

Solid-State Hydriding and Dehydriding of LiBH₄ + MgH₂ Enabled via Mechanical Activation and Nano-Engineering

**Leon L. Shaw, Tippawan Markmaitree, William Osborn,
Xuefei Wan, Kyle Crosby
University of Connecticut**

**Z. Gary Yang, Jianzhi Hu, Ja Hu Kwak
Pacific Northwest National Laboratory**

**May 18 – 22, 2009
2009 DOE Hydrogen Program Review**

Project ID: stp_44_shaw

Overview

Timeline:

- Project start date: December 2004
- Project end date: December 2009
- Percent complete: 85%

Budget:

- Total project funding:
 - DOE share: \$1.35 mil
 - Contractor share: \$0.4 mil
- Funding received in FY08: \$250,000 for UConn; \$80,000 for PNNL
- Funding for FY09: \$200,000 for UConn; \$70,000 for PNNL

Partners/Collaborators:

- Pacific Northwest National Laboratory – NMR analysis
- Universidad de Extremadura, Badajoz, Spain – X-ray analysis
- HRL Laboratories – Ball milling of $\text{LiBH}_4 + \text{MgH}_2$ at liquid N_2 temperature
- University of Pittsburgh – Information exchange

Barriers

- A. System weight and volume:
2 kWh/kg & 1.5 kWh/L
- E. Charging/discharging rates:
3 min for 5 kg

Technical Objectives – Relevance

Objective in FY 08:

- ❑ Establishing solid-state hydriding and dehydriding kinetics of $\text{LiBH}_4 + \text{MgH}_2$ systems**
- ❑ Enhancing solid-state hydriding and dehydriding kinetics of $\text{LiBH}_4 + \text{MgH}_2$ via doping of transition metals such as Mn and V**
- ❑ Enhancing solid-state hydriding and dehydriding kinetics of $\text{LiBH}_4 + \text{MgH}_2$ via milling additives such as graphite**

Objective in FY 09:

- ❑ Further improving the solid-state hydriding/dehydriding properties of $\text{LiBH}_4 + \text{MgH}_2$ via ball milling at liquid nitrogen temperature with the addition of transition metals and milling additives such as boron nitride**
- ❑ Investigating the hydriding and dehydriding reversibility of carbon aerogel confined LiBH_4 and increasing its storage capacity**
- ❑ Demonstrating hydrogen uptake and release of $\text{LiBH}_4 + \text{MgH}_2$ systems with a storage capacity of $\sim 10 \text{ wt}\% \text{ H}_2$ at 200°C**

Technical Impacts – Relevance

- Demonstrated hydriding and dehydriding reactions of LiBH_4 + MgH_2 systems at the solid state, i.e., below the melting point of LiBH_4 ($T_m = 280^\circ\text{C}$) with 9.3 wt% H_2 uptake and 4.5 wt% H_2 release;
- Established a two-step ball milling procedure to improve the solid-state hydriding and dehydriding kinetics of LiBH_4 + MgH_2 systems;
- Identified the solid-state hydriding and dehydriding mechanisms and established a partial ion exchange model to guide the improvement of the diffusion-controlled hydriding dehydriding reaction; and
- Demonstrated the release of H_2 from LiBH_4 at 80°C and the completion of H_2 release at 275°C via nano-engineering with carbon aerogel confinement.

Technical Methods – Approach

- **Identifying the mechanism and rate-controlling step of solid-state hydriding and dehydriding reactions of $\text{LiBH}_4 + \text{MgH}_2$ systems.**
- **Liquid nitrogen temperature ball milling combined with doping of transition metals and milling additives to enhance the solid-state hydriding and dehydriding kinetics.**
- **Developing the mechanistic understanding of the effect of mechanical activation and nano-engineering on hydriding and dehydriding properties.**
- **Applying the fundamental understanding of mechanical activation and the established reaction mechanism and rate-controlling step to enhancing the solid-state hydriding and dehydriding properties of $\text{LiBH}_4 + \text{MgH}_2$ systems.**

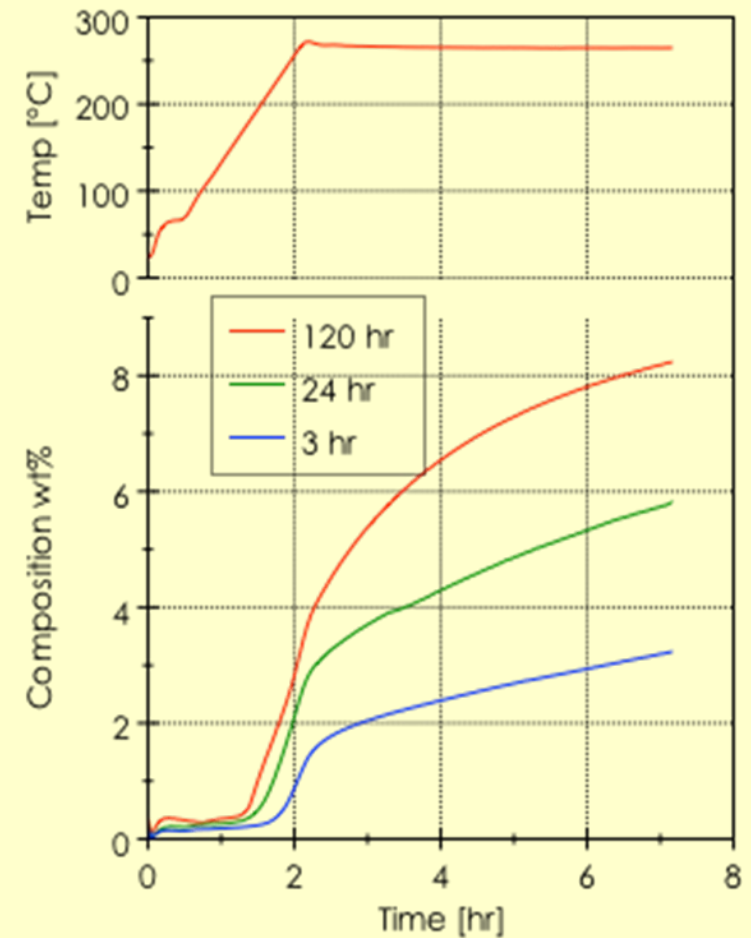
Milestones – Approach

Month/Year	Milestone or Go/No-Go Decision
Nov-08	<p><u>Milestone:</u></p> <ul style="list-style-type: none">(i) Establish the atomic level understanding of the mechanism and kinetics of solid-state hydriding/dehydriding reactions of mechanically activated, nano-engineered $\text{LiBH}_4 + \text{MgH}_2$ systems;(ii) Demonstrate hydriding and dehydriding reactions of $\text{LiBH}_4 + \text{MgH}_2$ systems at the solid state, i.e., below the melting point of LiBH_4 ($T_m = 280^\circ\text{C}$);(iii) Demonstrate hydrogen uptake and release of ($\text{LiBH}_4 + \text{MgH}_2$) systems with a storage capacity of $\sim 10 \text{ wt}\% \text{ H}_2$ at 200°C.
Dec-08	<p><u>Go/No-Go Decision:</u> Demonstrate hydrogen uptake and release of ($\text{LiBH}_4 + \text{MgH}_2$) systems with a storage capacity of $\sim 10 \text{ wt}\% \text{ H}_2$ at 200°C.</p> <ul style="list-style-type: none">(a) Milestones (i) and (ii) were met; however, milestone (iii) was not.(b) A no-go decision was made because milestone (iii) was not met.(c) This project with the original end date of December 2010 will be terminated in December 2009.
Dec-09	<p><u>Milestone:</u> Demonstrate hydrogen uptake and release of ($\text{LiBH}_4 + \text{MgH}_2$) systems with a storage capacity of $\sim 10 \text{ wt}\% \text{ H}_2$ at 200°C.</p>

Technical Accomplishments and Progress (FY08)

Solid-State Hydriding and Dehydriding of the $\text{LiBH}_4 + \text{MgH}_2$ Storage System

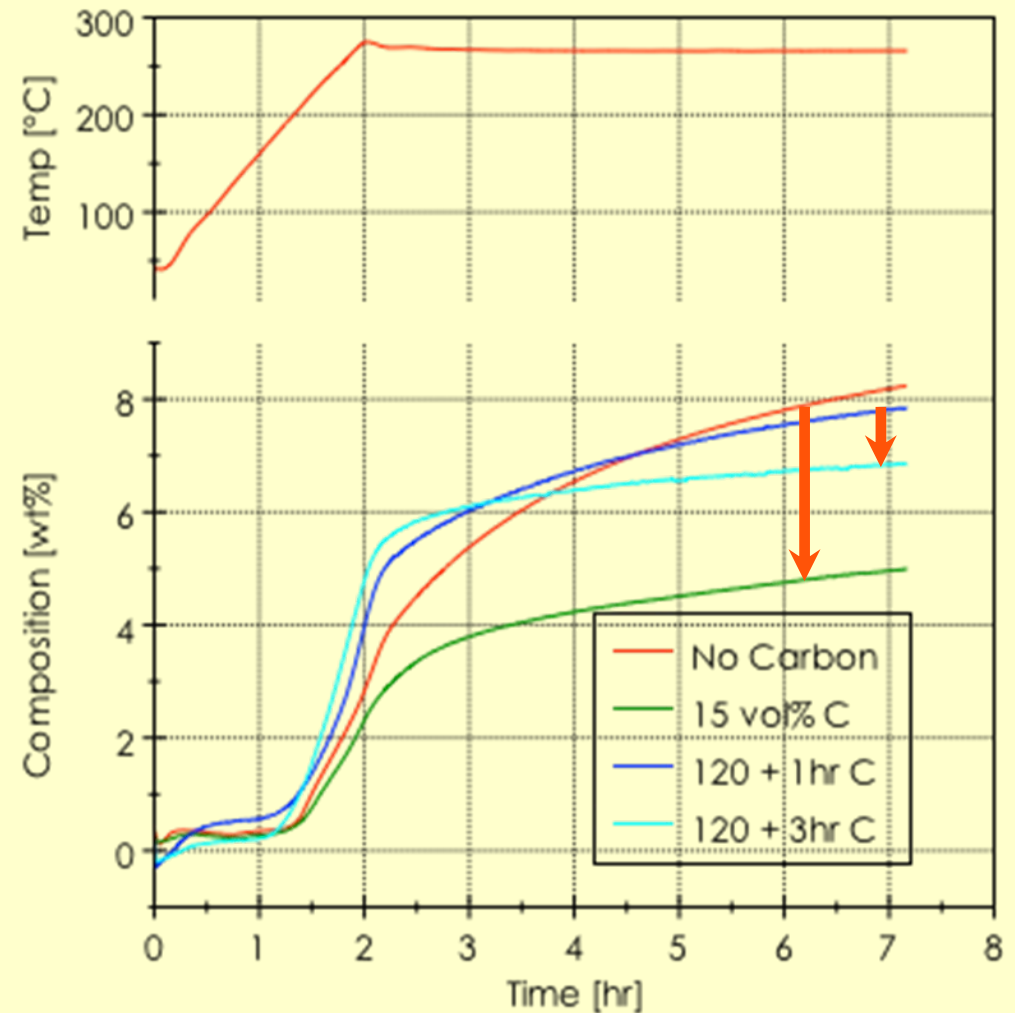
- $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 \leftrightarrow \text{LiH} + \frac{1}{2}\text{MgB}_2 + 2\text{H}_2$
 - 11.6 wt% H_2
 - $\Delta H = 44 \text{ kJ}\cdot\text{mol}^{-1} \text{H}_2$
 - $T_m(\text{LiBH}_4) = 280 \text{ }^\circ\text{C}$
 - $T = 265 \text{ }^\circ\text{C} \Rightarrow$ Solid State Operation
- Milled in the dehydrogenated state
- Milling duration greatly effects properties
- Solid-state hydriding and dehydriding accomplished by long-term ball milling – nano-particle formation & high crystal defects (high diffusion rates)



Technical Accomplishments and Progress (FY09)

Enhancing Hydriding & Dehydriding Properties via Milling Additives

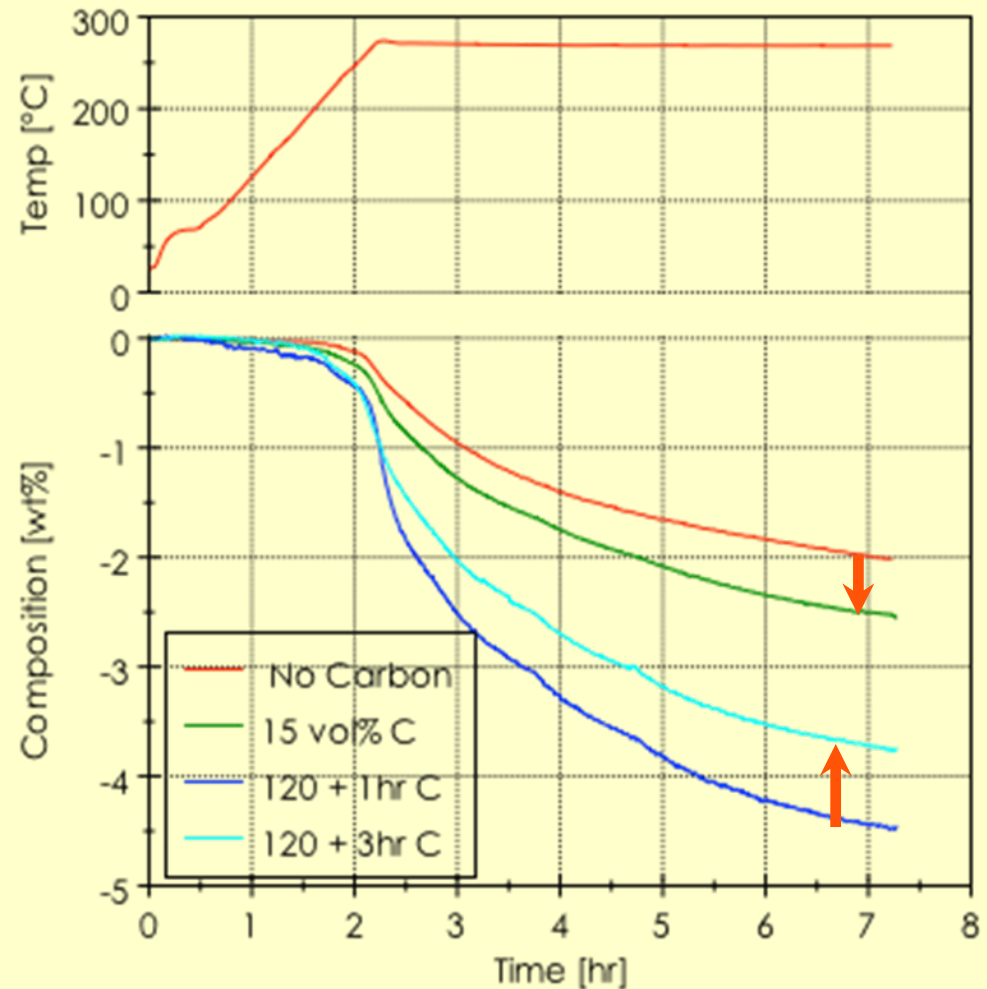
- Include graphite in ball milling of LiH+MgB₂ to improve milling efficiency and uniformity
- Normalized composition to exclude 15 vol% C
- Simply adding graphite reduces absorption by 40%
- LiH and C are reactive – *Two-step milling* to address this issue (e.g., 120h without C + 1h with C)



Technical Accomplishments and Progress (FY09)

Solid-State Hydrogen Release of $\text{LiBH}_4 + \text{MgH}_2$ Storage System

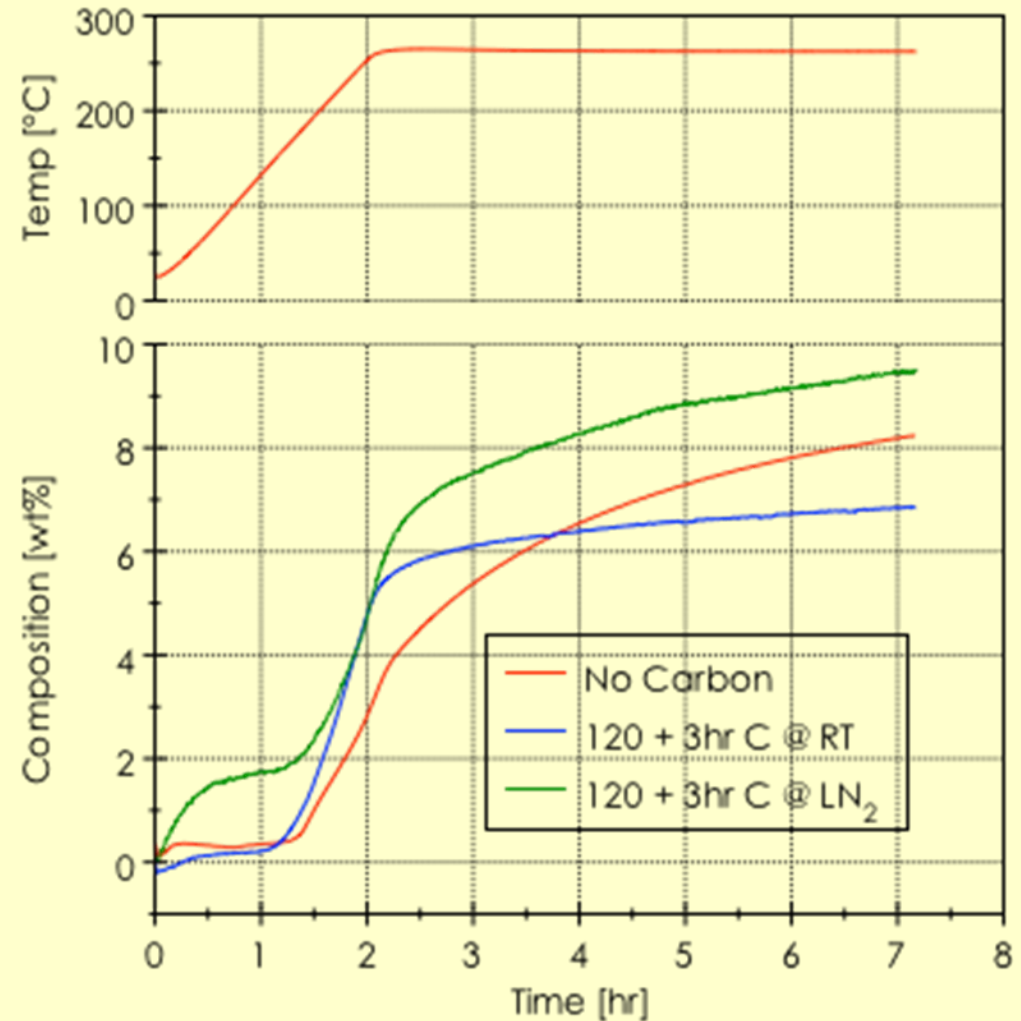
- 120 hr milling with C does improve release kinetics
- *Two-step milling*, i.e., 120+3 and 120+1 further enhances performance
- 120+1 milling is better than 120+3 milling because of the limited reaction between LiH and C
- Release of 4.5 wt% H_2 at 265°C accomplished.



Technical Accomplishments and Progress (FY09)

Further Enhancing the Solid-State Hydrogen Uptake/Release Kinetics via Milling at Liquid Nitrogen Temperature

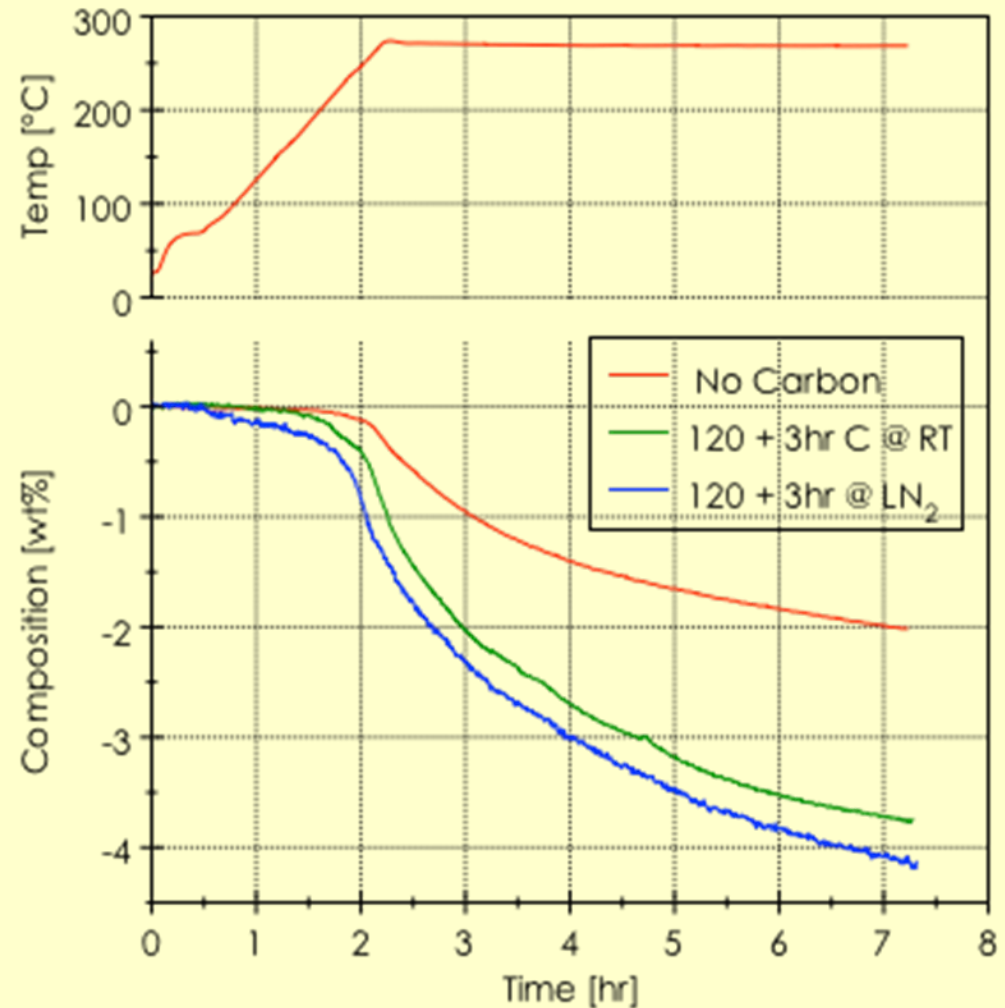
- 120hr RT milling for LiH and MgB₂, followed by Liq. N₂ milling – *Two-step milling at Liq. N₂*
- Liq. N₂ milling provides the best improvement because of the limited reaction between LiH and C
- 9.3 wt% H₂ uptake at 265°C accomplished
- Anomalous absorption during the temp ramp



Technical Accomplishments and Progress (FY09)

Further Enhancing the Solid-State Hydrogen Uptake/Release Kinetics via Milling at Liquid Nitrogen Temperature (Cont.)

- Samples milled in the dehydrogenated state are exposed to 5+ hours at 265 °C (97% T_m) → Growth
- 4.2 wt% H₂ release at 265 °C
- LN₂ milling does not offer large improvements in hydrogen release over RT milling, suggesting that hydriding & dehydriding kinetics are controlled by different mechanisms.



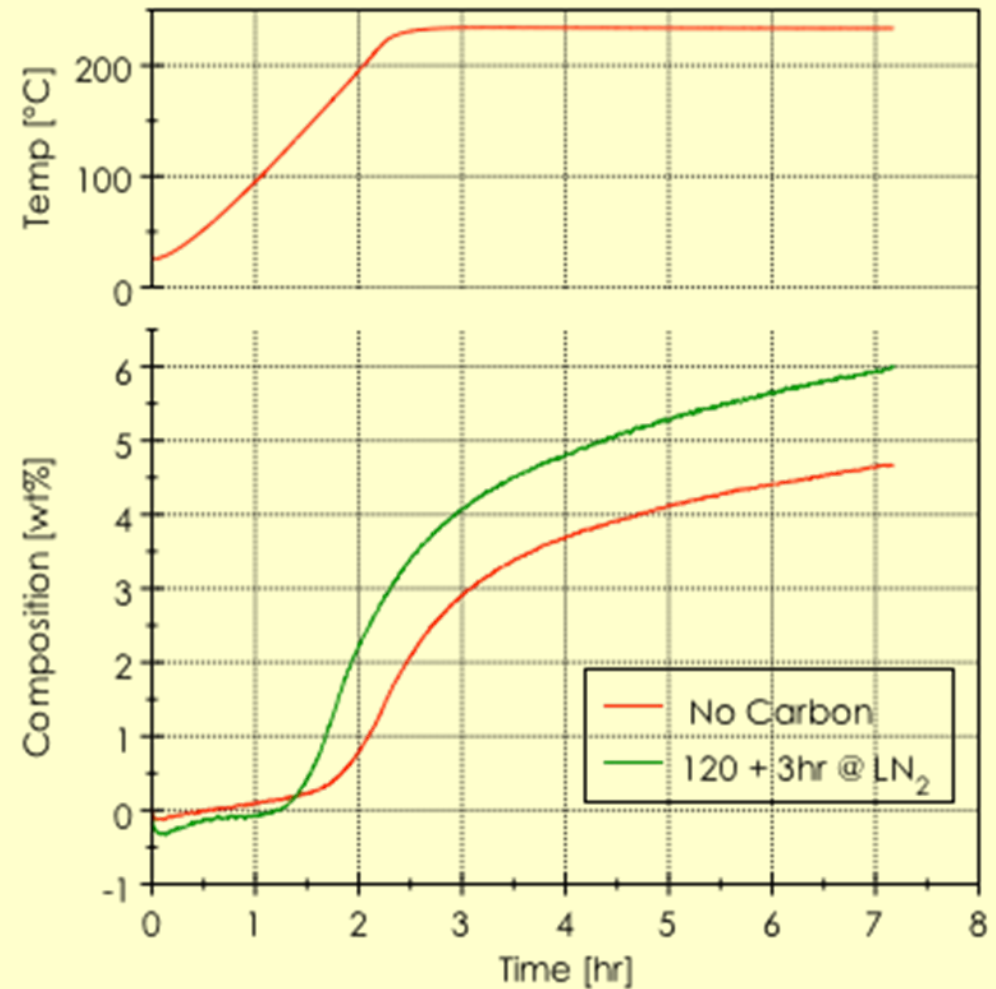
Technical Accomplishments and Progress (FY09)

Reducing the Solid-State Hydrogen Uptake and Release Temperature

- 265 °C allows solid-state, but is still too warm
- Diffusion rate is thermally activated

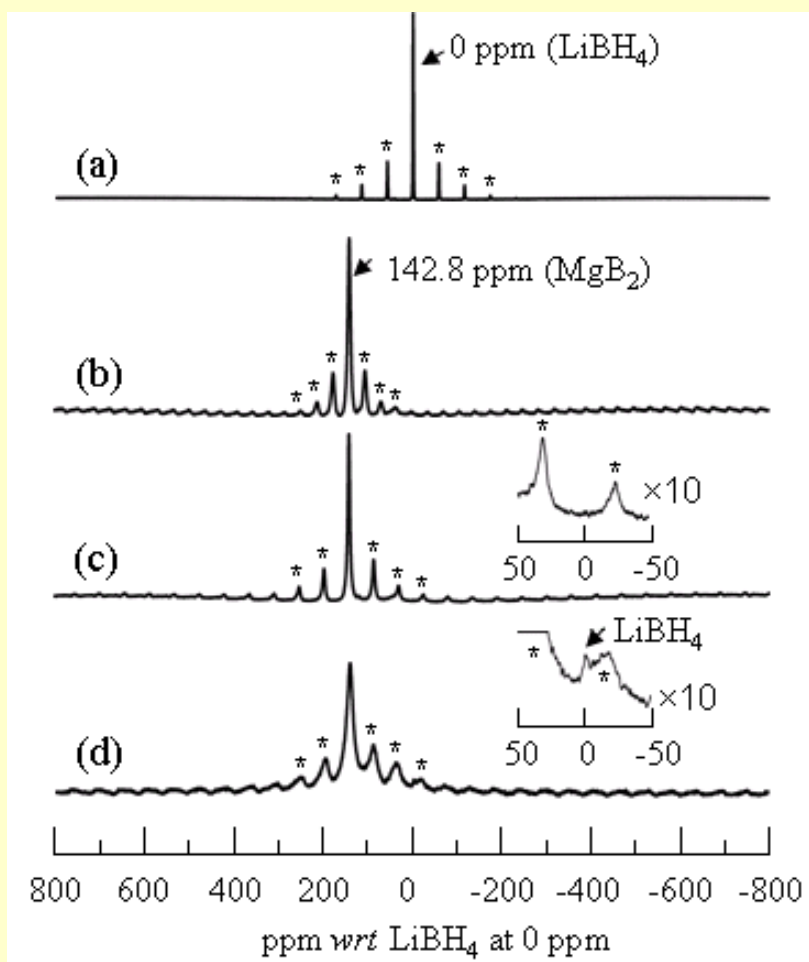
$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

- T = 235 °C & 6.1 wt% H₂ uptake



Technical Accomplishments and Progress (FY09)

High-Field NMR Analysis of Solid-State Hydriding/Dehydriding Mechanisms



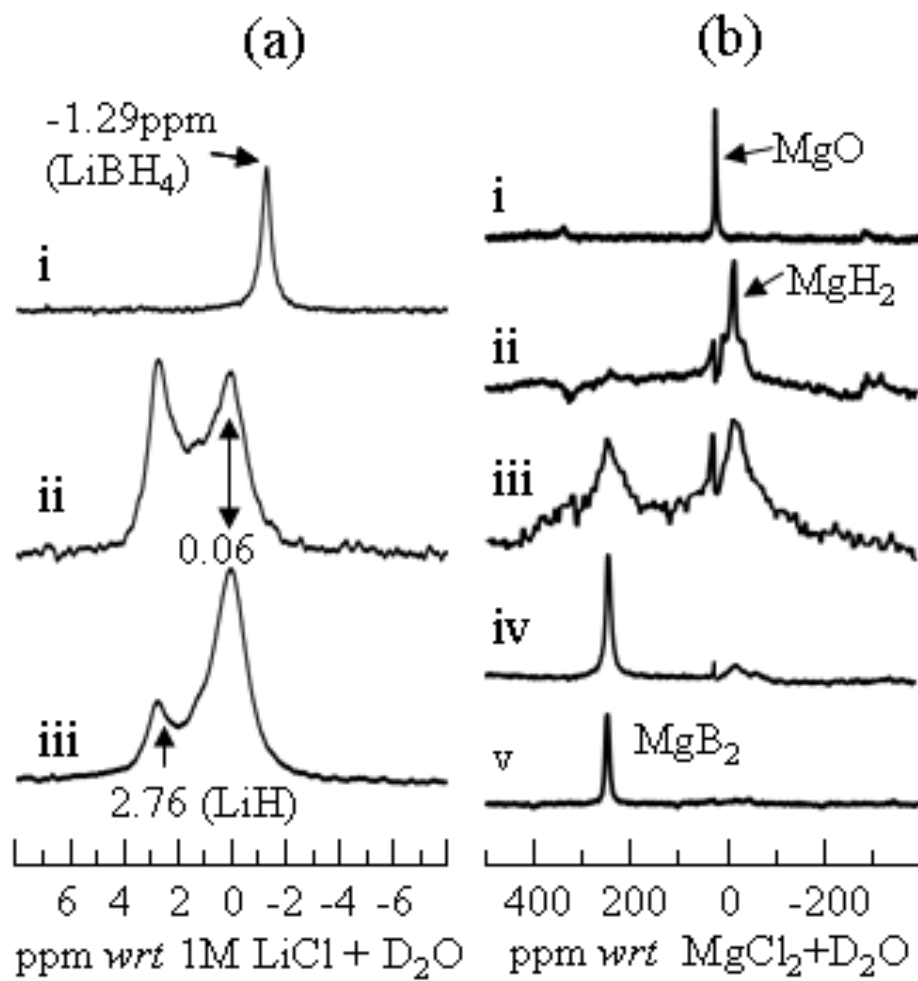
^{11}B MAS NMR spectra:

- Bulk LiBH_4
- Bulk MgB_2
- $\text{LiH} + \text{MgB}_2$ with 3hr ball milling
- $\text{LiH} + \text{MgB}_2$ with 120hr ball milling

- The similar ^{11}B MAS centerband peak positions of the 3hr and 120hr ball milled $\text{LiH} + \text{MgB}_2$ as that of pure MgB_2 indicates that the layered boron structure is unchanged during ball milling.
- The substantially increased centerband linewidth for the 120hr milled sample suggests that the MgB_2 particle size is dramatically decreased by ball milling.

Technical Accomplishments and Progress (FY09)

High-Field NMR Analysis of Solid-State Hydriding/Dehydriding Mechanisms (Cont.)



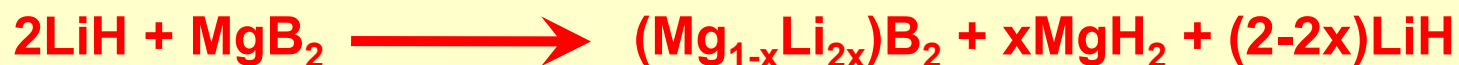
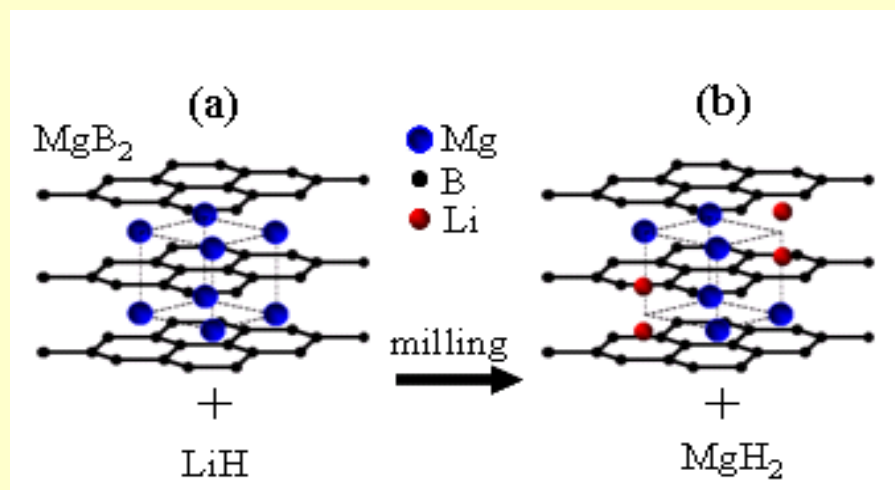
(a) ^6Li MAS NMR spectra: i) LiBH_4 , ii) $\text{LiH} + \text{MgB}_2$ with 3hr ball milling, iii) $\text{LiH} + \text{MgB}_2$ with 120 hrs ball milling,

(b) ^{25}Mg MAS NMR spectra: i) MgO , ii) MgH_2 , iii) $\text{LiH} + \text{MgB}_2$ with 120hr ball milling, iv) $\text{LiH} + \text{MgB}_2$ with 3hr ball milling, v) MgB_2

- The 2.76ppm ^6Li peak is assigned to LiH , while the 0.06ppm ^6Li peak is an intermediate in an ionic state. The quantity of the intermediate increases with the milling time.
- Long-term ball milling (120 h) leads to the formation of amorphous MgH_2 and the particle size refinement of MgB_2 .
- Approximately 50% of MgB_2 is converted to MgH_2 during 120h ball milling.

Technical Accomplishments and Progress (FY09)

High-Field NMR Analysis of Solid-State Hydriding/Dehydriding Mechanisms – A Partial Ion Exchange Model

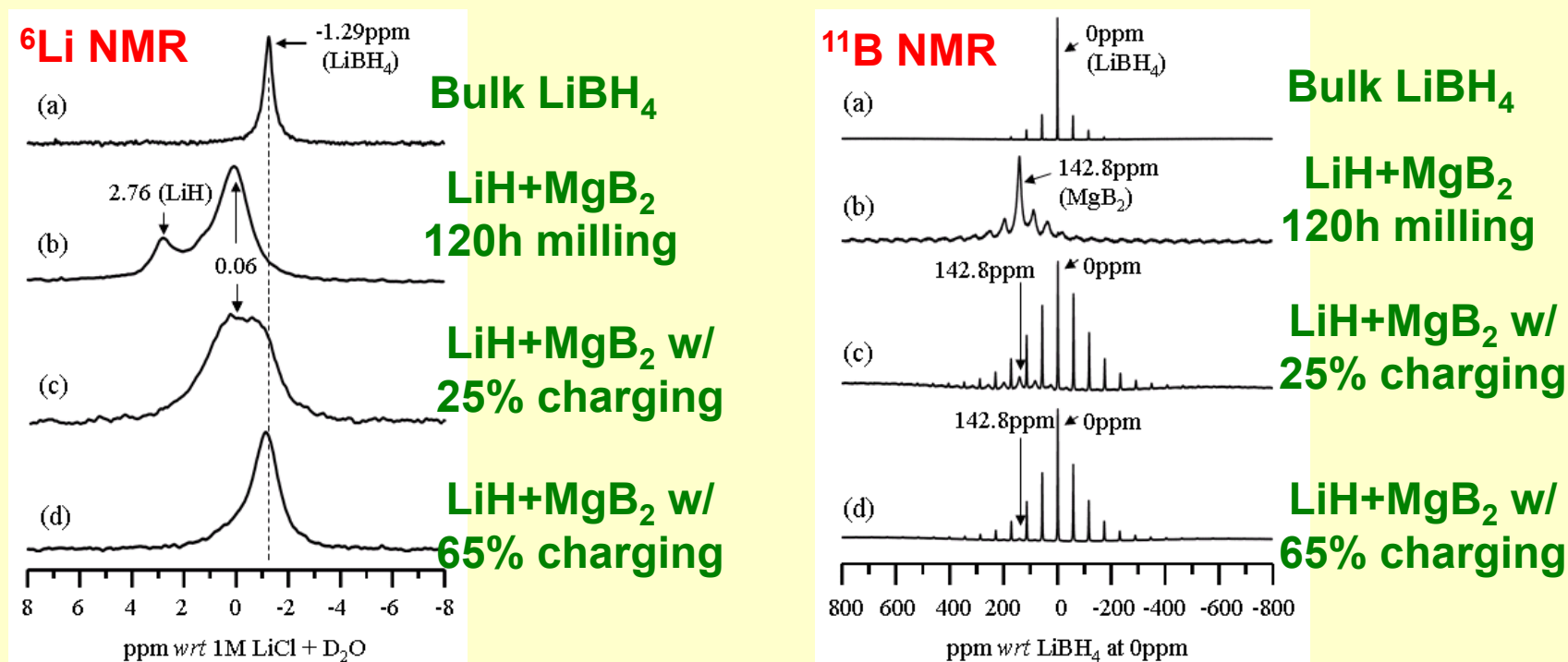


Ball milling & Hydriding

- Long-term ball milling results in the partial exchange of the Mg²⁺ ions in the MgB₂ crystal by the Li⁺ ions from the LiH crystal.
- This partial ion exchange results in the formation of a compound with a composition of (Mg_{1-x}Li_{2x})B₂ where x is a variable changing from 0 to less than 1.
- Each expelled magnesium combines with two protons from LiH to form MgH₂.
- Formation of (Mg_{1-x}Li_{2x})B₂ enhances the hydriding reaction because Mg needs to be expelled to form LiBH₄.

Technical Accomplishments and Progress (FY09)

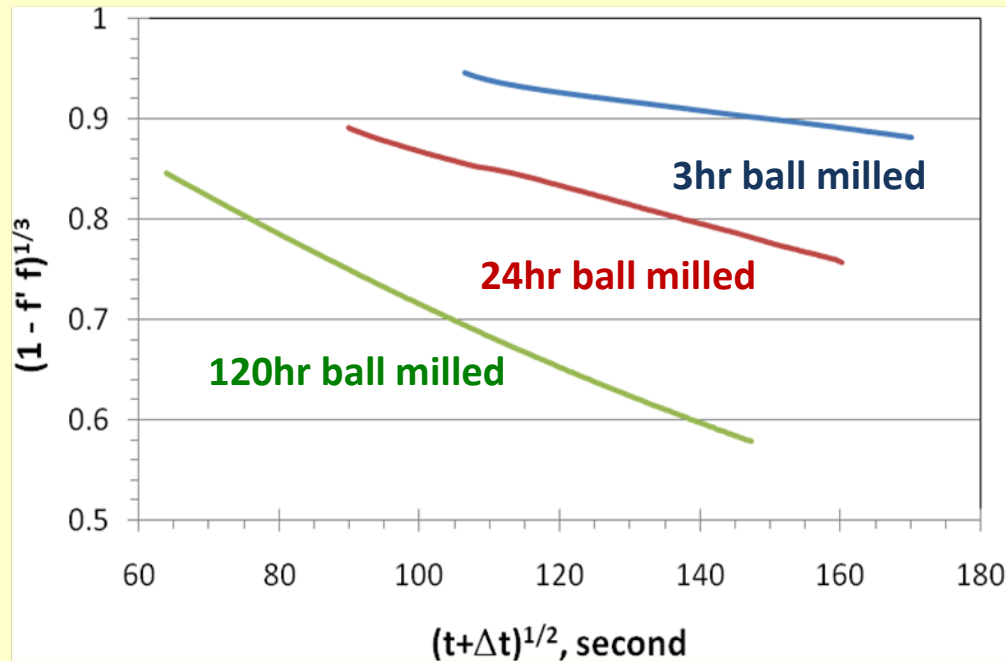
High-Field NMR Analysis of Solid-State Hydriding/Dehydriding Mechanisms – A Partial Ion Exchange Model (Cont.)



- During hydrogenation LiH continues to react with MgB_2 to form the intermediate $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ which is subsequently hydrided to form LiBH_4 , as shown by ^6Li MAS spectra.
- During hydrogenation MgB_2 continues to decrease while LiBH_4 increases, as shown by ^{11}B MAS spectra.
- During hydrogenation MgB_2 continues to decrease while MgH_2 increases, not shown here because of the space limitation.

Technical Accomplishments and Progress (FY09)

Diffusion-Controlled Solid-State Hydriding and Dehydriding Reactions of $\text{LiBH}_4 + \text{MgH}_2$

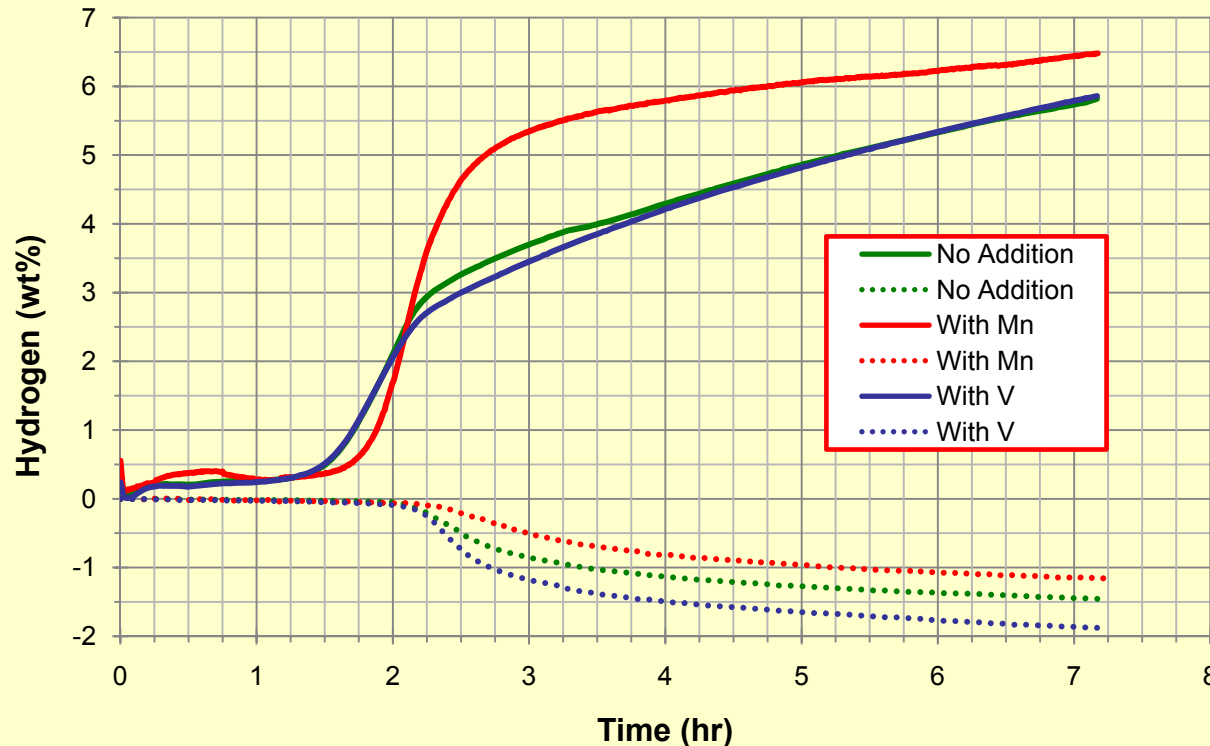


Analysis of the hydrogenation curves of the 120hr, 24hr, and 3hr ball-milled mixtures, based on the diffusion-controlled core/shell model.

- Solid-state hydriding and dehydriding of the $\text{LiBH}_4 + \text{MgH}_2$ system are diffusion-controlled.
- The diffusion control phenomenon is in good accordance with the partial ion exchange model identified.
- Thus, to enhance the hydriding and dehydriding kinetics of $\text{LiBH}_4 + \text{MgH}_2$, one needs nano-particles and fast diffusion rates.

Technical Accomplishments and Progress (FY09)

Enhancing Hydriding and Dehydriding Kinetics of $\text{LiBH}_4 + \text{MgH}_2$ via Doping of Transition Metals



Comparisons of 24h ball milled $\text{LiH} + \text{MgB}_2$ mixture with and without Mn or V

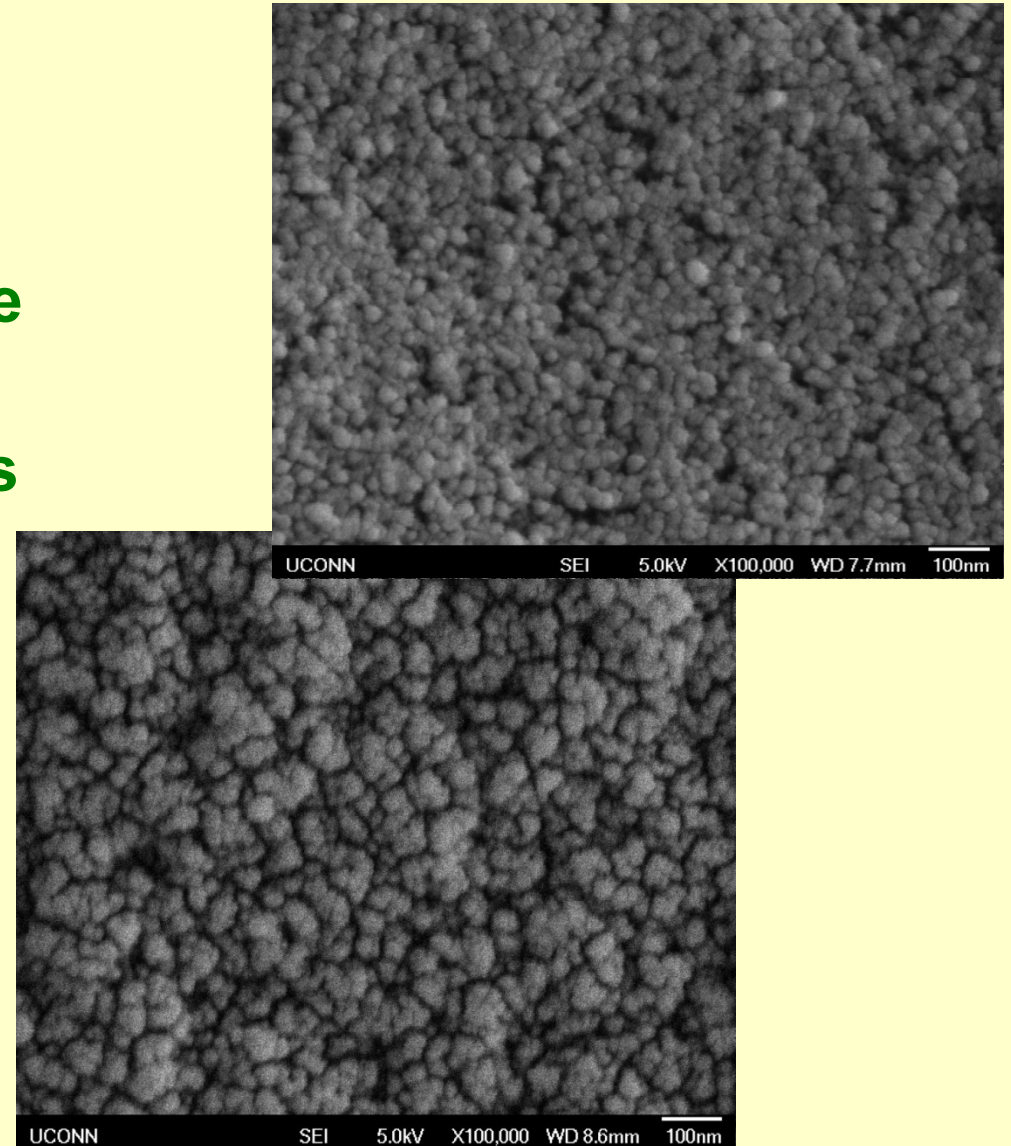
- Mn enhances hydrogenation because it dissolves in MgB_2 . However, it does not improve dehydrogenation.
- V does not enhance hydrogenation because it does not dissolve in MgB_2 . However, it improves dehydrogenation because V forms $\text{VH}_{0.81}$ during hydrogenation and $\text{VH}_{0.81}$ behaves like a hydrogen pump during dehydrogenation to induce decomposition of MgH_2 .

Technical Accomplishments and Progress (FY09)

Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement

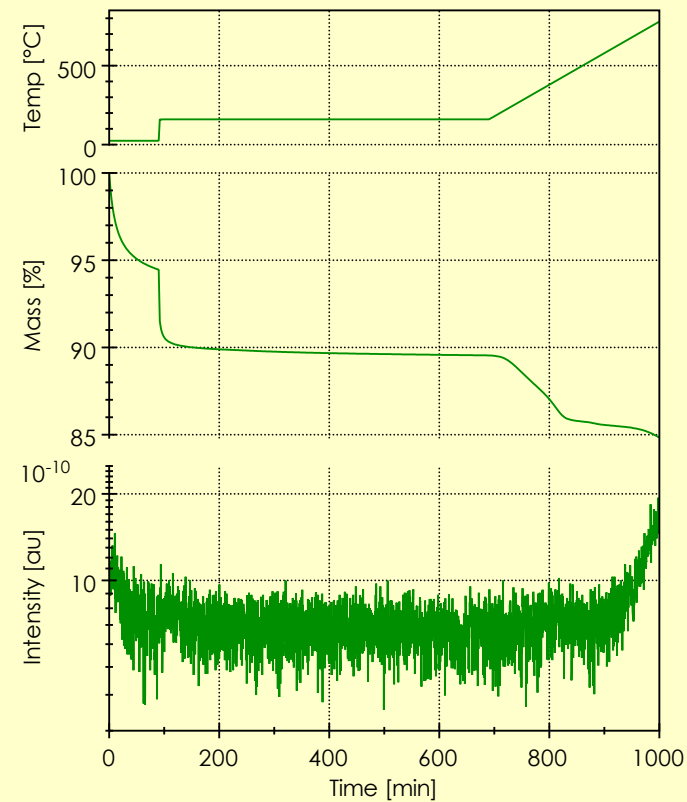
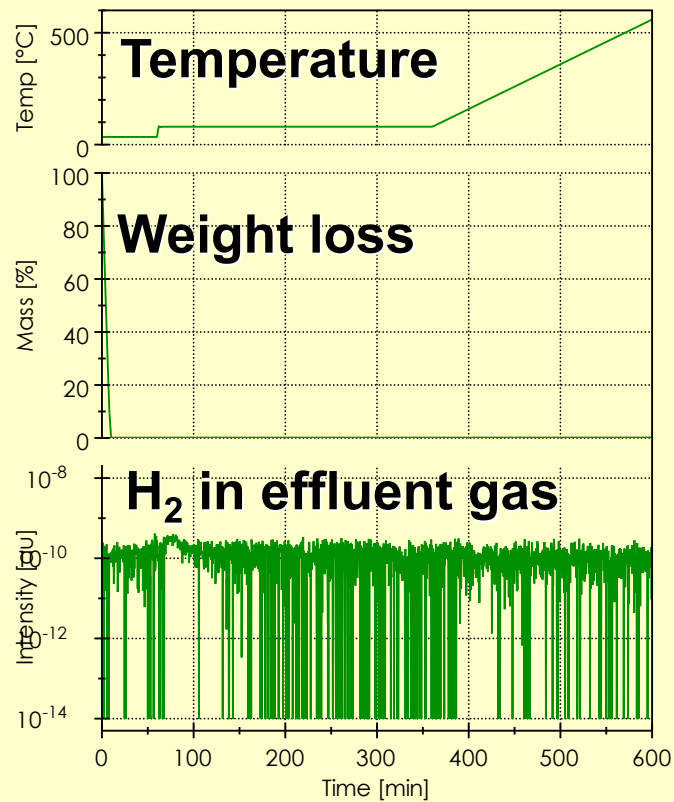
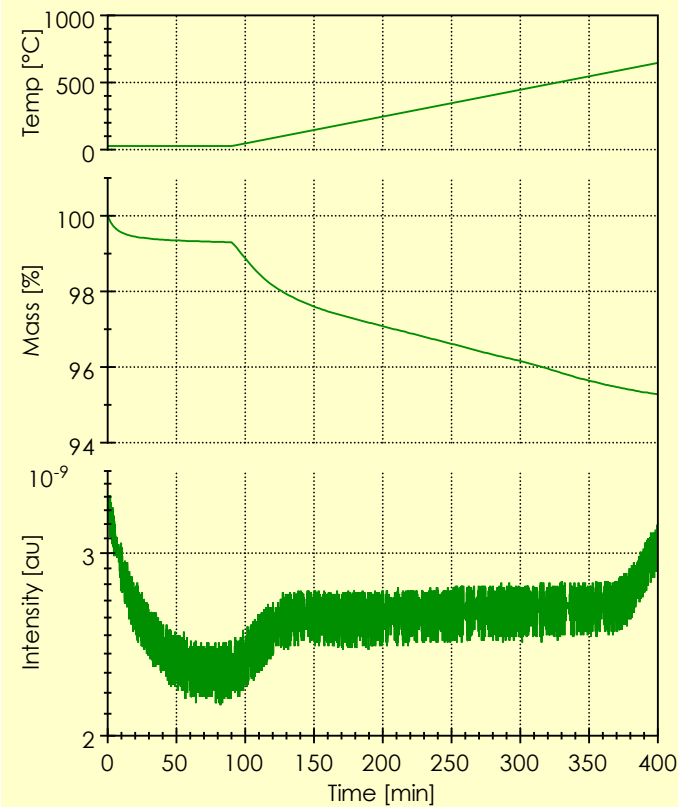
- Pore size distributions of CAs from 4 to 12 nm
- Confining LiBH_4 to CA pores eliminates long range microstructural growth
- Solvent infiltration provides good control of the size of LiBH_4
- Low concentrations for LiBH_4 in THF (0.5 M)

Carbon aerogel (CA) images



Technical Accomplishments and Progress (FY09)

Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement (Cont.)



As Received CA

THF Solvent

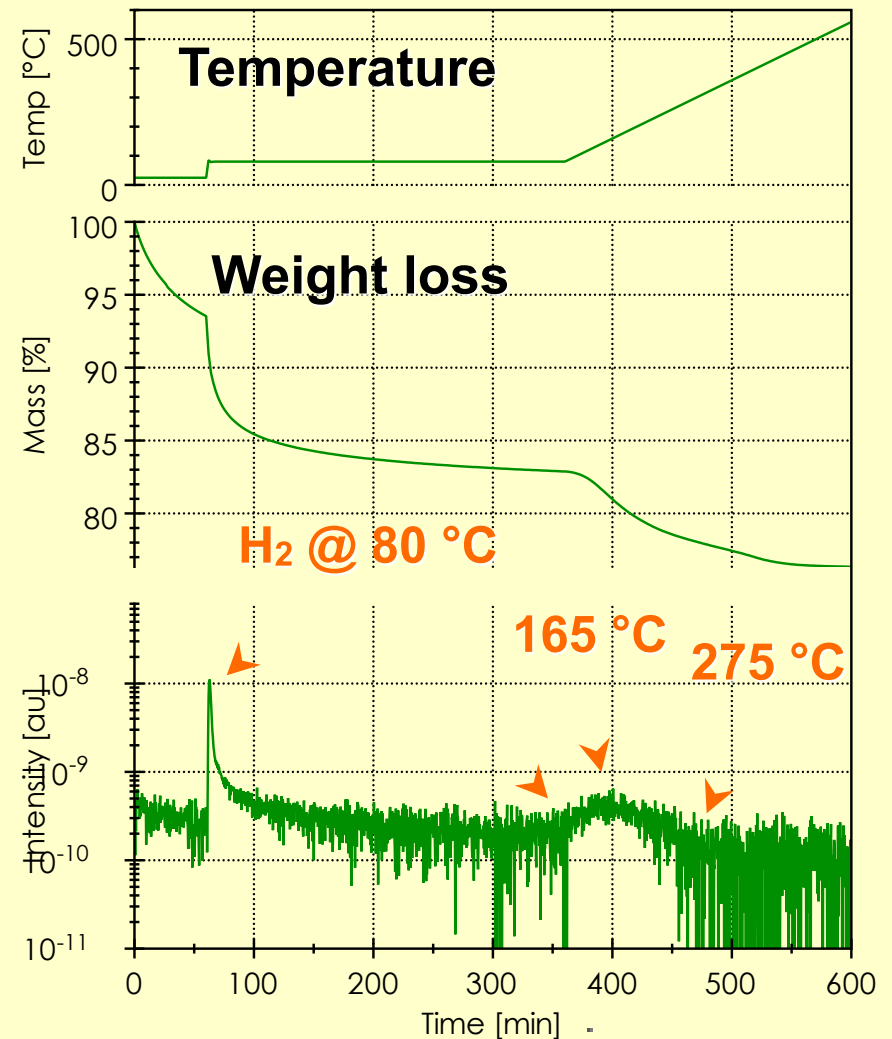
THF infiltrated CA

No H₂ Released by CA or THF

Technical Accomplishments and Progress (FY09)

Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement (Cont.)

- **0.5 M LiBH₄ in THF**
 - **Evacuate CA**
 - **Submerge in solution**
 - **Pressurize**
 - **Drain and vacuum dry (RT)**
- **0.5 M in a 5 nm pore**
→ **<1 nm LiBH₄ particle**
- **LiBH₄ released H₂ at 80°C!**
- **Completed H₂ release at 275°C!**
- **Change the thermodynamic properties?**



Technical Accomplishments and Progress (FY09)

Properties of Carbon Aerogels (CAs) before and after LiBH_4 infiltration and evaporation of the solvent under vacuum

	Mass of the material (g)	Mass increase (%)	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Peak pore diameter (nm)
CA before infiltration and drying*	0.0464	-	558.3	1.46	10.03
CA after infiltration and drying	0.0543	17 wt%	376.2	1.17	8.52

Infiltration of LiBH_4 into CAs results in a 17% weight gain and simultaneous decreases in the specific surface area, pore volume and peak pore diameter. Based on the peak pore diameter change, the thickness of LiBH_4 film or the particle diameter is ~ 0.75 nm.

Collaborations

- Pacific Northwest National Laboratory (Drs. Z. Gary Yang, Jianzhi Hu, and Ja-Hu Kwak within the DOE H₂ Program) – Extensive NMR analysis of hydrogen storage properties with the following joint publications.
 - J. Z. Hu, J. H. Kwak, Z. G. Yang, W. Osborn, T. Markmaitree, and L. Shaw, “Investigation of Mechanical Activation on Li-N-H Systems using ⁶Li MAS NMR at Ultrahigh Field,” *J. Power Sources*, 182, 278-283 (2008).
 - J. Z. Hu, J. H. Kwak, Z. G. Yang, W. Osborn, T. Markmaitree, and L. Shaw, “Probing the Reaction Pathway of Dehydrogenation of the LiNH₂ + LiH Mixture using In-Situ ¹H NMR Spectroscopy,” *J. Power Sources*, 181, 116-119 (2008).
 - C. Lu, J. Hu, J. H. Kwak, Z. G. Yang, R. Ren, T. Markmaitree, and L. Shaw, “Study the Effects of Mechanical Activation on Li-N-H Systems with ¹H and ⁶Li Solid-State NMR,” *J. Power Sources*, 170, 419-424 (2007).
 - W. Osborn, T. Markmaitree, L. Shaw, J. Z. Hu, J. H. Kwak, and Z. G. Yang, “Low Temperature Milling of the LiNH₂ + LiH Hydrogen Storage System,” *Int. J. Hydrogen Energy*, in press.
 - J. Z. Hu, J. H. Kwak, Z. Yang, X. Wan, and L. Shaw, “Direct Observation of Ion Exchange in Mechanically Activated LiH+MgB₂ System Using Ultra-High Field Nuclear Magnetic Resonance Spectroscopy,” *Appl. Phys. Lett.*, in press.
 - W. Osborn, T. Markmaitree, L. Shaw, R. Ren, J. Z. Hu, J. H. Kwak, and Z. G. Yang, “Overview: the LiNH₂ + LiH Hydrogen Storage System,” *JOM*, in press.

Collaborations (Cont.)

- HRL Laboratories (Dr. John Vajo within the DOE H₂ Program) – **Ball milling of LiBH₄ + MgH₂ at both RT and liquid N₂ temperature to investigate whether MgB₂ can be formed below the melting temperature of LiBH₄.**
- Universidad de Extremadura, Badajoz, Spain (Prof. Angel L. Ortiz outside the DOE H₂ Program) – **Detailed XRD analysis of hydrogen storage properties with the following joint publications.**
 - A. Ortiz, W. Osborn, T. Markmaitree and L. Shaw, “Crystallite Sizes of LiH before and after Ball Milling and Thermal Exposure,” *J. Alloys Compd.*, 454 [1-2] 297-305 (2008).
 - R. Ren, A. L. Ortiz, T. Markmaitree, W. Osborn, and L. Shaw, “Stability of Lithium Hydride in Argon and Air,” *J. Phys. Chem. B.*, 110, 10567 – 10575 (2006).
- University of Pittsburgh (Prof. Karl Johnson within the DOE H₂ Program) – **Information exchange on the prediction of the first-principles calculations**

Proposed Future Work

- **Quantify the storage capacity of carbon aerogel-confined LiBH_4 and investigate its hydriding and dehydriding reversibility.**
- **Increase the storage capacity of carbon aerogel-confined LiBH_4 through high loading of LiBH_4 in carbon aerogels and study the relationship between the LiBH_4 loading and the kinetics of hydriding and dehydriding processes.**
- **Investigate the effect of Sc and Al addition to ball milled $\text{LiH} + \text{MgB}_2$ mixtures on their hydriding and dehydriding properties.**
- **Enhance the hydriding and dehydriding properties of ball milled $\text{LiH} + \text{MgB}_2$ mixtures through boron nitride addition.**
- **Liquid N_2 temperature ball milling of $\text{LiBH}_4 + \text{MgH}_2$ to promote hydrogen release at low temperatures.**

Project Summary

- Relevance:** Explore fundamental mechanisms related to mechanical activation and nano-engineering necessary for improving kinetics of reversible hydrogen storage materials.
- Approach:** Investigate hydriding/dehydriding properties of $\text{LiBH}_4 + \text{MgH}_2$ materials with different degrees of mechanical activation and nano-engineering; Enhance the storage performance based on the understanding developed.
- Technical Accomplishments:** (i) Demonstrated hydriding and dehydriding reactions of $\text{LiBH}_4 + \text{MgH}_2$ systems at the solid state, i.e., below the melting point of LiBH_4 ($T_m = 280^\circ\text{C}$) with 9.3 wt% H_2 uptake and 4.5 wt% H_2 release; (ii) Enhanced hydriding and dehydriding kinetics via milling additives and doping of transition metals; (iii) Further improvement via liquid nitrogen temperature ball milling; (iv) Identify the solid-state hydriding and dehydriding mechanisms and established a partial ion exchange model to guide the improvement of the diffusion-controlled hydriding dehydriding reaction; and (v) Demonstrated the release of H_2 from LiBH_4 at 80°C and the completion of H_2 release at 275°C via nano-engineering with carbon aerogel confinement.