

# **Solid-State Hydriding and Dehydriding of LiBH<sub>4</sub> + MgH<sub>2</sub> Enabled via Mechanical Activation and Nano-Engineering**

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**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  $\text{N}_2$  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  $\text{LiBH}_4$  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  $200^\circ\text{C}$**

# **Technical Impacts – Relevance**

- Demonstrated hydriding and dehydriding reactions of  $\text{LiBH}_4$  +  $\text{MgH}_2$  systems at the solid state, i.e., below the melting point of  $\text{LiBH}_4$  ( $T_m = 280^\circ\text{C}$ ) with 9.3 wt%  $\text{H}_2$  uptake and 4.5 wt%  $\text{H}_2$  release;
- Established a two-step ball milling procedure to improve the solid-state hydriding and dehydriding kinetics of  $\text{LiBH}_4$  +  $\text{MgH}_2$  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  $\text{H}_2$  from  $\text{LiBH}_4$  at  $80^\circ\text{C}$  and the completion of  $\text{H}_2$  release at  $275^\circ\text{C}$  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.**

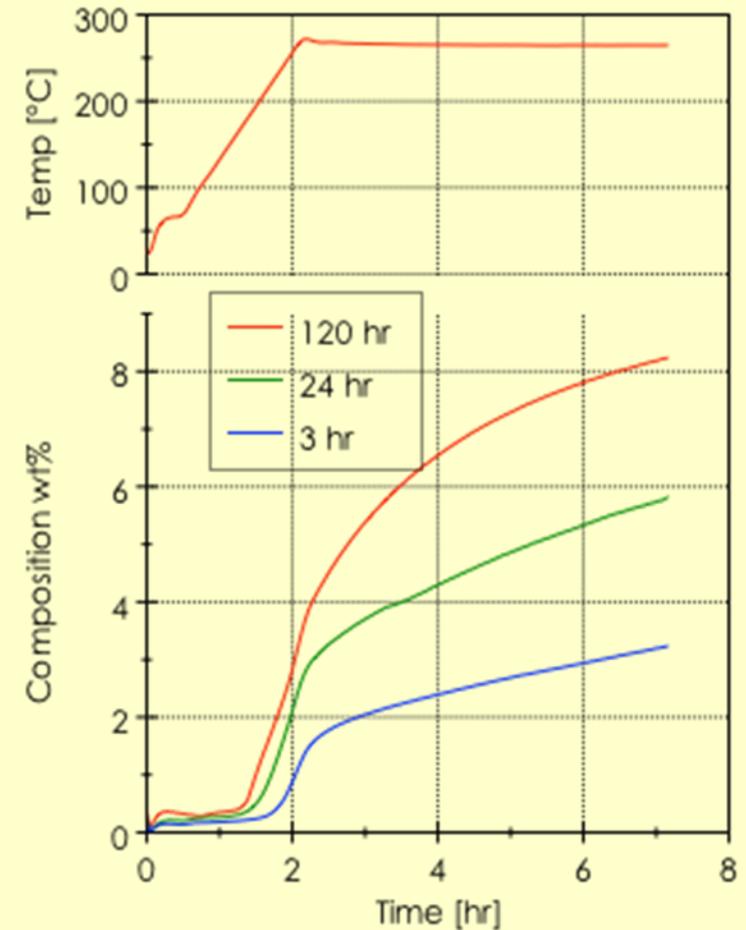
# Milestones – Approach

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

# Technical Accomplishments and Progress (FY08)

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

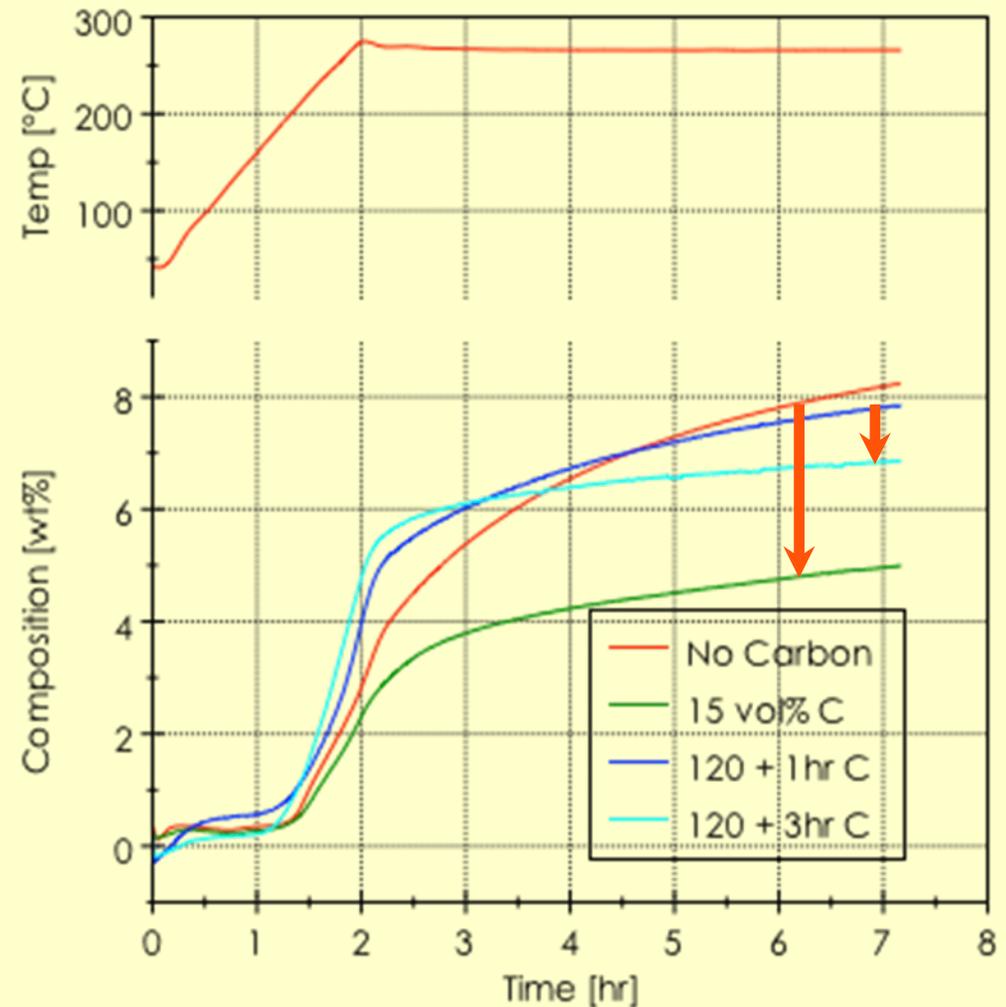
- $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 \leftrightarrow \text{LiH} + \frac{1}{2}\text{MgB}_2 + 2\text{H}_2$ 
  - 11.6 wt%  $\text{H}_2$
  - $\Delta H = 44 \text{ kJ}\cdot\text{mol}^{-1} \text{H}_2$
  - $T_m(\text{LiBH}_4) = 280 \text{ }^\circ\text{C}$
  - $T = 265 \text{ }^\circ\text{C} \Rightarrow$  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

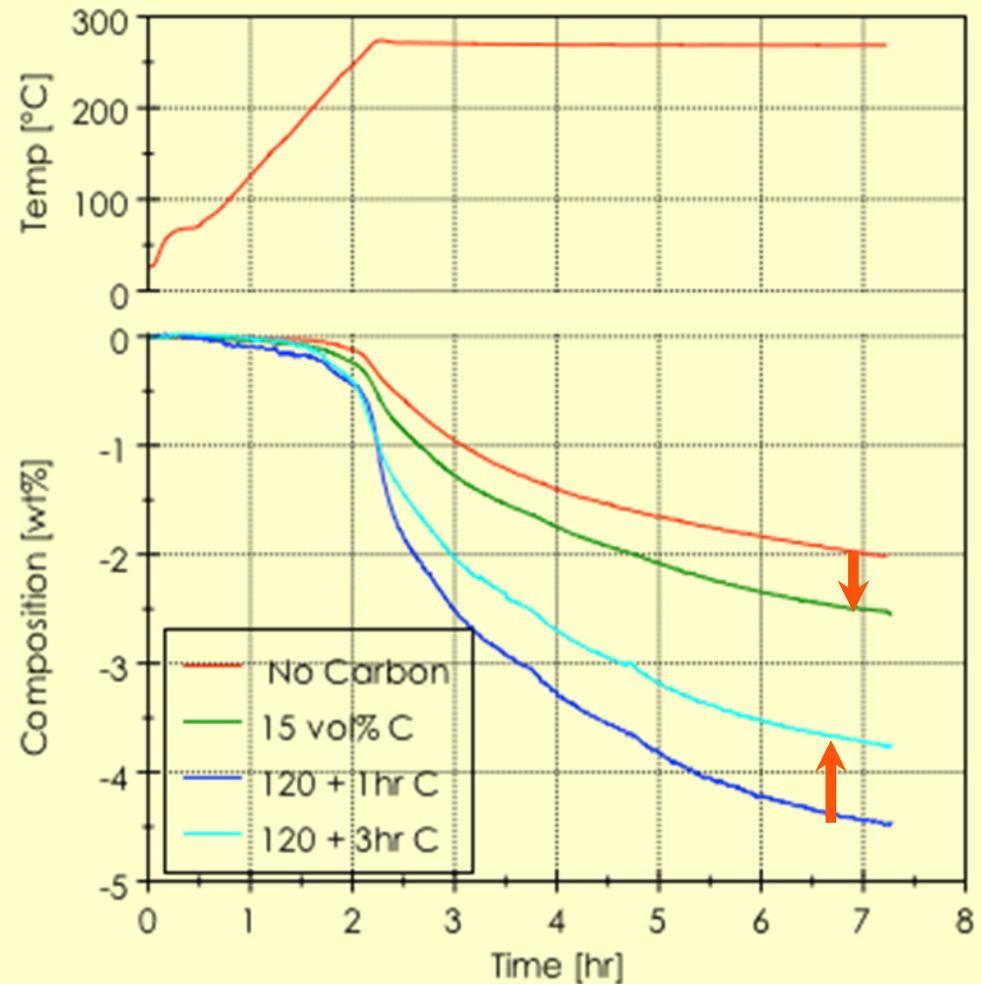
- Include graphite in ball milling of LiH+MgB<sub>2</sub> to improve milling efficiency and uniformity
- Normalized composition to exclude 15 vol% C
- Simply adding graphite reduces absorption by 40%
- LiH and C are reactive – *Two-step milling* to address this issue (e.g., 120h without C + 1h with C)



# Technical Accomplishments and Progress (FY09)

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

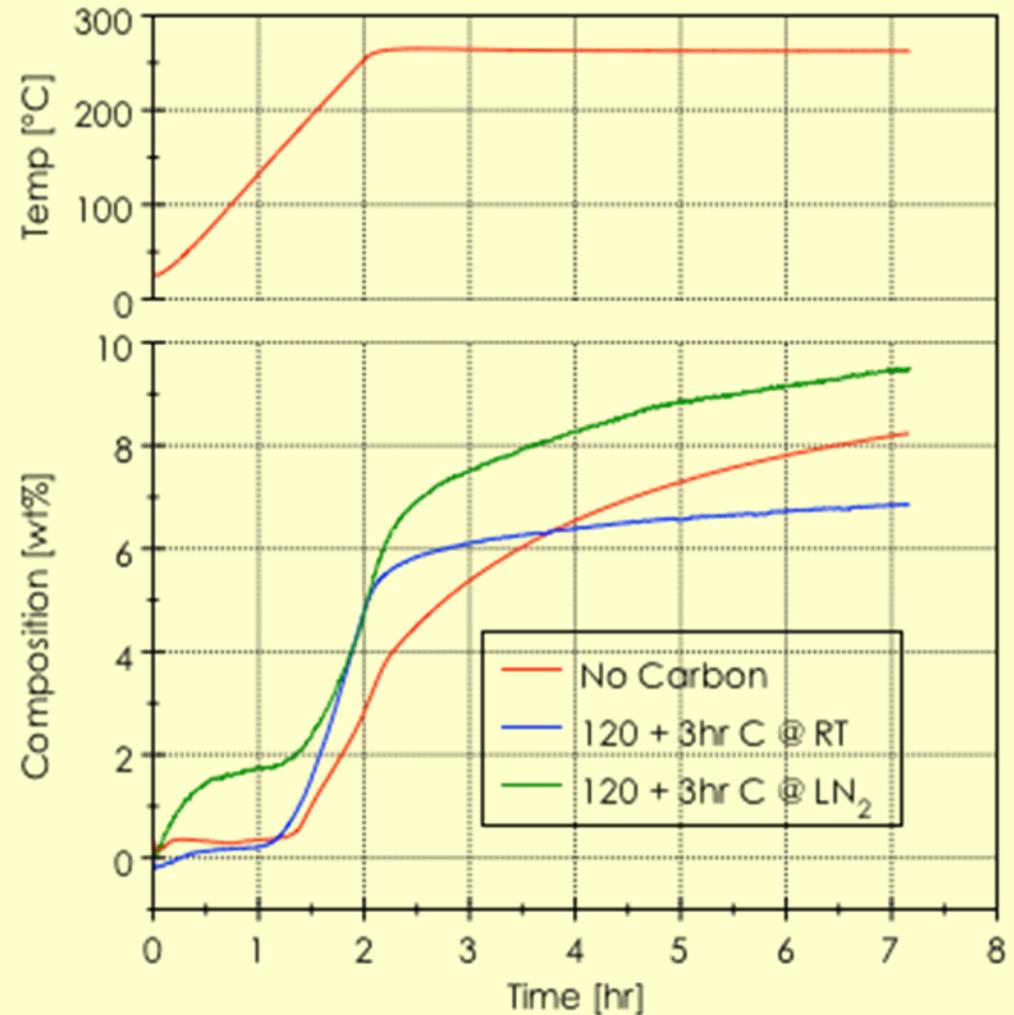
- 120 hr milling with C does improve release kinetics
- *Two-step milling*, i.e., 120+3 and 120+1 further enhances performance
- 120+1 milling is better than 120+3 milling because of the limited reaction between LiH and C
- Release of 4.5 wt%  $\text{H}_2$  at  $265^\circ\text{C}$  accomplished.



# Technical Accomplishments and Progress (FY09)

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

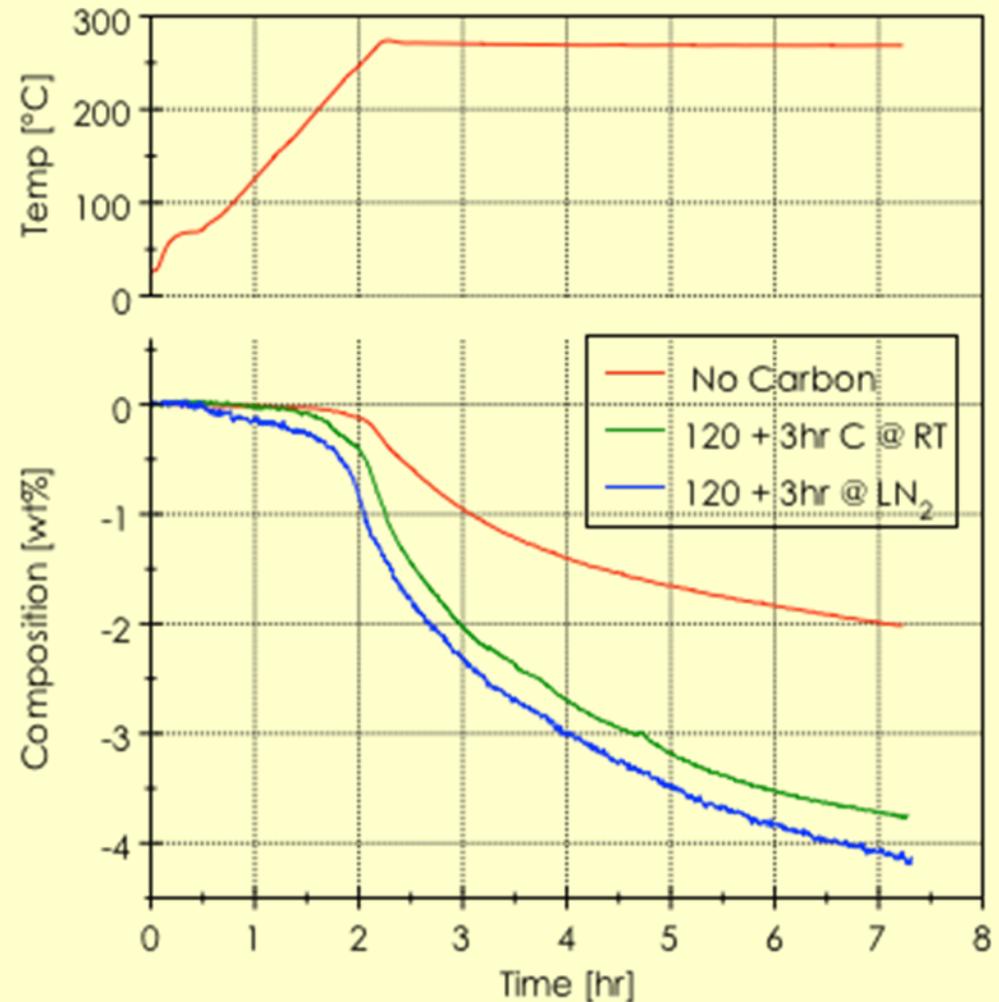
- 120hr RT milling for LiH and MgB<sub>2</sub>, followed by Liq. N<sub>2</sub> milling – *Two-step milling at Liq. N<sub>2</sub>*
- Liq. N<sub>2</sub> milling provides the best improvement because of the limited reaction between LiH and C
- 9.3 wt% H<sub>2</sub> uptake at 265°C accomplished
- Anomalous 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%  $H_2$  release at 265 °C
- $LN_2$  milling does not offer large improvements in hydrogen release over RT milling, suggesting that hydriding & dehydriding kinetics are controlled by different mechanisms.



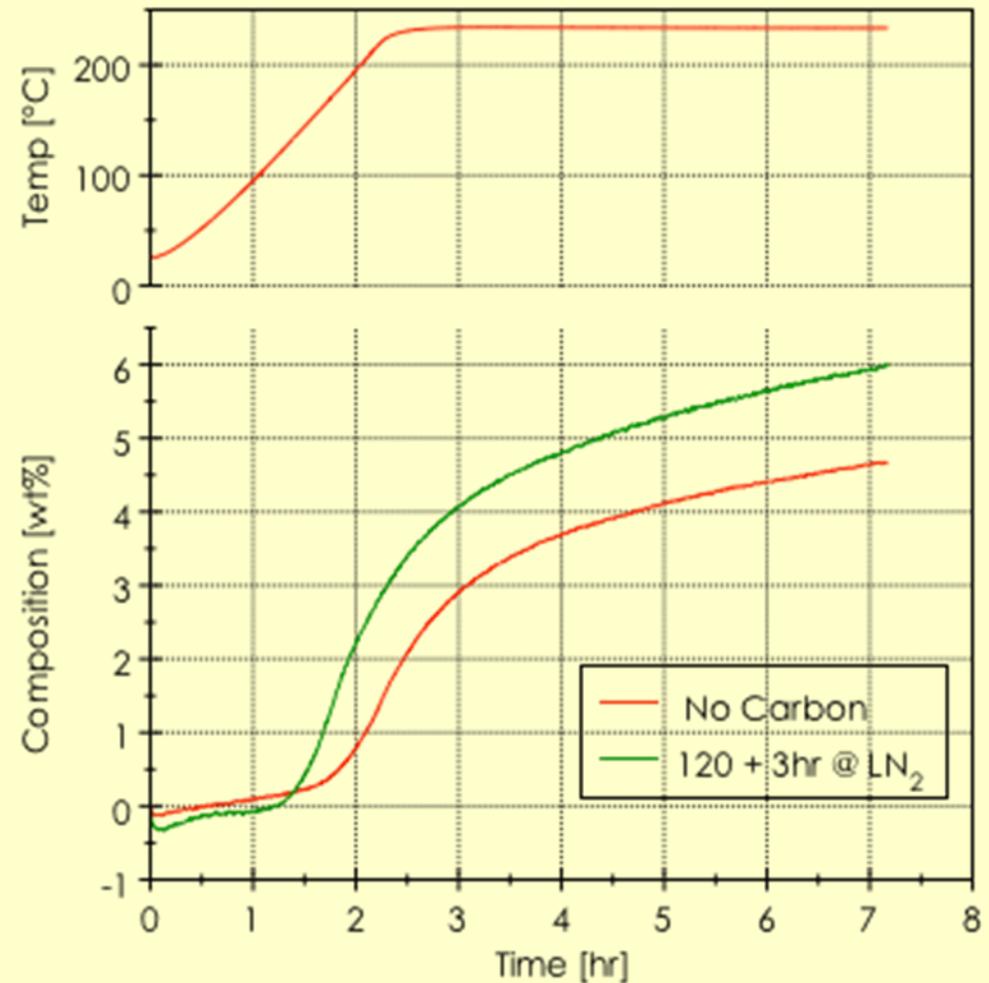
# Technical Accomplishments and Progress (FY09)

## Reducing the Solid-State Hydrogen Uptake and Release Temperature

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

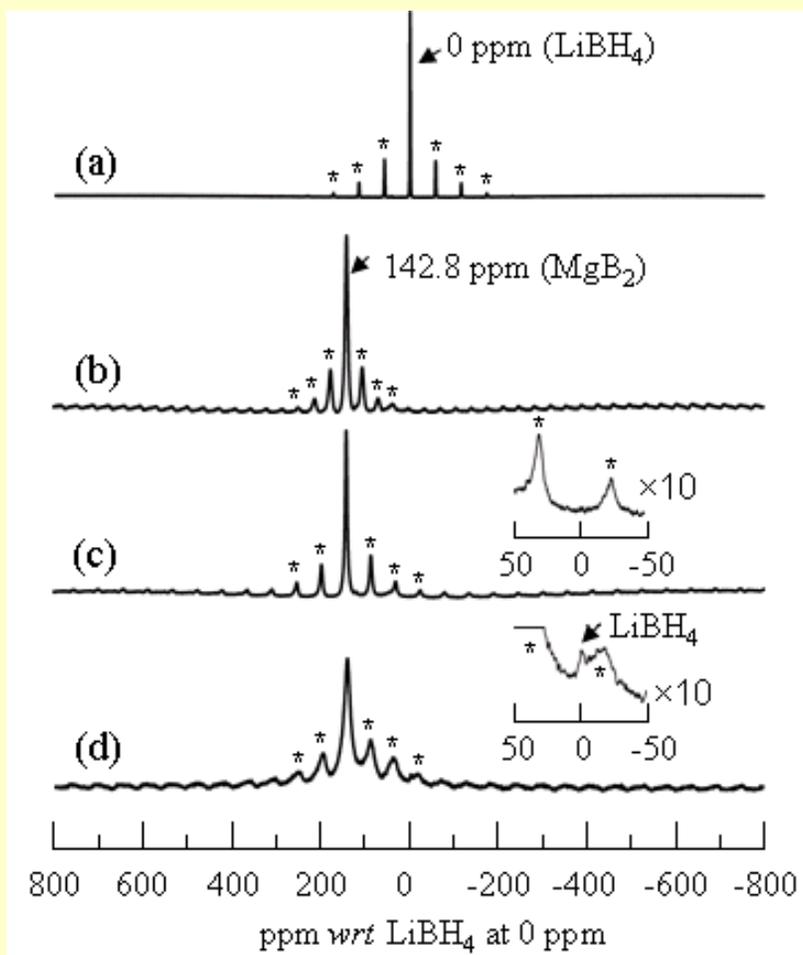
$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

- T = 235 °C & 6.1 wt% H<sub>2</sub> uptake



# Technical Accomplishments and Progress (FY09)

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



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

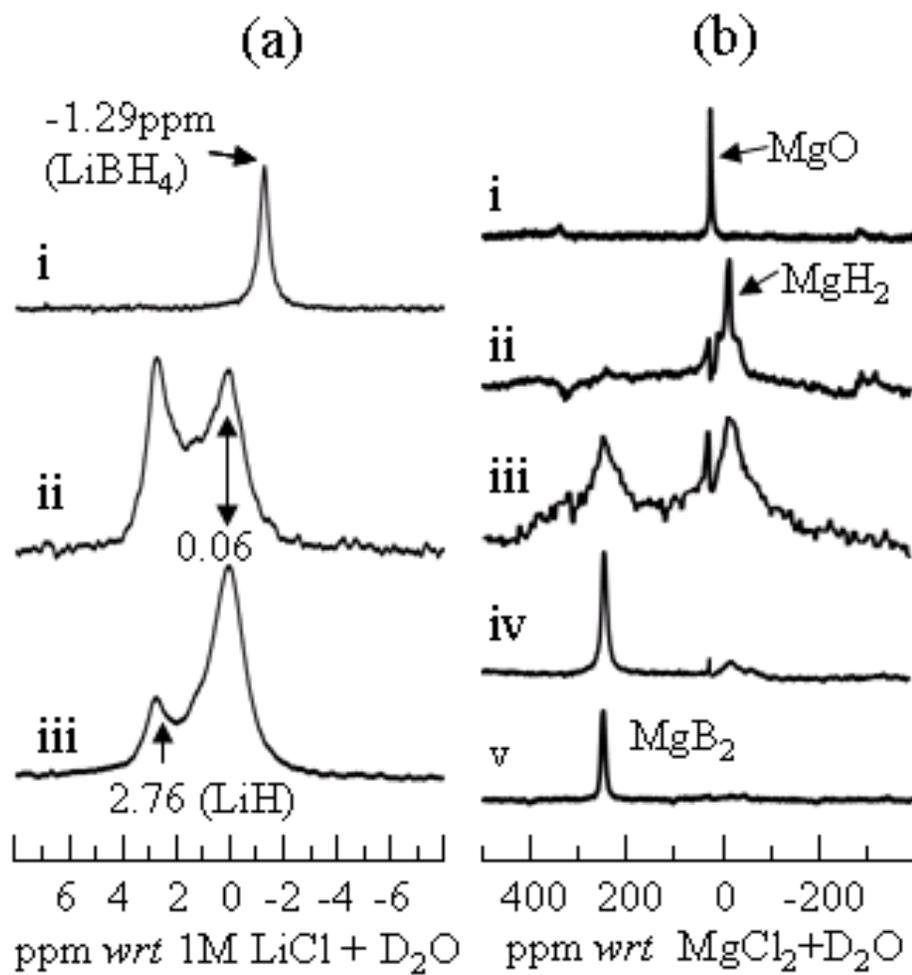
- Bulk  $\text{LiBH}_4$
- Bulk  $\text{MgB}_2$
- $\text{LiH} + \text{MgB}_2$  with 3hr ball milling
- $\text{LiH} + \text{MgB}_2$  with 120hr ball milling

➤ The similar  $^{11}\text{B}$  MAS centerband peak positions of the 3hr and 120hr ball milled  $\text{LiH} + \text{MgB}_2$  as that of pure  $\text{MgB}_2$  indicates that the layered boron structure is unchanged during ball milling.

➤ The substantially increased centerband linewidth for the 120hr milled sample suggests that the  $\text{MgB}_2$  particle size is dramatically decreased by ball milling.

# Technical Accomplishments and Progress (FY09)

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



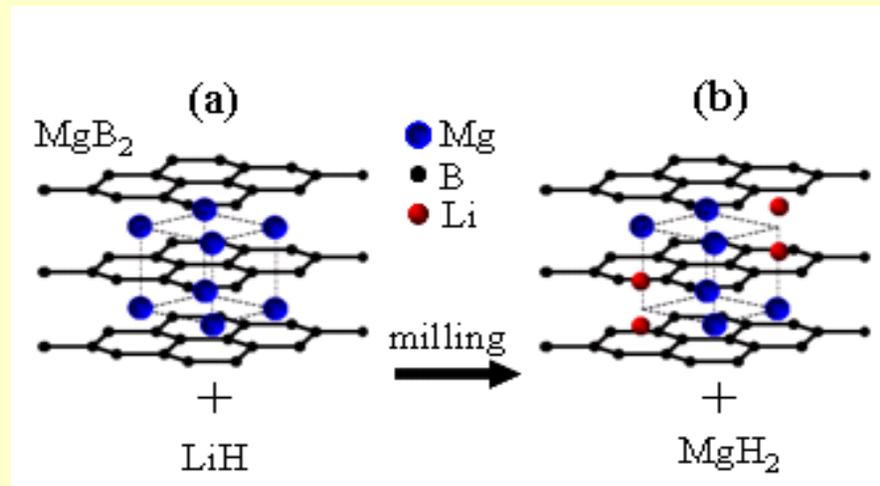
(a)  $^6\text{Li}$  MAS NMR spectra: i)  $\text{LiBH}_4$ , ii)  $\text{LiH} + \text{MgB}_2$  with 3hr ball milling, iii)  $\text{LiH} + \text{MgB}_2$  with 120 hrs ball milling,

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

- The 2.76ppm  $^6\text{Li}$  peak is assigned to  $\text{LiH}$ , while the 0.06ppm  $^6\text{Li}$  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  $\text{MgH}_2$  and the particle size refinement of  $\text{MgB}_2$ .
- Approximately 50% of  $\text{MgB}_2$  is converted to  $\text{MgH}_2$  during 120h ball milling.

# Technical Accomplishments and Progress (FY09)

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

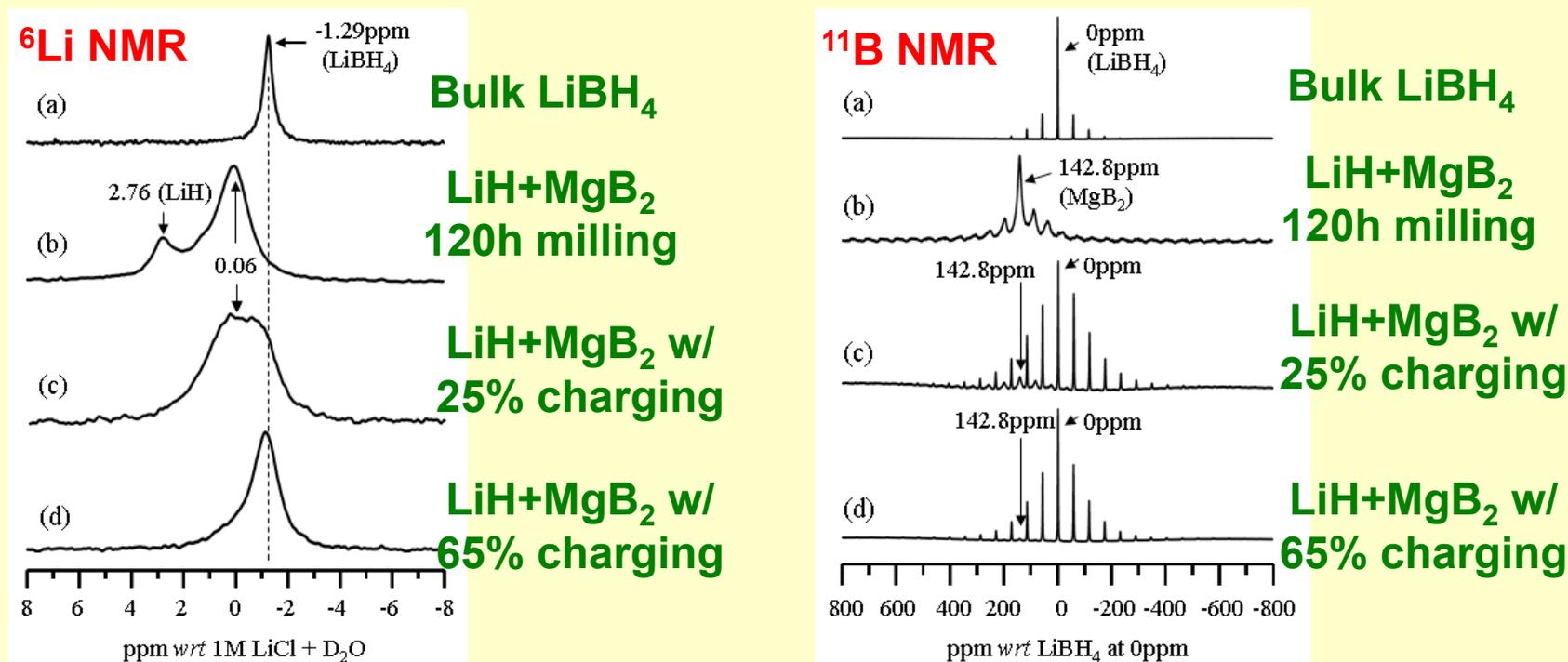


### Ball milling & Hydriding

- Long-term ball milling results in the partial exchange of the  $\text{Mg}^{2+}$  ions in the  $\text{MgB}_2$  crystal by the  $\text{Li}^+$  ions from the  $\text{LiH}$  crystal.
- This partial ion exchange results in the formation of a compound with a composition of  $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$  where  $x$  is a variable changing from 0 to less than 1.
- Each expelled magnesium combines with two protons from  $\text{LiH}$  to form  $\text{MgH}_2$ .
- Formation of  $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$  enhances the hydriding reaction because Mg needs to be expelled to form  $\text{LiBH}_4$ .

# Technical Accomplishments and Progress (FY09)

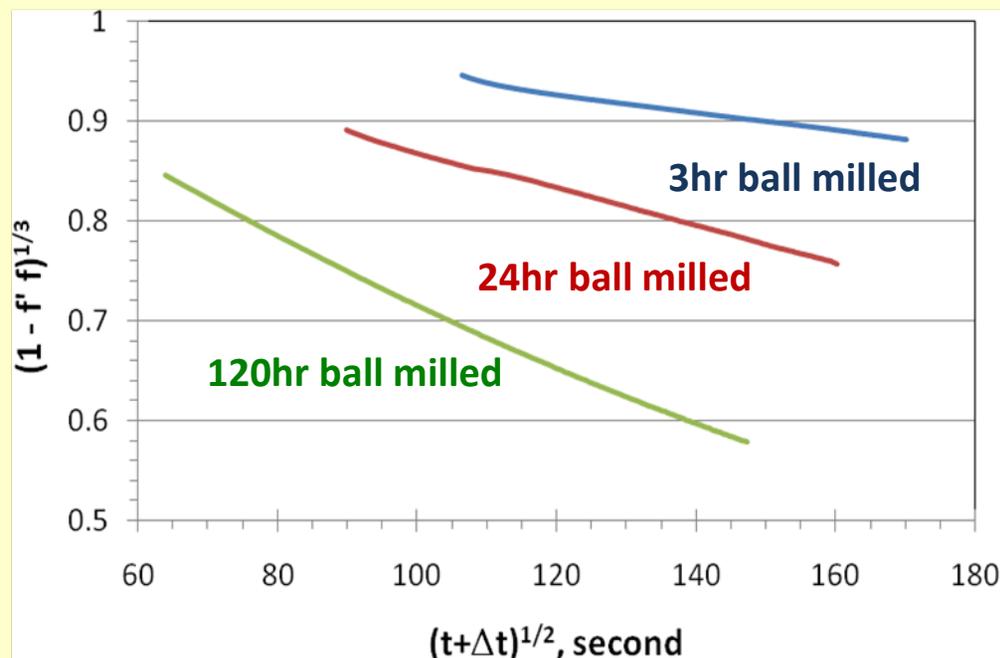
## High-Field NMR Analysis of Solid-State Hydriding/Dehydriding Mechanisms – A Partial Ion Exchange Model (Cont.)



- During hydrogenation LiH continues to react with MgB<sub>2</sub> to form the intermediate (Mg<sub>1-x</sub>Li<sub>2x</sub>)B<sub>2</sub> which is subsequently hydrided to form LiBH<sub>4</sub>, as shown by  $^6\text{Li}$  MAS spectra.
- During hydrogenation MgB<sub>2</sub> continues to decrease while LiBH<sub>4</sub> increases, as shown by  $^{11}\text{B}$  MAS spectra.
- During hydrogenation MgB<sub>2</sub> continues to decrease while MgH<sub>2</sub> increases, not shown here because of the space limitation.

# Technical Accomplishments and Progress (FY09)

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

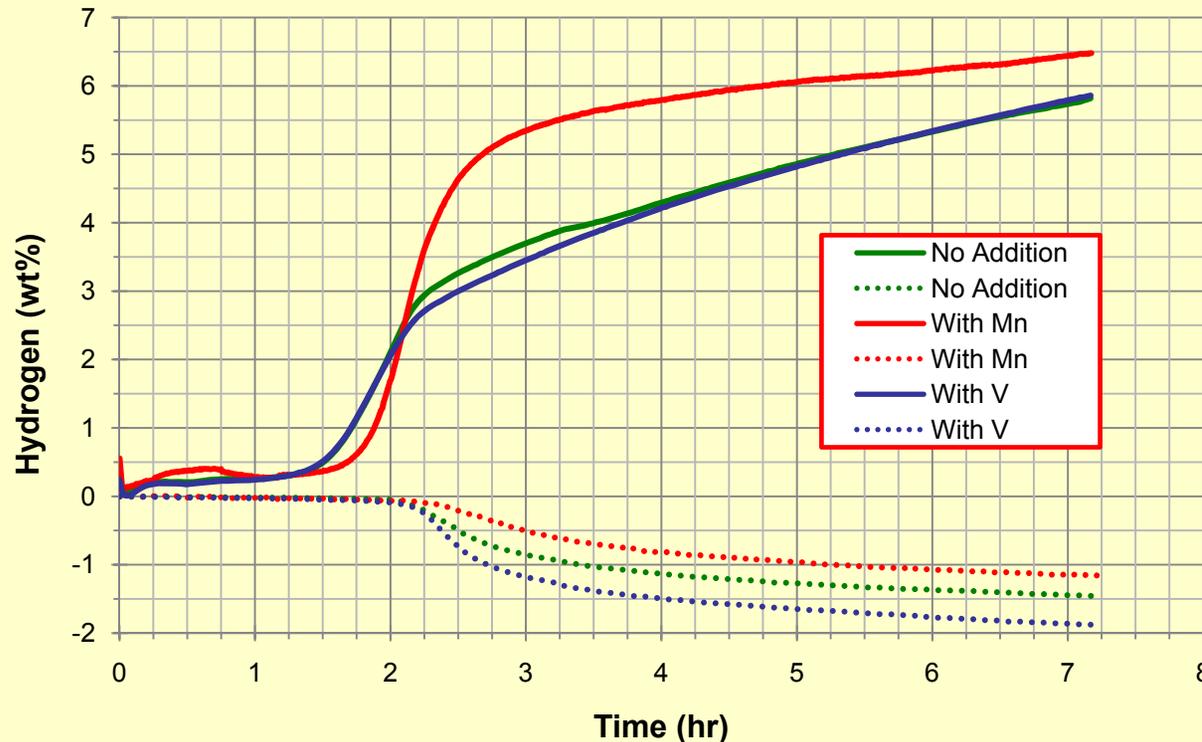


Analysis of the hydrogenation curves of the 120hr, 24hr, and 3hr ball-milled mixtures, based on the diffusion-controlled core/shell model.

- 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

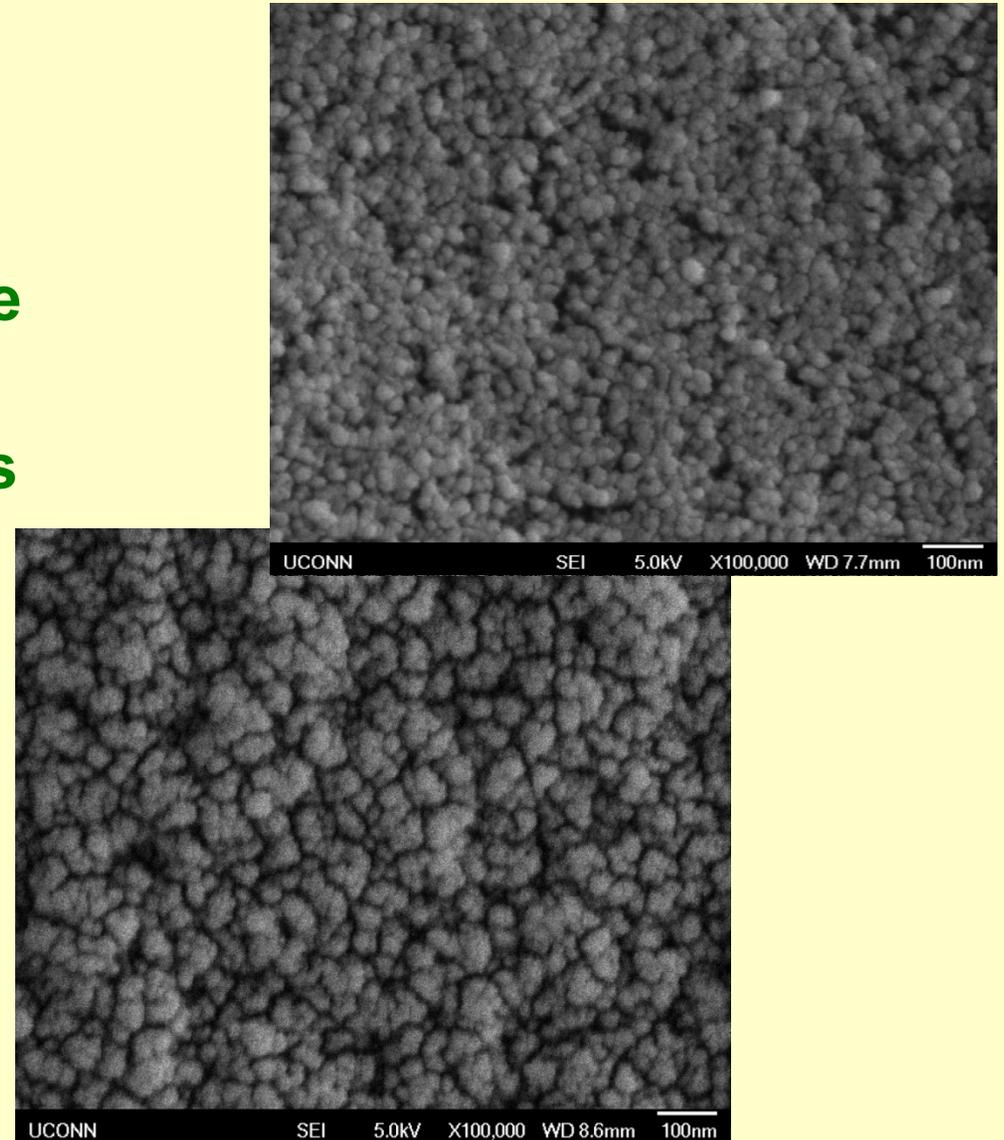
- Mn enhances hydrogenation because it dissolves in  $\text{MgB}_2$ . However, it does not improve dehydrogenation.
- V does not enhance hydrogenation because it does not dissolve in  $\text{MgB}_2$ . However, it improves dehydrogenation because V forms  $\text{VH}_{0.81}$  during hydrogenation and  $\text{VH}_{0.81}$  behaves like a hydrogen pump during dehydrogenation to induce decomposition of  $\text{MgH}_2$ .

# Technical Accomplishments and Progress (FY09)

## Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement

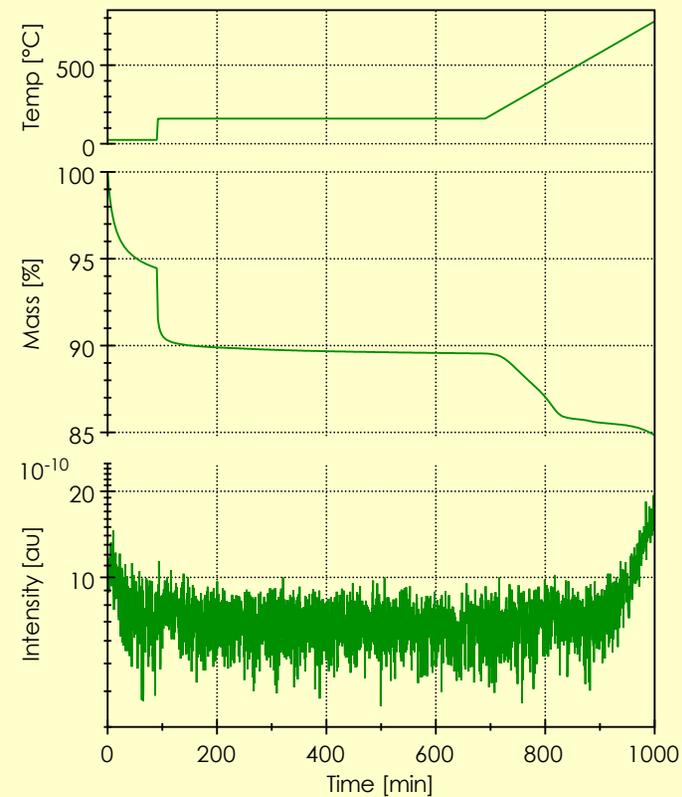
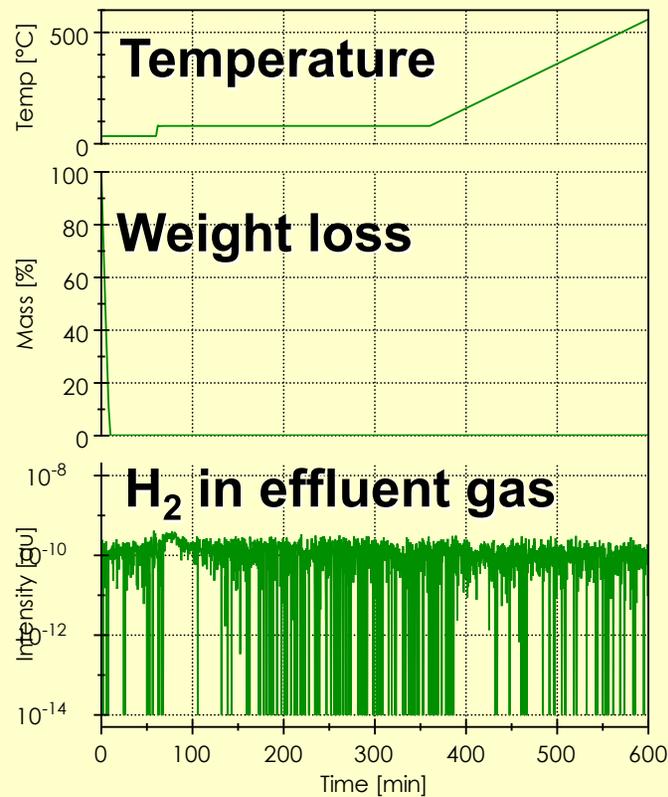
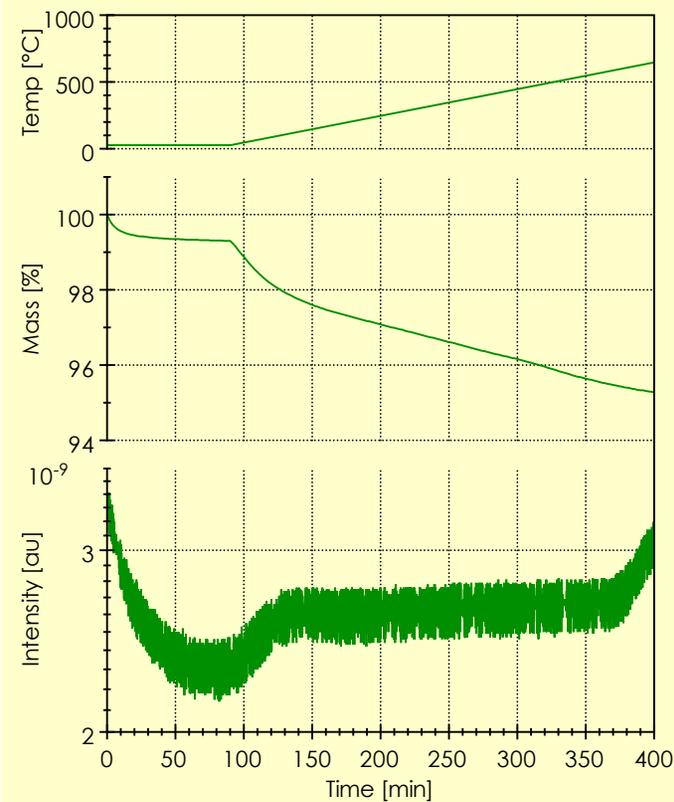
- Pore size distributions of CAs from 4 to 12 nm
- Confining  $\text{LiBH}_4$  to CA pores eliminates long range microstructural growth
- Solvent infiltration provides good control of the size of  $\text{LiBH}_4$
- Low concentrations for  $\text{LiBH}_4$  in THF (0.5 M)

Carbon aerogel (CA) images



# Technical Accomplishments and Progress (FY09)

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



**As Received CA**

**THF Solvent**

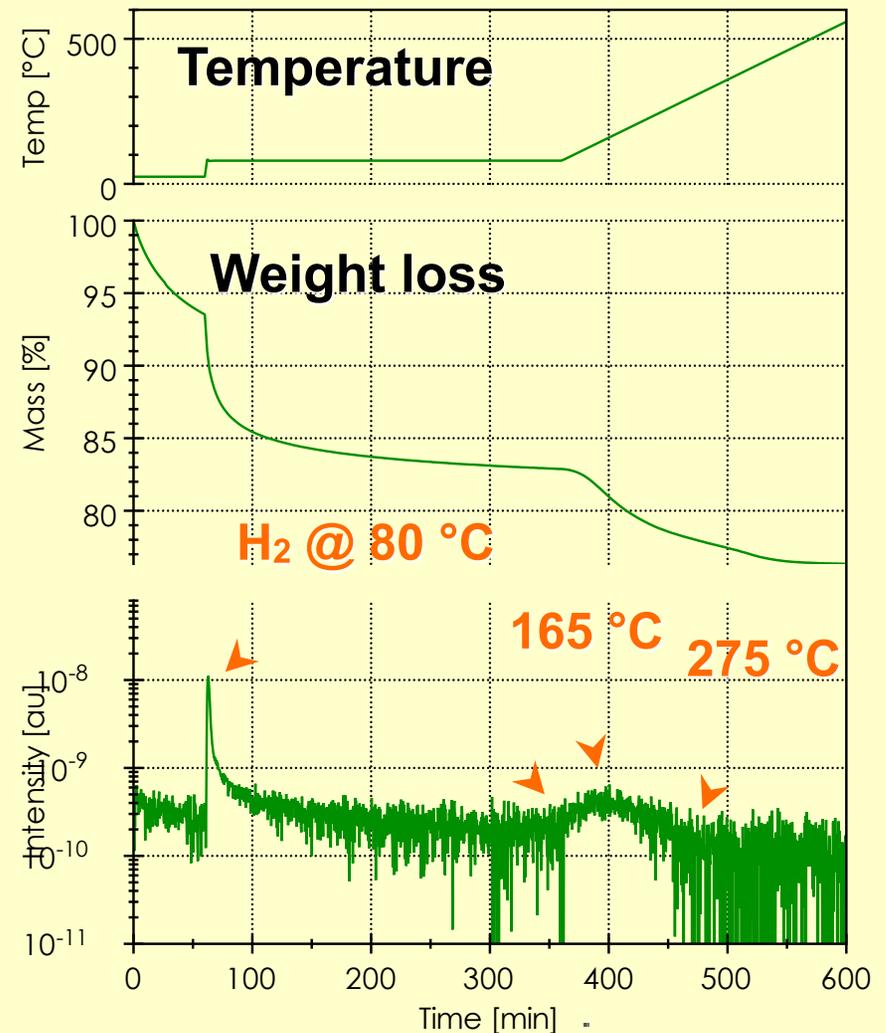
**THF infiltrated CA**

**No H<sub>2</sub> Released by CA or THF**

# Technical Accomplishments and Progress (FY09)

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

- **0.5 M LiBH<sub>4</sub> in THF**
  - **Evacuate CA**
  - **Submerge in solution**
  - **Pressurize**
  - **Drain and vacuum dry (RT)**
- **0.5 M in a 5 nm pore**  
→ **<1 nm LiBH<sub>4</sub> particle**
- **LiBH<sub>4</sub> released H<sub>2</sub> at 80°C!**
- **Completed H<sub>2</sub> release at 275°C!**
- **Change the thermodynamic properties?**



# Technical Accomplishments and Progress (FY09)

## Properties of Carbon Aerogels (CAs) before and after $\text{LiBH}_4$ infiltration and evaporation of the solvent under vacuum

	Mass of the material (g)	Mass increase (%)	Specific surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	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  $\text{LiBH}_4$  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  $\text{LiBH}_4$  film or the particle diameter is  $\sim 0.75$  nm.

# Collaborations

- Pacific Northwest National Laboratory (Drs. Z. Gary Yang, Jianzhi Hu, and Ja-Hu Kwak within the DOE H<sub>2</sub> 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 <sup>6</sup>Li 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 LiNH<sub>2</sub> + LiH Mixture using In-Situ <sup>1</sup>H 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 <sup>1</sup>H and <sup>6</sup>Li 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 LiNH<sub>2</sub> + 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+MgB<sub>2</sub> 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 LiNH<sub>2</sub> + LiH Hydrogen Storage System,” *JOM*, in press.

# Collaborations (Cont.)

- HRL Laboratories (Dr. John Vajo within the DOE H<sub>2</sub> Program) – **Ball milling of LiBH<sub>4</sub> + MgH<sub>2</sub> at both RT and liquid N<sub>2</sub> temperature to investigate whether MgB<sub>2</sub> can be formed below the melting temperature of LiBH<sub>4</sub>.**
- Universidad de Extremadura, Badajoz, Spain (Prof. Angel L. Ortiz outside the DOE H<sub>2</sub> 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 H<sub>2</sub> Program) – **Information exchange on the prediction of the first-principles calculations**

# **Proposed Future Work**

- **Quantify the storage capacity of carbon aerogel-confined  $\text{LiBH}_4$  and investigate its hydriding and dehydriding reversibility.**
- **Increase the storage capacity of carbon aerogel-confined  $\text{LiBH}_4$  through high loading of  $\text{LiBH}_4$  in carbon aerogels and study the relationship between the  $\text{LiBH}_4$  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  $\text{N}_2$  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  $\text{LiBH}_4$  ( $T_m = 280^\circ\text{C}$ ) with 9.3 wt%  $\text{H}_2$  uptake and 4.5 wt%  $\text{H}_2$  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  $\text{H}_2$  from  $\text{LiBH}_4$  at  $80^\circ\text{C}$  and the completion of  $\text{H}_2$  release at  $275^\circ\text{C}$  via nano-engineering with carbon aerogel confinement.