

# Advanced, High-Capacity Reversible Metal Hydrides

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UNIVERSITY  
of HAWAII<sup>®</sup>  
MĀNOA



ST 031

# Overview

## Timeline

- Start Date: March 2005
- End Date: September 2010
- 95% complete

## Budget

- Total project funding:  
\$2,945,058
  - DOE share: \$2,235,173
  - Contractor share: \$609,885
- Funding received in FY08:  
\$357,587
- Funding for FY09: \$285,173

## 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
- C. Ahn, S.J. Hwang; California Institute of Technology
- T. Autrey , E. Ronnebro; Pacific Northwest National Lab
- R. Cantelli; University of Rome
- B. Hauback, M. Sorby; Institute for Energy Technology
- H. Hagmann, R. Cerny; University of Geneva
- 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
- I. Robertson; University of Illinois
- T. Udovic; NIST
- S. Srinivasan; University of South Florida
- V. Stavila; Sandia National Laboratories
- J. Vajo, P. Liu; HRL

# Objectives and Relevance

Development of a new class of reversible complexes that has the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets.

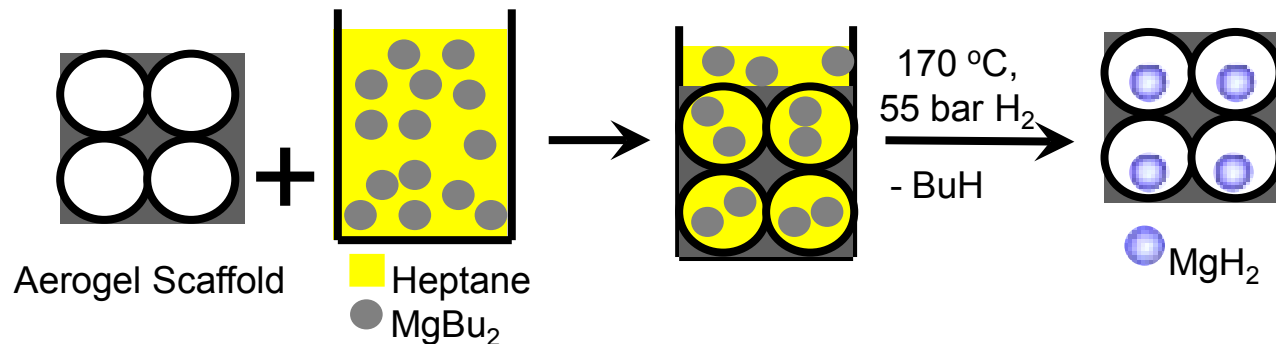
Current investigations include:

- $\text{Mg}(\text{BH}_4)_2$  nano-confined carbon aerogels.
- Reversible dehydrogenation of high capacity borohydrides at low temperatures.
- Development of a method for the hydrogenation  $\text{LiH}/\text{Al}$  to  $\text{LiAlH}_4$  at moderate conditions in unconventional solvents.

# Approach

## Nano-confined Al and Mg Compounds in Carbon Aerogels

- 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 of some ionic complexes such as  $\text{Na}_2\text{Zr}(\text{BH}_4)_6$ .
- > Altered thermodynamic stability might allow reversibility.

## $\text{Mg}(\text{BH}_4)_2$

- >  $\text{Mg}(\text{BH}_4)_2$  evolves **14 wt %**  $\text{H}_2$  upon dehydrogenation.
- > Ball-milled  $\text{MgB}_2$  undergoes **full, reversible** hydrogenation to  $\text{Mg}(\text{BH}_4)_2$  at 400 °C and 900 atm.
- > Dehydrogenation has been found to be a multi-step process, can partial reversible dehydrogenation be accomplished under milder conditions.

# Approach

## Re-hydrogenation in Non-conventional Solvents

- > 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 Nano-Confined Mg-Based Hydrides in Carbon Aerogels

## 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.

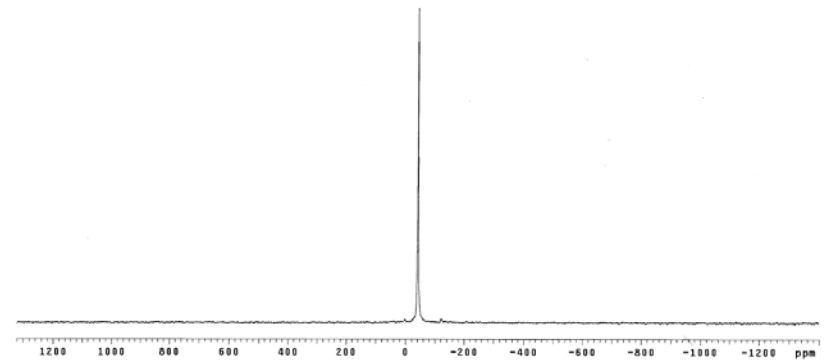
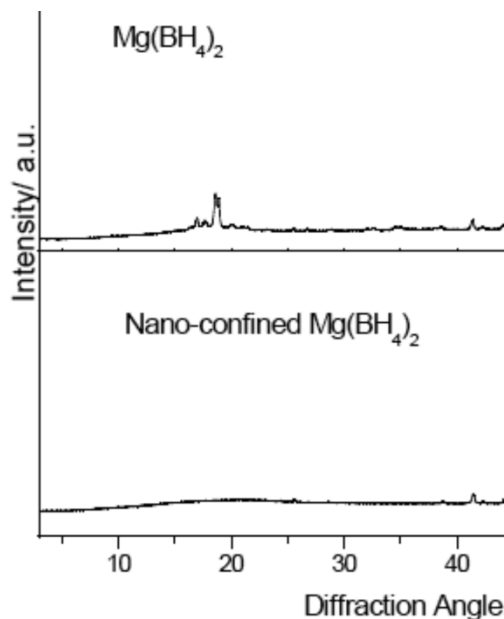
# Technical Accomplishments and Progress

## Nano-Confined Mg-Based Hydrides in Carbon Aerogels

### 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.

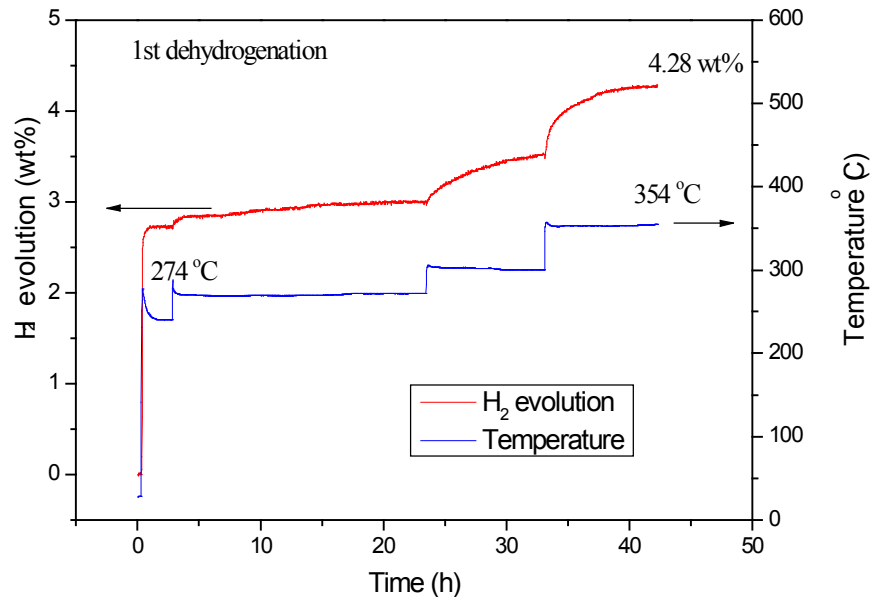


MAS  $^{11}\text{B}$  NMR spectrum of the hydride incorporated aerogel verifies that  $\text{Mg}(\text{BH}_4)_2$  is the only boron containing species present in the aerogel.



# Technical Accomplishments and Progress Nano-Confined Mg-Based Hydrides in Carbon Aerogels

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

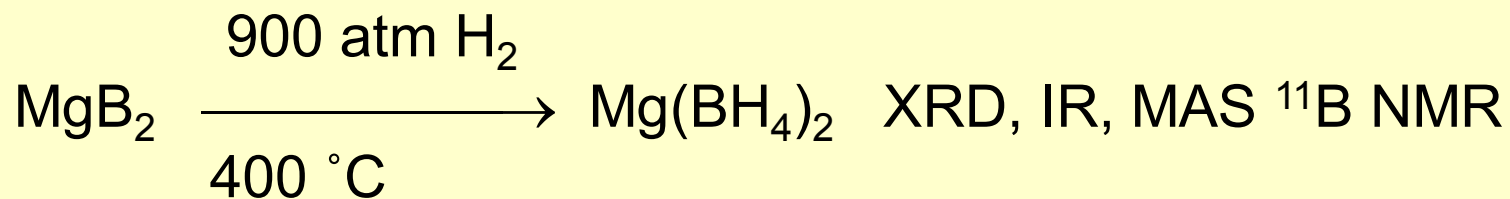


Hydrogen is evolved at the rate of 0.1 wt%/min at 270 °C during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting  $\text{MgB}_2$  under 120 atm at 220 °C gives rise to  $\text{Mg}(\text{B}_{12}\text{H}_{12})_2$  as occurs with bulk  $\text{Mg}(\text{BH}_4)_2$ .

# Technical Accomplishments and Progress Anionic Borohydrides

The  $\Delta H_{\text{dehyd}}$  of 42 kJ/mole suggests that it should be possible to hydrogenate  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  at moderate temperatures and pressures. Findings of incomplete re-hydrogenation is apparently the result of the high kinetic stability of  $\text{MgB}_{12}\text{H}_{12}$  intermediate.

## First Demonstration of Full Hydrogen Hydrogenation



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

Godwin Severa, Ewa Rönnebro, Craig M. Jensen; *Chemical Commun.* **2010**, 46, 421.

# Technical Accomplishments and Progress Borohydrides

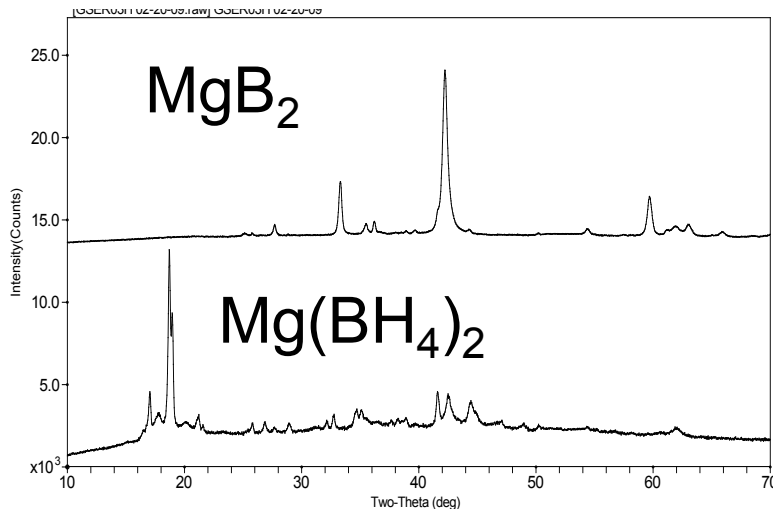
## Cycling Studies

XRD

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

After  
dehydrogenation  
at 530 °C.

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



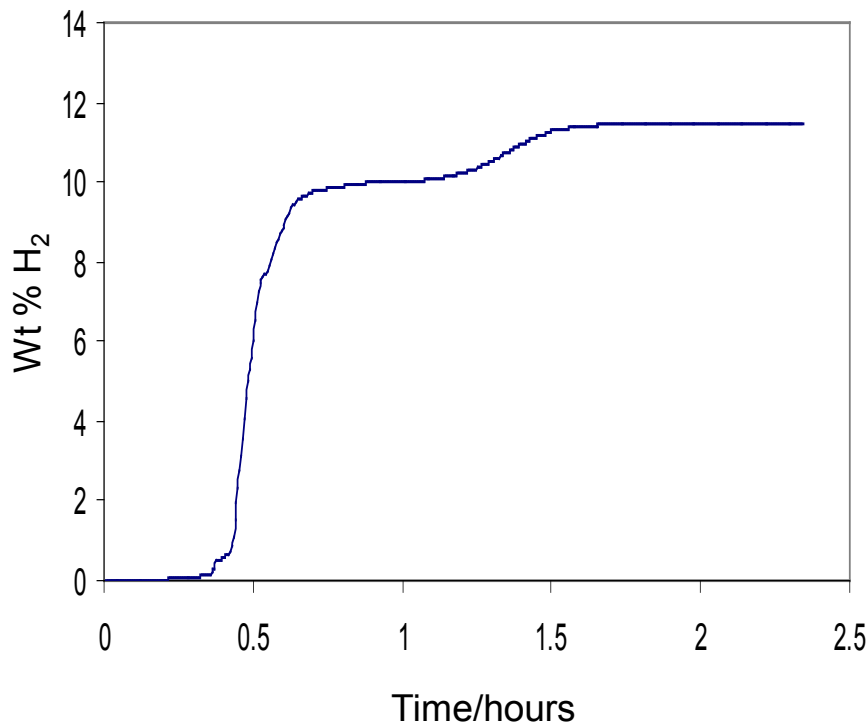
$\text{MgB}_2$

$\text{Mg}(\text{BH}_4)_2$

**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.**

# Technical Accomplishments and Progress Borohydrides

## 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 Borohydrides

## Cycling Under Mild Conditions Collaboration with PNL

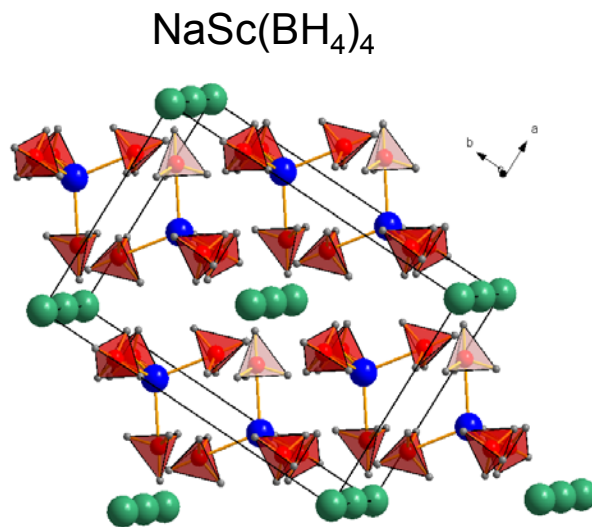
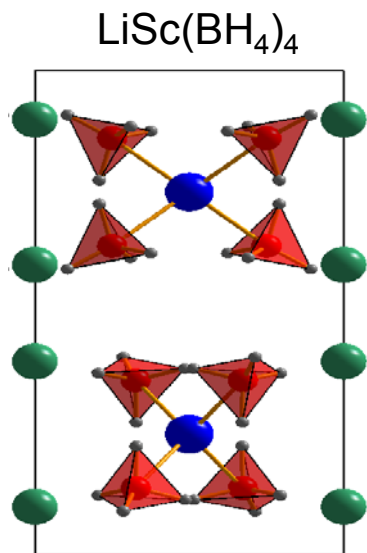
$\text{Mg}(\text{B}_{12}\text{H}_{12})$  is a thermodynamic sink whose formation precludes the reversible dehydrogenation  $\text{Mg}(\text{BH}_4)_2$  at moderate temperatures and pressures.

Orimo, S.; Nakamori, Y.; Ohba, N.; Miwa, K.; Aoki, M.; Towata, S.; Zuttel, A. *Appl. Phys. Lett.* **2006**, *89*, 21920.

R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour, C. C. Ahn, *J. Phys. Chem. C* **2008** *112*, 3164.

Mild conditions (<**200 °C**, <**100 atm**) have been found for the reversible elimination of 2.4 wt % hydrogen from  $\text{Mg}(\text{BH}_4)_2$  which circumvent the formation of  $\text{Mg}(\text{B}_{12}\text{H}_{12})$ .

# Technical Accomplishments and Progress Borohydrides



The **reversible** partial dehydrogenation of  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$  and  $\text{KSc}(\text{BH}_4)_4$  can also be achieved under conditions found for  $\text{Mg}(\text{BH}_4)_4$ .

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.

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.

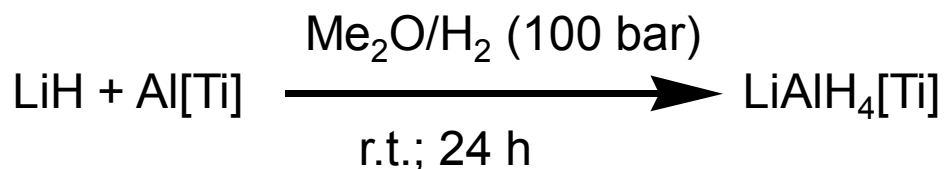
# Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

## BACKGROUND

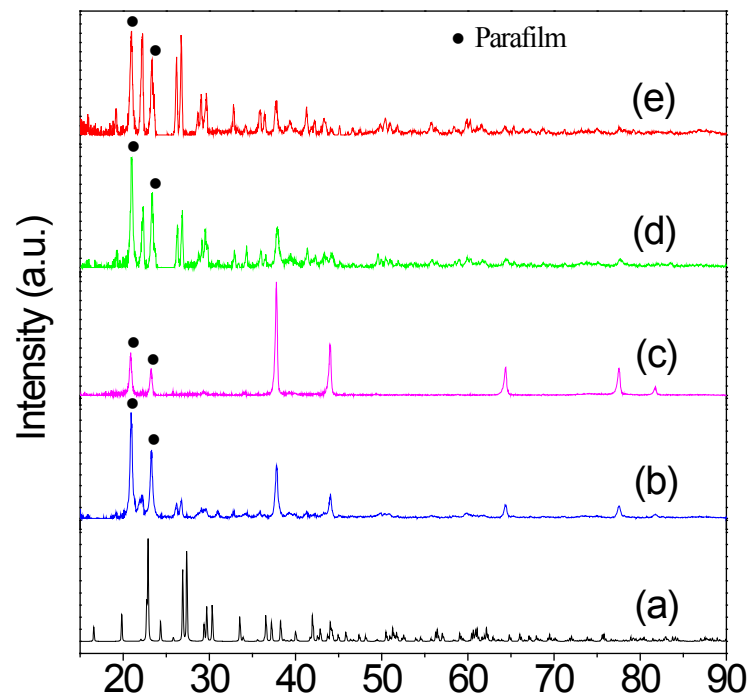
- Like sodium alanate, stepwise dehydrogenation, BUT first step is **exo**thermic.  
**Step 1:**  $3\text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \quad \Delta H = -30 \text{ kJ}$   
**Step 2:**  $\text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + 1.5\text{H}_2 \quad \Delta H = 38 \text{ kJ}$
- 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 °C for 6 h. Incompatible with Ti catalyst since dehydrogenation occurs at the temperature required for removal of THF.

# Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

## 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>).

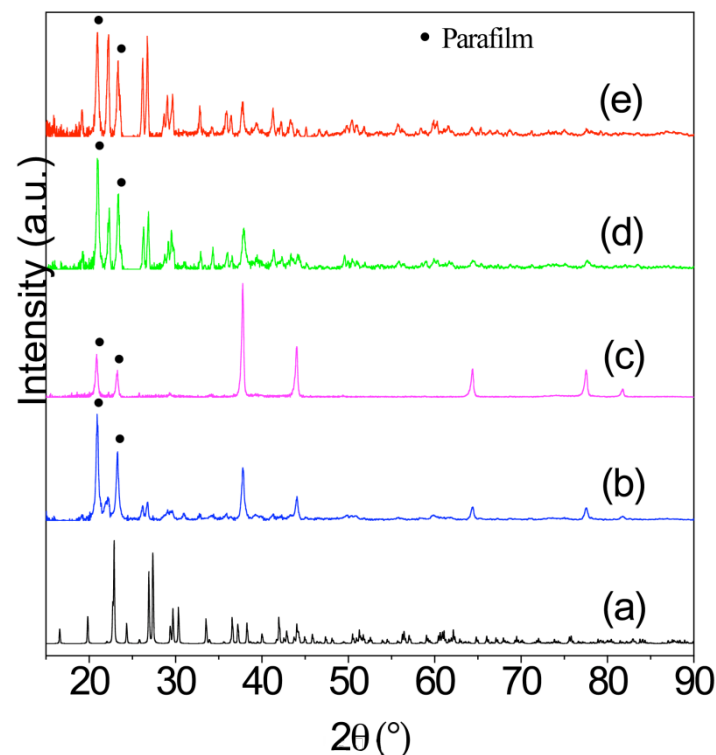


# Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

## 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.

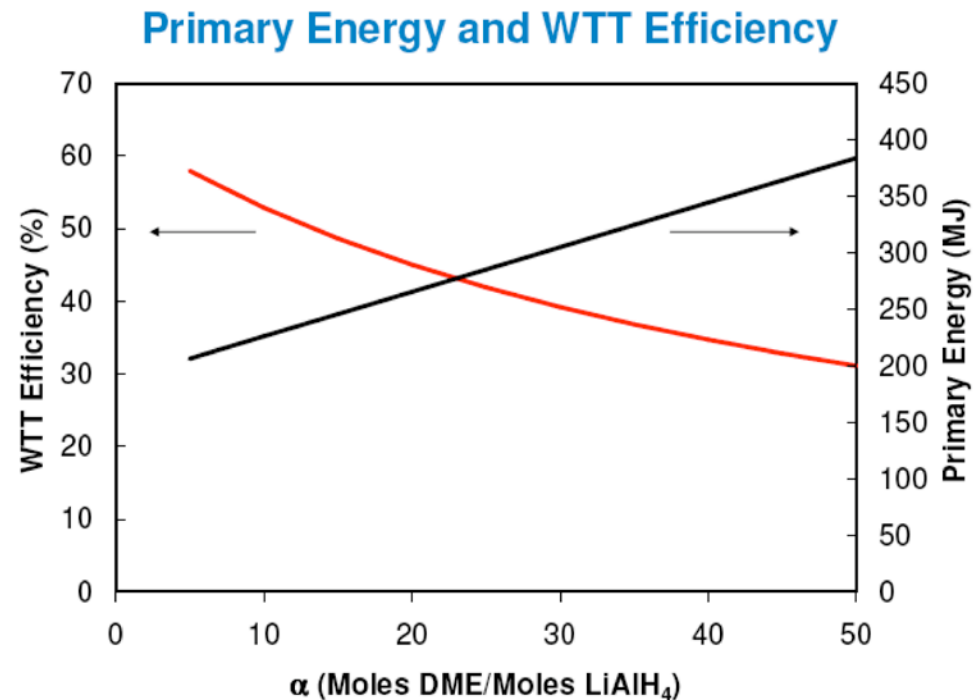


TPD plots for LiAlH<sub>4</sub> samples: (a) as-received; (b) milled with 2.0 mol% TiCl<sub>3</sub>; (c) re-H (2.0 mol% TiCl<sub>3</sub>); (d) re-H (1.0 mol% TiCl<sub>3</sub>); (e) re-H (0.5 mol% TiCl<sub>3</sub>); and (f) re-H (0.2 mol% TiCl<sub>3</sub>).

# Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

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

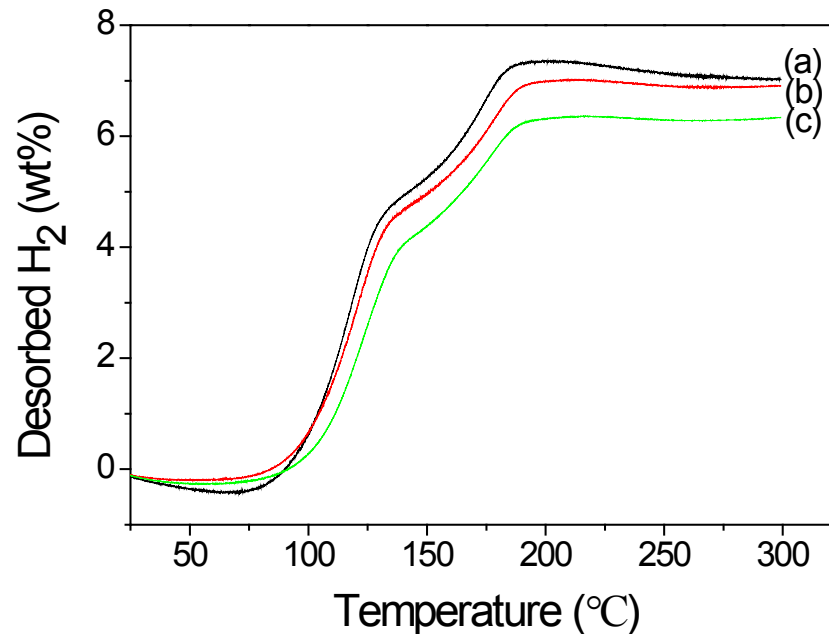
- Energy for compression of  $\text{Me}_2\text{O}$  and  $\text{H}_2$  is  $\sim 1/5$  that of  $\text{H}_2$  production.
- High  $\sim 5\text{M}$  solubility of  $\text{LiAlH}_4$  in  $\text{Me}_2\text{O}$  is the key in high efficiency.



# Technical Accomplishments and Progress

## Hydrogenation in Non-conventional Solvents

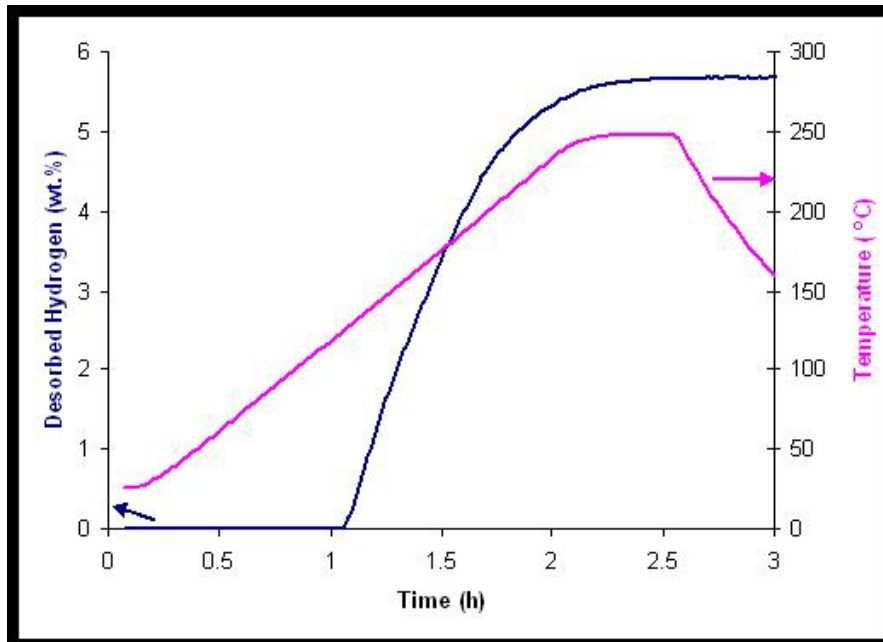
Ti-doped  $\text{LiAlH}_4$  shows a drop in capacity over several cycles due to formation of  $\text{Ti}_x\text{Al}_{1-x}$  phase.



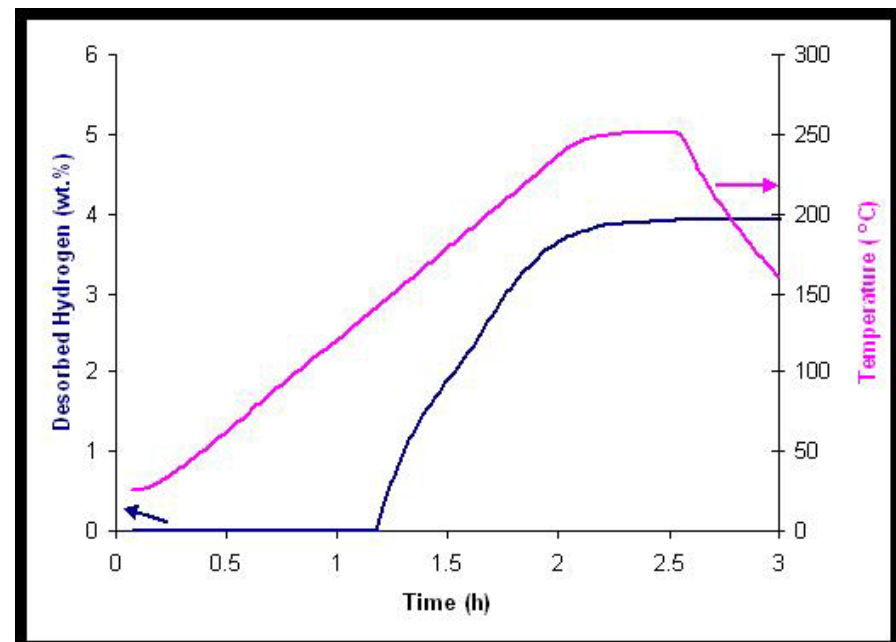
*Cycle performance of hydrogenated  $\text{LiH}/\text{Al}/\text{TiCl}_3$  (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.*

# Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

Attempt to circumvent the formation of  $Ti_xAl_{1-x}$  phase we circumvented by doping with supported Ti ( $TiCl_3$  on  $Al_2O_3$ )?



**First Dehydrogenation** Catalytic enhancement similar to that achieved with free Ti observed.



**Second Dehydrogenation** Hydrogen capacity lowered to >4 wt % and drops to zero after third cycle.

# Future Work

## Borohydrides

- Adjustment of conditions to maximize trade off between cycling capacity and temperature/pressures required for reversible dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{LiSc}(\text{BH}_4)_4$ , and  $\text{NaSc}(\text{BH}_4)_4$ .

## Hydrogenation in Non-conventional Solvents

- Explore maintenance of cycling capacity of doped  $\text{LiAlH}_4$  through variation of the dopants.
- Further evaluation of WTT efficiency of the  $\text{DME/LiAlH}_4$  system to be examined in collaboration with Argonne National Lab.

# Summary

## Nano-confined Mg in Carbon Aerogels

- High, (60 wt %) loadings  $\text{Mg}(\text{BH}_4)_2$  in carbon aerogel achieved using novel method.
- Nano-confinement of  $\text{Mg}(\text{BH}_4)_2$  improves dehydrogenation kinetics but does not change the re-hydrogenation reaction pathway.

## Borohydrides

- Demonstration of the reversible hydrogenation of  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  shown to cycle 12 wt% hydrogen.
- Mild conditions (<200 °C, <100 atm) have been for the reversible partial (2.4 wt %) dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  as well as (~2.0 wt%)  $\text{LiSc}(\text{BH}_4)_4$  and  $\text{NaSc}(\text{BH}_4)_4$ .

...

## Hydrogenation in Non-conventional Solvents

- Fully charged, Ti-doped  $\text{LiAlH}_4$  can be obtained in major yields from the direct hydrogenation of Ti-doped  $\text{LiH/Al}$  in liquefied dimethyl ether at room temperature under 100 bar of  $\text{Me}_2\text{O}/\text{H}_2$ .
- WTT efficiency of a  $\text{LiAlH}_4$  based hydrogen system utilizing liquid DME as a re-hydrogenation medium approaches the 60% target.

# Collaborations

## **Nano-confined Mg in Carbon Aerogels**

- C. Ahn; California Institute of Technology (Academic): Characterization by TEM imaging.
- J. Vajo, P. Liu; HRL (Industrial): Characterization by PCT.
- X. Tang; UTRC (Industrial); Confinement in alternative scaffolds.

## **Anionic Borohydrides and Complex Hydrides**

- E. Akiba, K. Sakaki; AIST, Tsukuba (Government): Characterization by positron annihilation.
- T. Autrey; PNNL (Government): Character by solution NMR analysis.
- 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.
- L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC (Industrial): Characterization by XRD and mass spectroscopy.

# Collaborations

## **Anionic Borohydrides and Complex Hydrides**

- R. Kuboto; KEK, Tsukuba (Government): characterization by muon spin resonance.
- S. Orimo; Tohoku University (Academic): Characterization by DSC and XRD. Synthesis.
- 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.
- T. Udovic; NIST (Government) Characterization by Inelastic Neutron Scattering.

## **Hydrogenation in Non-conventional Solvents**

- S. McGrady; University of New Brunswick (Academic): SCF reaction system.

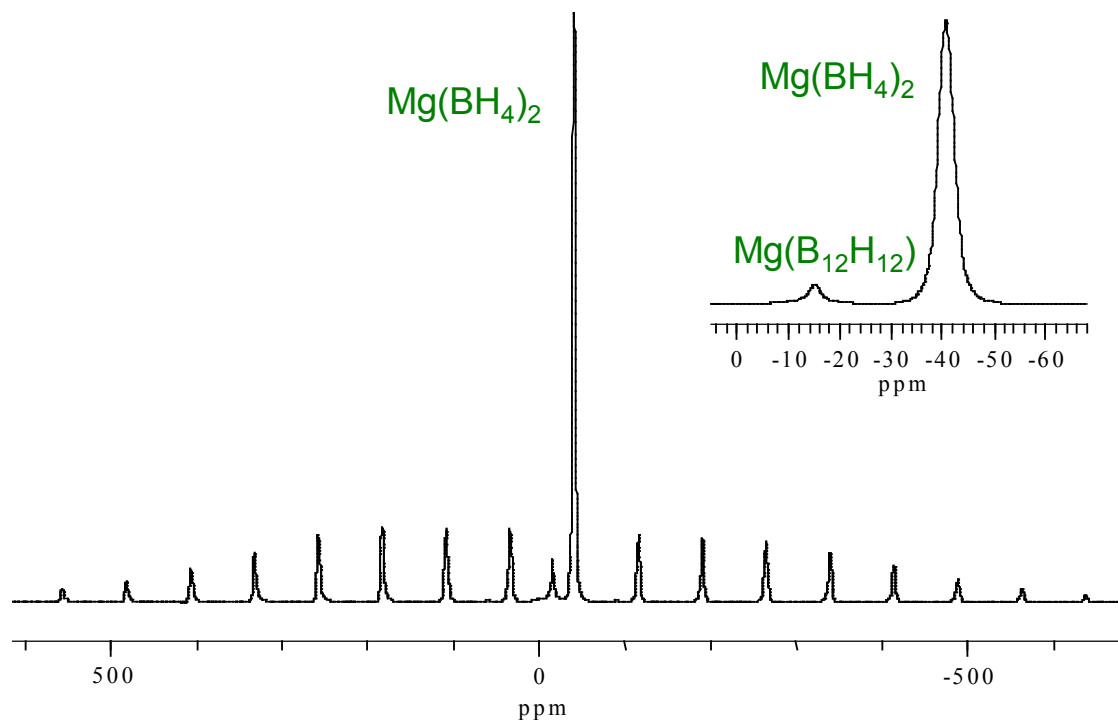


# Supplemental Slides

# Technical Accomplishments and Progress Anionic Borohydrides

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

- > XRD not generally used due to the highly amorphous nature of boranes and borohydrides.
- > 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.

MAS  $^{11}\text{B}$  NMR  $\text{MgB}_2$  + 2 mol % additive hydrogenated under 950 bar at 400 °C