

Advanced, High-Capacity Reversible Metal Hydrides

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of HAWAII[®]
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.

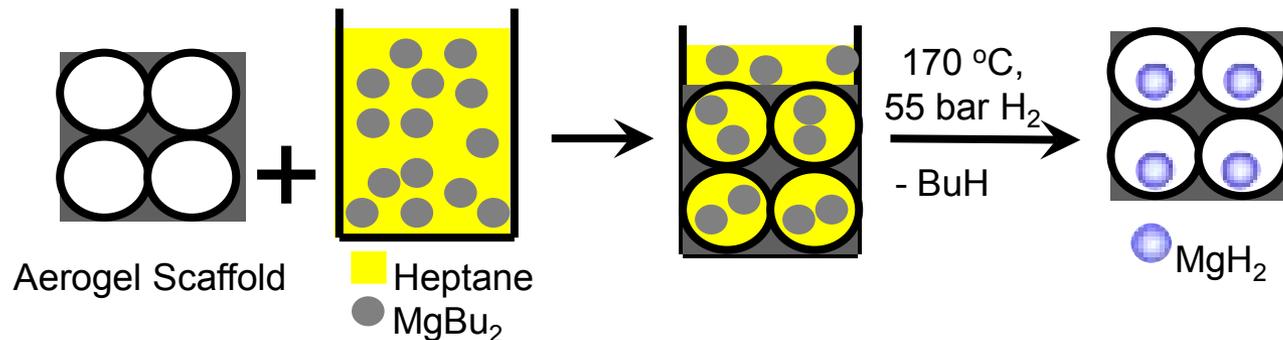
Current investigations include:

- $\text{Mg}(\text{BH}_4)_2$ nano-confined carbon aerogels.
- Reversible dehydrogenation of high capacity borohydrides at low temperatures.
- Development of a method for the hydrogenation LiH/Al to 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 %** H_2 upon dehydrogenation.
- > Ball-milled 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 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 Nano-Confined Mg-Based Hydrides in Carbon Aerogels

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.

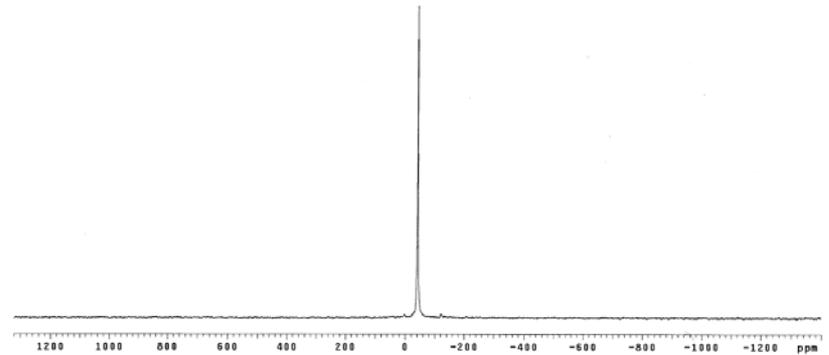
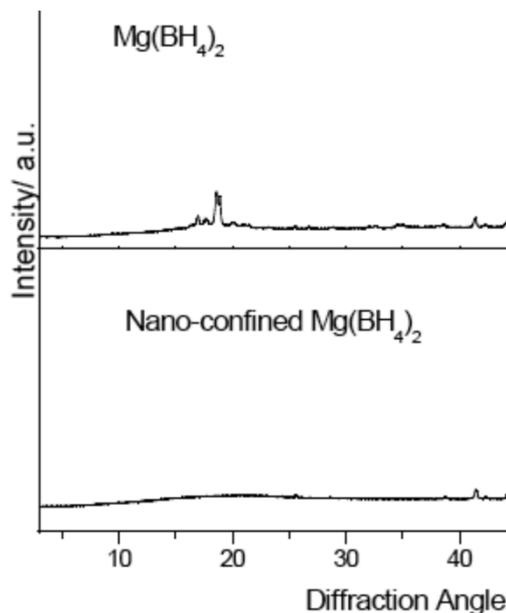
Technical Accomplishments and Progress

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.

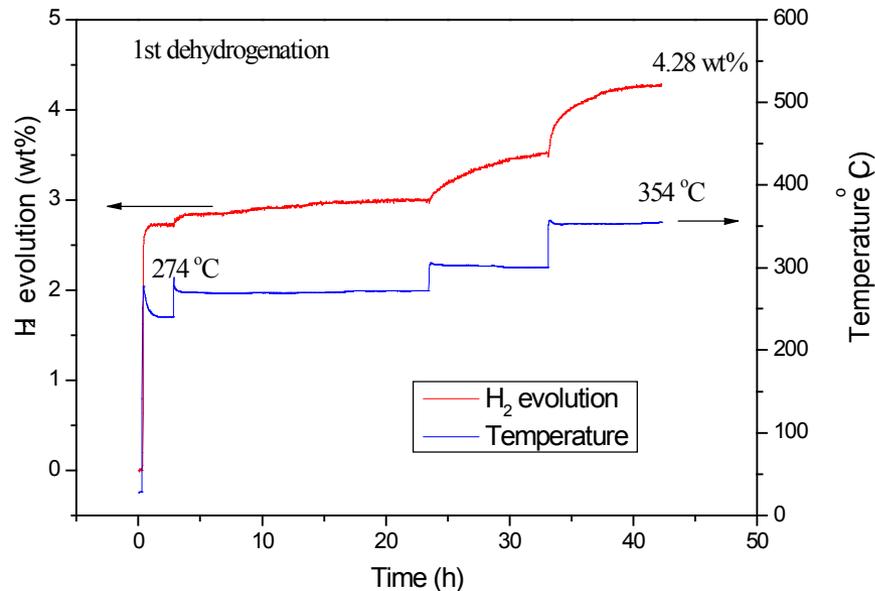


MAS ^{11}B NMR spectrum of the hydride incorporated aerogel verifies that $\text{Mg}(\text{BH}_4)_2$ is the only boron containing species present in the aerogel.

Technical Accomplishments and Progress

Nano-Confined Mg-Based Hydrides in Carbon Aerogels

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

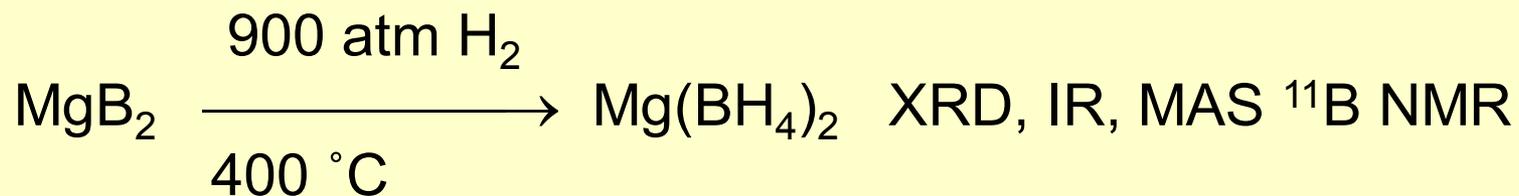


Hydrogen is evolved at the rate of 0.1 wt%/min at 270 °C during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting MgB_2 under 120 atm at 220 °C gives rise to $\text{Mg}(\text{B}_{12}\text{H}_{12})_2$ as occurs with bulk $\text{Mg}(\text{BH}_4)_2$.

Technical Accomplishments and Progress Anionic Borohydrides

The ΔH_{dehyd} of 42 kJ/mole suggests that it should be possible to hydrogenate 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

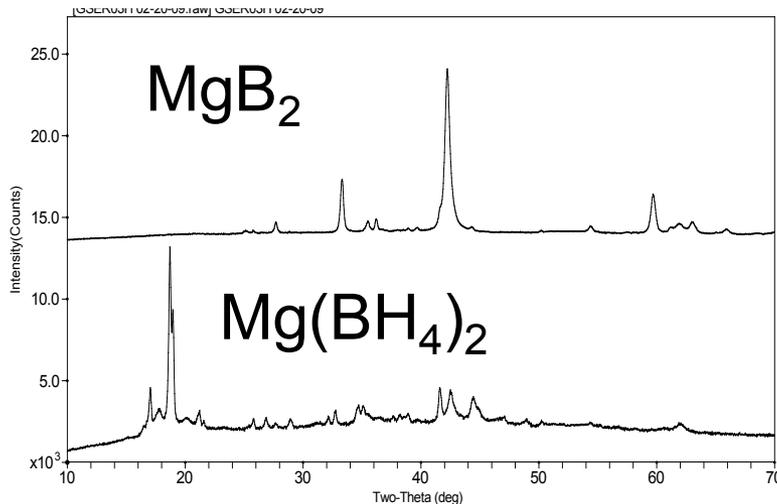
Cycling Studies

XRD

MAS ^{11}B NMR

After
dehydrogenation
at 530 °C.

After
hydrogenation at
400 °C under 950
atm H_2 .



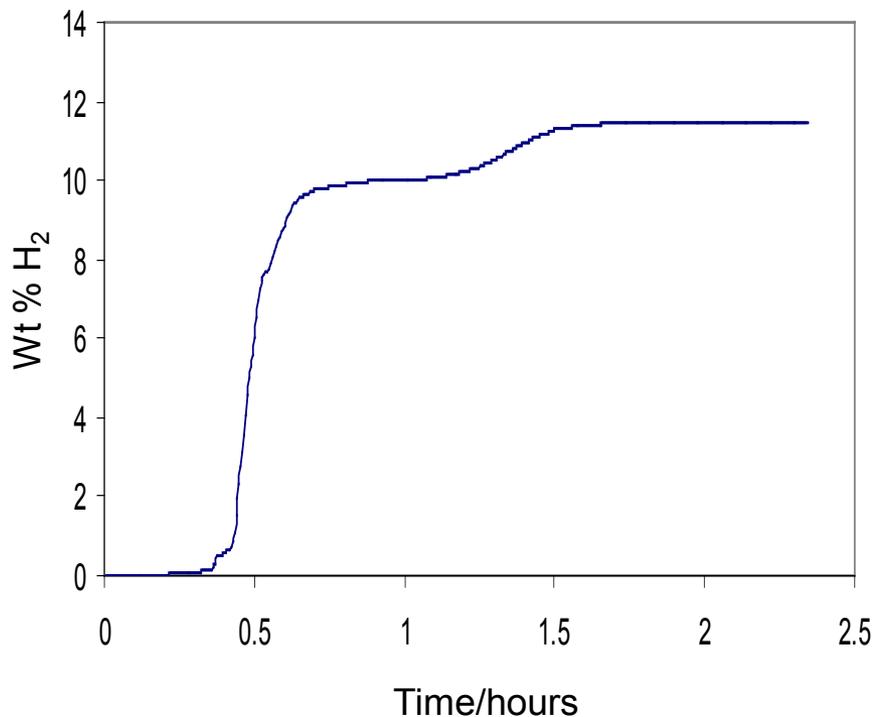
MgB_2

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

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.

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 MgB₂ might lead to cycling of >14 wt % hydrogen.

Technical Accomplishments and Progress Borohydrides

Cycling Under Mild Conditions Collaboration with PNL

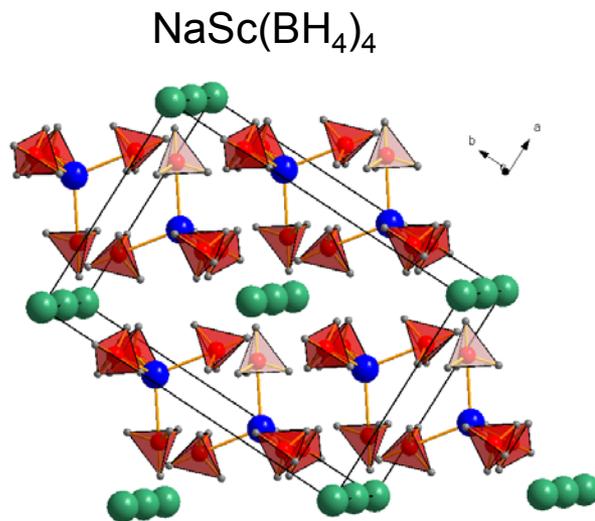
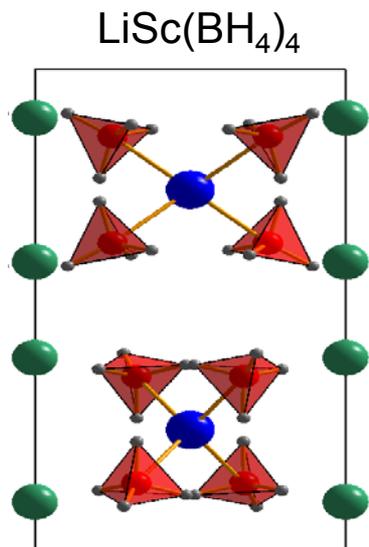
$\text{Mg}(\text{B}_{12}\text{H}_{12})$ is a thermodynamic sink whose formation precludes the reversible dehydrogenation $\text{Mg}(\text{BH}_4)_2$ at moderate temperatures and pressures.

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

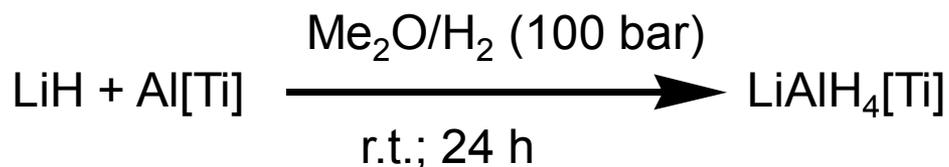
- Like sodium alanate, stepwise dehydrogenation, BUT first step is **exo**thermic.



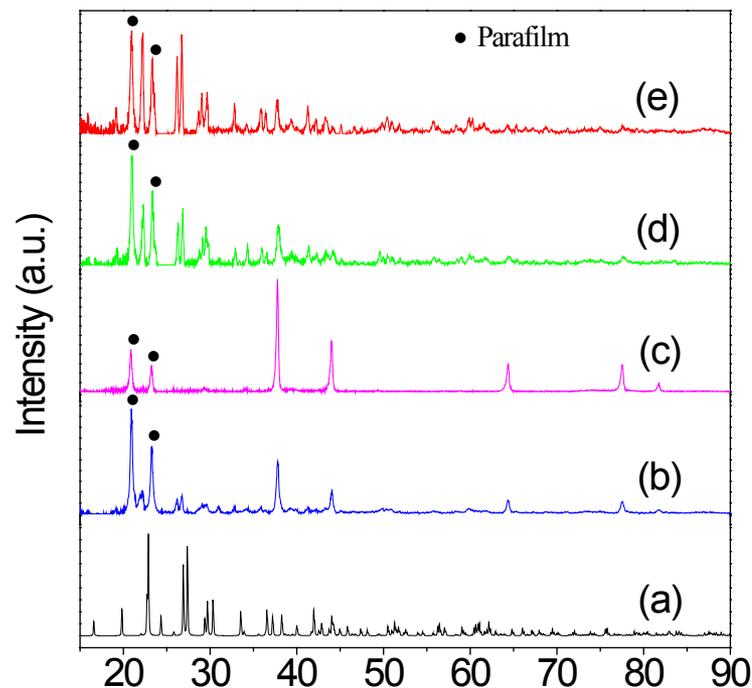
- Together steps 1 and 2 provide ~7.9 wt %H.
- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P).
- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle.
- Graetz (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 H₂
- Fully charged Ti-doped LiAlH₄ obtained
- Very low levels of Ti can be used (~500 ppm)



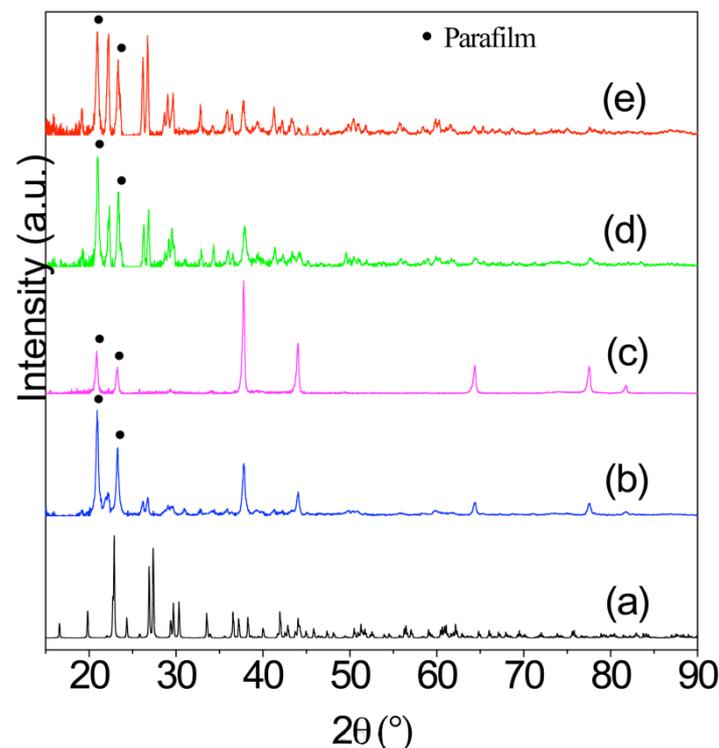
XRD patterns of LiAlH₄ samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl₃); (c) fully de-H (0.2 mol% TiCl₃); (d) re-H (2.0 mol% TiCl₃); (e) re-H (0.2 mol% TiCl₃).

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

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.

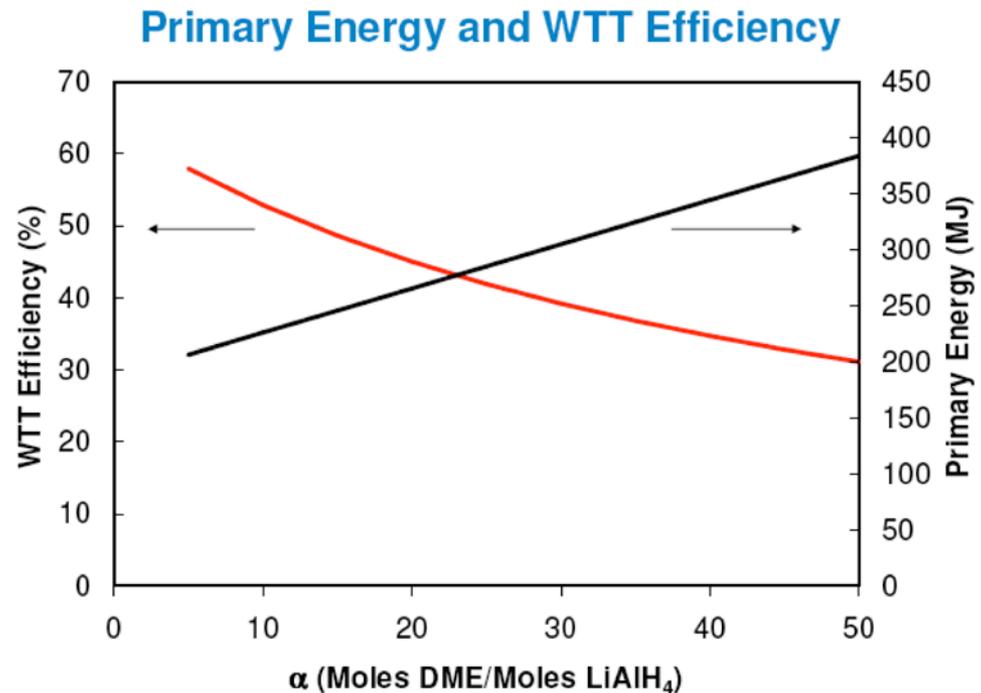


TPD plots for LiAlH₄ samples: (a) as-received; (b) milled with 2.0 mol% TiCl₃; (c) re-H (2.0 mol% TiCl₃); (d) re-H (1.0 mol% TiCl₃); (e) re-H (0.5 mol% TiCl₃); and (f) re-H (0.2 mol% TiCl₃).

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

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

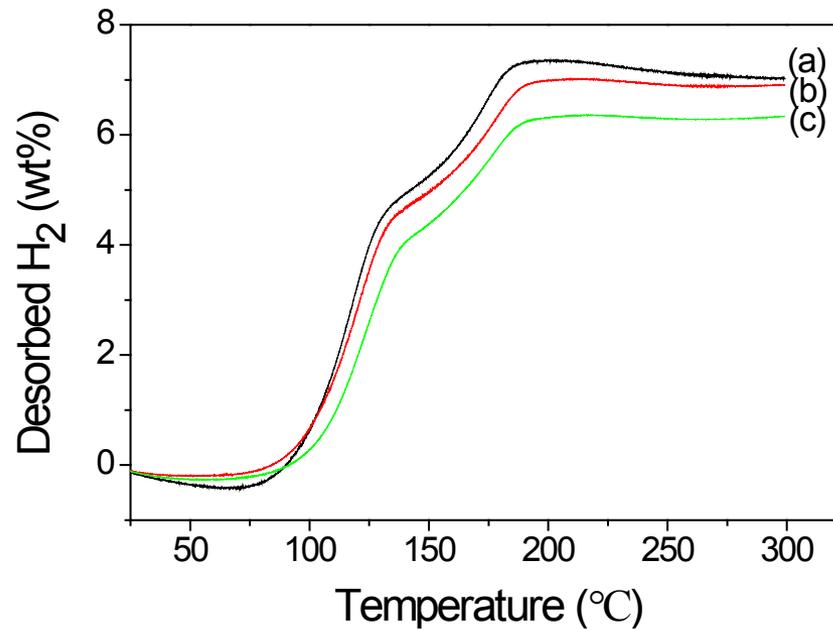
- Energy for compression of Me_2O and H_2 is $\sim 1/5$ that of H_2 production.
- High $\sim 5\text{M}$ solubility of LiAlH_4 in Me_2O is the key in high efficiency.



Technical Accomplishments and Progress

Hydrogenation in Non-conventional Solvents

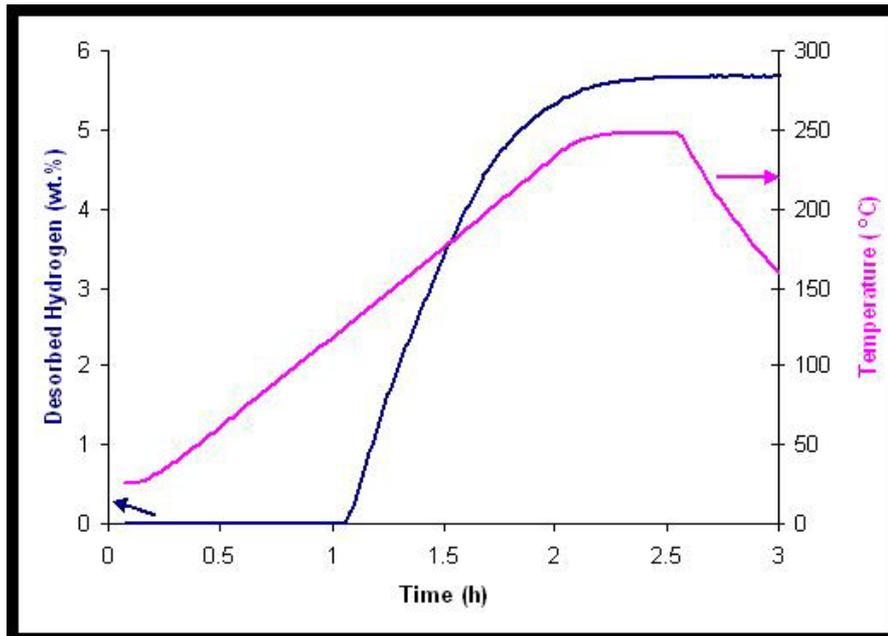
Ti-doped LiAlH_4 shows a drop in capacity over several cycles due to formation of $\text{Ti}_x\text{Al}_{1-x}$ phase.



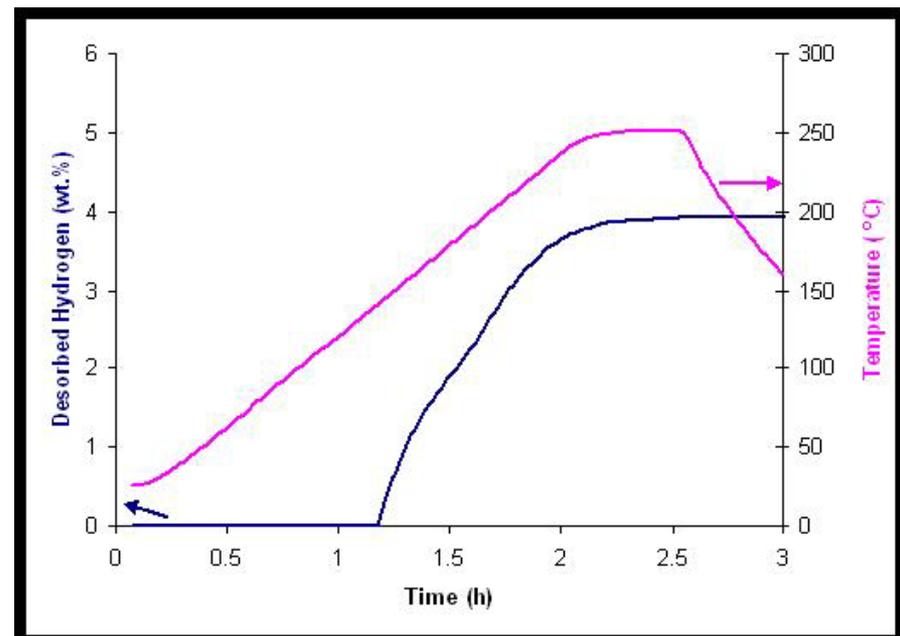
Cycle performance of hydrogenated $\text{LiH}/\text{Al}/\text{TiCl}_3$ (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.

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 LiAlH_4 through variation of the dopants.
- Further evaluation of WTT efficiency of the 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 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 LiAlH_4 can be obtained in major yields from the direct hydrogenation of Ti-doped 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 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

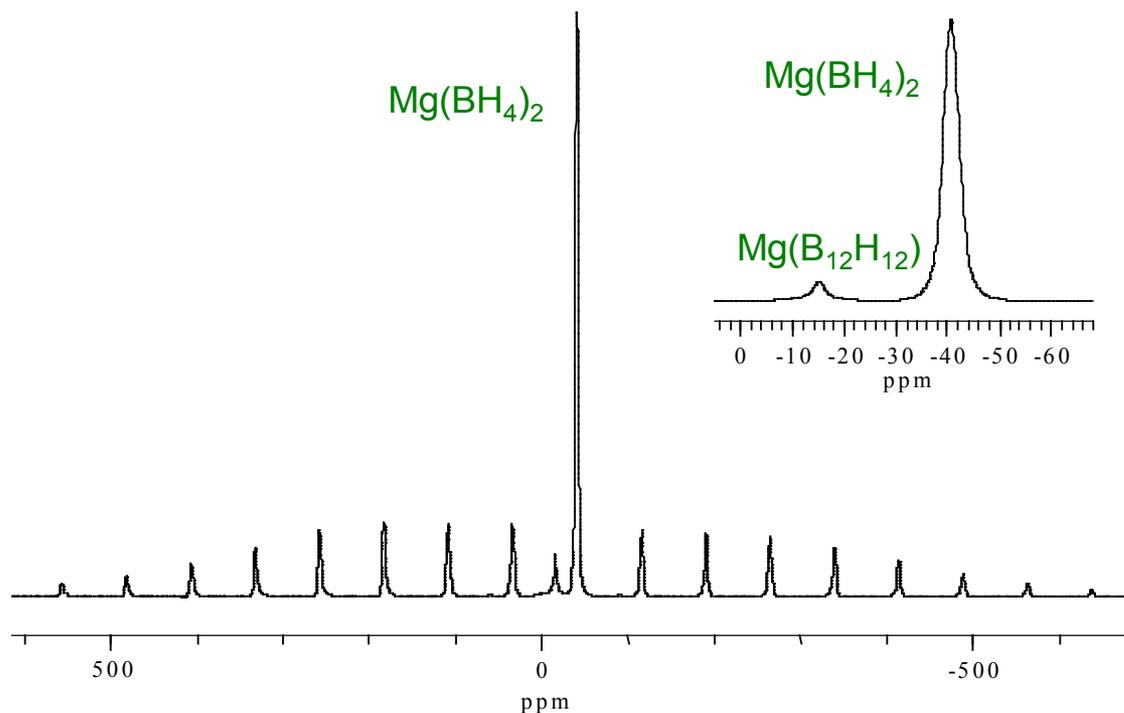
- S. McGrady; University of New Brunswick (Academic): SCF reaction system.

Supplemental Slides

Technical Accomplishments and Progress Anionic Borohydrides

MAS ^{11}B NMR

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

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