

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 12, 2011



UNIVERSITY
of HAWAII®
MĀNOA



ST 031

Overview

Timeline

- Start Date: March 2005
- End Date: September 2011
- 98% complete

Budget

- Total project funding:
\$2,945,058
 - DOE share: \$2,335,173
 - Contractor share: \$609,885
- Funding obligated for FY10:
\$0
- Funding for FY11: 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

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.

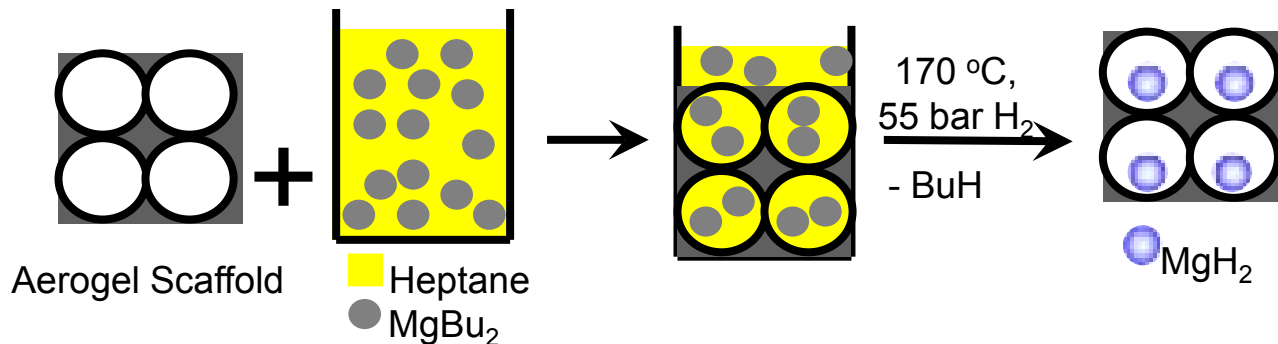
Investigations during FY11 focused on:

- Reversible dehydrogenation of MgBH_4 (14 wt % theoretical, >12 wt % **demonstrated** reversible capacity), $\text{LiSc}(\text{BH}_4)_4$ (14.7 wt %), $\text{NaSc}(\text{BH}_4)_4$ (12.8 wt %), and $\text{Na}_2\text{Mn}(\text{BH}_4)_4$ (6.9 wt %), at temperatures in the 100-220 °C temperature range.

Approach

Nano-confined Al and Mg Compounds in Carbon Aerogels (no further studies in FY11)

- 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

Group I and II Salts of Anionic Transition Metal Borohydride Complexes

- > Several potential improvements over neutral complexes:
 - Higher (9-13 wt %) hydrogen content than neutral TM borohydrides.
 - Ionic character reduces volatility and increases stability.
 - Very low levels of diborane are evolved during the dehydrogenation.
- > Altered thermodynamic stability might allow reversibility.

Mg(BH₄)₂

- > Mg(BH₄)₂ evolves **14.8 wt %** H₂ upon dehydrogenation.
- > $\Delta H_{\text{dehyd}} = 42 \text{ kJ/mol H}_2 \Rightarrow$ it should be possible to hydrogenate MgB₂ to Mg(BH₄)₂ at moderate temperatures and pressures.
- > Dehydrogenation has been found to be a multi-step process. Can reversible dehydrogenation of at least some steps be accomplished under milder conditions?

Approach

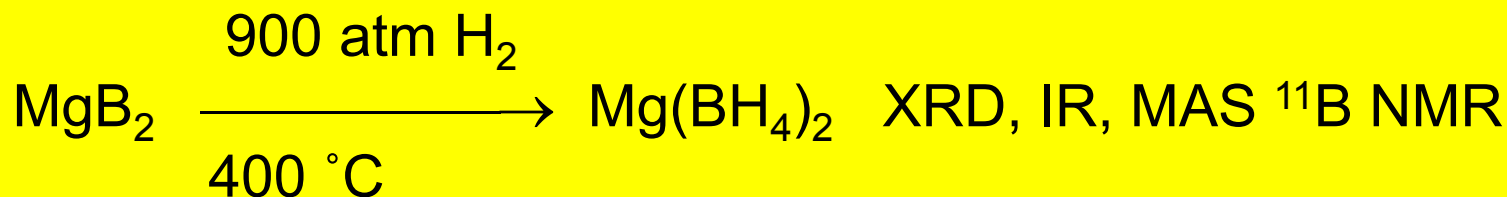
Re-hydrogenation in Non-conventional Solvents (no further studies in FY11)

- > Explore hydrogenation of Al to AlH_3 ; Al/MgH₂ to $\text{Mg}(\text{AlH}_4)_2$; 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.

Technical Accomplishments and Progress

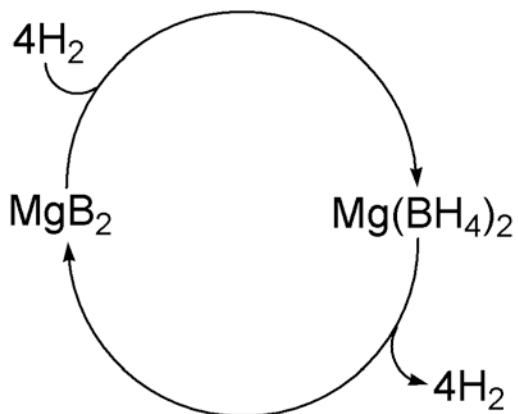
Studies by Orimo (Raman spectroscopy) and Hwang (NMR spectroscopy) indicated that incomplete re-hydrogenation is the result of the high kinetic stability of $\text{MgB}_{12}\text{H}_{12}$.

First Demonstration of Full Hydrogen Hydrogenation



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.

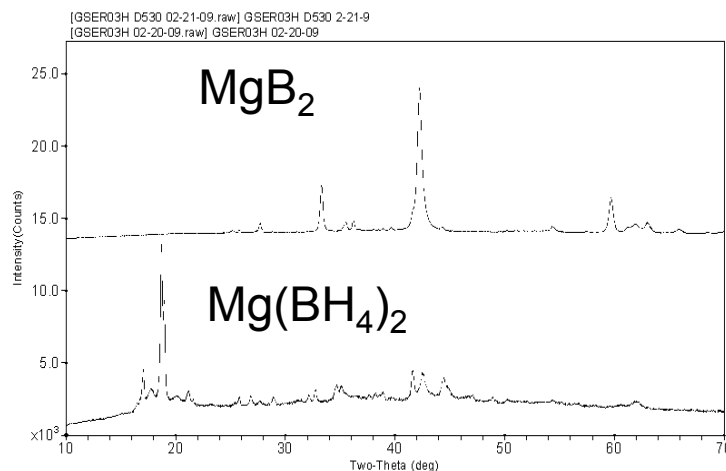
Technical Accomplishments and Progress



Cycling Studies

Cycling is mostly between MgB_2 and $\beta\text{-Mg}(\text{BH}_4)_2$. only minor amounts of MgO , MgB_2 , and $\text{MgB}_{12}\text{H}_{12}$ are observed.

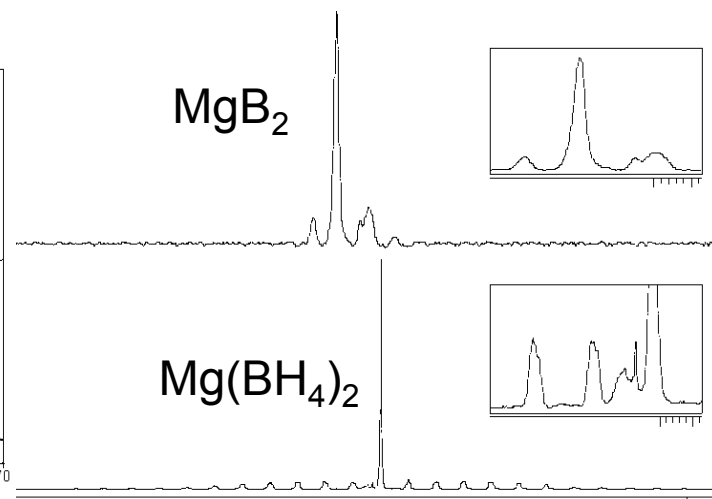
XRD



Dehydrogenation
at 530 °C.

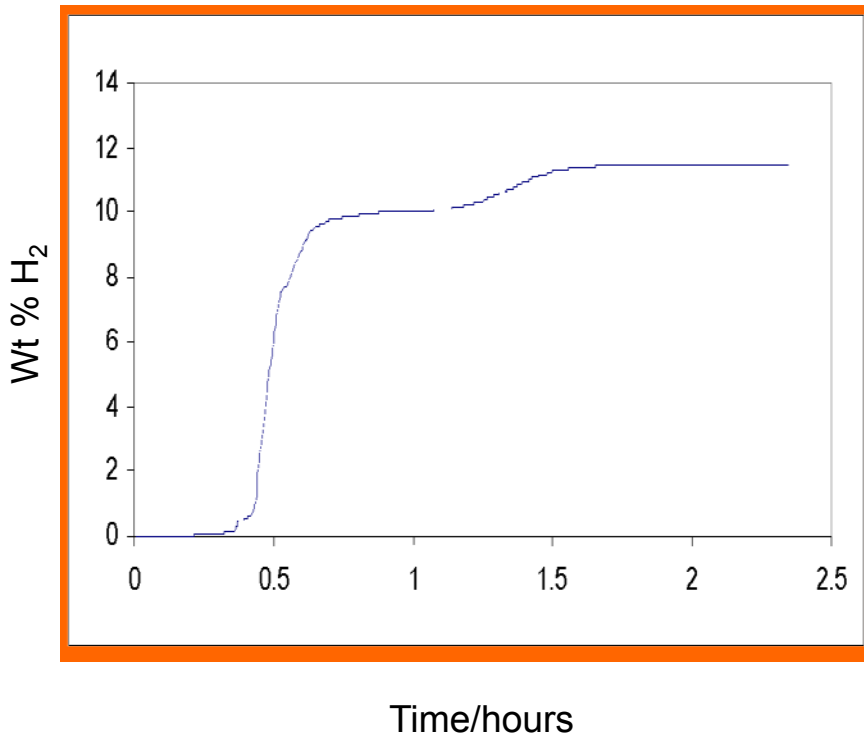
Hydrogenation
at 400 °C under
950 atm H_2 .

MAS ^{11}B NMR



Technical Accomplishments and Progress

12 wt % Cycling Capacity



12 wt % hydrogen was obtained upon dehydrogenation at 530 °C.

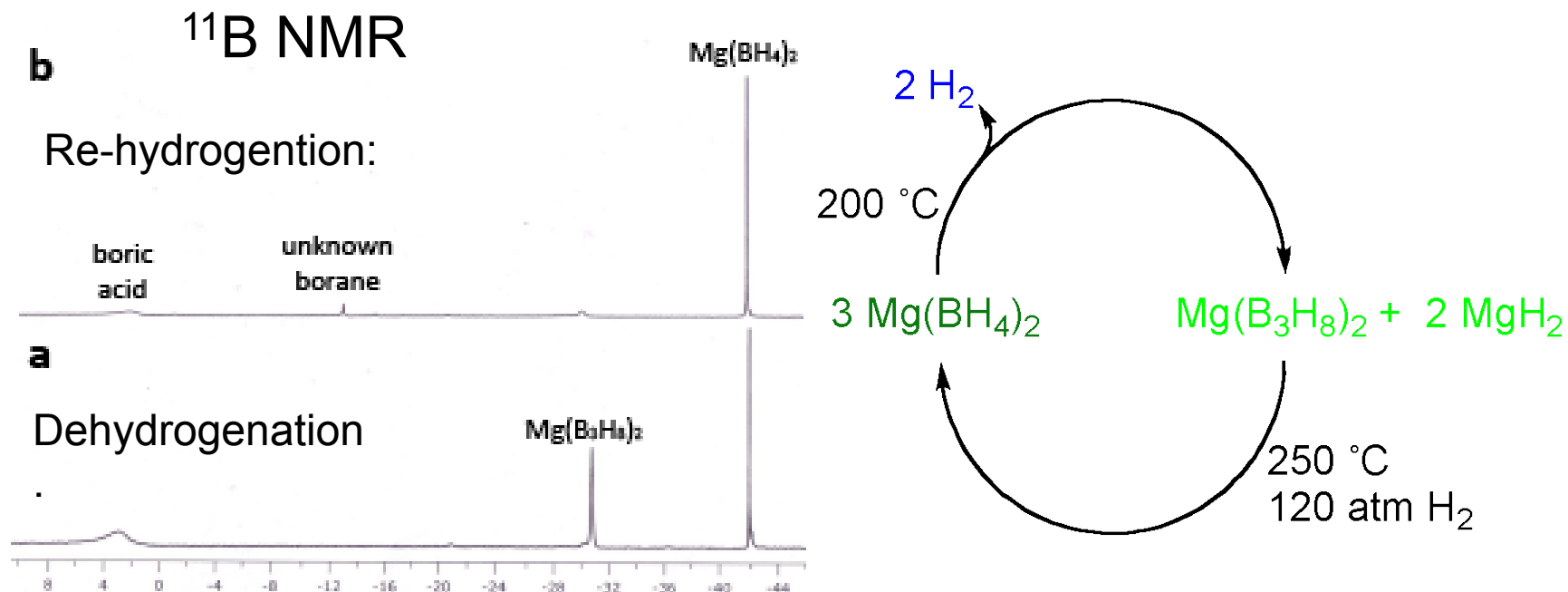
MgO arises during sampling, suggesting that 12.6 wt % hydrogen can be cycled.

Upon longer reaction times, higher levels of hydrogenation MgB₂ might lead to cycling of >14 wt % hydrogen.

Technical Accomplishments and Progress

Cycling Under Mild Conditions

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



Technical Accomplishments and Progress

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

Major products (mol %) formed in decomposition of $\text{Mg}(\text{BH}_4)_2$ determined from ^{11}B NMR

d/ppm	Species	300 1C	350 1C	400 1C
5	$\text{B}(\text{OH})_4^-$	86	87	83
-15.2	$(\text{B}_{12}\text{H}_{12})^{2-}$	0.4	1.5	4.5
-29.2	$(\text{B}_{10}\text{H}_{10})^{2-}$	0.8	0.2	0.0
-30.3	$(\text{B}_3\text{H}_8)^-$	12.6	9.0	6.5

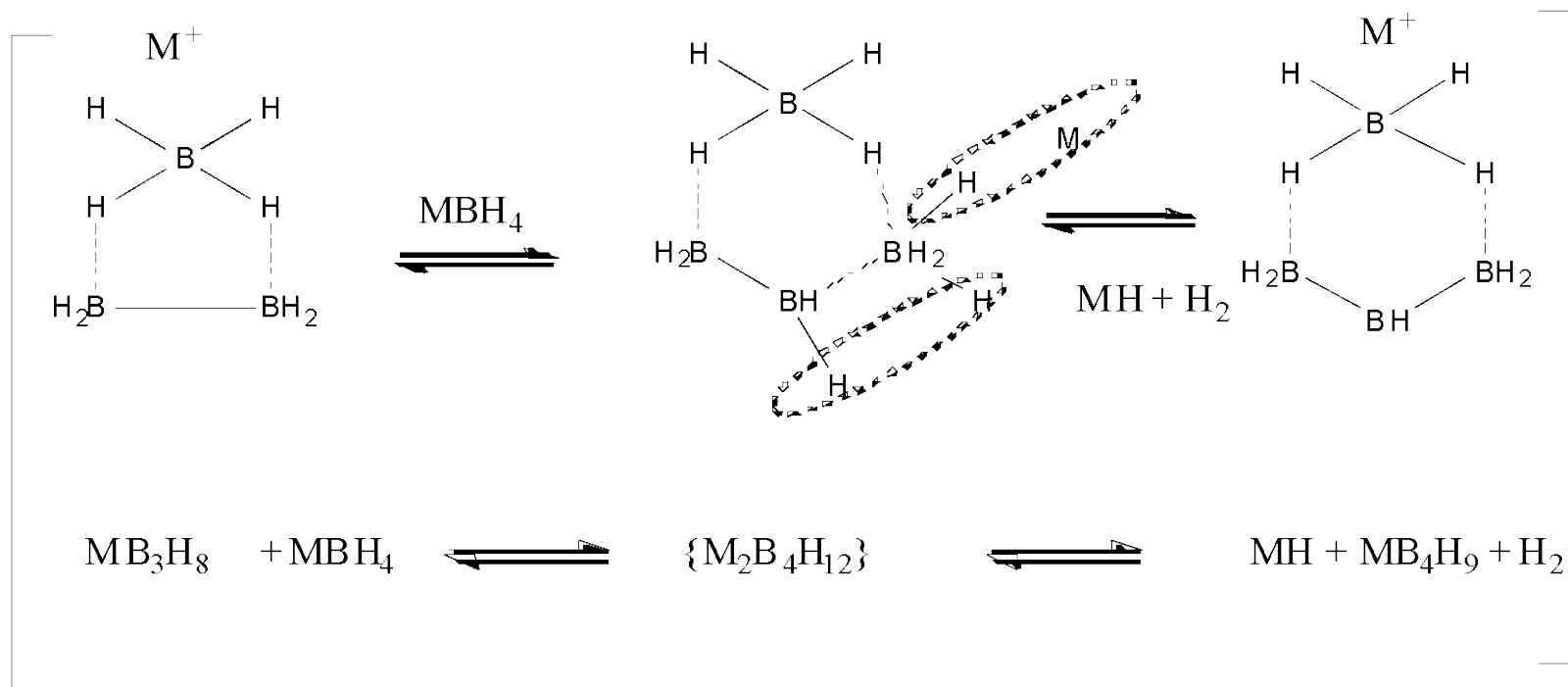
- Boric acid is major species observed in the ^{11}B NMR.
⇒ the major products are arachno- and nido- boranes.
- Concentration of the triborane increases lower temperatures.
⇒ First step in the decomposition of $\text{Mg}(\text{BH}_4)_2$ involves the formation of $\text{Mg}(\text{B}_3\text{H}_8)_2$.

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

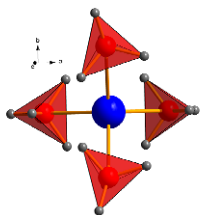
Technical Accomplishments and Progress

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

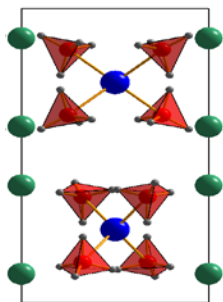
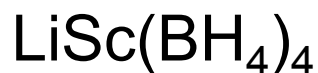
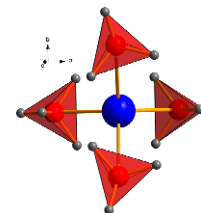
Metal ion assisted BH condensation pathway



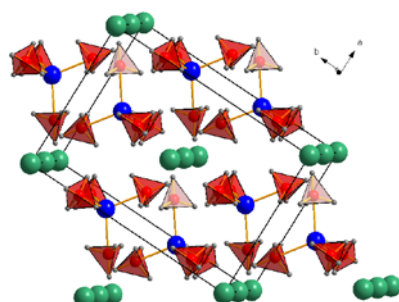
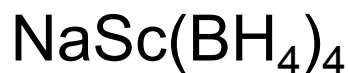
Technical Accomplishments and Progress



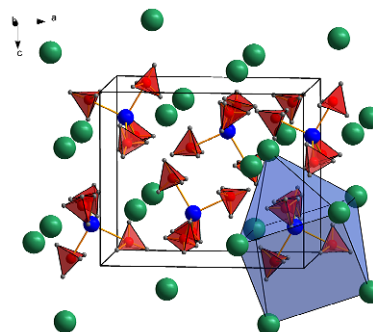
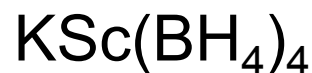
Synthesis and Characterization of Anionic Transition Metal Borohydrides



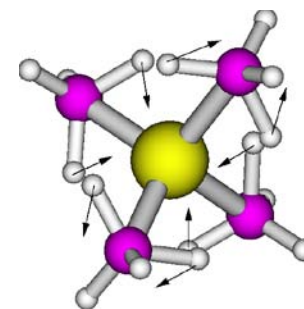
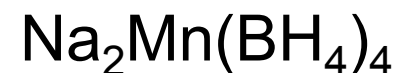
H. Hagemann, M. Longhini, J.W. Kaminski, T.A. Wesolowski, R. Černý, N. Penin, M.H. Sørby, B.C. Hauback, G. Severa and C.M. Jensen *J. Phys. Chem. B.* **2008**, *112*, 7551



R. Černý, 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.



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.



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

Technical Accomplishments and Progress

Reversibility?

- Release of high wt % hydrogen at high temperatures yields transition metal borides which can not be hydrogenated.
- Low dehydrogenation of $\text{LiSc}(\text{BH}_4)_4$, $\text{NaSc}(\text{BH}_4)_4$, and $\text{KSc}(\text{BH}_4)_4$ gives rise to materials that can be hydrogenated. However, the starting borohydrides are not regenerated.

Collaborations

FY11

- T. Autrey; PNNL (Government): Character by solution NMR analysis.
- H. Hagmann, R. Cerny; University of Geneva (Academic): Characterization by IR and Raman Spectroscopy and XRD.
- T. Jensen, Aarhus University, Denmark (Academic); Characterization by XRD.

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

Collaborations

Project (continued)

- R. Kuboto; KEK, Tsukuba (Government): characterization by muon spin resonance.
- R. Kumar; University of Nevada at Las Vegas (Academic) high pressure neutron diffraction studies.
- S. Orimo; Tohoku University (Academic): Characterization by DSC and XRD.
- 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; Sandia National Laboratory (Government); high pressure hydrogenation.
- X. Tang; UTRC (Industrial); Confinement in alternative scaffolds.
- 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 $\text{Mg}(\text{BH}_4)_2$.
- Determine if a material that undergoes reversible dehydrogenation under moderate conditions can be obtained from the initial dehydrogenation of $\text{LiSc}(\text{BH}_4)_4$, and/or $\text{NaSc}(\text{BH}_4)_4$ under mild conditions.

Hydrogenation in Non-conventional Solvents

- Further evaluation of WTT efficiency of the $\text{DME}/\text{LiAlH}_4$ system to be examined in collaboration with Argonne National Lab.

FY11 Summary

- Mild conditions (<200 °C, <100 atm) have been found for the reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ to $\text{Mg}(\text{B}_3\text{H}_8)_2$
- Dehydrogenation of (~2.0 wt%) from $\text{LiSc}(\text{BH}_4)_4$ and $\text{NaSc}(\text{BH}_4)_4$ gives rise to materials that can be hydrogenated at mild conditions (<200 °C, <100 atm).

...

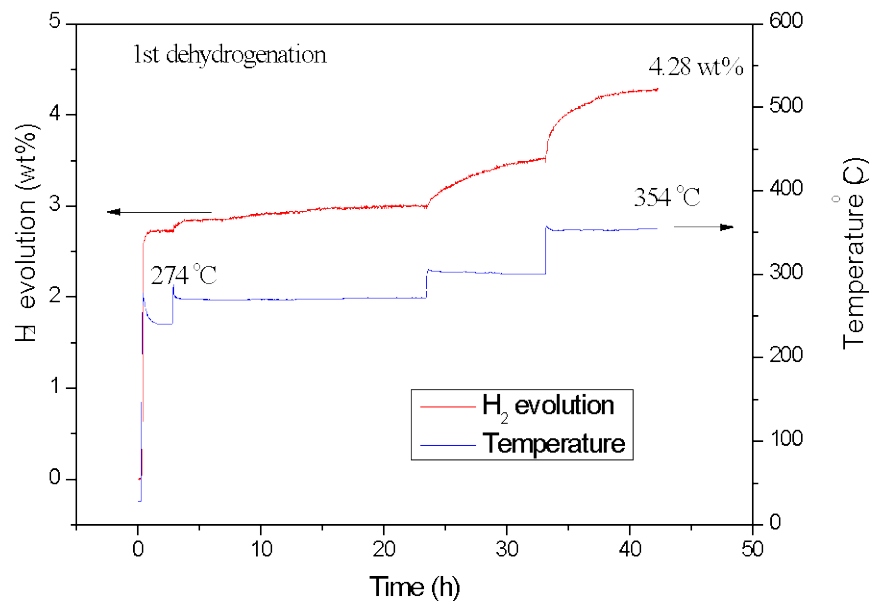
Back-up Technical Slide 1

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 dehydrogenation-rehydrogenation.

Back-up Technical Slide 2

Improved kinetics observed for nano-confined $\text{Mg}(\text{BH}_4)_2$



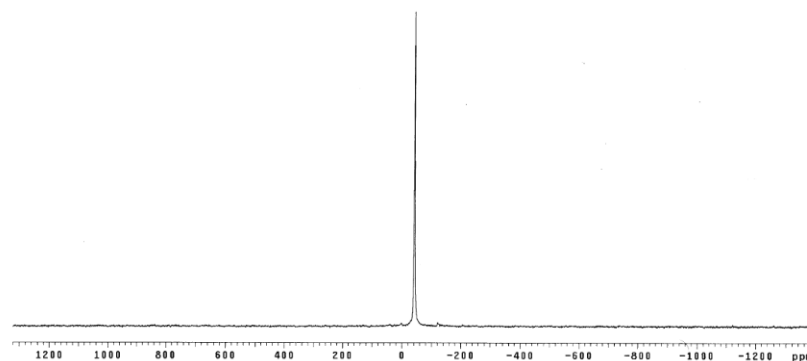
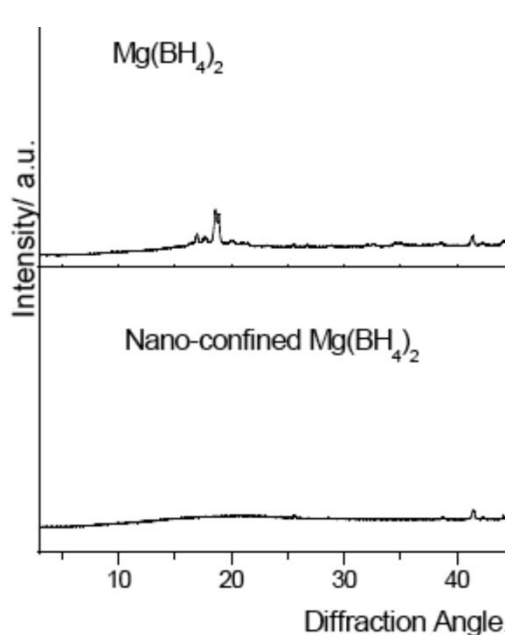
Hydrogen is evolved at the rate of 0.1 wt%/min at 270 $^\circ\text{C}$ during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting MgB_2 under 120 atm at 220 $^\circ\text{C}$ gives rise to $\text{Mg}(\text{B}_{12}\text{H}_{12})_2$ as occurs with bulk $\text{Mg}(\text{BH}_4)_2$.

Back-up Technical Slide 3

Synthesis of nano-confined $\text{Mg}(\text{BH}_4)_2$

- Hydride incorporated into carbon aerogel through immersion in molten $\text{Mg}(\text{BH}_4)_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. Diethyl ether adduct removed at 220 °C en vacuo.
- 60 wt% of $\text{Mg}(\text{BH}_4)_2$ is incorporated into aerogel.

Broaden of XRD peaks indicates incorporation into aerogel.



MAS ^{11}B NMR spectrum of the hydride incorporated aerogel verifies that $\text{Mg}(\text{BH}_4)_2$ is the only boron containing species present in the aerogel.

Back-up Technical Slide 4

BACKGROUND

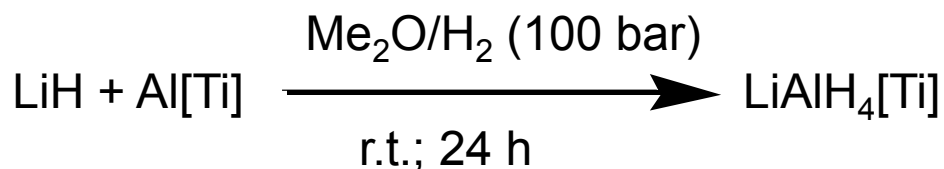
- Like sodium alanate, stepwise dehydrogenation, BUT first step is **exo**thermic.



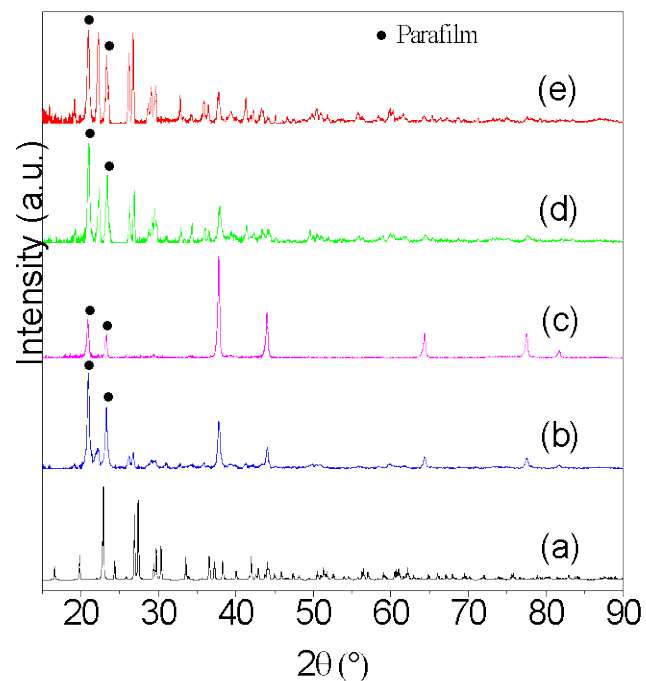
- Together steps 1 and 2 provide ~7.9 wt %H.
- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P).
- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle.
- Graetz (2008) – reversible in THF (low T and P) with Ti catalyst.
- THF removal requires heating to 60 °C 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



- Solvent vents immediately with H₂
- Fully charged Ti-doped LiAlH₄ obtained
- Very low levels of Ti can be used (~500 ppm)



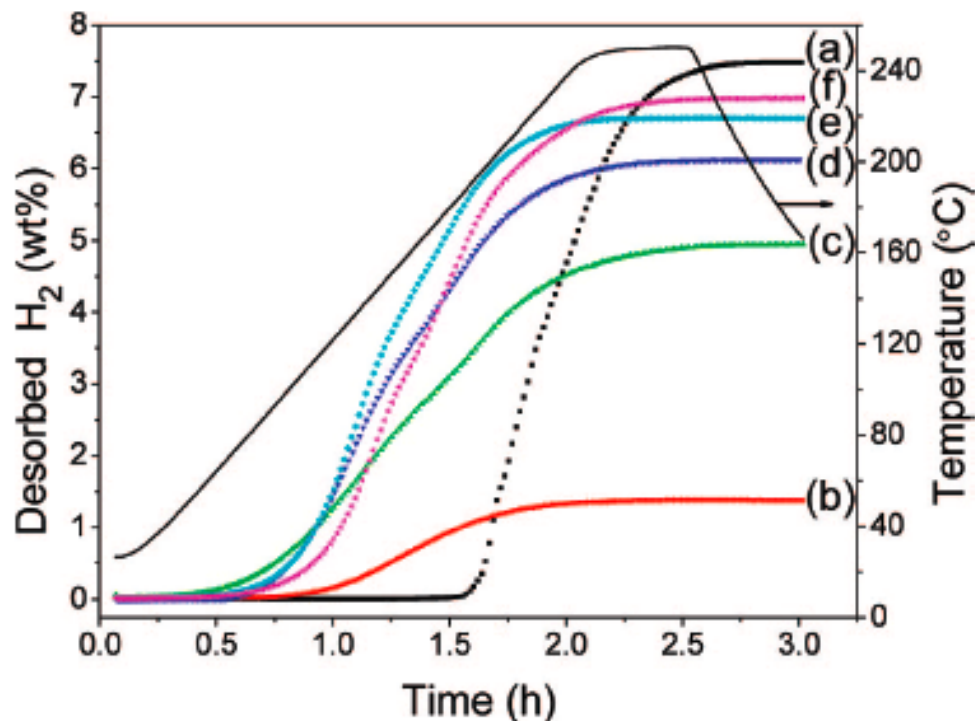
XRD patterns of LiAlH₄ samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl₃); (c) fully de-H (0.2 mol% TiCl₃); (d) re-H (2.0 mol% TiCl₃); (e) re-H (0.2 mol% TiCl₃).

Back-up Technical Slide 6

H₂ Desorption from Ti-Doped LiAlH₄

- 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 LiAlH₄ samples: (a) as-received; (b) milled with 2.0 mol% TiCl₃; (c) re-H (2.0 mol% TiCl₃); (d) re-H (1.0 mol% TiCl₃); (e) re-H (0.5 mol% TiCl₃); and (f) re-H (0.2 mol% TiCl₃).

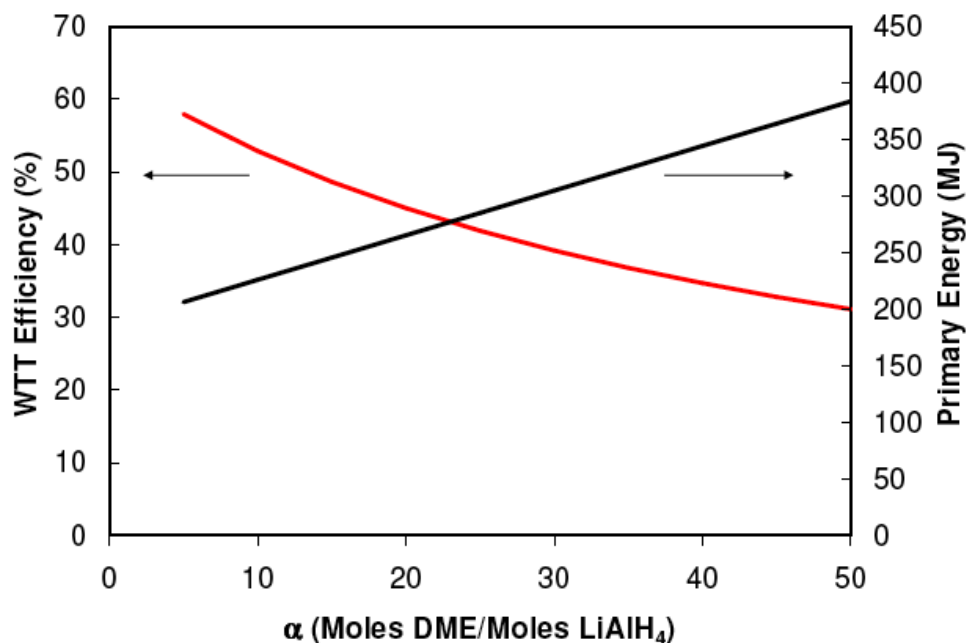
Back-up Technical Slide 7

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

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

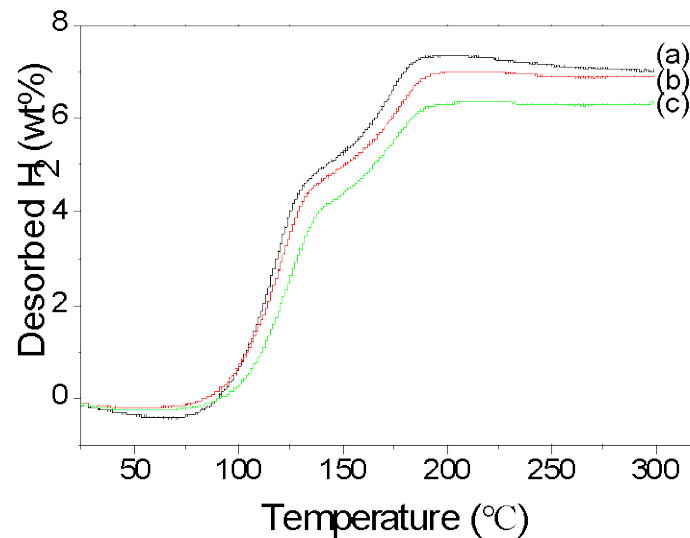


Primary Energy and WTT Efficiency



Back-up Technical Slide 8

Ti-doped LiAlH_4 shows a drop in capacity over several cycles due to formation of $\text{Ti}_x\text{Al}_{1-x}$ phase.

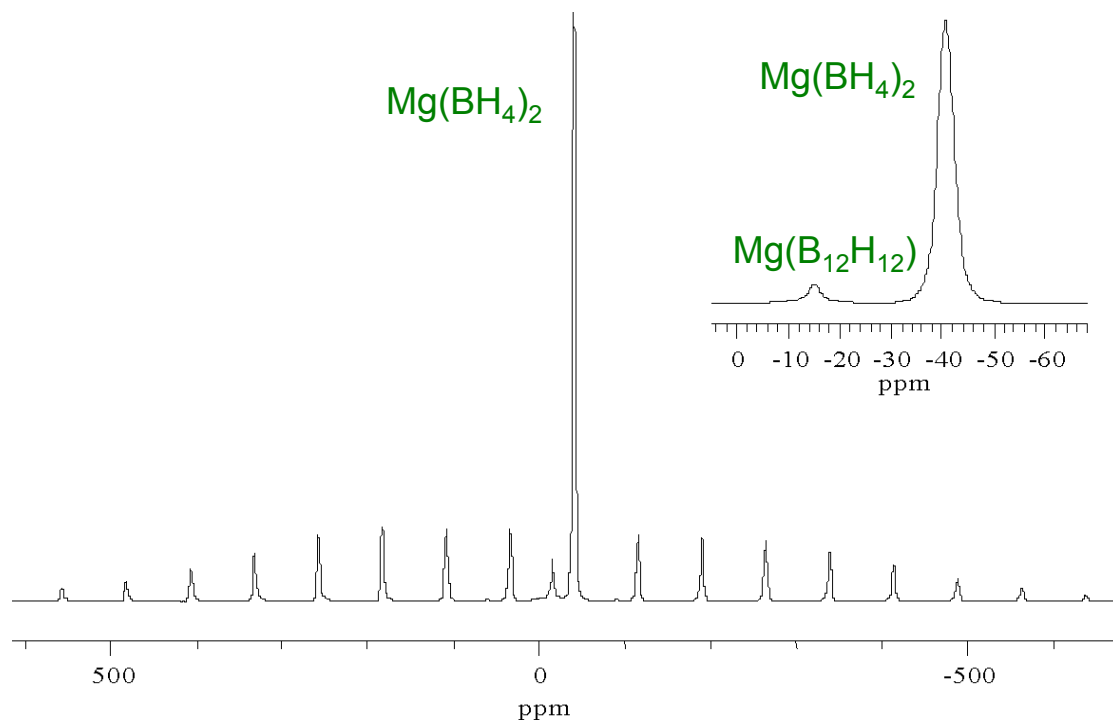


Cycle performance of hydrogenated $\text{LiH}/\text{Al}/\text{TiCl}_3$ (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.

Back-up Technical Slide 9

MAS ^{11}B NMR

- > XRD not generally used due to 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.



- > Full Hydrogenation of MgB_2 beyond $\text{MgB}_{12}\text{H}_{12}$ to $\text{Mg}(\text{BH}_4)_2$
- > One major boron containing product is observed.
- > Chemical shift of -41 ppm: $\text{Mg}(\text{BH}_4)_2$.
- > Minor signal observed for $\text{MgB}_{12}\text{H}_{12}$, at -24 ppm, represents < 5% of product mixture.
- > Not clear if the catalyzed reaction pathway is the same as the uncatalyzed pathway.