Advanced, High-Capacity Reversible Metal Hydrides

Craig M. Jensen, University of Hawaii
Sean McGrady, University of New Brunswick

US DOE Annual Merit Review Meeting

May 17, 2012

ST 031

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start Date: March 2005
- End Date: September 2012
- 99% complete

Budget

- Total project funding: $2,945,058
  - DOE share: $2,335,173
  - Contractor share: $609,885
- Funding for FY11: no cost extension only.
- Funding for FY12: no cost extension only.

Barriers

A. System Weight and Volume
E. Charging/Discharging Rates
F. Thermal management
P. Lack of understanding of hydrogen chemisorption and physisorption

Partners

- E. Akiba, K. Sakaki; AIST, Japan
- C. Ahn, S.J. Hwang; California Institute of Technology
- T. Autrey, Pacific Northwest National Lab
- R. Cantelli; University of Rome
- M Conradi, Washington University
- B. Hauback, Institute for Energy Technology, Norway
- H. Hagmann, R. Cerny; University of Geneva
- T. Jensen, Aarhus University, Denmark
- L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC
- R. Kuboto; KEK
- R. Kumar; University of Nevada at Las Vegas
- S. McGrady; University of New Brunswick
- S. Orimo, Y. Nakamori; Tohoku University, Japan
- I. Robertson; University of Illinois
- E. Ronnebro; SNL, PNNL
- T. Udovic; NIST
- J. Vajo, P. Liu; HRL
- A.Zuettel, E. Callinin, EMPA

Objectives and Relevance

Development of a new class of reversible complexes that has the potential to meet the DOE kinetic and system gravimetric storage capacity targets.

Investigations during FY12 focused on:

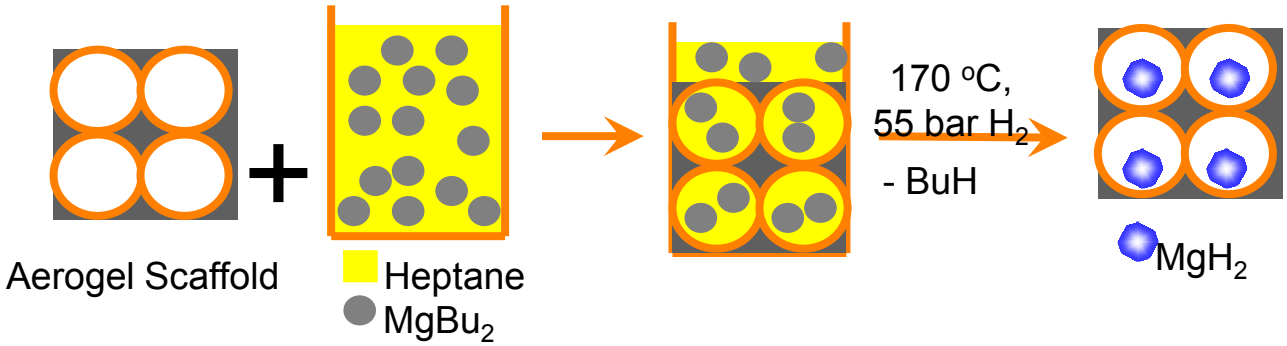
- Reversible dehydrogenation of $MgBH_4$ (14 wt % theoretical, >12 wt % **demonstrated** reversible capacity)

Approach

Nano-confined Al and Mg Compounds in Carbon Aerogels (no activity in FY12)

Collaboration with HRL

- Low temperature homogenous organometallic approach to incorporation of Al and Mg based hydrides into carbon aerogels results in unprecedented high loadings without degradation of nano-porous scaffold that occurs with melt intercalation.



- Determine the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of Al and Mg based hydrides.

Approach

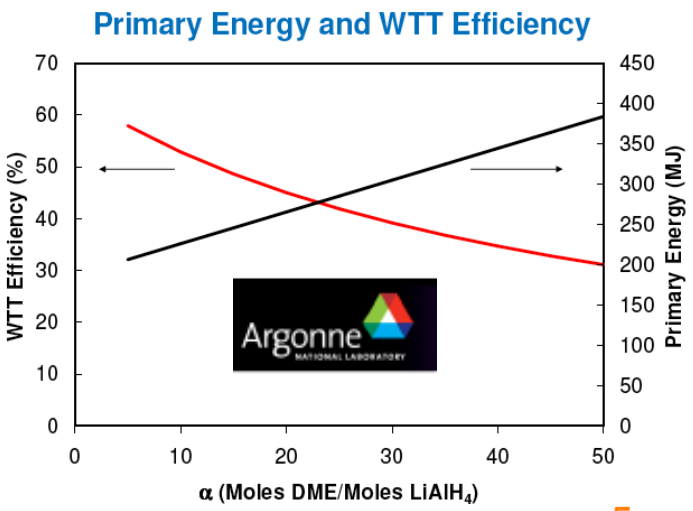
Re-hydrogenation in Non-conventional Solvents (no activity in FY12)

Collaboration with U. of New Brunswick

- Explore hydrogenation of Al to AlH_3; Al/MgH_2 to $Mg(AlH_4)_2$; and LiH/Al to $LiAlH_4$ in supercritical fluids and liquefied gases such as dimethyl ether which can form adducts during synthesis but are easily eliminated due to their high volatility.

$$LiH + Al[Ti] \xrightarrow[25\ ^{\circ}C\ 24\ h]{Me_2O/H_2\ 100\ bar} LiAlH_4[Ti]$$

- Solvent vents immediately with excess H_2
- Fully charged Ti-doped $LiAlH_4$ obtained
- Very low levels of Ti can be used (~500 ppm)

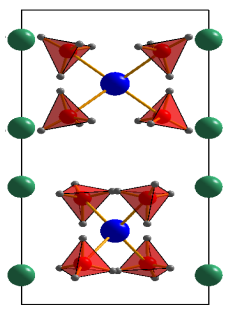


Approach

Mixed Metal Borohydrides

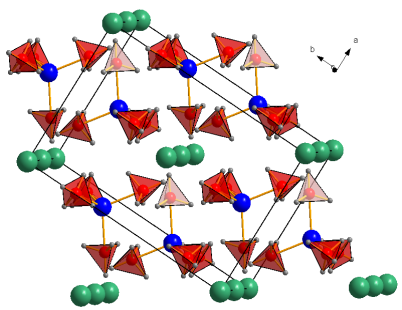
Collaboration with IFE, Aarhus U., and U. of Geneva

$LiSc(BH_4)_4$



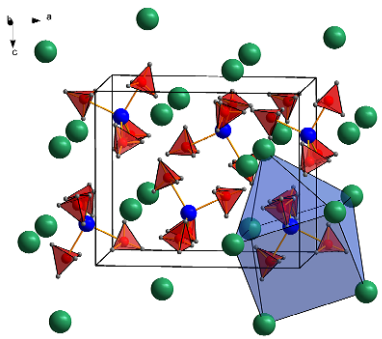
H. Hagemann, M. Longhini, J.W. Kaminski, T.A. Wesolowski, R. Černý, N. Penin, M.H. Sørby, B.C. Hauback, G. Severa and C.M. Jensen J. Phys. Chem B. **2008**, *112*, 7551

$NaSc(BH_4)_4$



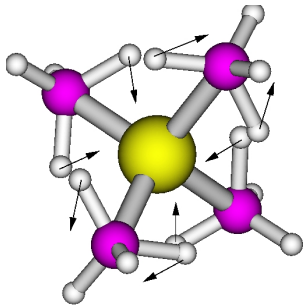
R. Černy, G. Severa, D. Ravnsbaek, Y. Filinchuk, V. d'Anna, H. Hagemann, Y. Cerenius, C.M. Jensen, T.R. Jensen *J. Phys. Chem. C* **2010**, *114*, 1357.

$KSc(BH_4)_4$



R. Cerny, D.B. Ravnsbaek , G. Severa, Y. Filinchuk, V. d'Anna , H. Hagemann, D. Haase, C.M. Jensen, T.R. Jensen; *J. Phys. Chem. C.* **2010**, , *114*, 19540.

$Na_2Mn(BH_4)_4$



G. Severa, H. Hagemann, M. Longhini, J.W.Kaminski, T.A. Wesolowski, C.M. Jensen; *J. Phys. Chem. C.* **2010**, *114,* 15516.

Approach

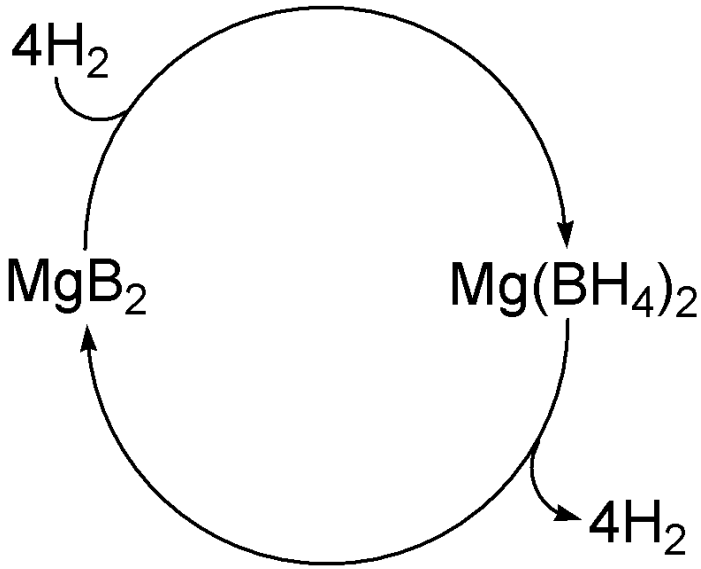
Reversible Dehydrogenation of $Mg(BH_4)_2$

Collaboration with Sandia and Pacific Northwest National Laboratories

Demonstration of Cycling of 12% wt H

$$MgB_2 \xrightarrow[400\ ^\circ C]{900\ atm\ H_2} Mg(BH_4)_2$$

XRD, IR, MAS ^{11}B NMR



Rönnebro, Jensen, and Severa US patent application U.S. Patent 12/553,633.

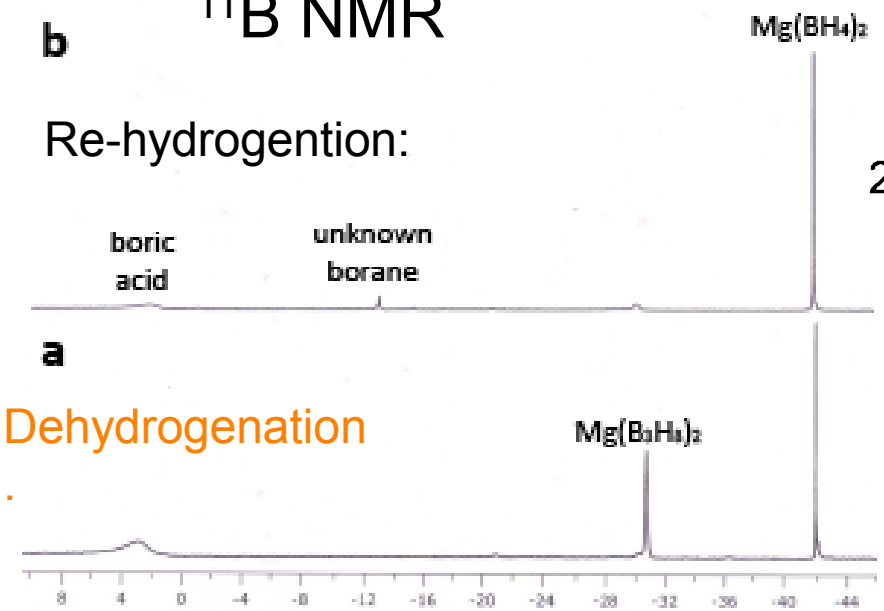
G. Severa, E. Rönnebro, C.M.Jensen; *Chemical Commun.* **2010**, *46,* 421.

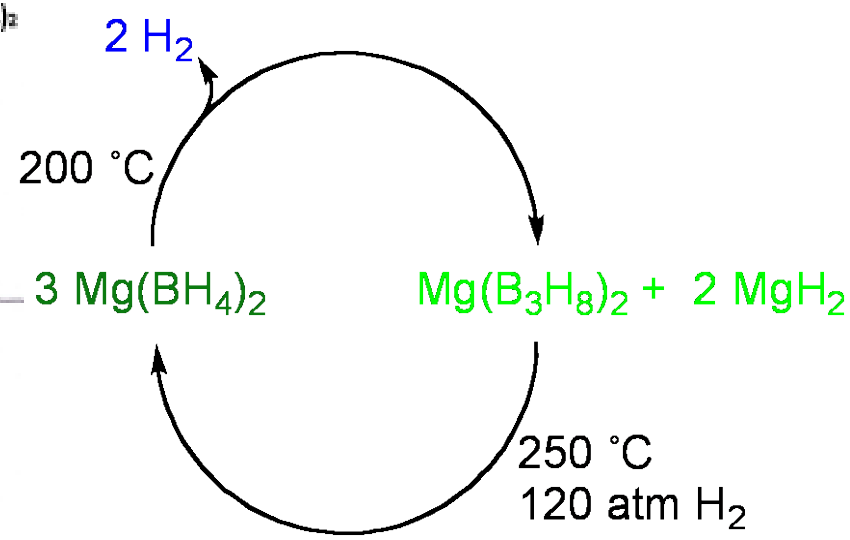
Accomplishments (FY11)

Hydrogen Cycling of $Mg(BH_4)_2$ Under Mild Conditions

First example of the **reversible**, solid state dehydrogenation of a borohydride at temperatures below 350 ˚C.

^{11}B NMR





M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

FY12 Accomplishments

Independent Synthesis $Mg(B_3H_8)_2$

$$BH_3THF + MgHg\ amalgam \xrightarrow{25\ ^\circ C} Mg(B_3H_8)_2\ \ 95\%\ yield$$

FY12 Accomplishments

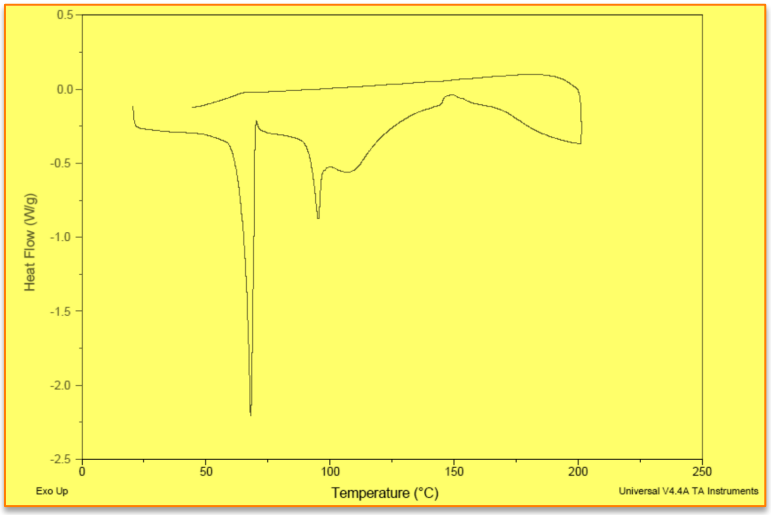
Hydrogenation Reaction

$$2\ MgH_2 + Mg(B_3H_8)_2 \xrightarrow[100\ ^\circ C,\ 3\ h]{5\ atm\ H_2} 3\ Mg(BH_4)_2$$

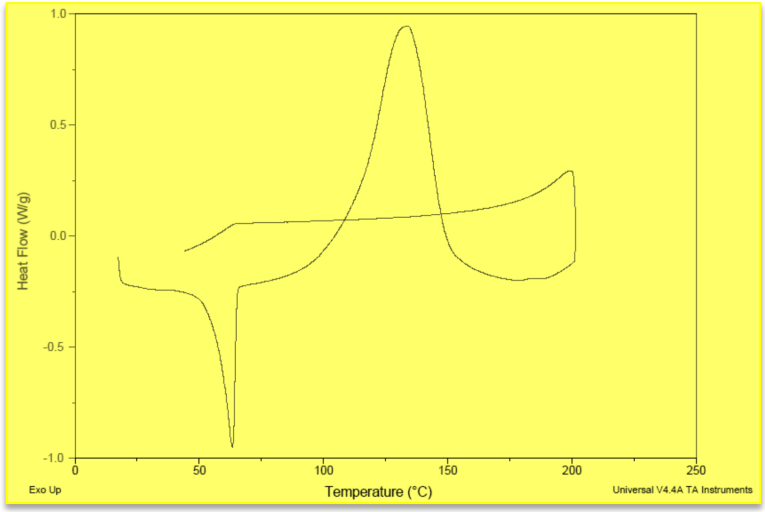
- MgH_2 must be activated by ball milling
- $MgB_{12}H_{12}$ is formed if reaction mixture contains <2 equivalents of MgH_2. → Condensation to higher boranes **does not require** metal hydride.
- MAS ^{11}B NMR shows that hydrogenation of $Mg(B_3H_8)_2$ with 4 equivalents of LiH or NaH also gives $[BH_4]^-$.

FY12 Accomplishments

DSC Studies $Mg(B_3H_8)_2$ and $Mg(B_3H_8)_2$ /MgH_2 Collaboration with Tohoku U.



$Mg(B_3H_8)_2$ alone shows a strong exotherm due to melting at 60 ˚C. MAS ^{11}B NMR confirms $[B_3H_8]^-$ still intact.



$Mg(B_3H_8)_2$/ 2 MgH_2 under 50 atm H_2 shows that after melting a strong endothermic peak occurs at ~130°C. ^{11}B NMR a shows at this point B is predominantly BH_4^-

FY12 Accomplishments

Diborane emission from $MSc(BH_4)_4$ (M = Li,Na,K) – collaboration with Callini and Zuettel EMPA

- Discrepancies in the literature regarding diborane resulting from thermal decomposition of $MSc(BH_4)_4$ (M = Li,Na,K).
- EMPA equipment for IR detection and quantification of diborane emission from borohydrides.
- Results indicate thermal decomposition proceeds via:

$$MSc(BH_4)_4 \longrightarrow MBH_4 + Sc(BH_4)_3$$

$$Sc(BH_4)_3 \longrightarrow x\ B_2H_6 + y\ H_2 + Sc(?)$$

Collaborations

FY12

T. Autrey; PNNL (Government): Character by solution NMR analysis
S. Orimo; Tohuku University (Academic): Characterization by DSC and XRD.
A. Zuettel, E. Callini, EMPA (Academic), Detection and Quantification of diborane by IR

Project

C. Ahn; California Institute of Technology (Academic): Characterization by TEM imaging
E. Akiba, K. Sakaki; AIST, Tsukuba (Government): Characterization by positron annihilation.
R. Cantelli; University of Rome (Academic): Characterization by anelastic spectroscopy.
H. Hagmann, R. Cerny; University of Geneva (Academic): Characterization by IR and Raman Spectroscopy and XRD.
B. Hauback, M. Sorby; Institute for Energy Technology (Government, Norway): Characterization by Synchrotron X-ray and Neutron Diffraction.
S-J. Hwang; R. Bowman California Institute of Technology, JPL (Academic, Government): Characterization by solid state NMR spectroscopy.
T. Jensen, Aahus University, Denmark (Academic); Characterization by XRD.

Collaborations

Project (continued)

L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC (Industrial): Characterization by XRD and mass spectroscopy.

R. Kuboto; KEK, Tsukbua (Government): characterization by muon spin resonance.

R. Kumar; University of Nevada at Las Vegas (Academic) high pressure neutron diffraction studies.

I. Robertson; University of Illinois (Academic): Characterization by TEM.

E. Ronnebro; SNL (now with PNNL), Government: High pressure studies.

S. Srinivasan; University of South Florida (Academic): Characterization by DSC.

V, Stavila; Sanida National Laboratory (Government); high pressure hydrogenation.

X. Tang: UTRC (Industrial); Confinement in alternative scafolds.

T. Udovic; NIST (Government) Characterization by Inelastic neutron scattering.

J. Vajo, P. Liu; HRL (Industrial): Characterization by PCT.

Future Work

Borohydrides

- Adjustment of conditions to maximize trade off between cycling capacity and temperature/pressures required for reversible dehydrogenation of $Mg(BH_4)_2$.

Hydrogenation in Non-conventional Solvents

- Further evaluation of WTT efficiency of the DME/$LiAlH_4$ system to be examined in collaboration with Argonne National Lab.

FY12 Summary

- $Mg(B_3H_8)_2$/2 MgH_2 undergoes rapid hydrogenation to $Mg(BH_4)_2$ at **100 ˚C** under **50 atm** of H_2. The rapid kinetics are at least in part due to the fact that $Mg(B_3H_8)_2$ is in the liquid state above 60 ˚C. This finding points to the possibility of finding mild, PEM fuel relevant conditions for the reversible dehydrogenation of borohydrides that avoid the thermodynamic sinks such as $[B_{12}H_{12}\}^{2-}$.

- The thermal decompostion of $MSc(BH_4)_4$ (M= Li, Na, and K) gives rise to MBH_4 and $Sc(BH_4)_3$. The neutral Sc borohydride is unstable and decomposes to produce diborane. Thus $MSc(BH_4)_4$ will not undergo reversible dehydrogenation.

Supplemental Slides

Back-up Technical Slide 1

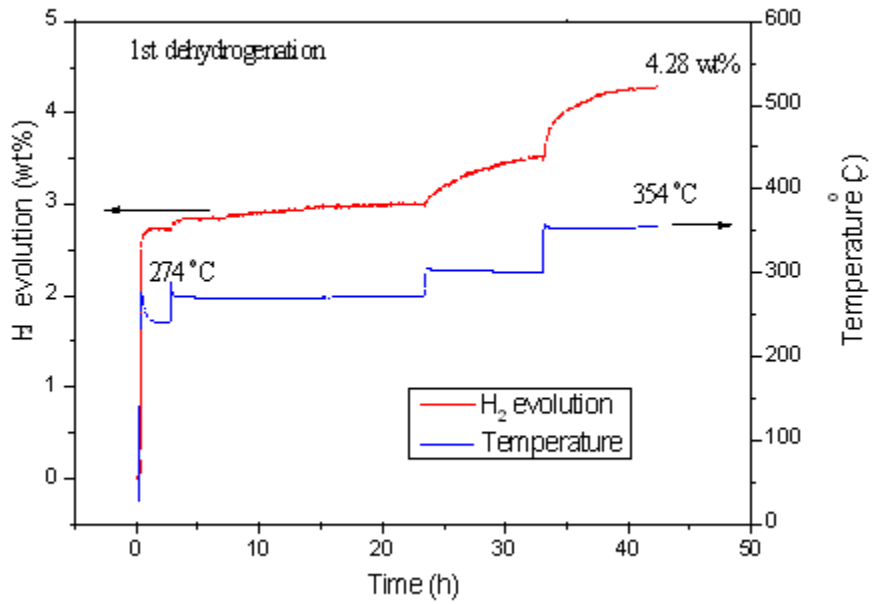
Previous Results

- High, (9-16 wt % confirmed by TEM, EDS, and XRD) MgH_2 loadings of carbon aerogel without host degradation are obtained using the organometallic method.
- The rate of dehydrogenation at 252 ˚C is >5 times faster than the initial rate found for ball milled MgH_2 and comparable to those found for nano-confined MgH_2 in carbon aerogels by alternative methods at HRL. The rate remains the same over 4 cycles of dehyrogenation-rehydrogenation.

HRL LABORATORIES

Back-up Technical Slide 2

Improved kinetics observed for nano-confined $Mg(BH_4)_2$



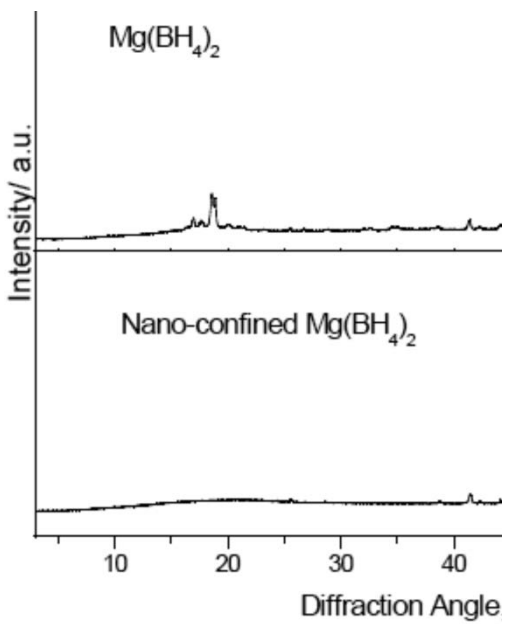
Hydrogen is evolved at the rate of 0.1 wt%/min at 270 ˚C during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting MgB_2 under 120 atm at 220 ˚C gives rise to $Mg(B_{12}H_{12})_2$ as occurs with bulk $Mg(BH_4)_2$.

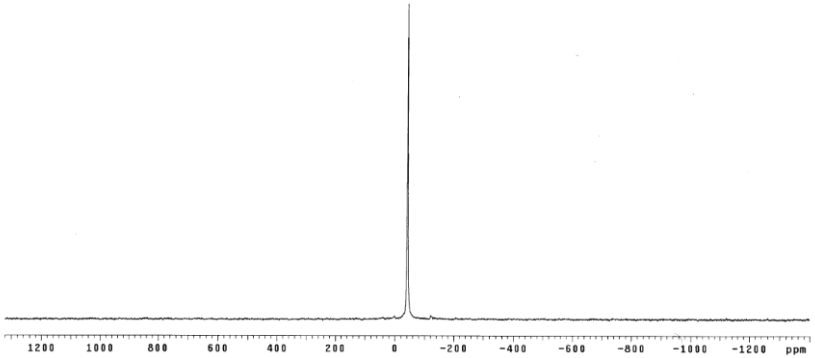
Back-up Technical Slide 3

Synthesis of nano-confined $Mg(BH_4)_2$

- Hydride incorporated into carbon aerogel through immersion in molten $Mg(BH_4)_2 \cdot O(C_2H_5)_2$. Diethyl ether adduct removed at 220 ˚C en vacuo.
- 60 wt% of $Mg(BH_4)_2$ is incorporated into aerogel.

Broaden of XRD peaks indicates incorporation into aerogel.





MAS 11B NMR spectrum of the hydride incorporated aerogel verifies that $Mg(BH_4)_2$ is the only boron containing species present in the aerogel.

Back-up Technical Slide 4

BACKGROUND

- Like sodium alanate, stepwise dehydrogenation, BUT first step is exothermic.

  Step 1: $3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$ $\Delta H = -30$ kJ

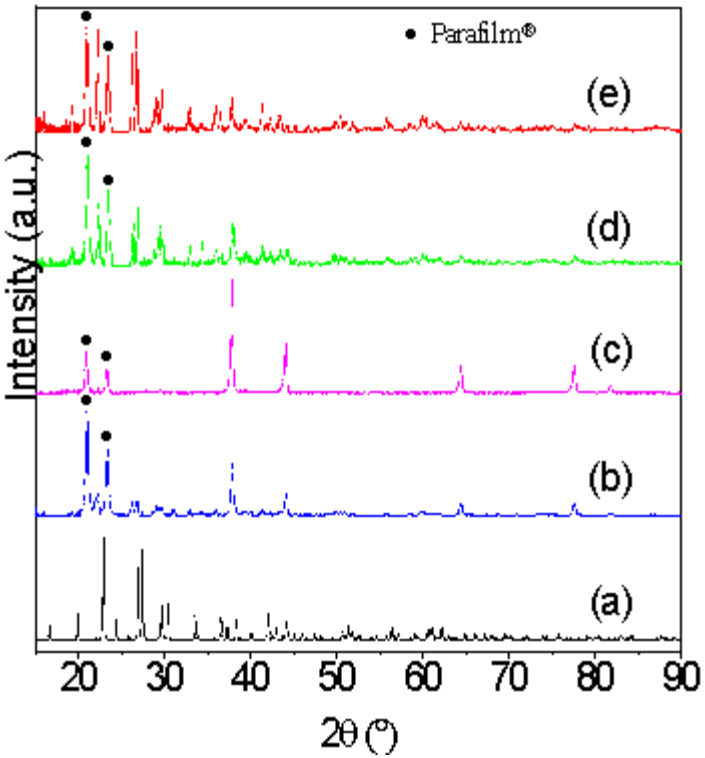
  Step 2: $Li_3AlH_6 \rightarrow 3LiH + Al + 1.5H_2$ $\Delta H = 38$ kJ
- Together steps 1 and 2 provide ~7.9 wt %H.
- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P).
- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle.
- Graetz (2008) – reversible in THF (low T and P) with Ti catalyst.
- THF removal requires heating to 60 ºC for 6 h.Incompatible with Ti catalyst since dehydrogenation occurs at the temperature required for removal of THF.

Back-up Technical Slide 5

Using liquid dimethyl ether as solvent eliminates adduct removal issues

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

- Solvent vents immediately with H_2
- Fully charged Ti-doped $LiAlH_4$ obtained
- Very low levels of Ti can be used (~500 ppm)



XRD patterns of $LiAlH_4$ samples: (a) ICDD ref; (b) ball milled (2.0 mol% $TiCl_3$); (c) fully de-H (0.2 mol% $TiCl_3$); (d) re-H (2.0 mol% $TiCl_3$); (e) re-H (0.2 mol% $TiCl_3$).

UNB
UNIVERSITY OF NEW BRUNSWICK

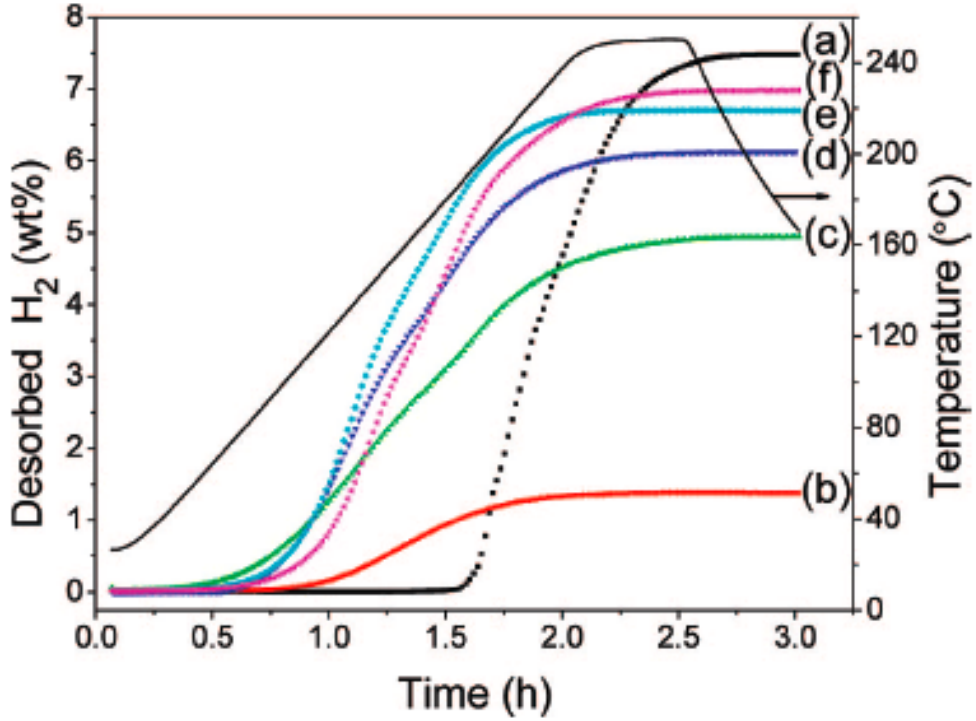
G.S. McGrady and C.M. Jensen U.S. Patent Application 60/945,650.

Back-up Technical Slide 6

H_2 Desorption from Ti-Doped $LiAlH_4$

- 0.5-0.2 mol% Ti optimal
- ~7 wt% H at 80-180 °C
- Excellent kinetics

Xi. Liu, G.S. McGrady, H. W. Langmi, C.M. Jensen; *J. Am. Chem. Soc.* **2009**, 131, 5032.



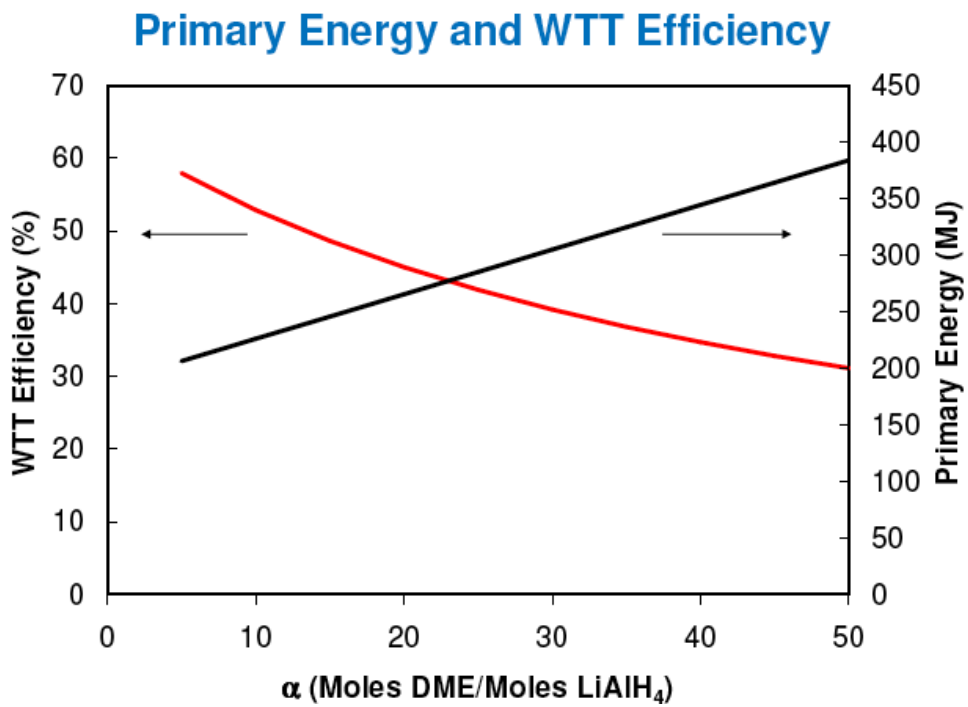
TPD plots for $LiAlH_4$ samples: (a) as-received; (b) milled with 2.0 mol% $TiCl_3$; (c) re-H (2.0 mol% $TiCl_3$); (d) re-H (1.0 mol% $TiCl_3$); (e) re-H(0.5 mol% $TiCl_3$); and (f) re-H (0.2 mol% $TiCl_3$).

UNB
UNIVERSITY OF NEW BRUNSWICK

Back-up Technical Slide 7

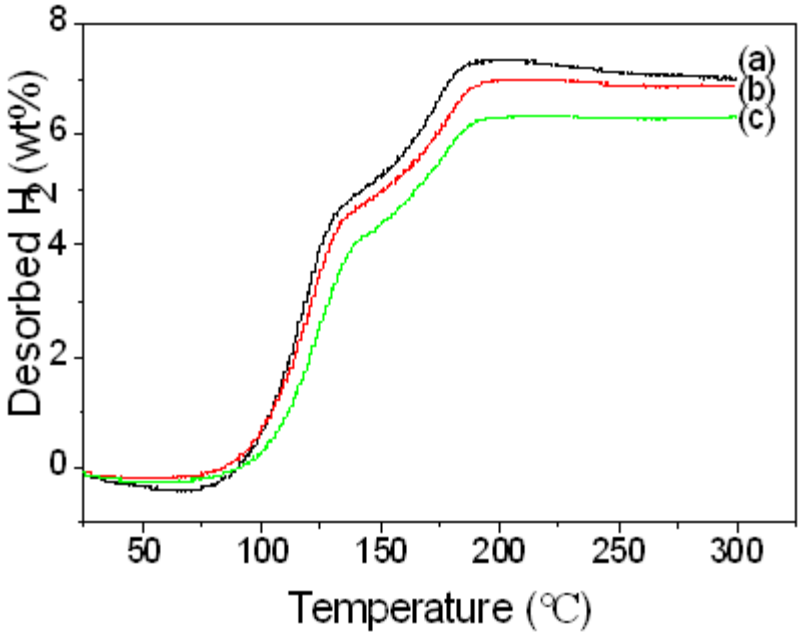
WTT energy efficiency approach 70% US DOE target for off-board recharging!

- Energy for compression of Me_2O and H_2 is ~ 1/5 that of H_2 production.
- High ~ 5M solubility of $LiAlH_4$ in Me_2O is the key in high efficiency.



Back-up Technical Slide 8

Ti-doped $LiAlH_4$ shows a drop in capacity over several cycles due to formation of Ti_xAl_{1-x} phase.



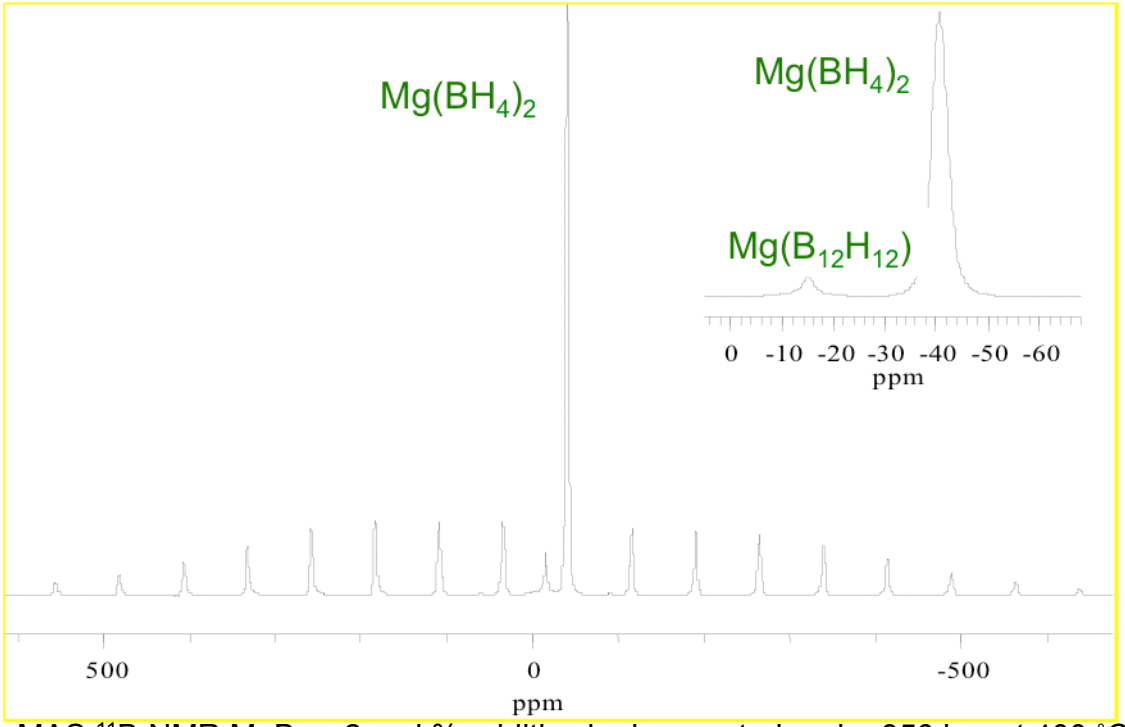
Cycle performance of hydrogenatedLiH/Al/$TiCl_3$ (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.

Back-up Technical Slide 9

MAS ^{11}B NMR

> XRD not generally used due the highly amorphous nature of boranes and bororhydrides.

> MAS ^{11}B NMR spectroscopy allows detection and differentiation of all the boron containing species that are present.



MAS ^{11}B NMR MgB_2 + 2 mol % additive hydrogenated under 950 bar at 400 ˚C

> Full Hydrogenation of MgB_2 beyond $MgB_{12}H_{12}$ to $Mg(BH_4)_2$

> One major boron containing product is observed.

> Chemical shift of -41 ppm: $Mg(BH_4)_2$.

> Minor signal observed for $MgB_{12}H_{12}$, at -24 ppm, represents < 5% of product mixture.

> Not clear if the catalyzed reaction pathway is the same as the uncatalyzed pathway.

Back-up Technical Slide 10

Identification and Quantification of Borane Products Produced from Higher From Dehydrogenation at Higher Temperatures - Collaboration with PNNL

Major products (mol %) formed in decomposition of $Mg(BH_4)_2$ determined from ^{11}B NMR

d/ppm	Species	300 1C	350 1C	400 1C
5	$B(OH)_4^-$	86	87	83
−15.2	$(B_{12}H_{12})^{2-}$	0.4	1.5	4.5
−29.2	$(B_{10}H_{10})^{2-}$	0.8	0.2	0.0
−30.3	$(B_3H_8)^-$	12.6	9.0	6.5

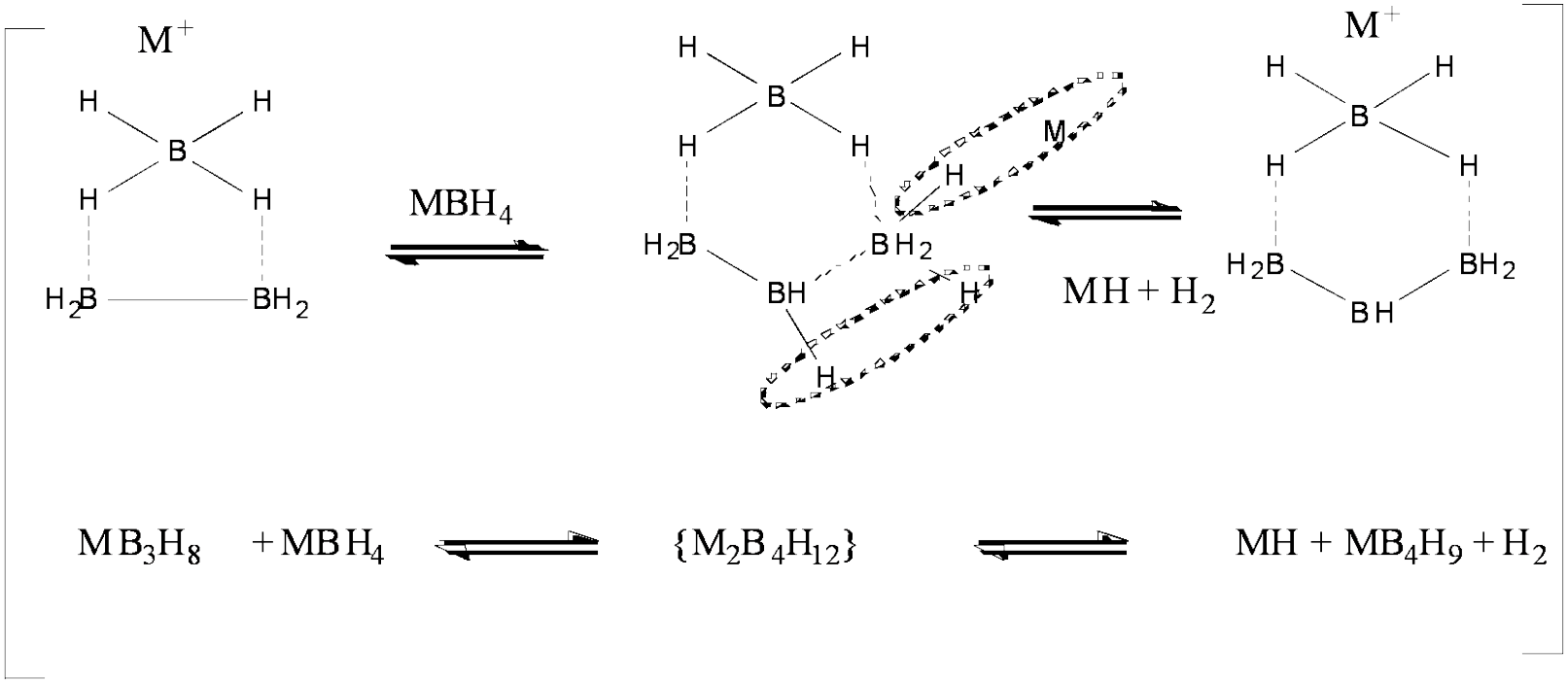
- Boric is acid is major species observed in the ^{11}B NMR.
  - ⇒ the major products are arachno- and nido- boranes.
- Concentration of the triborane increases lower temperatures.
  - ⇒ First step in the decomposition of $Mg(BH_4)_2$ involves the formation of $Mg(B_3H_8)_2$.

M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

Back-up Technical Slide 11

Mechanism of the Build-up of the Increasing Higher B_nH_{n+x} Species

Metal ion assisted BH condensation pathway



M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

Back-up Technical Slide 12

High Hydrogen Capacities
Low Dehydrogenation Temperatures

	wt% H theory	wt% H exp	T_D (˚C)	level of diborane
$LiSc(BH_4)_4$	14.6	3.5	175, 260	ppm
$NaSc(BH_4)_4$	12.8	1.0	170, 225	ppm
$KSc(BH_4)_4$	11.3	1.0	190, 240	ppm
$Na_2[Mn(BH_4)_4]$	6.9	2.9	120	50:1 H_2:B_2H_6 due to
$Mn(BH_4)_2$				contamination