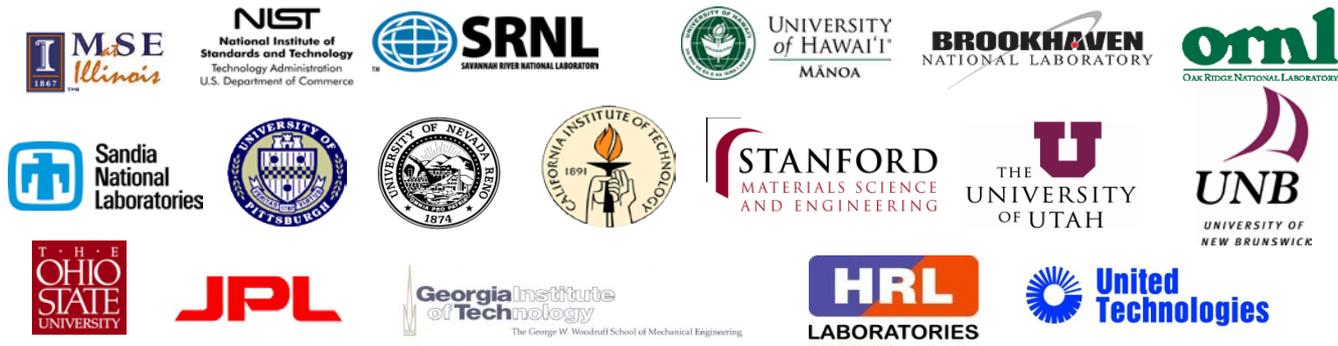


# 5-Year Review of Metal Hydride Center of Excellence



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

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

ST029

# 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*

# MHCoE Objectives

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*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*

## 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  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$  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

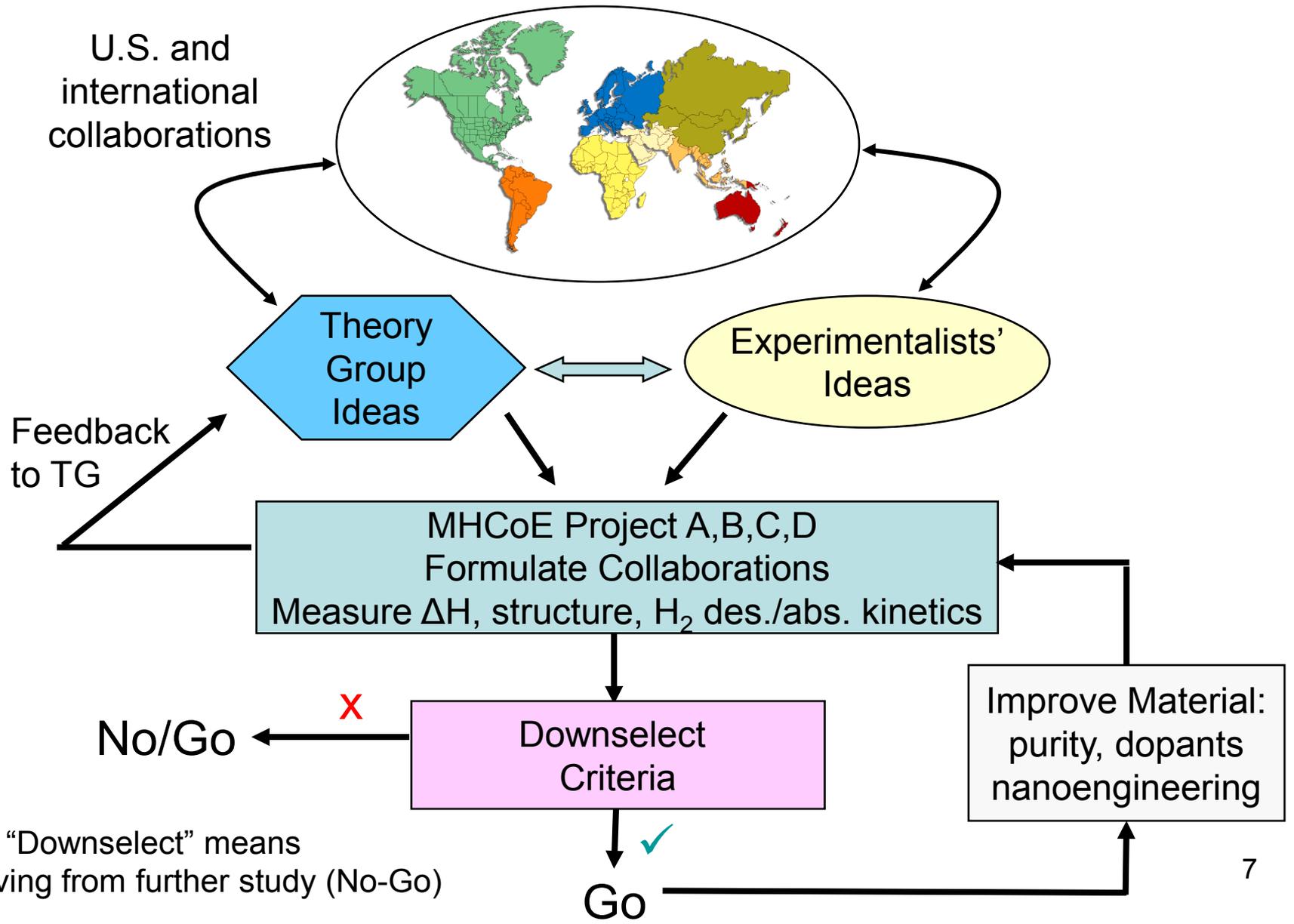
**D**

### Alane (AlH<sub>3</sub>)

- **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



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

# We Have Established Extensive Domestic Collaborations the Past 5 Years

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<u>MHCoE Partner</u>	<u>US Institution (not MHCoE)</u>	<u>US Collaborator and Topic</u>
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 <sub>3</sub> chem., structure)
BNL	U. Geneva (Switzerland)	K. Yvon, (oxidation of AlH <sub>3</sub> , synchrotron)
UH	KEK	R. Kuboto (muon spin resonance)
UH	AIST ( <i>Japan</i> )	E. Akiba, K. Sakaki (positron annihilation studies)
UH	Tohoku University ( <i>Japan</i> )	S. Orimo, Y. Nakamori (synthesis, DSC and XRD)
UH/UNR	U. Rome ( <i>Italy</i> )	R. Cantelli (analastic spectroscopy)
UH	IFE ( <i>Norway</i> )	B. Hauback, M. Sorby; (Sync. X-ray, Neutron Diff.)
UH	U. Geneva ( <i>Switzerland</i> )	H. Hagmann, R. Černý; (XRD, IR, Raman Spec.)
UNR	U. Geneva ( <i>Switzerland</i> )	K. Yvon (sabbatical host, XRD studies)
GA Tech/Pitt	U. Geneva ( <i>Switzerland</i> )	R. Černý (High res. XRD, neutron scattering)
SNL/UNR	ESRF ( <i>France</i> )	Y. Filinchuk (Synchrotron X-ray Diffraction)
U. Utah	Dalian Institute ( <i>China</i> )	P. Chen (amide synthesis)
SNL	Mahidol U. ( <i>Thailand</i> )	N. Poonyayant, P. Pakawatpanurut (synthesis)

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

# Technical Accomplishments By The Numbers

<b>YEAR (12 month interval)</b>	<b><i>Publications</i></b>	<b><i>Joint Partner Publications</i></b>	<b><i>Presentations</i></b>	<b><i>Patents</i></b>
<b>2005/2006</b>	<b>53</b>	<b>6</b>	<b>121</b>	<b>0</b>
<b>2006/2007</b>	<b>62</b>	<b>20</b>	<b>87</b>	<b>10</b>
<b>2007/2008</b>	<b>60</b>	<b>25</b>	<b>97</b>	<b>4</b>
<b>2008/2009</b>	<b>61</b>	<b>26</b>	<b>71</b>	<b>5</b>
<b>2009/2010</b>	<b>65</b>	<b>29</b>	<b>76</b>	<b>5</b>

**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.....

# 5-Year Technical Highlights and Summary

# Mg(BH<sub>4</sub>)<sub>2</sub> Releases 12 Wt. % H<sub>2</sub>

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

## Mg(BH<sub>4</sub>)<sub>2</sub> Prior to 2005:

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

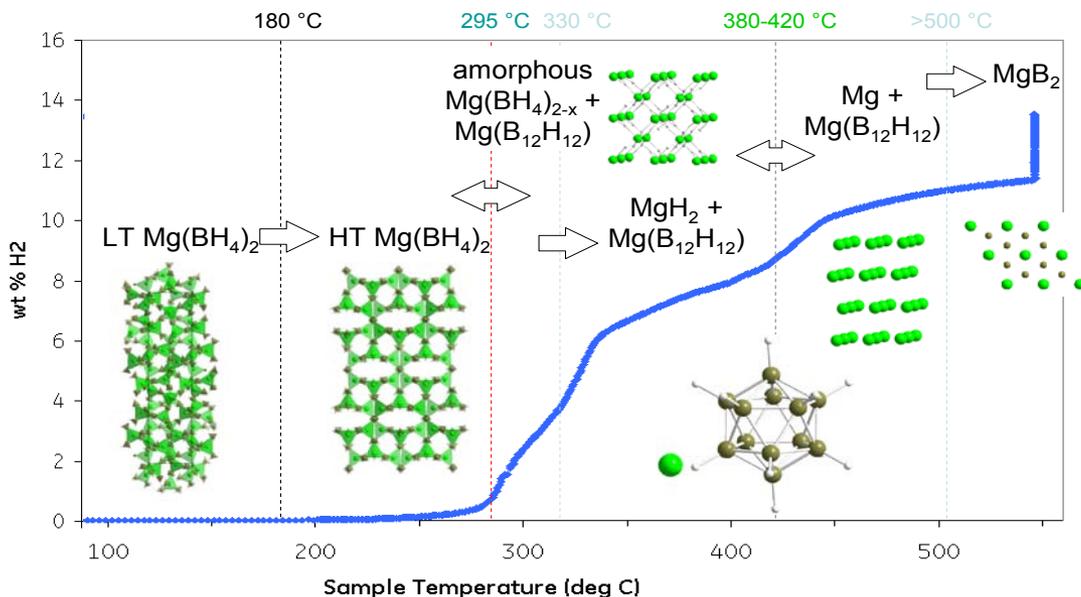
Prior work reports H desorption above 320 °C, ΔH ~ 53 kJ/mole H<sub>2</sub>.

## Mg(BH<sub>4</sub>)<sub>2</sub> In MHCoe:

**--theoretical wt.% = 14.9**

GE synthesized material in 2005

GE, JPL, Caltech examine desorption, structure and mechanisms. [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> identified as a prominent intermediate in borohydride reactions



-- a much better understanding of Mg(BH<sub>4</sub>)<sub>2</sub> desorption mechanism

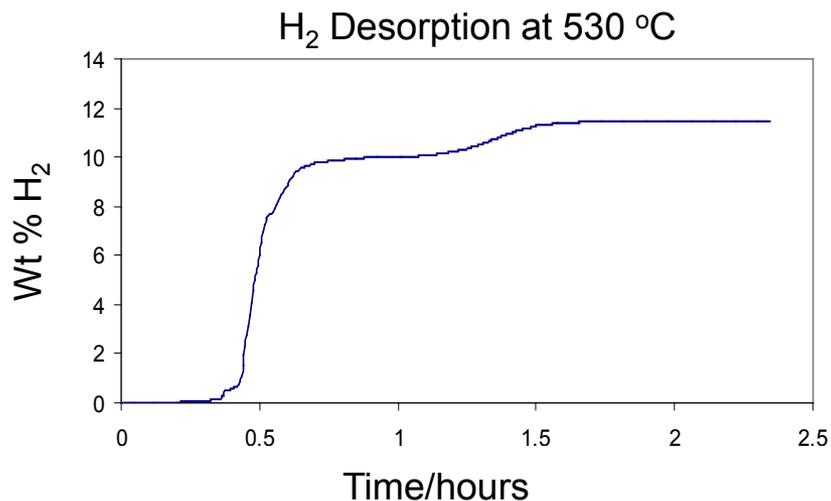
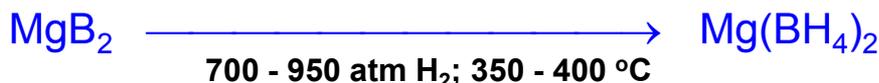


# Mg(BH<sub>4</sub>)<sub>2</sub> Reversibility Demonstrated

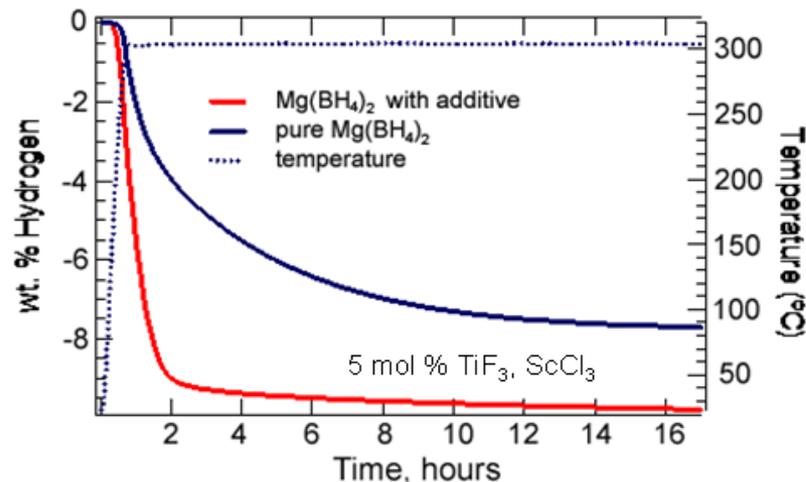
**Mg(BH<sub>4</sub>)<sub>2</sub> H<sub>2</sub> release is reversible; Additives aid desorption kinetics.**

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.



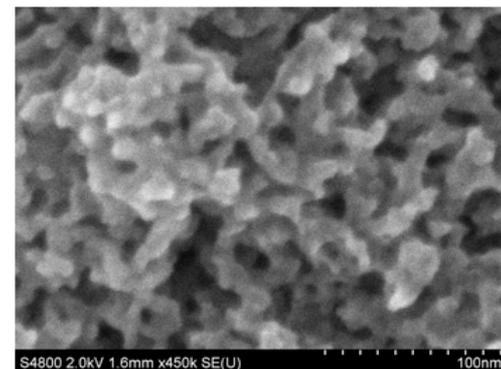
12 wt.% released from Mg(BH<sub>4</sub>)<sub>2</sub>  
derived from MgB<sub>2</sub>, at 530 °C



Additives aid kinetics of H<sub>2</sub>  
release from Mg(BH<sub>4</sub>)<sub>2</sub>

## Concept: Modify kinetics by incorporating hydrides into nanoporous scaffolds

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



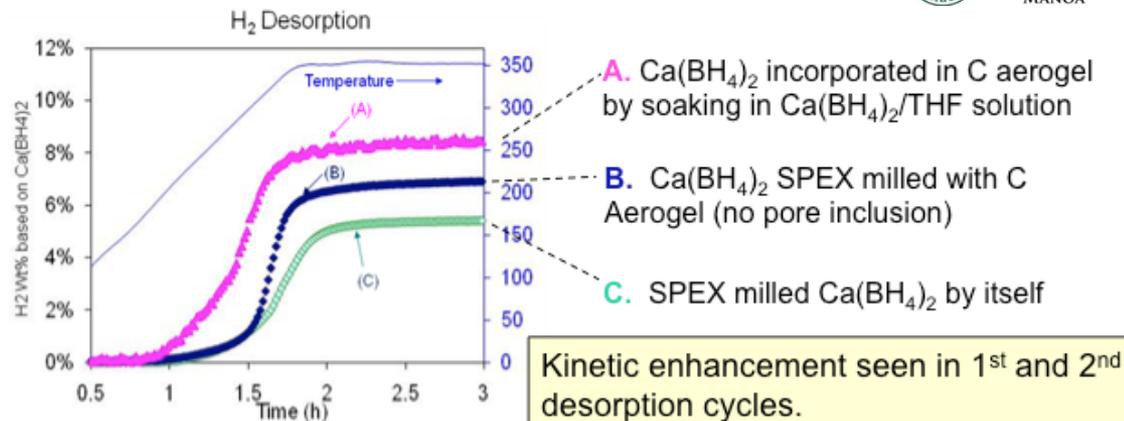
Carbon aerogel with 13 nm pores

## Prior to ~2005: Early reports

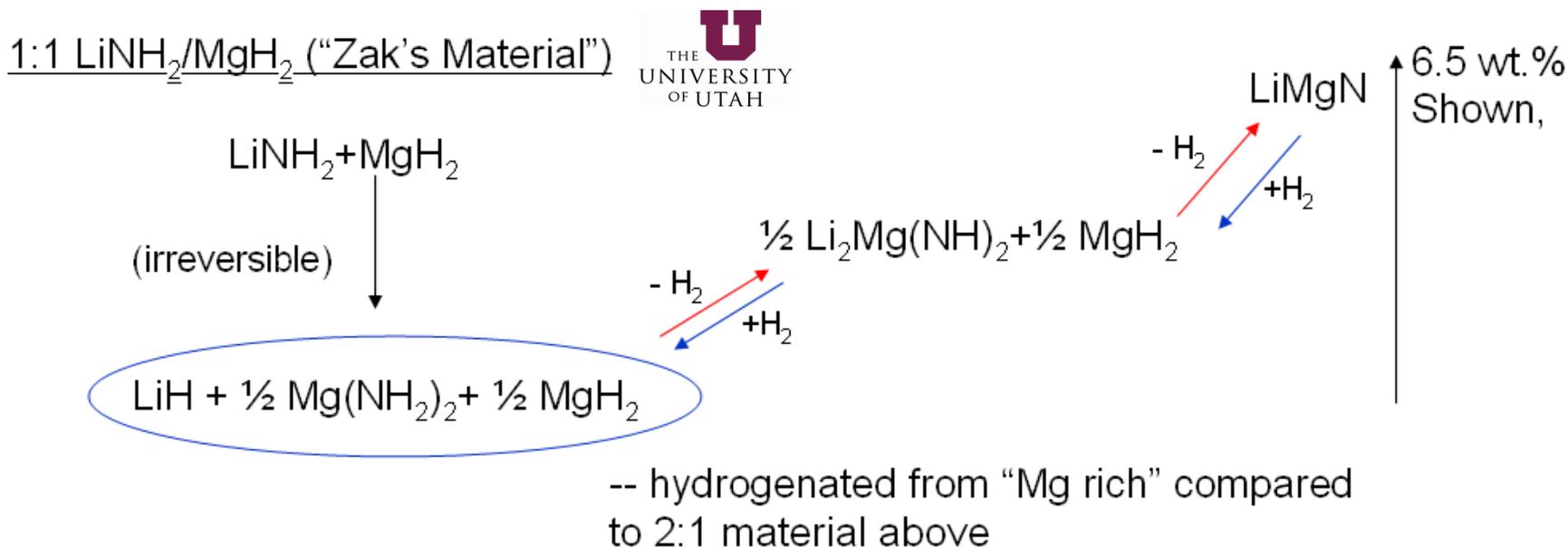
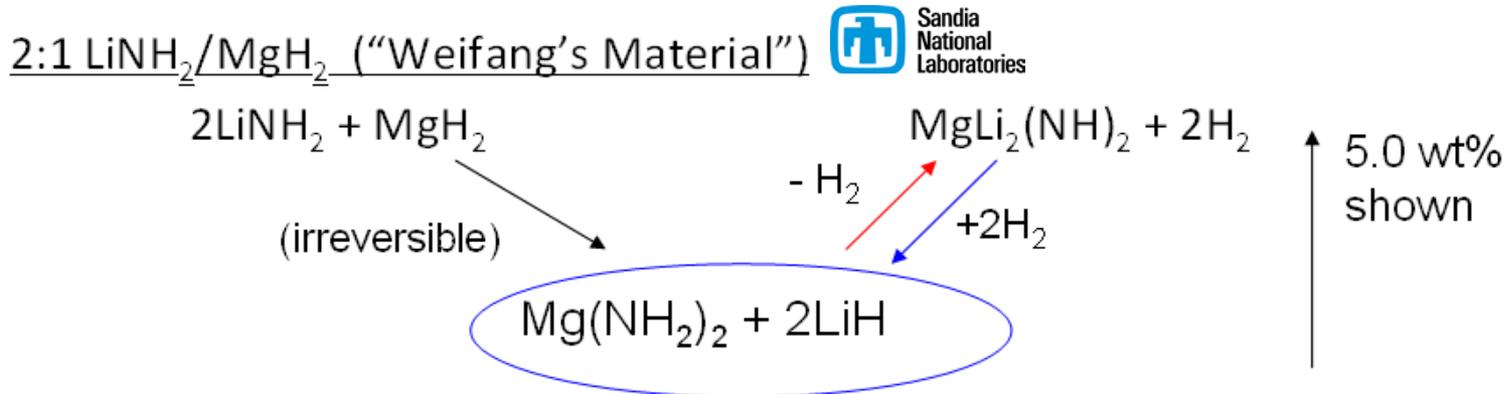
- $\text{BH}_3\text{NH}_3$ @mesoporous silica, from PNNL (*improved kinetics and altered thermodynamics*)
- $\text{NaAlH}_4$ @carbon aerogel, from MPI (*improved kinetics*)

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

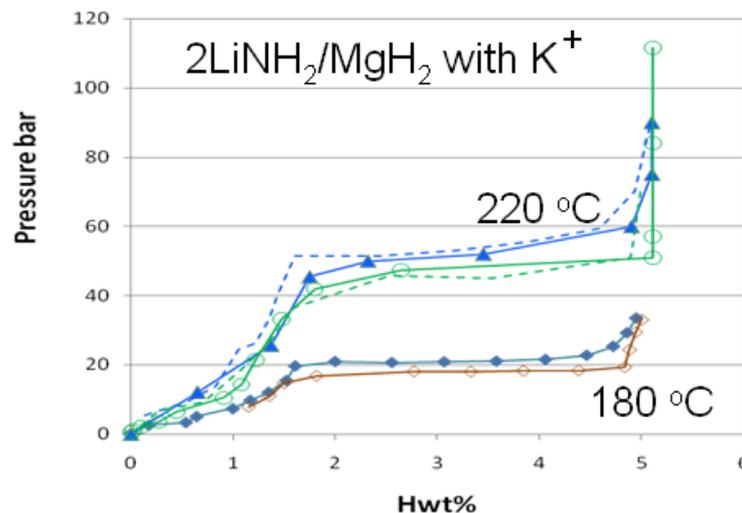
- $\text{LiBH}_4$ @carbon aerogels (*60X increase in dehydrogenation rate at 300 °C, improved reversibility from ~35% to 70%*)
- $\text{MgH}_2$ @carbon aerogels (*achieved rates comparable to best catalyzed material*)
- $\text{Ca}(\text{BH}_4)_2$ @carbon aerogels (*lowered rxn temperatures*)
- $\text{LiBH}_4/\text{MgH}_2$ @aerogel (*achieved sequential incorporation but cycling was poor; still working on simultaneous incorporation*)



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



# 2LiNH<sub>2</sub>/MgH<sub>2</sub> Has Been Recommended to the HSECoE as a “Near-Term” Material



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

- Potassium doping dramatically improves absorption rate.
- $\Delta H_{\text{des.}} = 41.8 \text{ kJ/mole H}_2$
- Proven reversible hydrogen capacity of 5wt%, 1wt% more than NaAlH<sub>4</sub>
- Excellent Cyclability: 264 cycles demonstrated, with 23% loss in capacity
- Manageable NH<sub>3</sub> release (200 ppm at 180 °C), but needs improvement

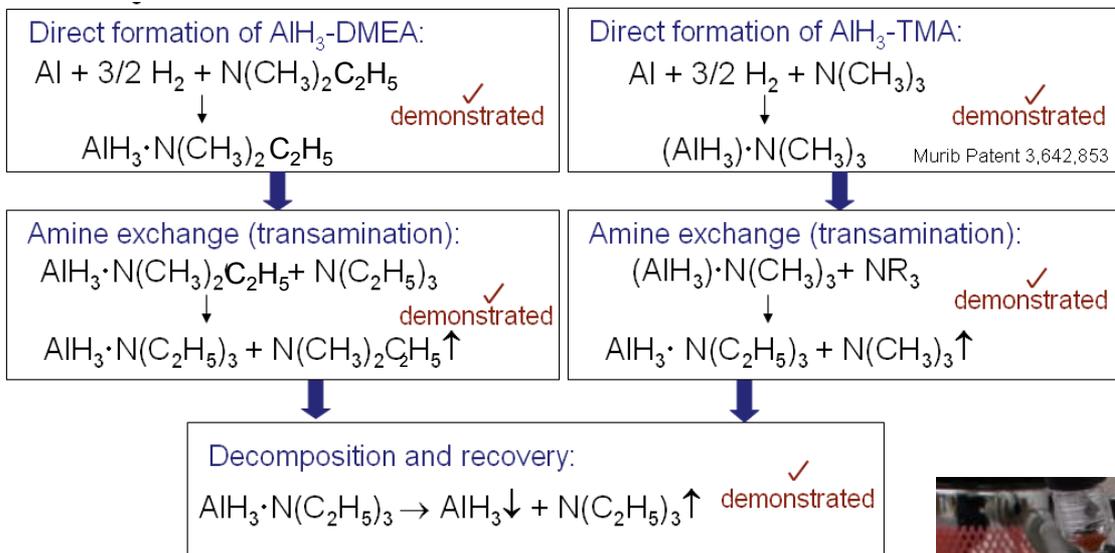
**More capacity possible with 1:1 LiNH<sub>2</sub>/MgH<sub>2</sub> material, but need to improve pressure of 1st plateau region, cyclability**

# AlH<sub>3</sub> Regeneration

**AlH<sub>3</sub> can be regenerated with good WTT energy efficiency**

**-- AlH<sub>3</sub> recommended to the HSECoE as a "near-term" material**

## I. Organometallic Approach (BNL)



## II. Electrochemical Approach (SRNL)

- Gram quantities produced
- High purity AlH<sub>3</sub>
- High H<sub>2</sub> capacity
- A closed material regeneration cycle was developed



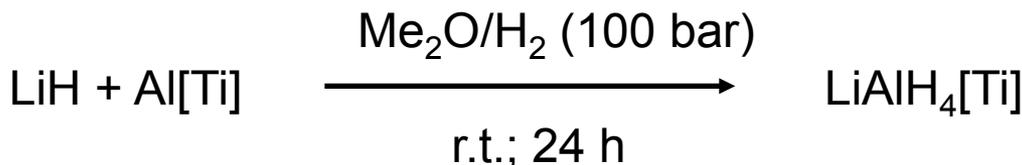
AlH<sub>3</sub>-TEDA 17

# Energy-efficient Rehydrogenation of $\text{LiAlH}_4$



$\text{LiAlH}_4$  possesses good hydrogen release properties, but could not be easily reversed

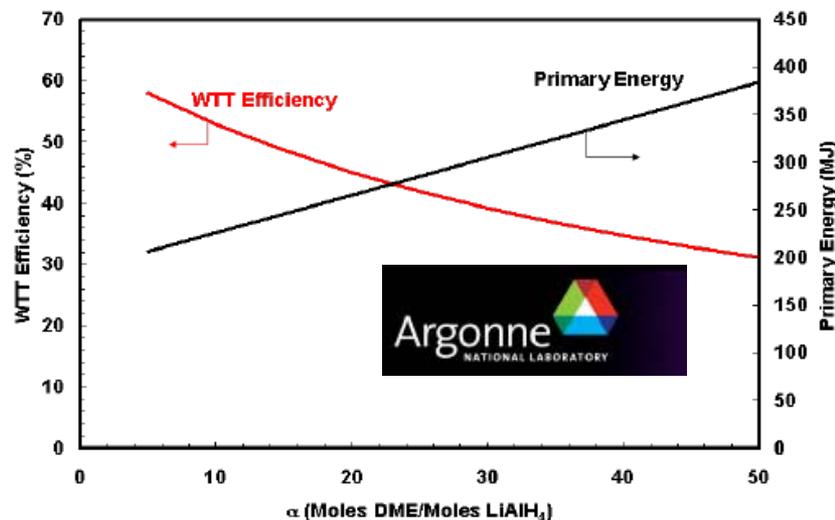
∴ Explored “off-board” routes:



$\text{Me}_2\text{O}$  solvent vents immediately with  $\text{H}_2$   
Regeneration with mild conditions (low T, P)

$\text{LiAlH}_4$  releases 7 wt.%  $\text{H}_2$  80 – 180 °C,  
excellent kinetics, only ~100ppm Ti needed

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.



**WTT efficiency approaches DOE target**

-- due to:

- Low compression energy for  $\text{Me}_2\text{O}$
- ~ 5M solubility of  $\text{LiAlH}_4$  in  $\text{Me}_2\text{O}$

--  $\text{LiAlH}_4$  recommended to the  
HSECoE as a “near-term” material

## ***State of Modeling & Theory in 2005:***

1. Density functional theory (DFT) had been used to compute the thermodynamics of 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<sub>2</sub> 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  $\Delta H$  and  $\Delta G$  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)

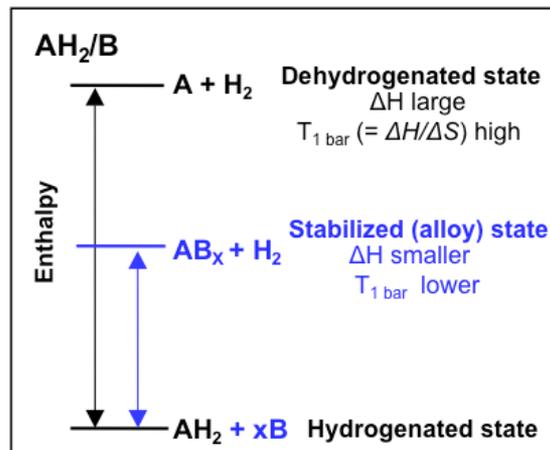
3. Theory predicting important rxn. intermediates ( $[B_{12}H_{12}]^{2-}$ ), confirmed by experiment.

4. Developed PEGS technique for predicting crystal structures, enabling thermo. study

5. Using Factsage to study the role of non-H<sub>2</sub> gas-phase species in MH reactions

## Prior to 2005: HRL advances “Destabilization” scheme

- LiH/Si system demonstrated ( $T_{1bar} > 400$  °C, but reduced from  $> 900$  °C)
- MgH<sub>2</sub>/Si system studied (est.  $T_{1bar} \sim 50$  °C but no reversibility in bulk)
- LiBH<sub>4</sub>/MgH<sub>2</sub> system demonstrated (~10 wt%,  $T_{1bar} = 225$  °C; however, reaction occurred in 2 steps and  $T \sim 400$  °C needed for reasonable kinetics)



## 2005 – 2010: Extended Destabilization Concept

- Tested ~ 20 new systems, > 300 proposed computationally (Johnson/Sholl)
- Studied systems including LiBH<sub>4</sub>/MgX (X = F, Cl, I, S, Se, CO<sub>3</sub>, Si, Cu), LiH/B<sub>4</sub>C, LiBH<sub>4</sub>/Si, CaSiN<sub>2</sub>, MgSiN<sub>2</sub>, LiBC, Mg(BC)<sub>2</sub>, LiH/TiO<sub>2</sub>, LiH/SiO<sub>2</sub>, LiBH<sub>4</sub>/SiO<sub>2</sub> (most systems did not hydrogenate or showed no reversibility, LiBH<sub>4</sub>/MgX (X = F, S, and Se were partially reversible, full reversibility achieved recently for X = F)
- LiBH<sub>4</sub>/Mg<sub>2</sub>NiH<sub>4</sub> system studied (first reversible system to clearly show kinetic coupling, nearly ideal thermodynamics; however, only 2.6 wt% theoretical capacity)
- Proposed LiBH<sub>4</sub>/M<sub>n</sub>TmH<sub>y</sub> (Tm = transition metal) systems (many Tm complex hydride anions are known that may be catalytic and undergo destabilization reactions)
- Examined LiBH<sub>4</sub>/Sch<sub>2</sub>, but the reaction never “coupled”.

# Material Downselect Procedures

## Provide R&D Focus for MHCoE

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***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<sub>2</sub> for T < 350 °C
- 4) The material's non-H<sub>2</sub> volatilization products should not exceed 1000 ppm for a single thermal cycle
- 5) The material should release and reabsorb H<sub>2</sub> 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<sub>2</sub> 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.

## Bulk Materials No Longer Pursued:

$\text{MgH}_2/\text{Si}$ : not reversible X

$\text{LiBH}_4/\text{MgH}_2$ : kinetically limited ( $T > 350\text{ }^\circ\text{C}$ ) X

$\text{Li}_2\text{Zn}(\text{BH}_4)_4$ :  $\text{B}_2\text{H}_6/\text{H}_2$  ratio of 0.3 X

## Materials Still Being Pursued as of 10/2007:

$\text{Ca}(\text{BH}_4)_2$  ✓

$\text{LiBH}_4/\text{MgH}_2$  in aerogels ✓

$\text{LiMgN}$ ,  $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$  ✓

$\text{AlH}_3$ , and 22 other systems ✓

## *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



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

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

$\text{Ca}(\text{BH}_4)_2$	(poor cycling, high $\Delta H$ )
$\text{Mn}(\text{BH}_4)_2$	(not reversible)
$\text{Ca}(\text{BH}_4)_2 \cdot \text{NH}_3$	(ammonia release)
$\text{LiCa}(\text{BH}_4)_3 \cdot \text{NH}_3$	(ammonia release)
$\text{Na}_2\text{Zr}(\text{BH}_4)_6$	(not reversible)
$\text{K}_2\text{Zr}(\text{BH}_4)_6$	(not reversible)
$\text{LiMn}(\text{BH}_4)_3$	(not reversible)
$\text{Li}_2\text{Zr}(\text{BH}_4)_6$	(not reversible)
$\text{Na}_2\text{Mn}(\text{BH}_4)_4$	(not reversible)
$\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$	(LiMgN better)
$\text{ScH}_2\text{-LiBH}_4$	(no destabilization rxn.)

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

Borohydrides: e.g.  $\text{Mg}(\text{BH}_4)_2$

Amides: e.g.  $2\text{LiNH}_2/\text{MgH}_2$

Closoboranes:  $[\text{B}_{12}\text{H}_{12}]^{2-}$

$\text{AlH}_3$ ,  $\text{LiAlH}_4$

Nanostructured materials:

---  $\text{LiBH}_4/\text{MgH}_2$  in aerogel

**And also working on newly discovered materials....**

Mixtures of  $\text{NH}_2/\text{BH}_4$  compounds

Mixtures of  $\text{AlH}_4/\text{BH}_4$  compounds

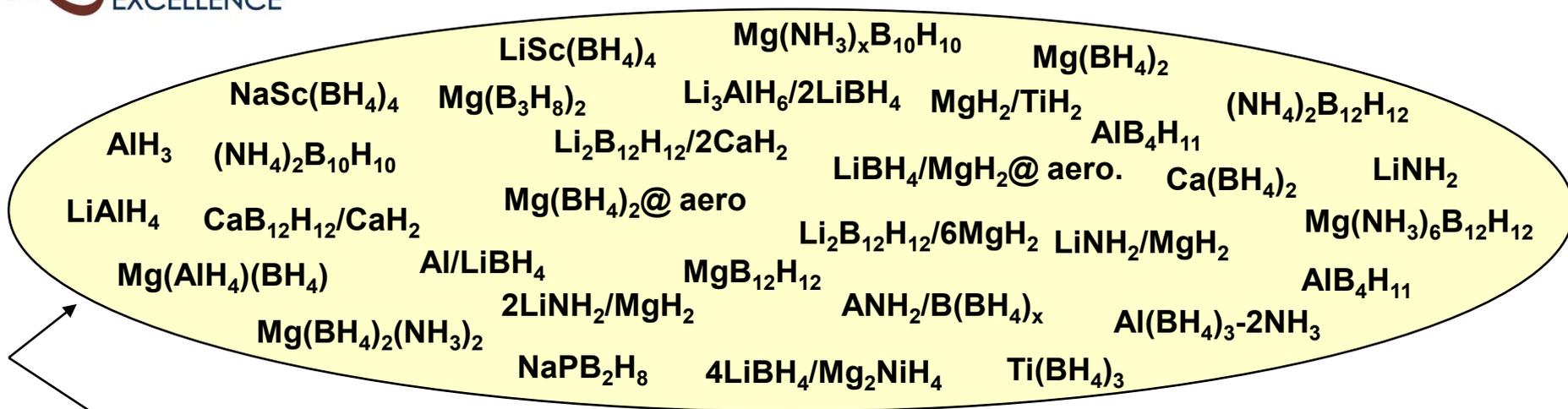
$\text{NH}_3$  Adducts of Borohydrides

$\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$

$\text{MgH}_2/\text{TiH}_2$

P-based compounds:  $\text{NaPB}_2\text{H}_8$

# Final Year Downselection Path



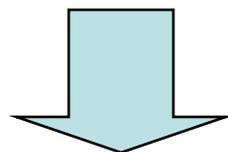
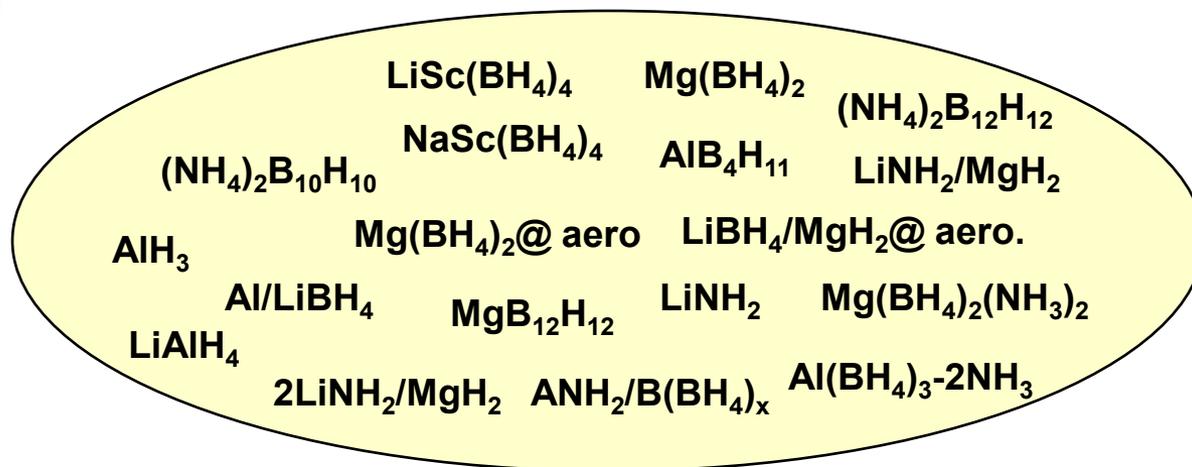
**Materials examined in  
final year of the MHCoe**

**11 More Downselects  
(Removing from Study)**

$4\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  (low wt. %)  
 $\text{Mg}(\text{B}_3\text{H}_8)_2$  (too unstable)  
 $\text{Li}_2\text{B}_{12}\text{H}_{12}/2\text{CaH}_2$  (too high  $T_{\text{des}}$ )  
 $\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$  ( $\text{NH}_3$  release)  
 $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$  ( $\text{NH}_3$  release)

$\text{CaB}_{12}\text{H}_{12}/\text{CaH}_2$  (not reversible)  
 $\text{Li}_2\text{B}_{12}\text{H}_{12}/6\text{MgH}_2$  (too high  $T_{\text{des}}$ )  
 $\text{Ti}(\text{BH}_4)_3$  (not reversible)  
 $\text{Li}_3\text{AlH}_6/2\text{LiBH}_4$  (too high  $T_{\text{des}}$ )  
 $\text{Li}(\text{NH}_3)_x\text{B}_{12}\text{H}_{12}$  ( $\text{NH}_3$  release)  
 $\text{NaBP}_2\text{H}_8$  (not reversible)

# Leaving Us With....



recommendations

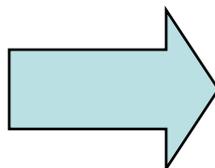
## 3 High-Level MHCoE Goals For The Final Project Year: Focus for the Future

1. Identify a near-term material for collaboration and subsystem testing in the HSECoE ✓ **Recommended  $2\text{LiNH}_2/\text{MgH}_2$ ,  $\text{AlH}_3$ ,  $\text{LiAlH}_4$**
2. Identify medium-term materials that need more R&D, but would also be of eventual interest for HSECoE examination and subsystem testing  
 ✓ **Recommend  $\text{LiNH}_2/\text{MgH}_2$ , 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 <sub>2</sub> /kg-system	4.5%
System Vol.: gH <sub>2</sub> /L system	28
System Fill Time (5kg H <sub>2</sub> ): mins	4.2
Operational Cycle Life: cycles	1000
Hydrogen Purity	99.97% (dry)

Convert to inferred materials properties for making Spider Charts

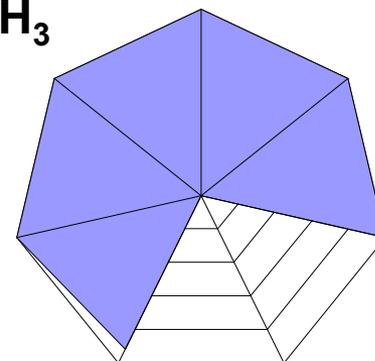
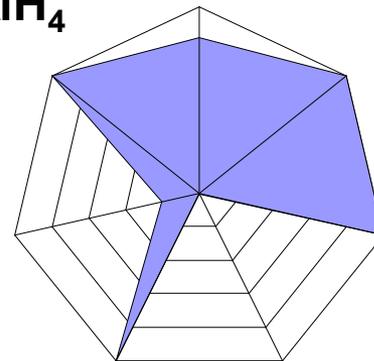
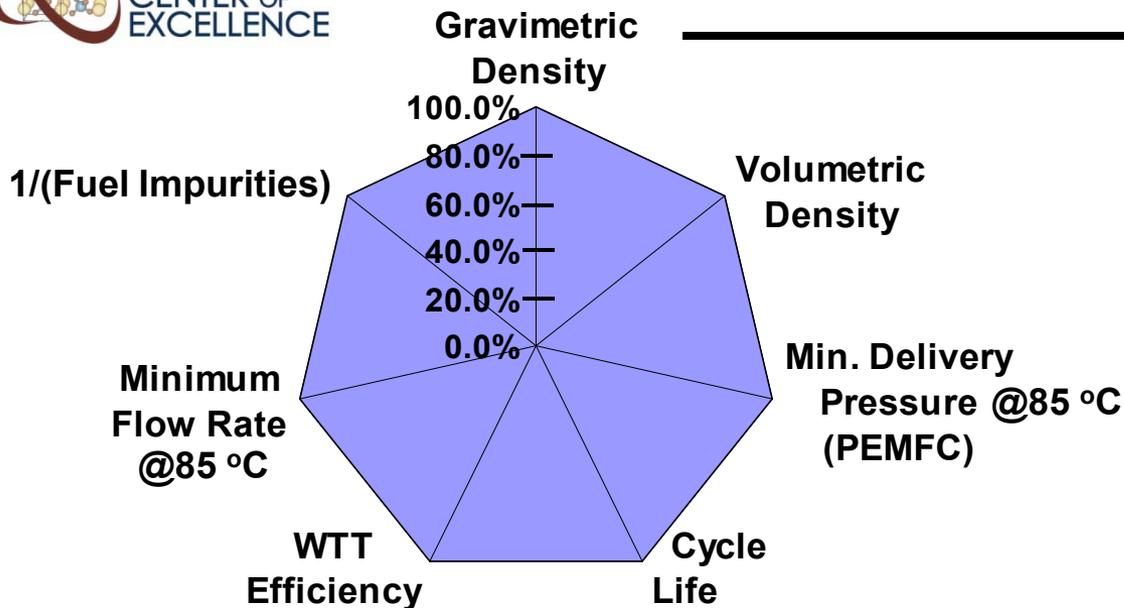


Storage Material Parameter	"Goal"
Material Grav.: kgH <sub>2</sub> /kg-material	9.0%*
System Vol.: gH <sub>2</sub> /L material	56**
1/(Fill Time) Min <sup>-1</sup>	0.238
Operational Cycle Life: cycles	1000
1/(Fuel Impurities) ppm <sup>-1</sup>	0.01

\* Assumes 50% system gravimetric penalty

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

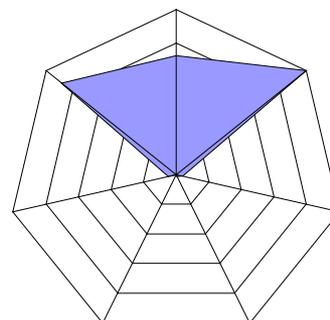
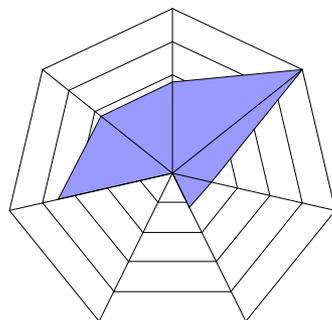
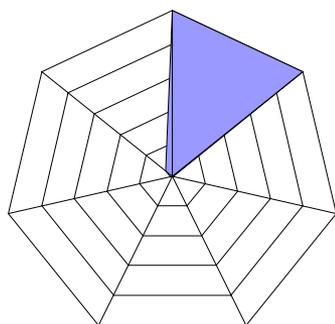
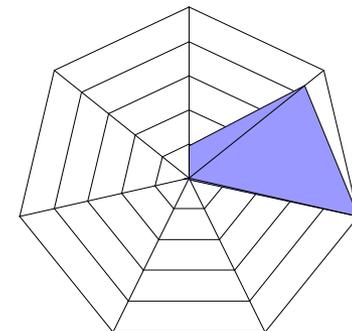
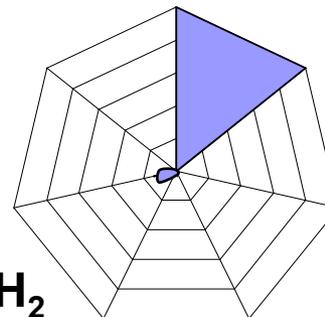
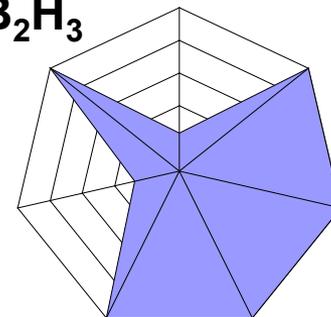
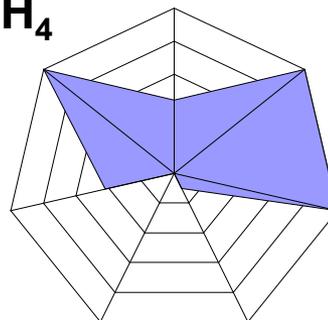
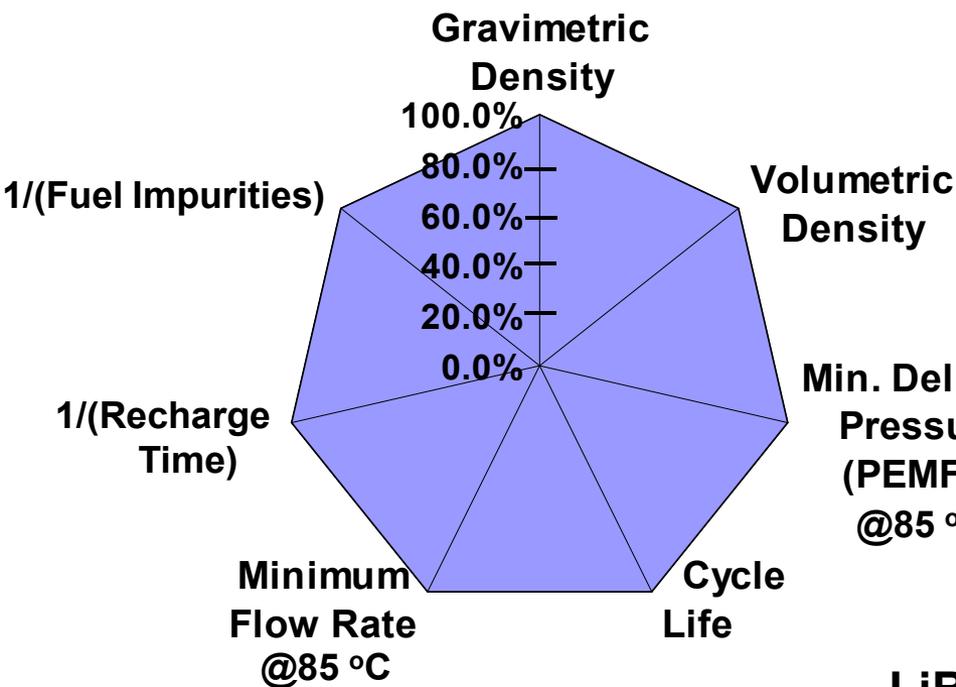
# “Off-board” Reversible MH



Materials “Goals”		$\text{LiAlH}_4$	$\text{AlH}_3$
Gravimetric Density (wt. %)	9%	7.5%	9.8%
Volumetric Density ( $\text{gH}_2/\text{L}$ )	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 ( $\text{gH}_2/\text{sec}$ ) @ 85 °C	1	0.2	1
1/(Fuel Impurities = 100 ppm) $\text{ppm}^{-1}$	0.01	$\infty$	$\infty$

$\text{LiAlH}_4$  and  $\text{AlH}_3$  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



H<sub>2</sub> capacity (wt. %) was improved with high volumetric density and good H<sub>2</sub> purity. However, the “on-board” materials have poor kinetics at 85 °C, and robust cycling has not been shown

# “On-Board” Reversible Chart Input

2010 Materials “Goals”		$\text{LiBH}_4/\text{MgH}_2$	$\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$	$2\text{LiNH}_2/\text{MgH}_2$	$\text{Mg}(\text{BH}_4)_2$	$\text{LiNH}_2/\text{MgH}_2$	$\text{AB}_2\text{H}_3$ A = Ti, Zr B = V, Cr, Mn	$\text{NaAlH}_4$
<b>Gravimetric Density (wt. %)</b>	9%	10%	1.7%	5%	11%	6.5%	2.1%	4%
<b>Volumetric Density (gH<sub>2</sub>/L)</b>	56	95	48	70	147	107	110	80
<b>Min. Delivery Pressure @ 85 °C (PEMFC) (bar)</b>	5	0.022	10	1.2	0.035	0.2	70	0
<b>Cycle Life</b>	1000	10	10	235	2	10	1000	100
<b>Minimum Flow Rate (gH<sub>2</sub>/sec) @ 85 °C</b>	1	~0	~0	~0	~0	~0	1.5	~0
<b>1/(Recharge Time = 4.2 min), min<sup>-1</sup></b>	0.238	0.0333	0.0083	0.1667	0.0028	0.0110	0.0660	0.1
<b>1/(Fuel Impurities = 100 ppm), ppm<sup>-1</sup></b>	0.010	unknown	unknown	0.0056	0.0005	0.0088	∞	∞

## Thermodynamics:

We really need  $\Delta H$  to be  $\sim 30$  kJ/mole, but the materials we have been finding generally have  $\Delta H \sim 40 - 80$  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

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***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  $\text{LiNH}_2/\text{MgH}_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{AlH}_3$ , etc.). That level of collaboration is highly unlikely without the funding and structure of a Center.**

Were Hard Problems Solved? -- YES, but the  $\text{H}_2$  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  $\text{H}_2$  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