

# Advanced, High-Capacity Reversible Metal Hydrides

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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.

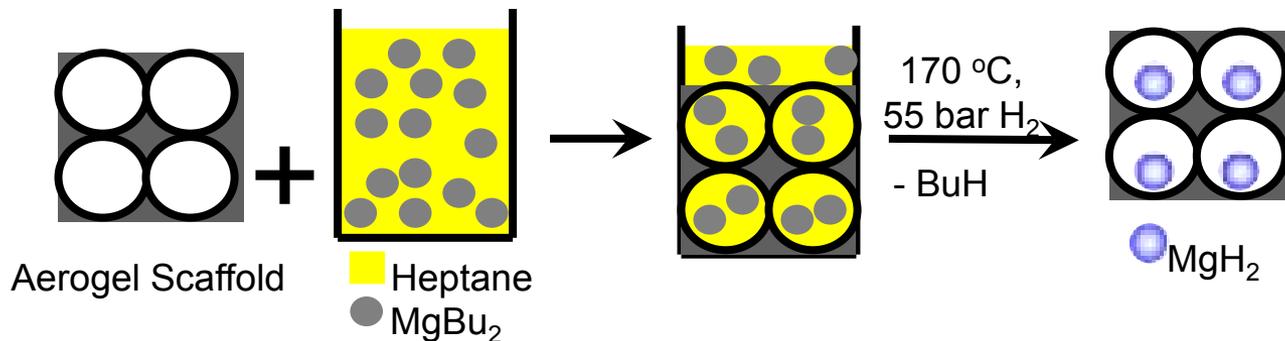
Investigations during FY11 focused on:

- Reversible dehydrogenation of  $\text{MgBH}_4$  (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(BH<sub>4</sub>)<sub>2</sub>

- > Mg(BH<sub>4</sub>)<sub>2</sub> evolves **14.8 wt %** H<sub>2</sub> upon dehydrogenation.
- >  $\Delta H_{\text{dehyd}} = 42 \text{ kJ/mol H}_2 \Rightarrow$  it should be possible to hydrogenate MgB<sub>2</sub> to Mg(BH<sub>4</sub>)<sub>2</sub> 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  $\text{AlH}_3$ ; Al/MgH<sub>2</sub> to  $\text{Mg}(\text{AlH}_4)_2$ ; and LiH/Al to  $\text{LiAlH}_4$  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

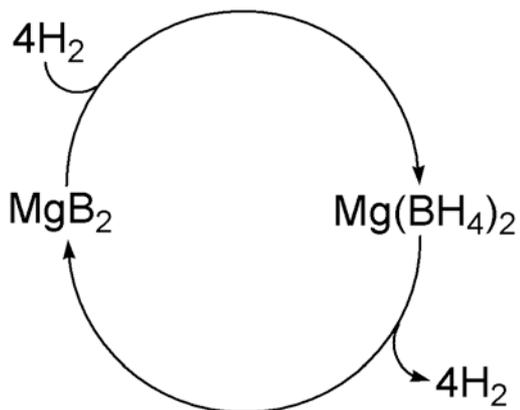
Studies by Orimo (Raman spectroscopy) and Hwang (NMR spectroscopy) indicated that incomplete re-hydrogenation is the result of the high kinetic stability of  $\text{MgB}_{12}\text{H}_{12}$ .

## 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.

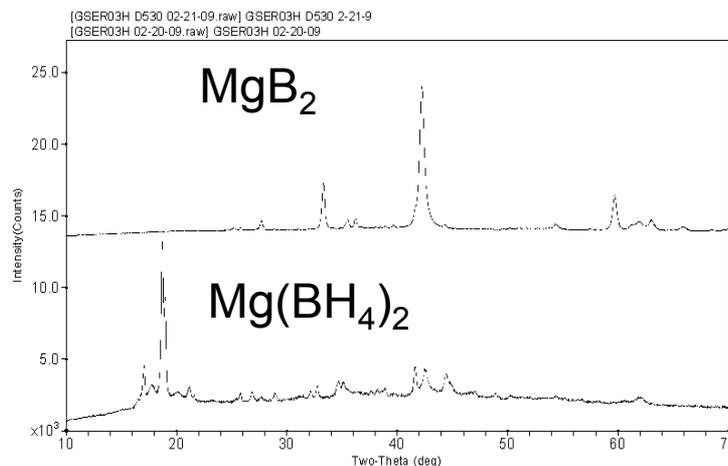
# Technical Accomplishments and Progress



## Cycling Studies

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

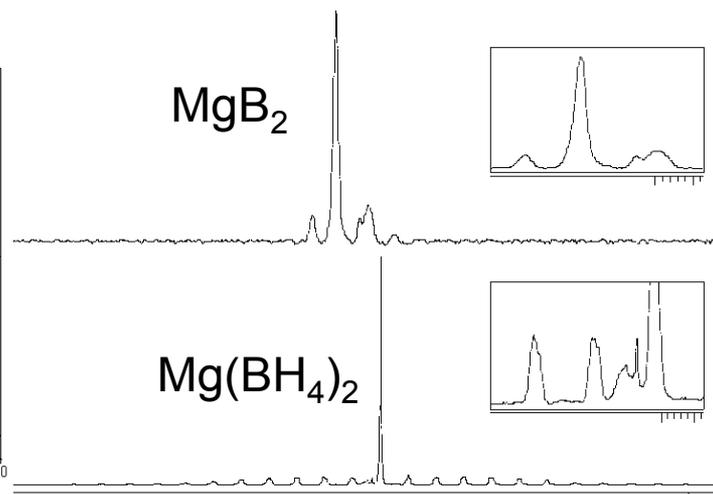
XRD



Dehydrogenation  
at 530 °C.

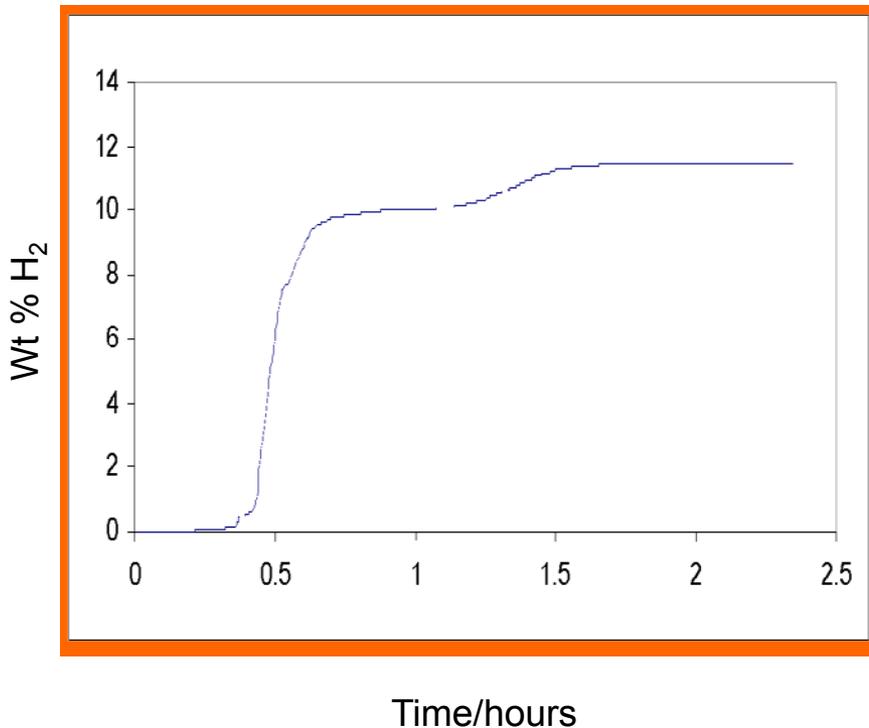
Hydrogenation  
at 400 °C under  
950 atm  $\text{H}_2$ .

MAS  $^{11}\text{B}$  NMR



# Technical Accomplishments and Progress

## 12 wt % Cycling Capacity



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

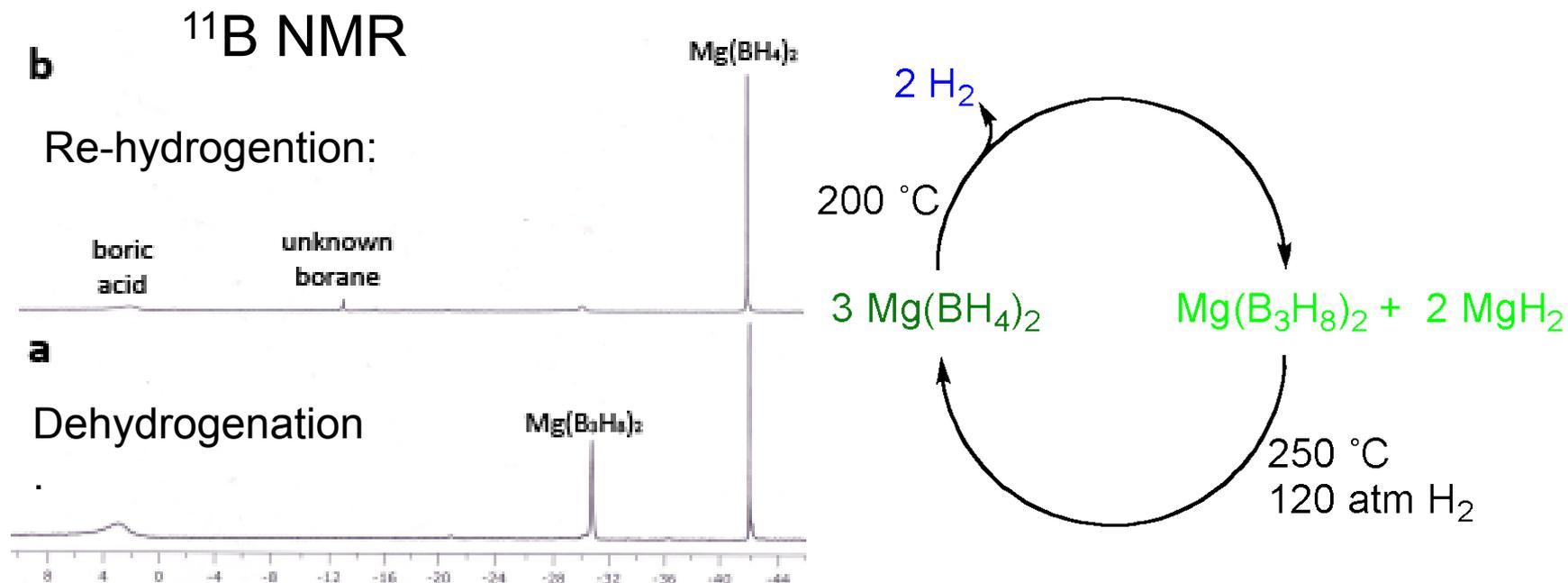
MgO arises during sampling, suggesting that 12.6 wt % hydrogen can be cycled.

Upon longer reaction times, higher levels of hydrogenation MgB<sub>2</sub> 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  $^{11}\text{B}$  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

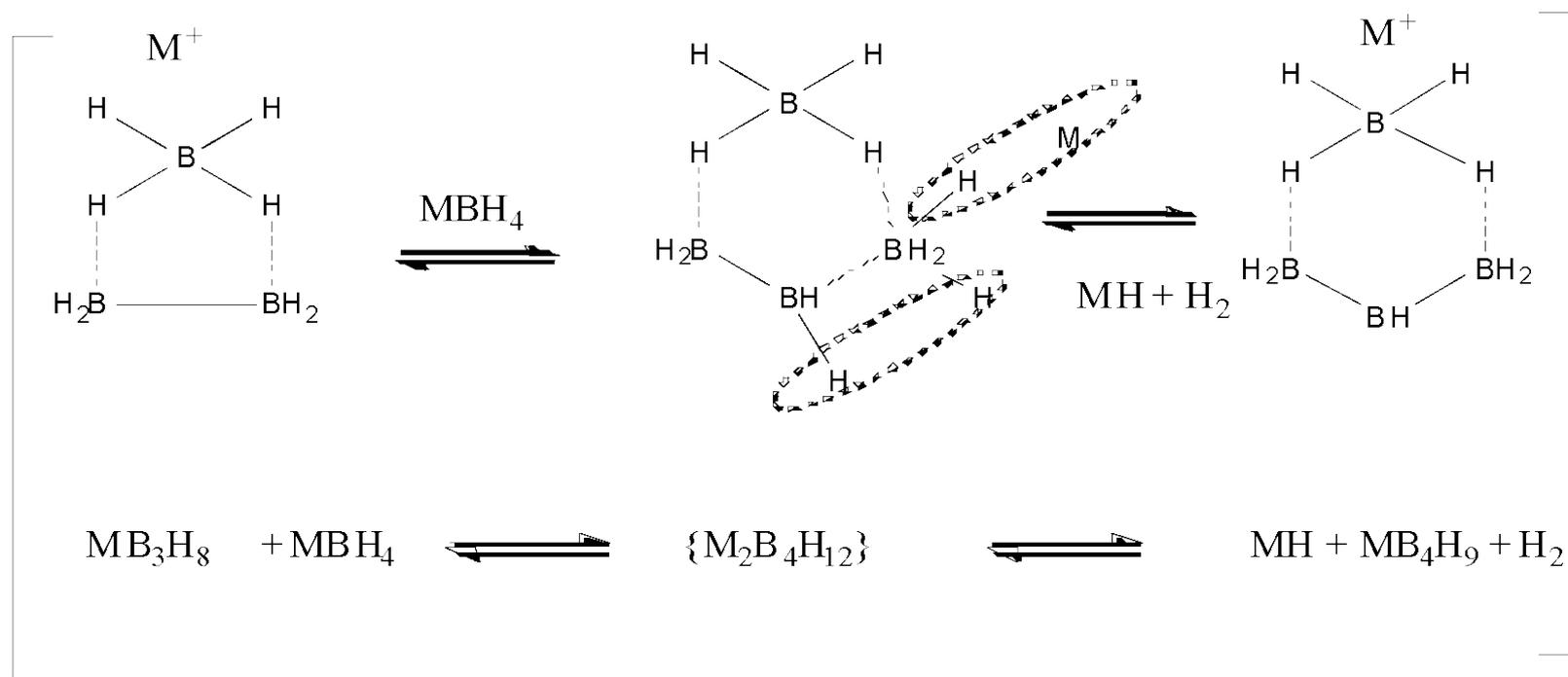
- Boric acid is major species observed in the  $^{11}\text{B}$  NMR.  
⇒ the major products are arachno- and nido- boranes.
- Concentration of the triborane increases lower temperatures.  
⇒ First step in the decomposition of  $\text{Mg}(\text{BH}_4)_2$  involves the formation of  $\text{Mg}(\text{B}_3\text{H}_8)_2$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

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

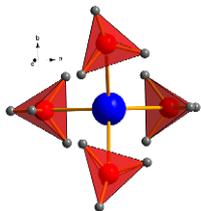
# Technical Accomplishments and Progress

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

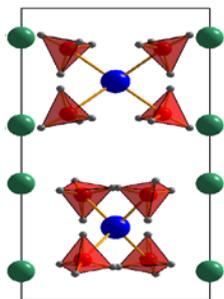
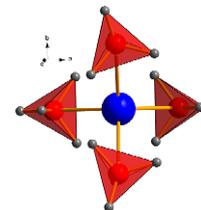
Metal ion assisted BH condensation pathway



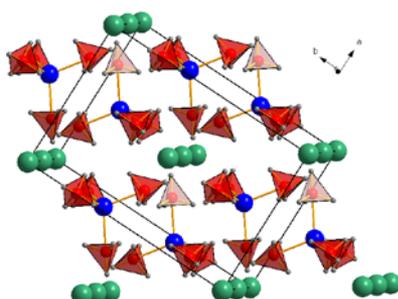
# Technical Accomplishments and Progress



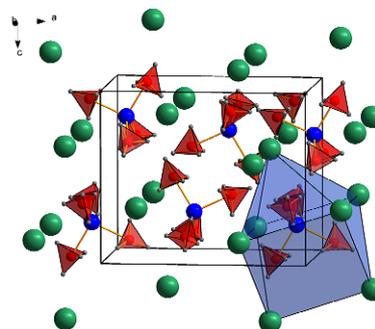
## Synthesis and Characterization of Anionic Transition Metal Borohydrides



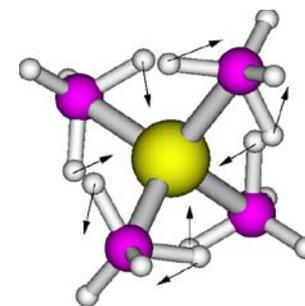
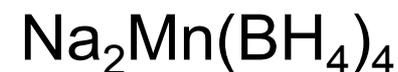
H. Hagemann, M. Longhini, J.W. Kaminski, T.A. Wesolowski, R. Černý, N. Penin, M.H. Sørby, B.C. Hauback, G. Severa and C.M. Jensen *J. Phys. Chem. B.* **2008**, *112*, 7551



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

## High Hydrogen Capacities Low Dehydrogenation Temperatures

	<u>wt% H</u> <u>theory</u>	<u>wt% H</u> <u>exp</u>	<u>T<sub>D</sub> (°C)</u>	<u>level of</u> <u>diborane</u>
<u>LiSc(BH<sub>4</sub>)<sub>4</sub></u>	14.6	3.5	175, 260	ppm
NaSc(BH <sub>4</sub> ) <sub>4</sub>	12.8	1.0	170, 225	ppm
KSc(BH <sub>4</sub> ) <sub>4</sub>	11.3	1.0	190, 240	ppm
Na <sub>2</sub> [Mn(BH <sub>4</sub> ) <sub>4</sub> ]	6.9	2.9	120	50:1 H <sub>2</sub> :B <sub>2</sub> H <sub>6</sub> due to Mn(BH <sub>4</sub> ) <sub>2</sub> contamination

# 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).

...

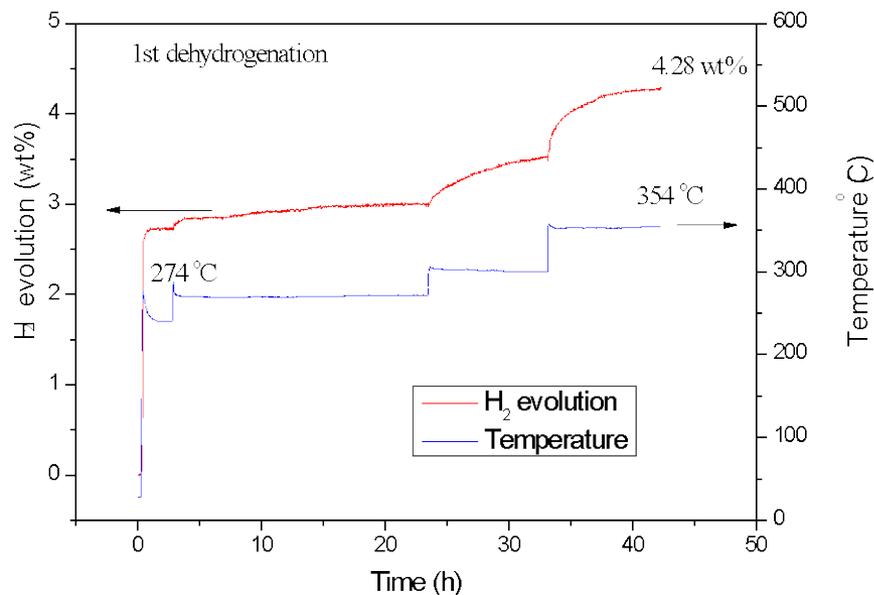
# Back-up Technical Slide 1

## Previous Results

- High, (9-16 wt % confirmed by TEM, EDS, and XRD)  $\text{MgH}_2$  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  $\text{MgH}_2$  and comparable to those found for nano-confined  $\text{MgH}_2$  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  $\text{Mg}(\text{BH}_4)_2$



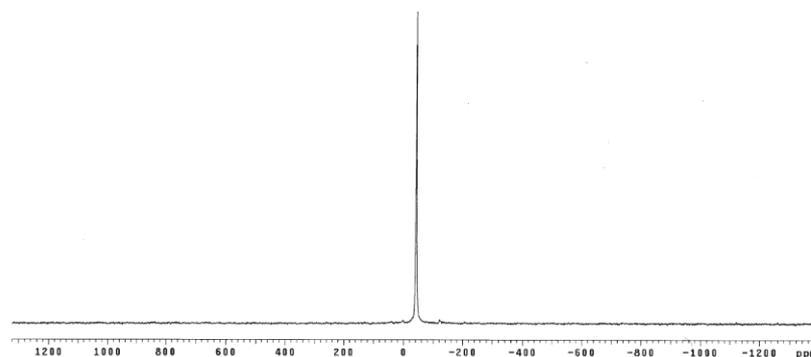
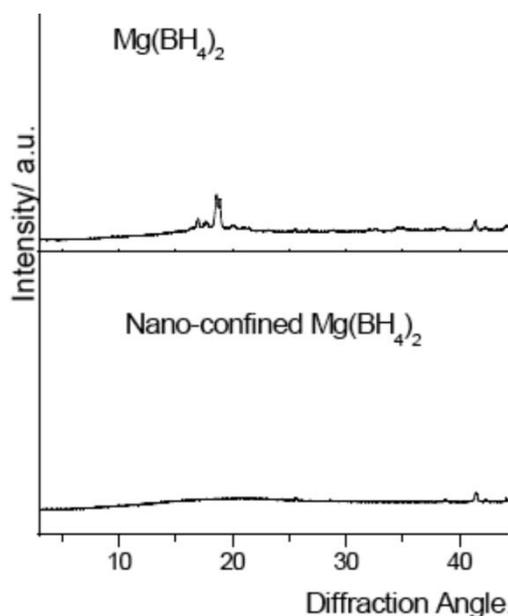
Hydrogen is evolved at the rate of 0.1 wt%/min at 270  $^\circ\text{C}$  during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting  $\text{MgB}_2$  under 120 atm at 220  $^\circ\text{C}$  gives rise to  $\text{Mg}(\text{B}_{12}\text{H}_{12})_2$  as occurs with bulk  $\text{Mg}(\text{BH}_4)_2$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

# 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  $^{11}\text{B}$  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

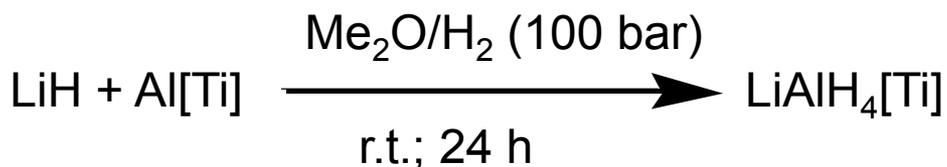
- Like sodium alanate, stepwise dehydrogenation, BUT first step is **exo**thermic.



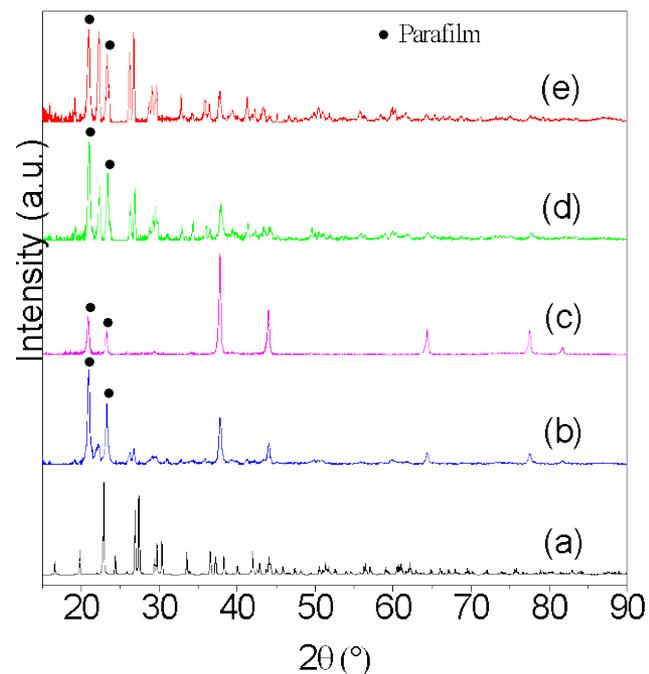
- Together steps 1 and 2 provide ~7.9 wt %H.
- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P).
- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle.
- Graetz (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 H<sub>2</sub>
- Fully charged Ti-doped LiAlH<sub>4</sub> obtained
- Very low levels of Ti can be used (~500 ppm)



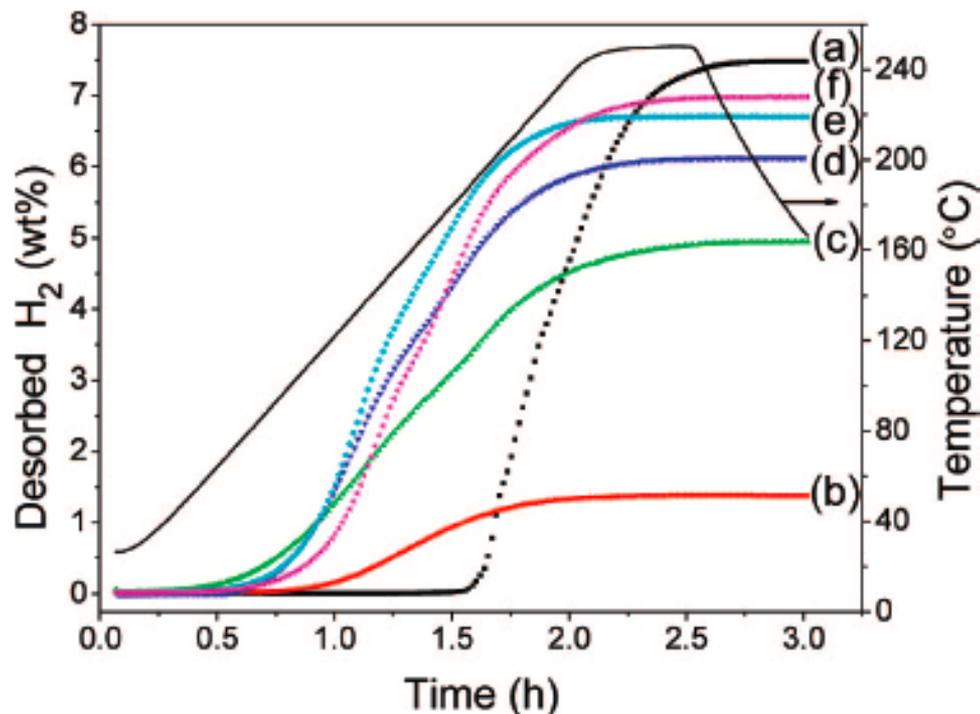
XRD patterns of LiAlH<sub>4</sub> samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl<sub>3</sub>); (c) fully de-H (0.2 mol% TiCl<sub>3</sub>); (d) re-H (2.0 mol% TiCl<sub>3</sub>); (e) re-H (0.2 mol% TiCl<sub>3</sub>).

# Back-up Technical Slide 6

## H<sub>2</sub> Desorption from Ti-Doped LiAlH<sub>4</sub>

- 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<sub>4</sub> samples: (a) as-received; (b) milled with 2.0 mol% TiCl<sub>3</sub>; (c) re-H (2.0 mol% TiCl<sub>3</sub>); (d) re-H (1.0 mol% TiCl<sub>3</sub>); (e) re-H (0.5 mol% TiCl<sub>3</sub>); and (f) re-H (0.2 mol% TiCl<sub>3</sub>).

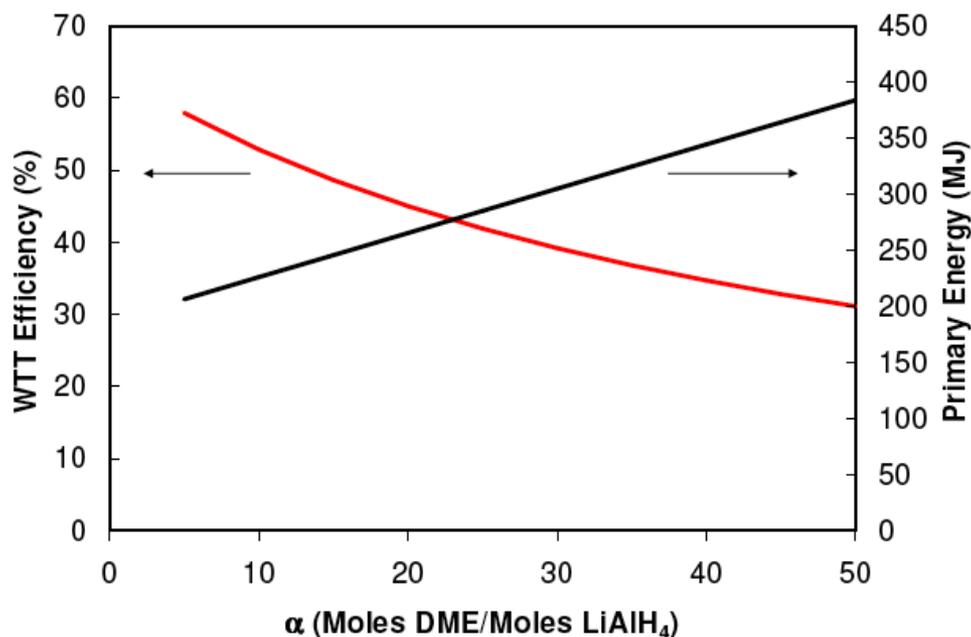
# Back-up Technical Slide 7

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

- Energy for compression of  $\text{Me}_2\text{O}$  and  $\text{H}_2$  is  $\sim 1/5$  that of  $\text{H}_2$  production.
- High  $\sim 5\text{M}$  solubility of  $\text{LiAlH}_4$  in  $\text{Me}_2\text{O}$  is the key in high efficiency.

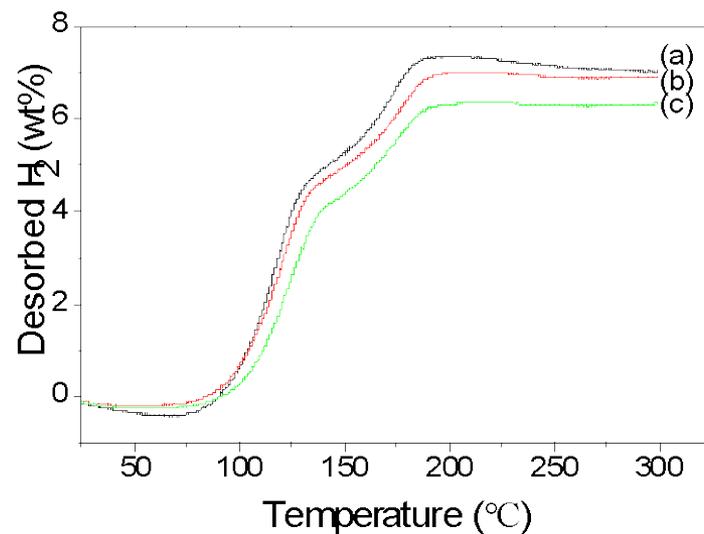


Primary Energy and WTT Efficiency



# Back-up Technical Slide 8

Ti-doped  $\text{LiAlH}_4$  shows a drop in capacity over several cycles due to formation of  $\text{Ti}_x\text{Al}_{1-x}$  phase.

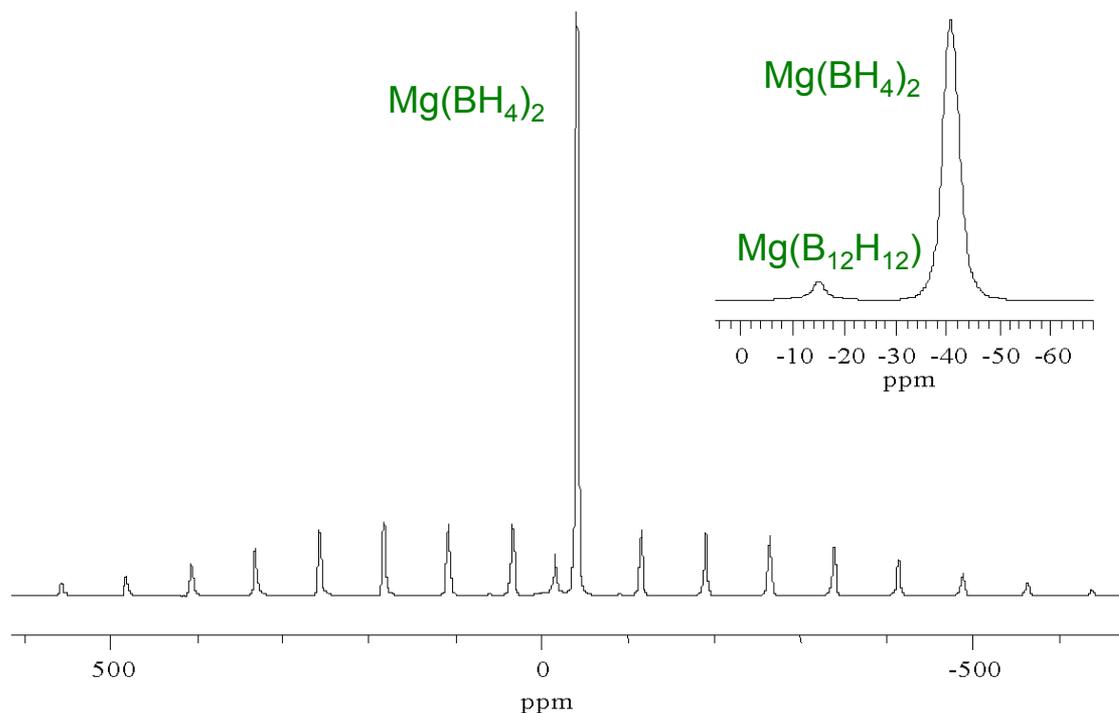


*Cycle performance of hydrogenated  $\text{LiH}/\text{Al}/\text{TiCl}_3$  (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.*

# Back-up Technical Slide 9

## MAS $^{11}\text{B}$ NMR

- > XRD not generally used due to the highly amorphous nature of boranes and bororhydrides.
- > MAS  $^{11}\text{B}$  NMR spectroscopy allows detection and differentiation of all the boron containing species that are present.



- > Full Hydrogenation of  $\text{MgB}_2$  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.