5-Year Review of Metal Hydride Center of Excellence

Lennie Klebanoff, Director (presenting)

Jay Keller, Sandia Hydrogen Program Manager

http://www.ca.sandia.gov/MHCoE/ ST029

(This presentation does not contain any proprietary information)

MHCoE Overview Outline

- *MHCoE Objectives*
- *Approach to Technical Targets*
- *MHCoE Structure*
- *Collaborations*
- *Accomplishments By the Numbers*
- *5-Year Technical Highlights and Summaries*
- *Material Downselects and Recommendations to HSECoE*
- *Comparing Material Properties to Material Goals*
- *Remaining Technical Challenges*
- *Some Thoughts on Center Concept*

METAL HYDRIDE CENTER OF EXCELLENCE

MHCoE Objectives

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

Approach to Technical Targets

H Capacity:

– Synthesize and characterize hydride materials with high hydrogen capacity and favorable thermodynamics, as guided by theory

Charge/Discharge Rates:

– Develop materials that are fully reversible, assess nanoengineering and catalysis as means for promoting kinetics

Hydrogen Purity (from Storage Material) :

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

Cycle Life:

– Assess durability of materials, cycling behavior, effects of contaminants, structural stability, release of volatiles

Overview

Timeline

- Project started in March 2005
- Project ends June 2010

MHCoE Budget

FY 2005: $5.0M (½ yr)
FY 2006: $6.3M
FY 2007: $8.6M
FY 2008: $9.3M
FY 2009: $10.7M
FY 2010: $5.0M (planned ½ yr.)

Partners

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

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

Industry: UTRC, HRL, GE*, Intematix*

* = former partner

Approach to R&D- Center Structure

DOE

Coordinating Council (2008-2010)

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

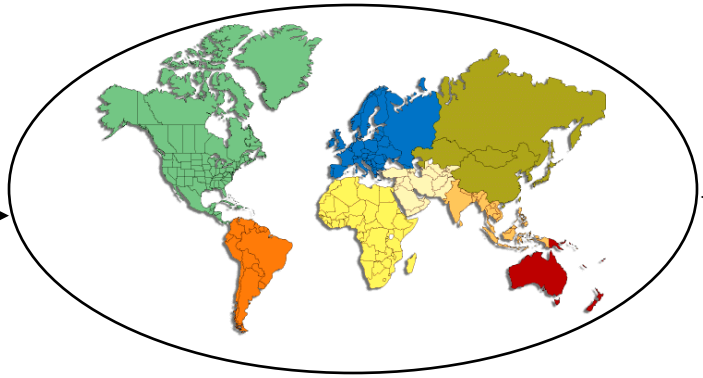
D

Alane (AlH_3)

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

Note: Original Project E (Eng.) discontinued in July 2008 due to HSECoE

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

Downselect Criteria

X

No/Go

✓

Go

Improve Material: purity, dopants nanoengineering

Note: "Downselect" means removing from further study (No-Go)

We Have Established Extensive Domestic Collaborations the Past 5 Years

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

…as well as 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	Dalian Institute (*China*)	P. Chen (amide synthesis)
SNL	Mahidol U. *(Thailand)*	N. Poonyayant, P. Pakawatpanurut (synthesis)

-- we collaborate with 9 foreign institutions that are not partners in the MHCoE

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Technical Accomplishments By The Numbers

YEAR (12 month interval)	*Publications*	*Joint Partner Publications*	*Presentations*	*Patents*
2005/2006	53	6	121	0
2006/2007	62	20	87	10
2007/2008	60	25	97	4
2008/2009	61	26	71	5
2009/2010	65	29	76	5
Totals:	**301**	**106**	**452**	**24**

Published in:

Phys. Rev. Lett., 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. and others…….

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5-Year Technical Highlights and Summary

$Mg(BH_4)_2$ Releases 12 Wt. % H_2

Note: We have investigated ~50 B-containing materials in the MHCoE

$Mg(BH_4)_2$ Prior to 2005:

First synthesized by V.N. Konoplev: Zhurnal Neorganicheskoi Khimii 25 1739 (1980).

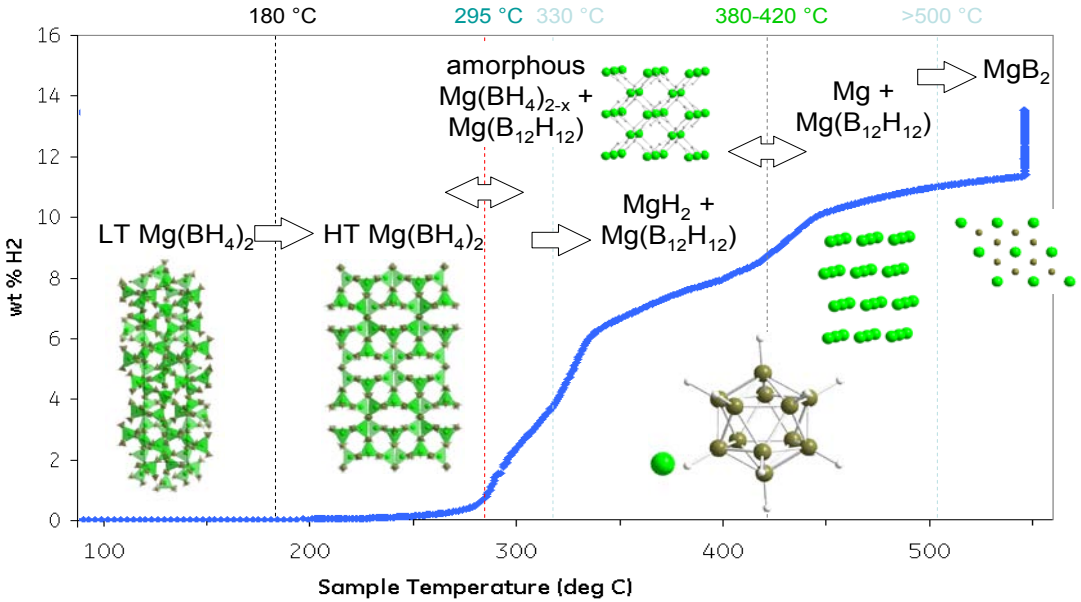
Prior work reports H desorption above 320 °C, $\Delta H \sim 53$ kJ/mole H_2.

--theoretical wt.% = 14.9

$Mg(BH_4)_2$ In MHCoE:

GE synthesized material in 2005

GE, JPL, Caltech examine desorption, structure and mechanisms. $[B_{12}H_{12}]^{2-}$ identified as a prominent intermediate in borohydride reactions



-- a much better understanding of $Mg(BH_4)_2$ desorption mechanism

$Mg(BH_4)_2$ Reversibility Demonstrated

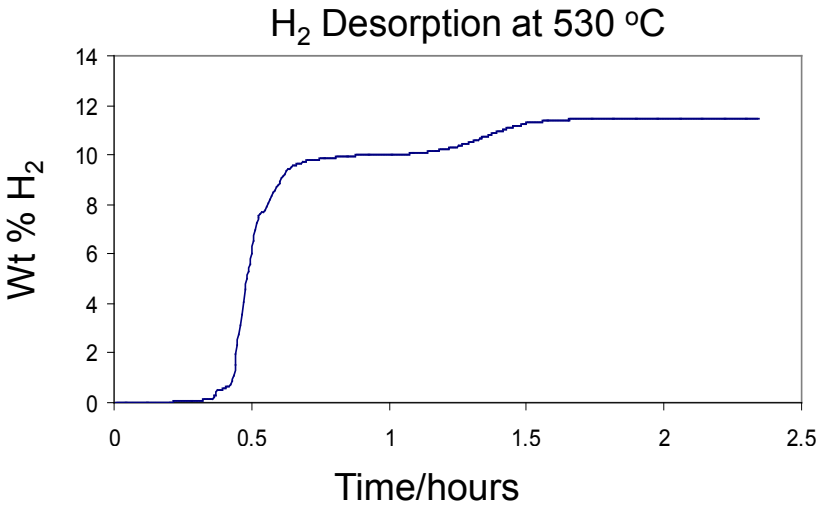
$Mg(BH_4)_2$ H_2 release is reversible; Additives aid desorption kinetics.

G. Severa, E. Rönnebro, and C.M. Jensen *Chem. Commun.* 2010, 46, 421-423

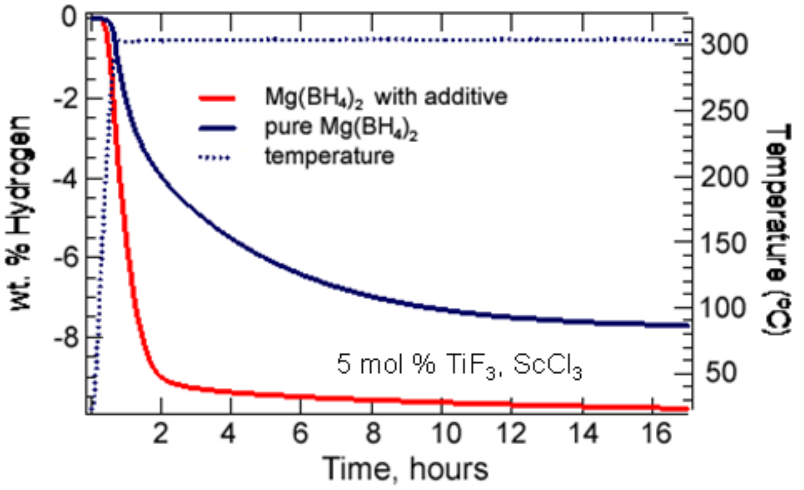
E. Rönnebro, C.M. Jensen, and G. Severa US patent application 61/093,937.

$$MgB_2 \xrightarrow[700 - 950 \text{ atm } H_2;\ 350 - 400\ ^oC]{} Mg(BH_4)_2$$

$$Mg(BH_4)_2 \xrightarrow[400\ ^oC]{} MgB_2$$



12 wt.% released from $Mg(BH_4)_2$ derived from MgB_2, at 530 °C

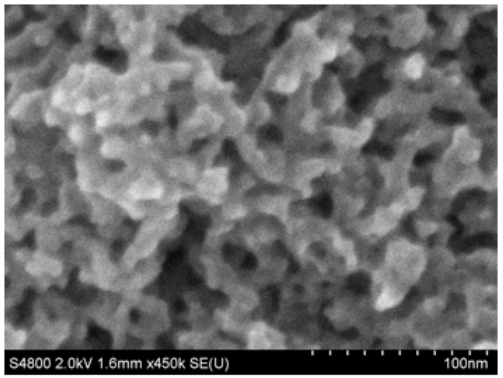


Additives aid kinetics of H_2 release from $Mg(BH_4)_2$

Scaffolds Improve Materials Kinetics

Concept: Modify kinetics by incorporating hydrides into nanoporous scaffolds

- **scaffold templates with nanoscale (< ~*50 nm*) structure**
- **nanoscale structure reduces diffusion times ($t \sim l^2/D$)**
- **scaffold provides confinement (*prevents sintering*)**



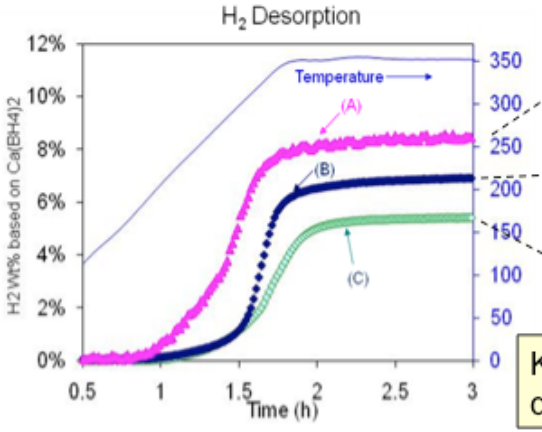
Carbon aerogel with 13 nm pores

Prior to ~2005: Early reports

- **BH_3NH_3@mesoporous silica, from PNNL (*improved kinetics and altered thermodynamics*)**
- **$NaAlH_4$@carbon aerogel, from MPI (*improved kinetics*)**

2005 – 2010: Further developed/tested concept, evaluated practicality

- **$LiBH_4$@carbon aerogels (*60X increase in dehydrogenation rate at 300 ℃, improved reversibility from ~35% to 70%*)**
- **MgH_2@carbon aerogels (*achieved rates comparable to best catalyzed material*)**
- **$Ca(BH_4)_2$@carbon aerogels (*lowered rxn temperatures*)**
- **$LiBH_4/MgH_2$@aerogel (*achieved sequential incorporation but cycling was poor; still working on simultaneous incorporation*)**



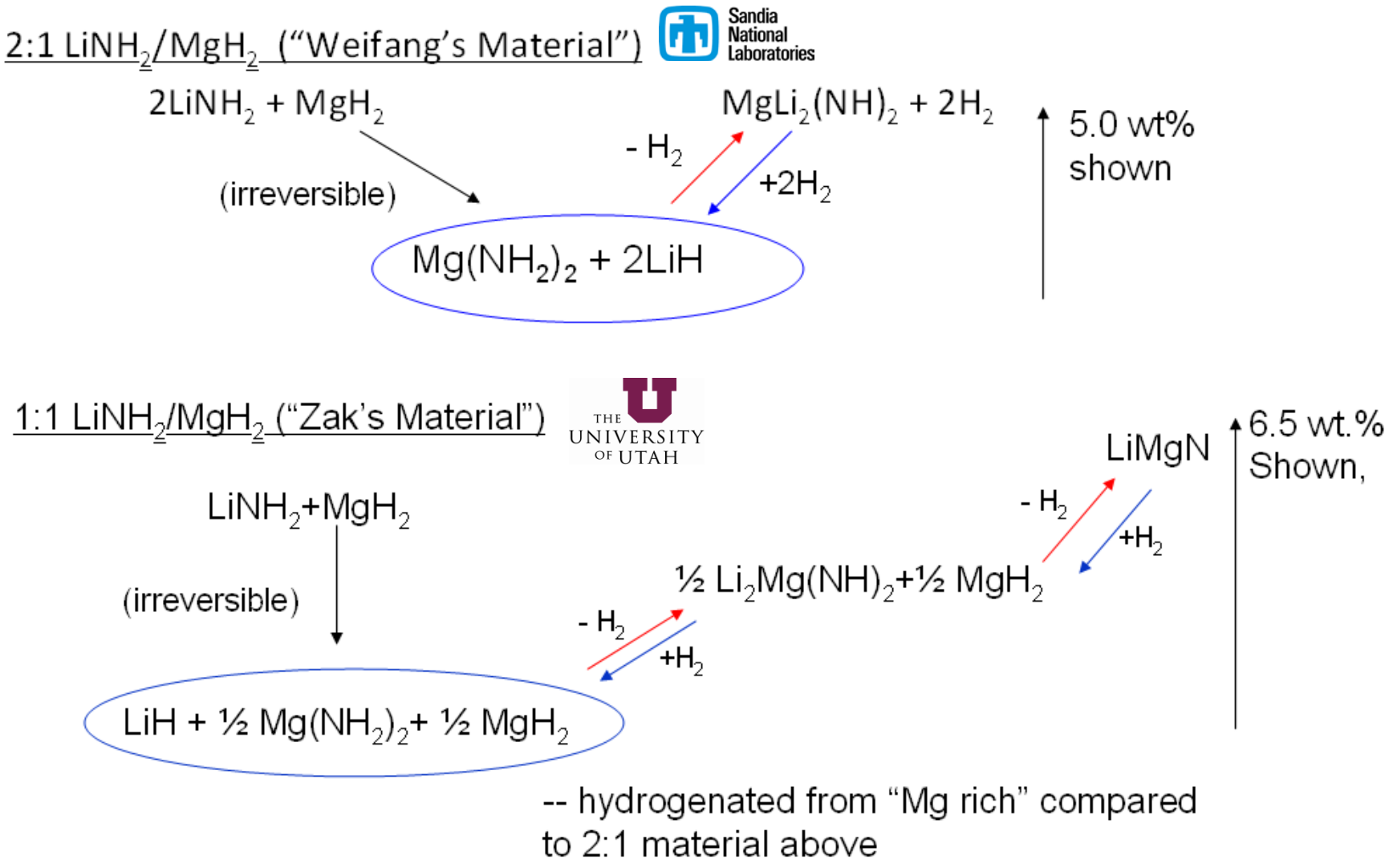
A. $Ca(BH_4)_2$ incorporated in C aerogel by soaking in $Ca(BH_4)_2$/THF solution

B. $Ca(BH_4)_2$ SPEX milled with C Aerogel (no pore inclusion)

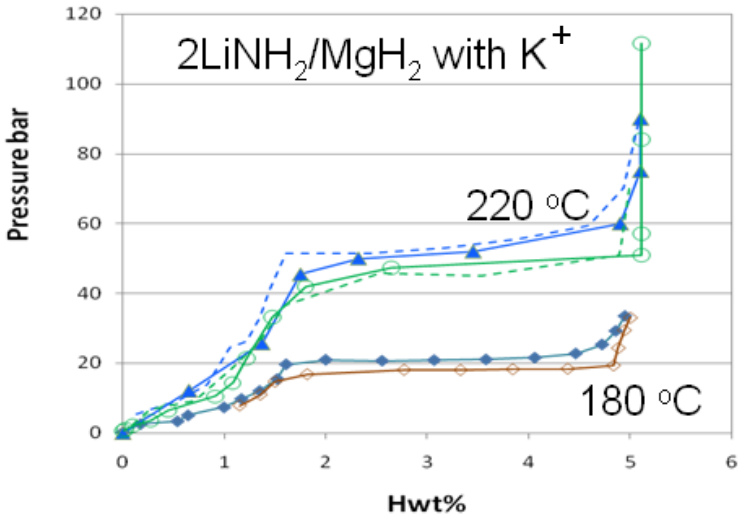
C. SPEX milled $Ca(BH_4)_2$ by itself

Kinetic enhancement seen in 1st and 2nd desorption cycles.

2 Promising Materials Have Been Discovered in the Li-Mg-N-H Family



$2LiNH_2/MgH_2$ Has Been Recommended to the HSECoE as a "Near-Term" Material



Sandia National Laboratories

K^+ catalysis first observed by P. Chen et al. Angew. Chem. Int. ed. **2009**, 48, 5828

- **Potassium doping dramatically improves absorption rate.**
- **$\Delta H_{des.}$ = 41.8 kJ/mole H_2**
- **Proven reversible hydrogen capacity of 5wt%, 1wt% more than $NaAlH_4$**
- **Excellent Cyclability: 264 cycles demonstrated, with 23% loss in capacity**
- **Manageable NH_3 release (200 ppm at 180 °C), but needs improvement**

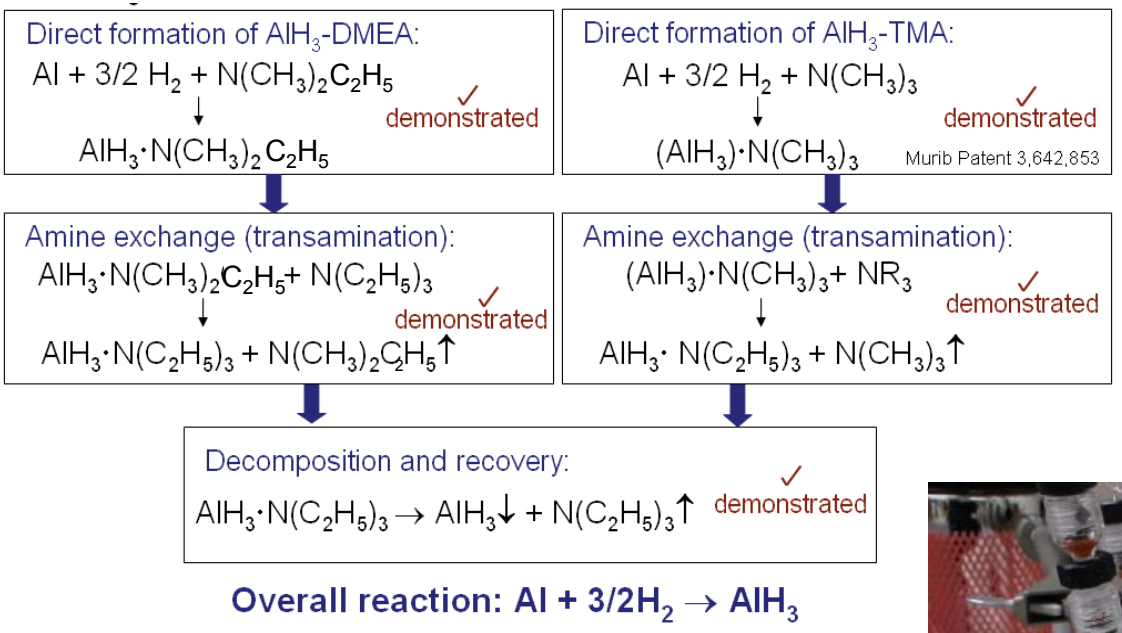
More capacity possible with 1:1 $LiNH_2/MgH_2$ material, but need to improve pressure of 1st plateau region, cyclability

AlH_3 Regeneration

AlH_3 can be regenerated with good WTT energy efficiency

I. Organometallic Approach (BNL)

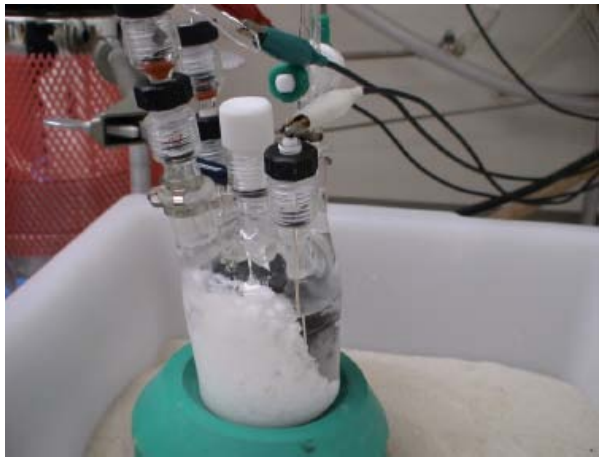
-- AlH_3 recommended to the HSECoE as a "near-term" material



Overall reaction: $Al + 3/2H_2 \rightarrow AlH_3$

II. Electrochemical Approach (SRNL)

- Gram quantities produced
- High purity AlH_3
- High H_2 capacity
- A closed material regeneration cycle was developed



AlH_3-TEDA

Energy-efficient Rehydrogenation of $LiAlH_4$

$3LiAlH_4 \longrightarrow Li_3AlH_6 + 2Al + 3H_2$ 5.3 wt.%H $\Delta H = -10$ kJ mol^{-1} Step 1

$Li_3AlH_6 \longrightarrow 3LiH + Al + 1.5H_2$ 2.6 wt.%H $\Delta H = +25$ kJ mol^{-1} Step 2

$LiAlH_4$ possesses good hydrogen release properties, but could not be easily reversed

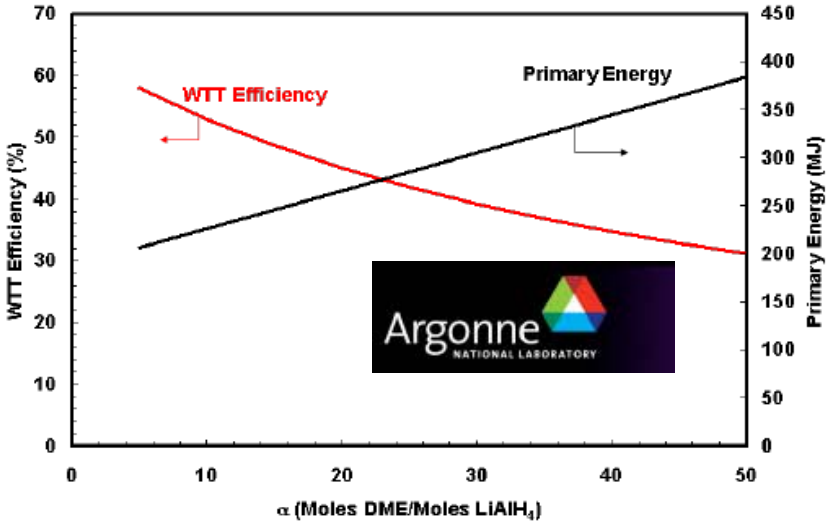
∴ **Explored "off-board" routes:**

$$LiH + Al[Ti] \xrightarrow[\text{r.t.; 24 h}]{Me_2O/H_2\ (100\ bar)} LiAlH_4[Ti]$$

Me_2O solvent vents immediately with H_2

Regeneration with mild conditions (low T, P)

$LiAlH_4$ releases 7 wt.% H_2 80 – 180 °C, excellent kinetics, only ~100ppm Ti needed



WTT efficiency approaches DOE target

-- due to:

- **Low compression energy for Me_2O**
- **~ 5M solubility of $LiAlH_4$ in Me_2O**

-- $LiAlH_4$ recommended to the HSECoE as a "near-term" material

G.S. McGrady and C.M. Jensen, US Patent Application 60/945.650
X. Liu, G.S. McGrady, H.W. Langmi, C.M. Jensen,
*JACS 2009, **131** (14), 5032–5033.*

Major Advances in Modeling & Theory

State of Modeling & Theory in 2005:

1. Density functional theory (DFT) had been used to compute the thermodynamics of a only a few individual metal hydride compounds.
   -- See e.g. Wolverton et al., PRB, **69**, 144109 (2004)
2. There was no way to predict phase diagrams/van't Hoff plots for metal hydrides
3. Theory could not account for rxn complexities (eg. meta-stable and multi-step rxns) that can occur in solid-state H_2 desorption/absorption reactions
4. Virtually no theoretical work had been done on amorphous MH materials or kinetics

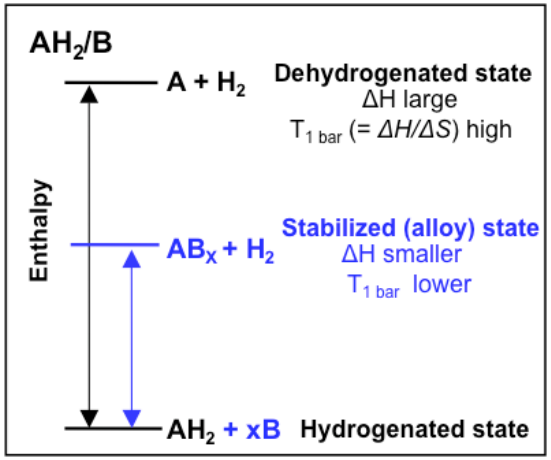
Advances Made in the MHCoE as of 2010:

1. DFT is now routinely used to predict the ΔH and ΔG of complex metal hydrides
2. Developed the ability to predict reactions over wide ranges of P, T and composition, thereby focusing experimental efforts on promising compounds. Linear search methods have scanned millions of different reaction conditions (composition, T, P)
3. Theory predicting important rxn. intermediates ($[B_{12}H_{12}]^{2-}$), confirmed by experiment.
4. Developed PEGS technique for predicting crystal structures, enabling thermo. study
5. Using Factsage to study the role of non-H_2 gas-phase species in MH reactions

Explored "Destabilization" Strategy

Prior to 2005: HRL advances "Destabilization" scheme

- **LiH/Si system demonstrated (*T_{1bar} > 400 ℃, but reduced from > 900 ℃*)**
- **MgH_2/Si system studied (*est. T_{1bar} ~ 50 ℃ but no reversibility in bulk*)**
- **$LiBH_4$/MgH_2 system demonstrated (*~10 wt%, T_{1bar} = 225 ℃; however, reaction occurred in 2 steps and T ~ 400 ℃ needed for reasonable kinetics*)**



2005 – 2010: Extended Destabilization Concept

- **Tested ~ 20 new systems, > 300 proposed computationally (Johnson/Sholl)**
- **Studied systems including $LiBH_4$/MgX (X = F, Cl, I, S, Se, CO_3, Si, Cu), LiH/B_4C, $LiBH_4$/Si, $CaSiN_2$, $MgSiN_2$, LiBC, $Mg(BC)_2$, LiH/TiO_2, LiH/SiO_2, $LiBH_4$/SiO_2 (*most systems did not hydrogenate or showed no reversibility, $LiBH_4$/MgX (X = F, S, and Se were partially reversible, full reversibility achieved recently for X = F*)**
- **$LiBH_4$/Mg_2NiH_4 system studied (*first reversible system to clearly show kinetic coupling, nearly ideal thermodynamics; however, only 2.6 wt% theoretical capacity*)**
- **Proposed $LiBH_4$/M_nTmH_y (Tm = transition metal) systems (*many Tm complex hydride anions are known that may be catalytic and undergo destabilization reactions*)**
- **Examined $LiBH_4$/ScH_2, but the reaction never "coupled".**

Material Downselect Procedures Provide R&D Focus for MHCoE

The MHCoE focused on 5 primary performance criteria on which Go/No-Go material 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 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 did they substitute for the full DOE system targets for on-board H_2 storage.

Material Downselects: 2005-2007

- From 2005-2007, 51 material systems were investigated in the MHCoE. Of these 51 materials, 24 were "downselected," removing them from further study. 27 satisfied the 5 performance metrics and were studied further.

In fulfillment of the end of FY2007 Materials Downselect 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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Bulk Materials No Longer Pursued:

MgH_2/Si: not reversible **X**

$LiBH_4/MgH_2$: kinetically limited (T >350 ºC) **X**

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

Materials Still Being Pursued as of 10/2007:

$Ca(BH_4)_2$ ✓

$LiBH_4/MgH_2$ in aerogels ✓

LiMgN, $Li_3AlH_6/3LiNH_2$ ✓

AlH_3 , and 22 other systems ✓

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

More Downselects, up to 6/2009

From 2007 to 2009, the following 11 materials were synthesized and characterized, but were downselected:

$Ca(BH_4)_2$	(poor cycling, high ΔH)
$Mn(BH_4)_2$	(not reversible)
$Ca(BH_4)_2 \cdot NH_3$	(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)
$LiMn(BH_4)_3$	(not reversible)
$Li_2Zr(BH_4)_6$	(not reversible)
$Na_2Mn(BH_4)_4$	(not reversible)
$Li_3AlH_6/3LiNH_2$	(LiMgN better)
ScH_2-$LiBH_4$	(no destabilization rxn.)

As of 6/2009 we were pursuing the following bulk materials:

Borohydrides: e.g. $Mg(BH_4)_2$

Amides: e.g. $2LiNH_2/MgH_2$

Closoboranes: $[B_{12}H_{12}]^{2-}$

AlH_3, $LiAlH_4$

Nanostructured materials:

--- $LiBH_4/MgH_2$ in aerogel

And also working on newly discovered materials….

Mixtures of NH_2/BH_4 compounds

Mixtures of AlH_4/BH_4 compounds

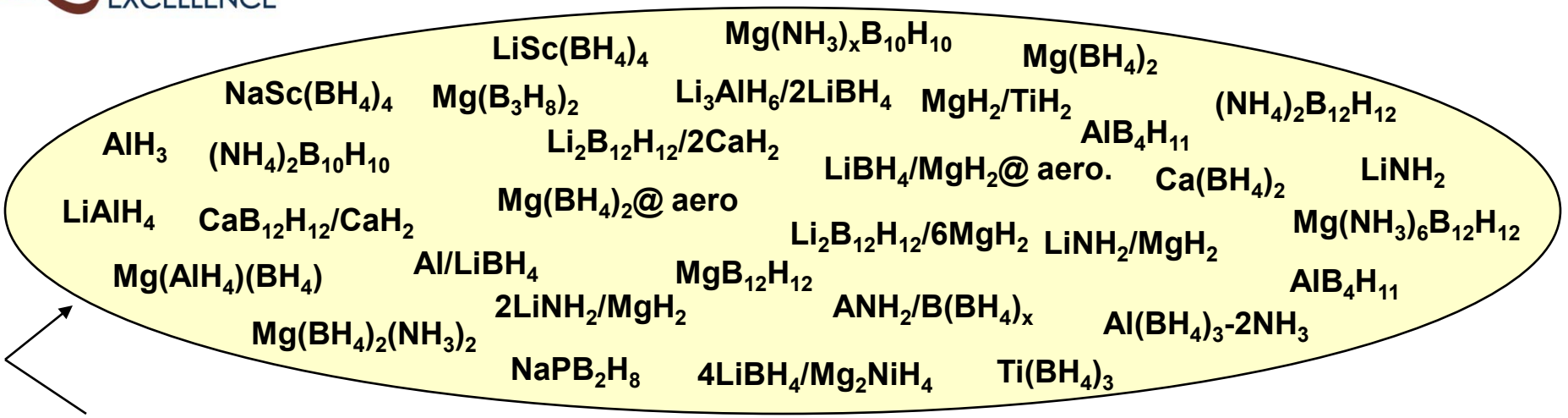
NH_3 Adducts of Borohydrides

$LiBH_4/Mg_2NiH_4$

MgH_2/TiH_2

P-based compounds: $NaPB_2H_8$

Final Year Downselection Path



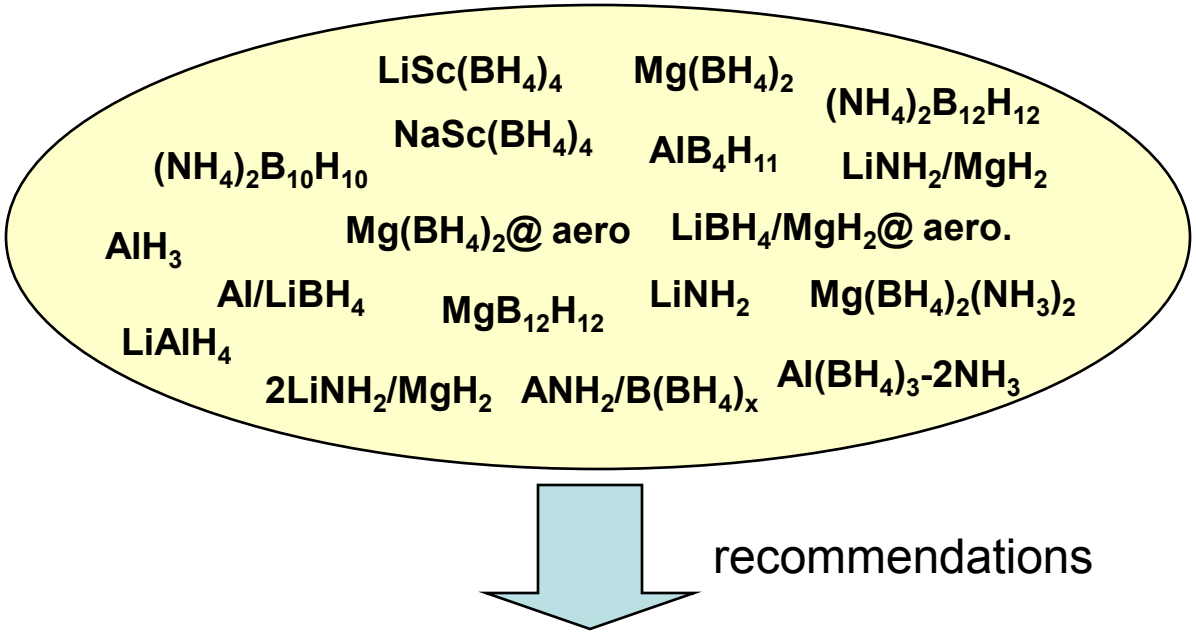
Materials examined in final year of the MHCoE

11 More Downselects
(Removing from Study)

$4LiBH_4/Mg_2NiH_4$	(low wt. %)
$Mg(B_3H_8)_2$	(too unstable)
$Li_2B_{12}H_{12}/2CaH_2$	(too high T_{des})
$Mg(NH_3)_xB_{10}H_{10}$	(NH_3 release)
$Mg(NH_3)_6B_{12}H_{12}$	(NH_3 release)

$CaB_{12}H_{12}/CaH_2$	(not reversible)
$Li_2B_{12}H_{12}/6MgH_2$	(too high T_{des})
$Ti(BH_4)_3$	(not reversible)
$Li_3AlH_6/2LiBH_4$	(too high T_{des})
$Li(NH_3)_xB_{12}H_{12}$	(NH_3 release)
$NaBP_2H_8$	(not reversible)

Leaving Us With….



recommendations

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 ✓ Recommended $2LiNH_2/MgH_2$, AlH_3, $LiAlH_4$

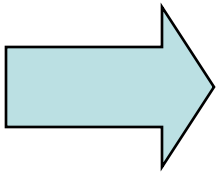
2. Identify medium-term materials that need more R&D, but would also be of eventual interest for HSECoE examination and subsystem testing
   ✓ Recommend $LiNH_2/MgH_2$, others (TBD)

3. Identify areas of further R&D that in the long-term have promise for fulfilling the 2015 targets

Comparing to the 2010 DOE Targets

Storage System Parameter	2010 DOE Target (New)
System Grav.: kgH_2/kg-system	4.5%
System Vol.: gH_2/L system	28
System Fill Time (5kg H_2): mins	4.2
Operational Cycle Life: cycles	1000
Hydrogen Purity	99.97% (dry)

Convert to inferred materials properties for making Spider Charts

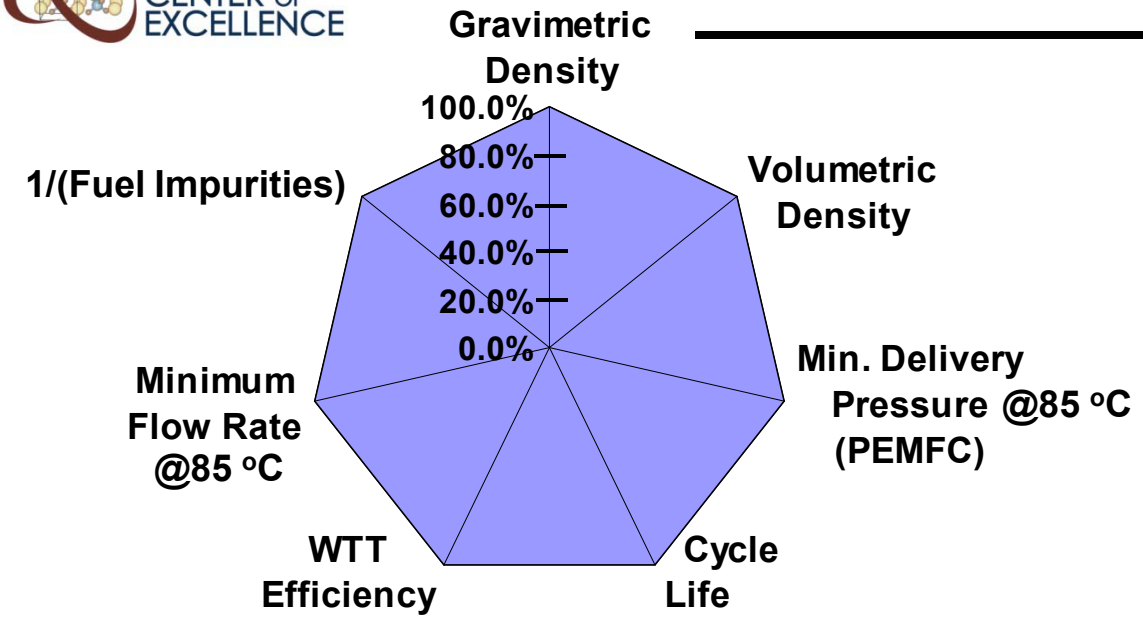


Storage Material Parameter	"Goal"
Material Grav.: kgH_2/kg-material	9.0%*
System Vol.: gH_2/L material	56**
1/(Fill Time) Min^{-1}	0.238
Operational Cycle Life: cycles	1000
1/(Fuel Impurities) ppm^{-1}	0.01

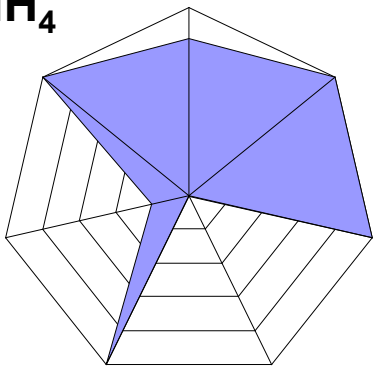
* Assumes 50% system gravimetric penalty

** Assumes 50% system volumetric penalty (including packing density penalty)

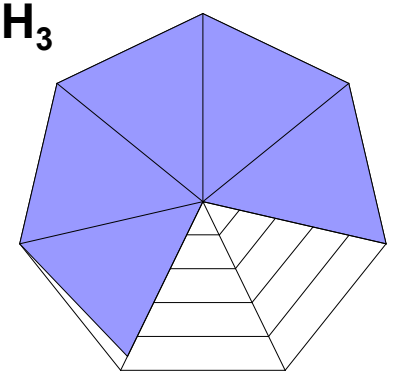
"Off-board" Reversible MH



$LiAlH_4$



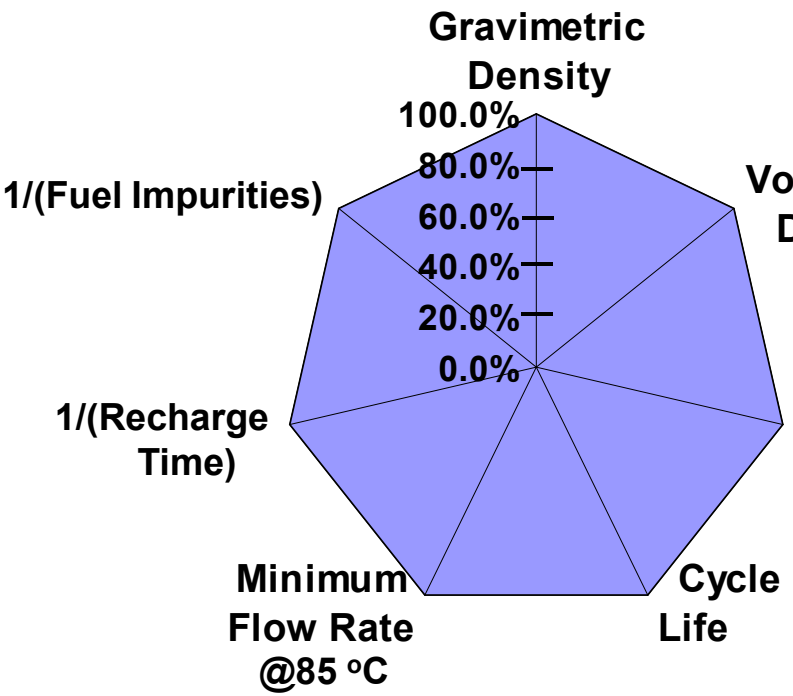
AlH_3



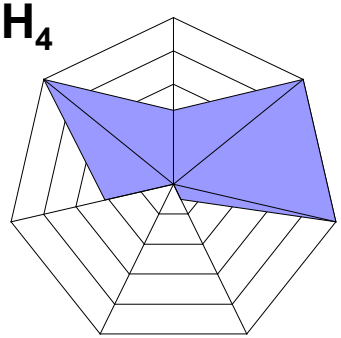
Materials "Goals"		$LiAlH_4$	AlH_3
Gravimetric Density (wt. %)	9%	7.5%	9.8%
Volumetric Density (gH_2/L)	56	74	139
Min. Delivery Pressure @ 85°C (PEMFC) (bar)	5	5	>5
Cycle Life	1000	5	1
WTT Efficiency	60	60	55
Minimum Flow Rate (gH_2/sec) @ 85 °C	1	0.2	1
1/(Fuel Impurities = 100 ppm) ppm^{-1}	0.01	∞	∞

$LiAlH_4$ and AlH_3 are viable "off-board" reversible materials. Very promising regeneration methods have been found, but robust cycle life has not been demonstrated.

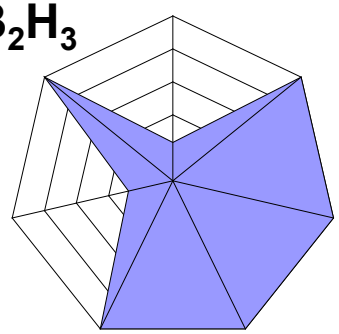
"On-board" Reversible MH



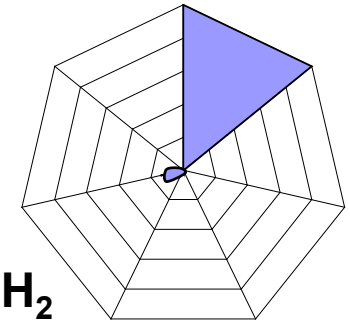
$NaAlH_4$



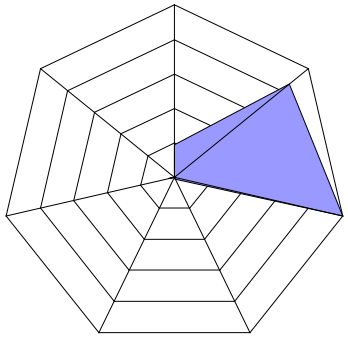
AB_2H_3



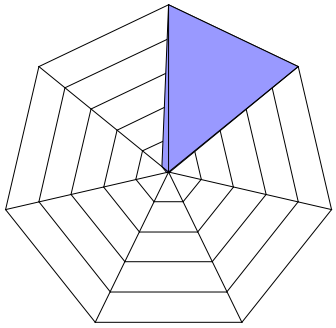
$LiBH_4/MgH_2$



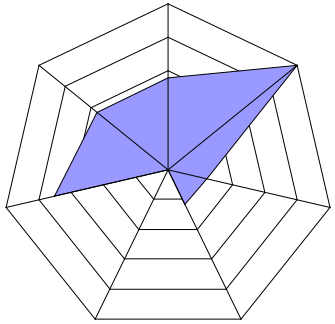
$LiBH_4/Mg_2NiH_4$



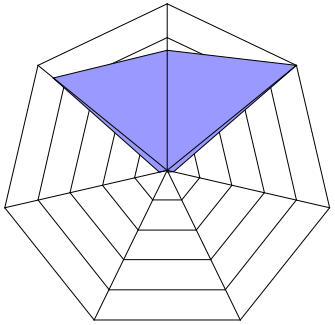
$Mg(BH_4)_2$



$2LiNH_2/MgH_2$



$LiNH_2/MgH_2$



H_2 capacity (wt. %) was improved with high volumetric density and good H_2 purity. However, the "on-board" materials have poor kinetics at 85 °C, and robust cycling has not been shown

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"On-Board" Reversible Chart Input

2010 Materials "Goals"		$LiBH_4/MgH_2$	$LiBH_4/Mg_2NiH_4$	$2LiNH_2/MgH_2$	$Mg(BH_4)_2$	$LiNH_2/MgH_2$	AB_2H_3 A = Ti, Zr B = V, Cr, Mn	$NaAlH_4$
Gravimetric Density (wt. %)	9%	10%	1.7%	5%	11%	6.5%	2.1%	4%
Volumetric Density (gH_2/L)	56	95	48	70	147	107	110	80
Min. Delivery Pressure @ 85 °C (PEMFC) (bar)	5	0.022	10	1.2	0.035	0.2	70	0
Cycle Life	1000	10	10	235	2	10	1000	100
Minimum Flow Rate (gH_2/sec) @ 85 °C	1	~0	~0	~0	~0	~0	1.5	~0
1/(Recharge Time = 4.2 min), min^{-1}	0.238	0.0333	0.0083	0.1667	0.0028	0.0110	0.0660	0.1
1/(Fuel Impurities = 100 ppm), ppm^{-1}	0.010	unknown	unknown	0.0056	0.0005	0.0088	∞	∞

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Remaining Technical Challenges

Thermodynamics:

We really need ΔH to be ~ 30 kJ/mole, but the materials we have been finding generally have ΔH ~ 40 – 80 kJ/mole. Thus, the H_2 release T's are too high.

-- Our understanding of intermediates ($[B_{12}H_{12}]^{2-}$, N-H species) and reaction pathways improved with time. Our theoretical methods advanced to predict more accurately the thermodynamics of reactions.

Reversibility at High Wt.%:

The biggest reason for downselecting a material has been poor reversibility. This has been especially true of high wt. % materials. We have poor mechanistic understanding of why.

-- Our experience with $Mg(BH_4)_2$ offers some hope. We have been able to reverse this high wt. % material, albeit with high T, P. We need to understand the borohydrides better as they have promising properties.

Kinetics at High Wt. %:

All of the materials seem to be challenged kinetically, particularly in the rehydrogenation step. We don't have a theoretical handle on the kinetics problem.

-- Catalysts exist that can dramatically aid kinetics (e.g. K^+ for $2LiNH_2/MgH_2$) but finding them has been slow, and we don't have a guiding understanding

Some Thoughts on Center Concept

The purpose of a Center is to solve hard technical problems requiring collaborations that cannot be established otherwise.

Was Collaboration Unique to a Center Achieved? -- YES

Collaborations between 2 individuals is easy without a Center. Collaborations between 3 individuals/institutions is harder, but can be done. In the MHCoE, sometimes 5 or 6 partners worked together on particular materials (1:1 $LiNH_2/MgH_2$, $Mg(BH_4)_2$, AlH_3, etc.). That level of collaboration is highly unlikely without the funding and structure of a Center.

Were Hard Problems Solved? -- YES, but the H_2 storage materials still need to be improved.

We did not find one material that simultaneously supports all of the DOE targets. However, we gained critical understanding on many topics, and solved important "sub-problems" (theory, synthesis, regeneration) that lay the foundation for developing an optimal solid-state H_2 storage material.

The Center concept was very successful for making rapid progress in this field

Many Thanks to the Following

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(cc) = co-chair at some point