

# Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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**Malibu, CA**

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**Project ID #**  
**ST\_09\_Liu**

## Timeline

- Project start date: March 2005
- Project end date: Feb 2010
- Percent complete: 80%

## Budget

- **Total Project Funding:**

*Phase I and II: \$ 2.75M*

- DOE Share: \$2.0M
- Contractor Share: \$0.75M

- **Funding received in FY08:**

\$350K (DOE),  
\$150K (cost share)

- **Funding for FY09 (planned):**

\$400K (DOE),  
\$150K (cost share)

## Technical Barriers

- A. System weight and volume
- C. Efficiency
- E. Charging and discharge rates

## Partners

- **MHCoE collaborations:**

- U. Pitt, Georgia Tech: modeling of new systems and kinetic barriers
- Stanford: thin film systems
- Hawaii: hydride synthesis
- Caltech, JPL, NIST: scaffolds characterization

- **DOE collaborations:**

- LLNL, PNNL: carbon scaffold synthesis
- UConn: destabilized systems

## Overall

To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for reversible on-board hydrogen storage

## 2008/2009

### 1. Characterize $\text{LiBH}_4/\text{MgX}$ , $\text{X} = \text{Ni}$ destabilized hydride system

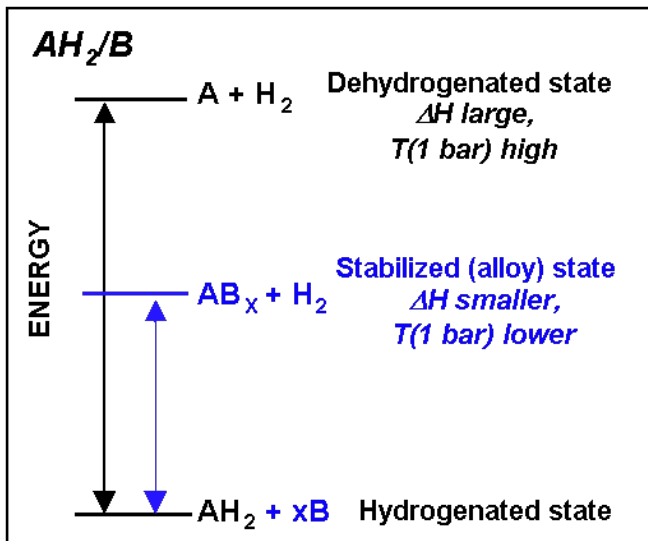
- New destabilized hydride system with reversible theoretical capacity of 8.3% (6.5% observed) and lower temperature than  $\text{X} = \text{H}_2$  for hydrogen exchange
- Addresses Barriers A, C, and E.

### 2. Incorporate complete $\text{LiBH}_4/\text{MgH}_2$ destabilized hydride system into carbon aerogel

- Increase hydrogen exchange rate through nano-engineering
- Addresses Barriers C and E

### 3. Investigate new scaffold structures

- Increase hydrogen exchange rate through nano-engineering
- Addresses Barriers C and E



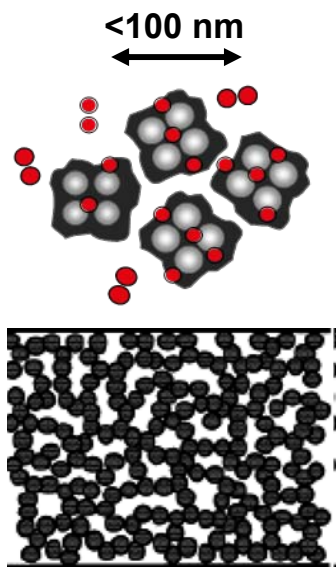
## Hydride Destabilization

(addresses thermodynamics)

**Reduce reaction enthalpy by forming dehydrogenated alloy**

- If alloy is stable w.r.t metal then hydride is destabilized
- System cycles between H-containing state and metal alloy  
→ lower  $\Delta H$

**Destabilization results in lower  $\Delta H$  and  $T_{1 \text{ bar}}$**



## Nano-engineering

(addresses kinetics)

**Decrease diffusion distances, nanoporous scaffolding**

- Shorter diffusion distances: *faster hydrogen exchange*
- More efficient catalysis pathways
- Nano-scaffolds as hosts for nanostructured hydrides:  
→ *structure-directing agents, mitigate particle agglomeration*

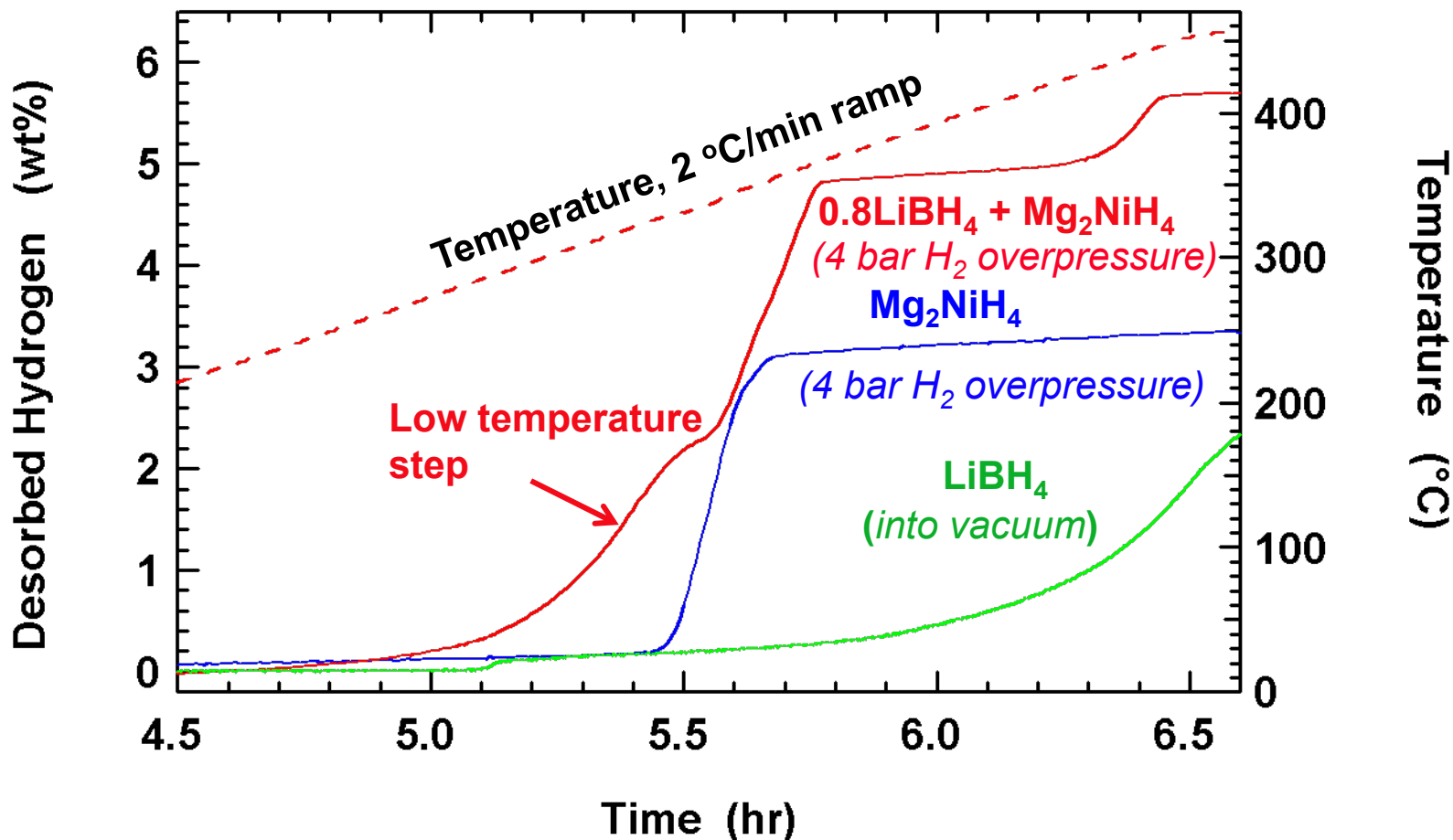
**Enhanced reaction rate and improved cycling**

## Status as of March 2008:

- Observed reversible capacity of 6.5% for the  $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  system; ternary boride formation identified
- Incorporated and characterized  $\text{LiBH}_4$  in carbon aerogel
- Incorporated Mg into Ni loaded carbon aerogel through melting

Month/Year	Milestone or Go/No-Go Decision
Sept-08	<b>Milestone: Incorporate the <math>\text{LiBH}_4/\text{MgH}_2</math> destabilized system into nanoscale scaffold.</b> Successfully incorporated $\text{LiBH}_4/\text{MgH}_2$ destabilized system. Observed reduced reaction temperature with hydrogen release.
Sept-09	<b>Milestone: Complete investigation of ternary boride system.</b> Complete work on Mg-Ni-B systems, search for other ternary boride systems with higher capacities and lower reaction temperatures.

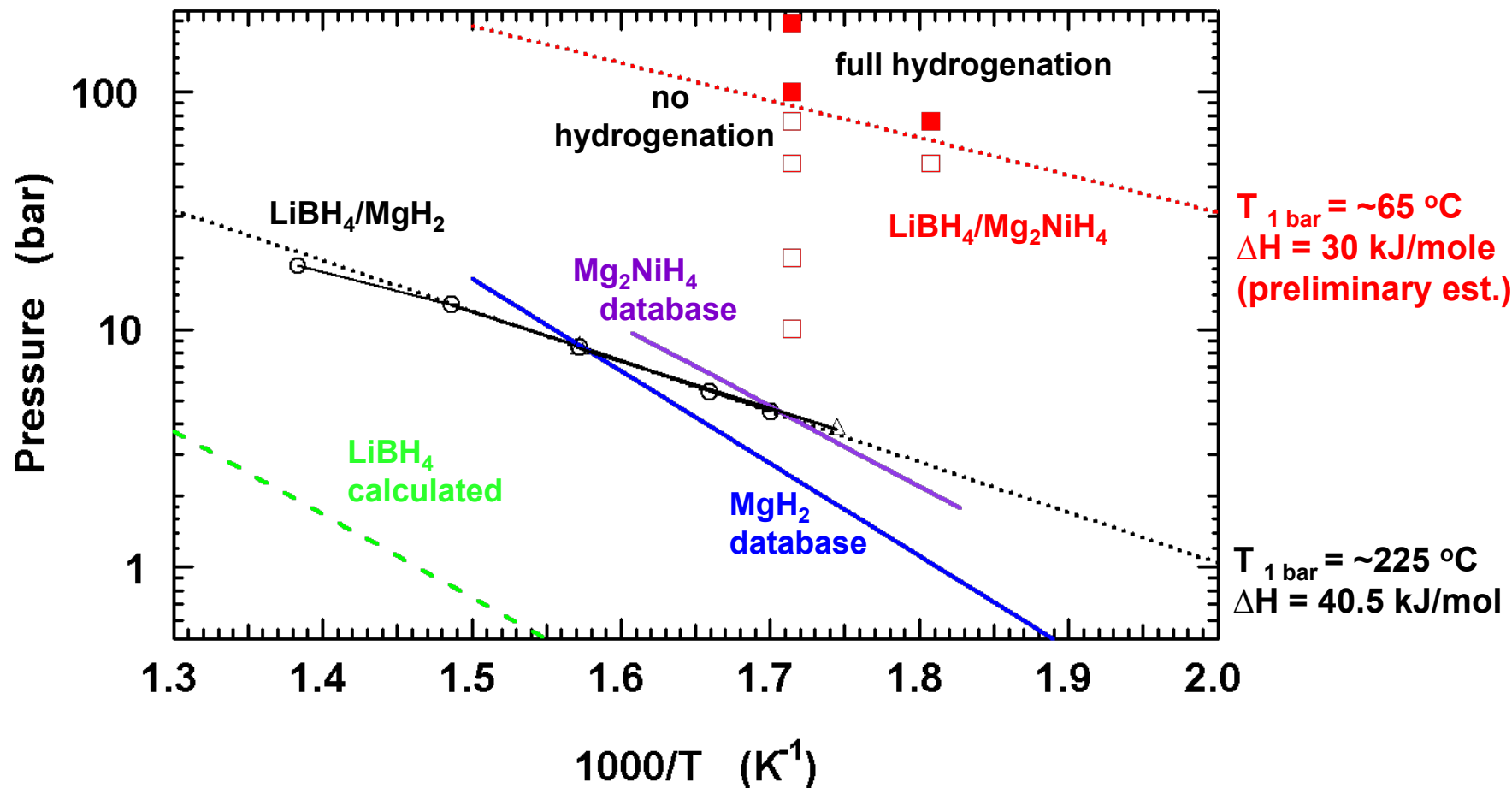
# 1. $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ Destabilized System



- IR spectra shows complete consumption of  $\text{LiBH}_4$  by  $345^\circ\text{C}$
- Possible Rxn:  $4\text{LiBH}_4 + 5\text{Mg}_2\text{NiH}_4 \rightarrow 2\text{MgNi}_{2.5}\text{B}_2 + 4\text{LiH} + 8\text{MgH}_2 + 2.5\text{ wt\% H}_2$
- Low temperature step does not occur for either  $\text{Mg}_2\text{NiH}_4$  or  $\text{LiBH}_4$  individually

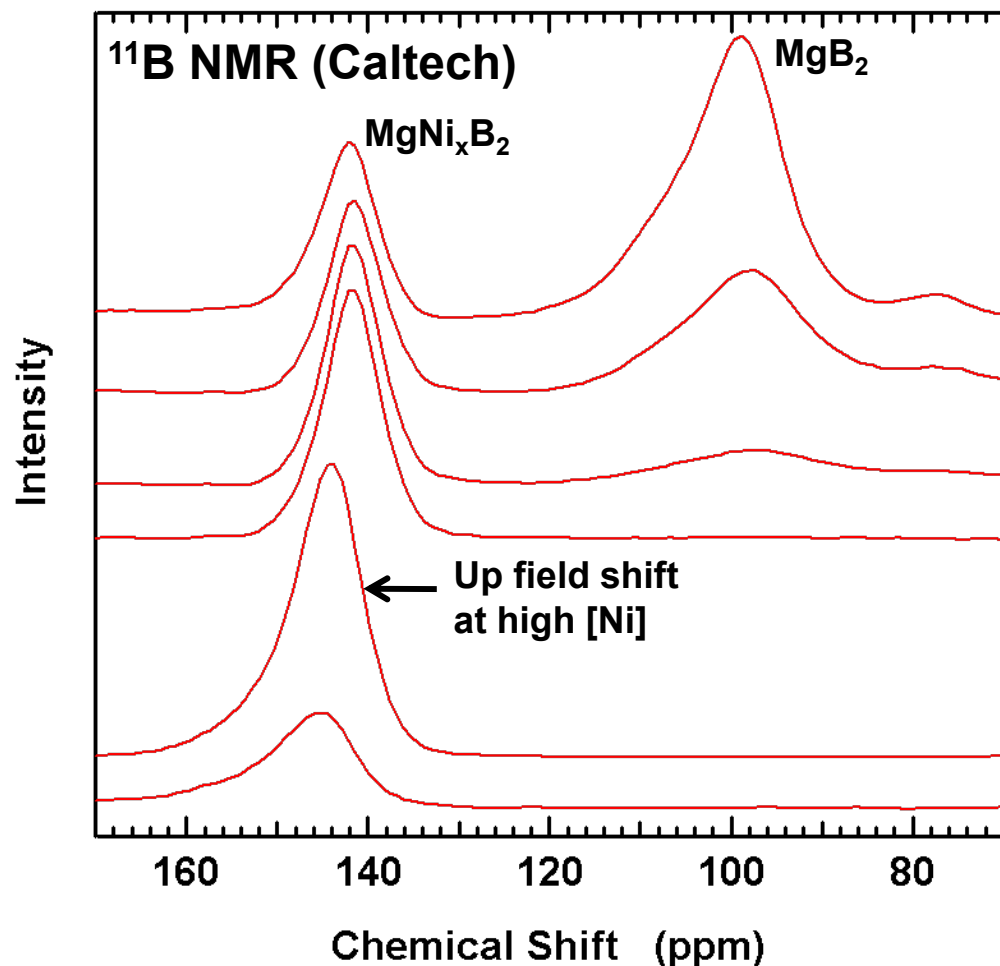
First example of *kinetically* destabilized system

Preliminary data from variable pressure hydrogenation/dehydrogenation cycles



- Preliminary data gives  $P_{\text{eq}} \sim 30\text{x}$  higher than  $\text{LiBH}_4/\text{MgH}_2$  system
- Full isotherms need to be done (*planned*)

Alloys synthesized from milled mixtures of  $\text{MgB}_2 + x\text{Ni}$ , sintered at  $800\text{ }^\circ\text{C}$ , 24 hr

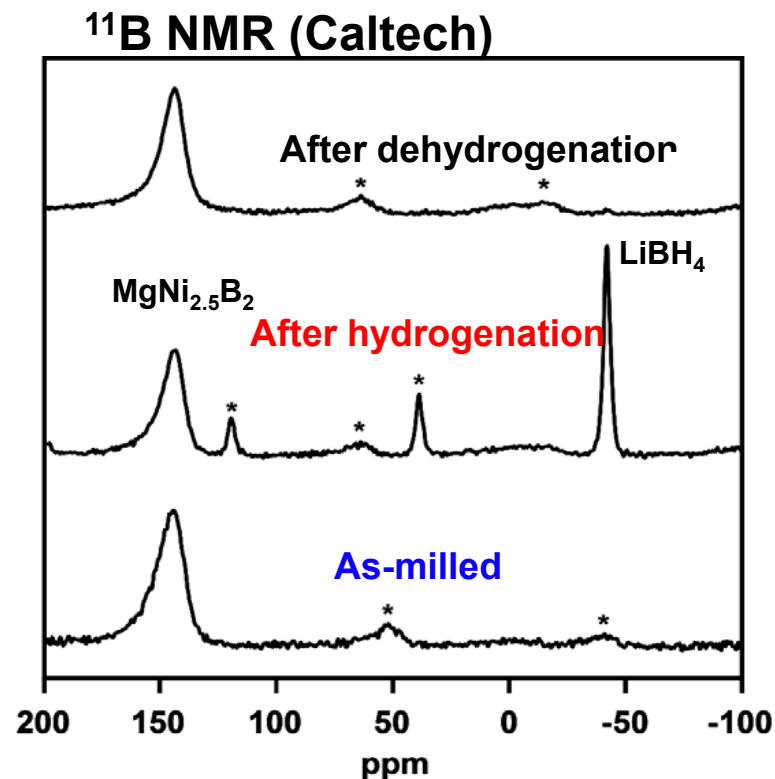
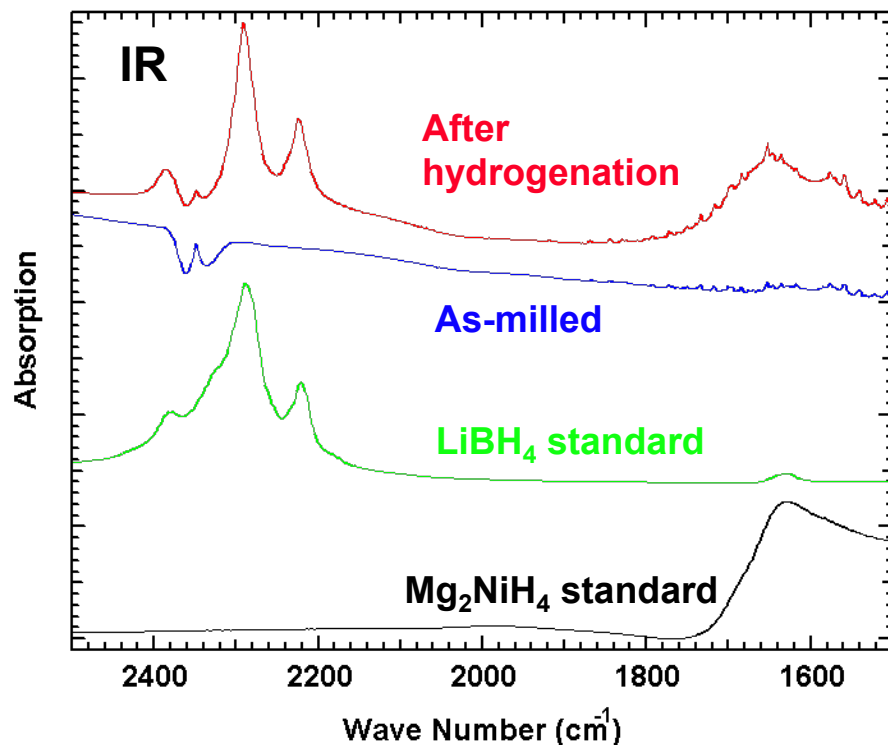


Ni composition	Approximate actual composition
$x = 0.5$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 2\text{MgB}_2$
$x = 0.75$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 1\text{MgB}_2$
$x = 1.0$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 0.5\text{MgB}_2$
$x = 2.0$	$\text{MgNi}_2\text{B}_2$
$x = 2.5$	$\text{MgNi}_{2.5}\text{B}_2$
$x = 3.0$	$\text{MgNi}_{\sim 3}\text{B}_2 + \text{small Ni}_2\text{B}$

- All compositions show identical XRD pattern without peak shifts
- Ni concentration in ternary can vary from  $\sim 1.5$  to  $\sim 3$



Hydrogenation of milled  $MgNi_{2.5}B_2 + 2LiH + 4MgH_2$  at 350 °C, 100 bar  $H_2$ , 4 hr

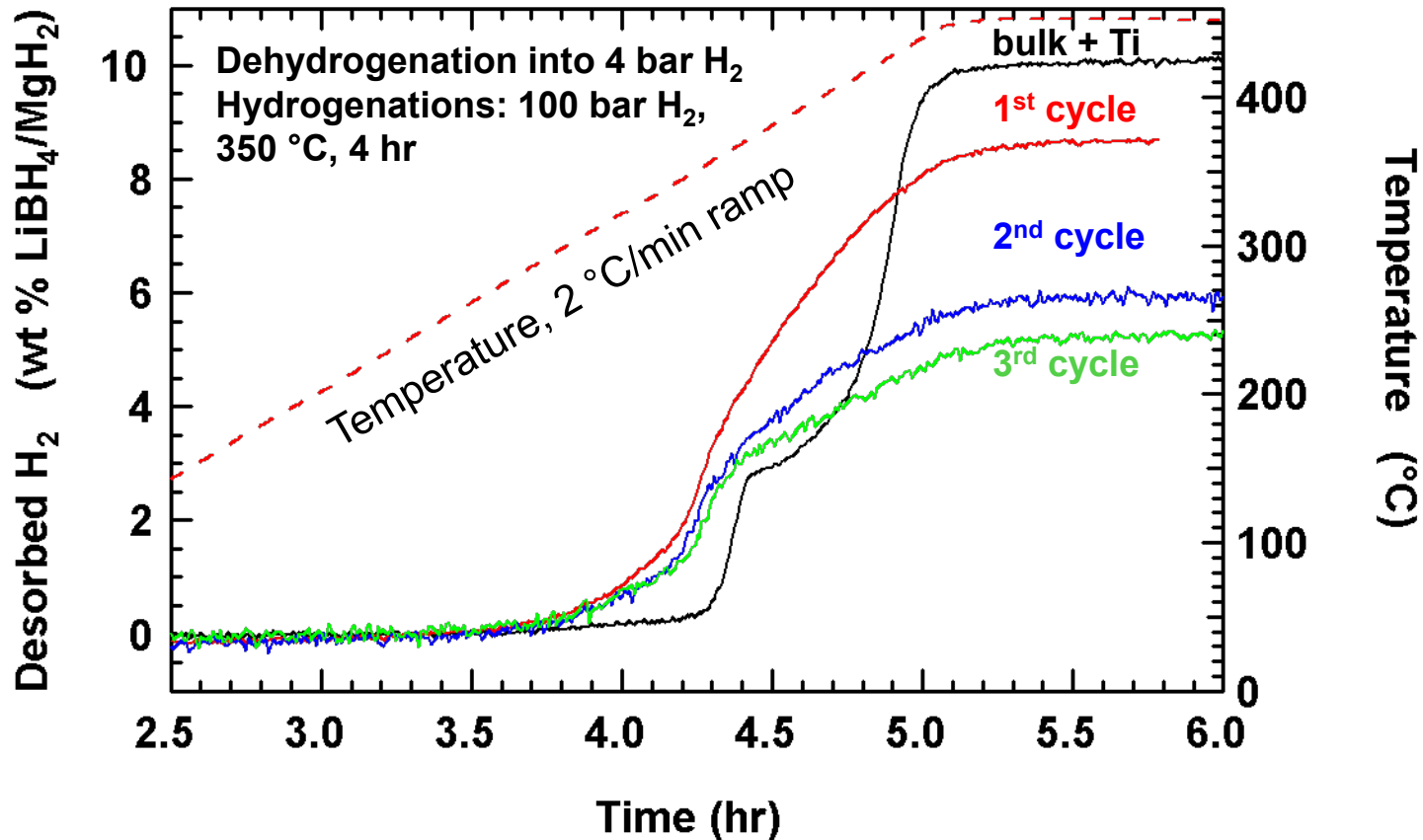


- Ternary boride ( $x = 2.5$ ) can be hydrogenated partially (~30%)
- Only boride other than  $MgB_2$  that readily reacts with hydrogen

Other reactive ternary (or higher order) borides may exist to offer higher capacities and lower reaction temperatures

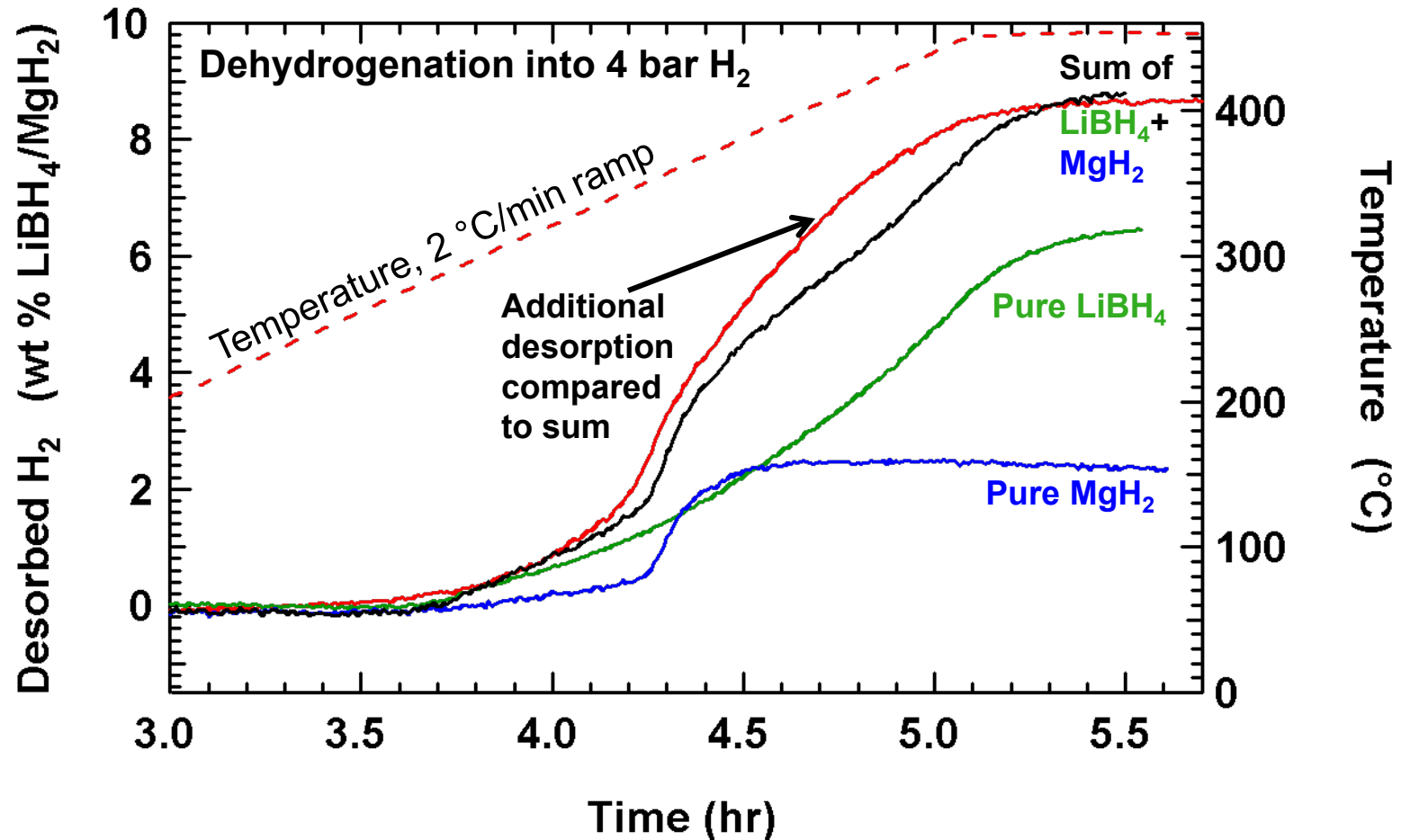
## 2. $\text{LiBH}_4/\text{MgH}_2$ System in Carbon Aerogel

$\text{MgH}_2$  incorporated 1<sup>st</sup> at U. Hawaii from  $\text{Bu}_2\text{Mg}$ , then  $\text{LiBH}_4$  at HRL  
 Overall composition is  $2 \text{LiBH}_4 + \text{MgH}_2$  in aerogel at a loading of 25 wt%



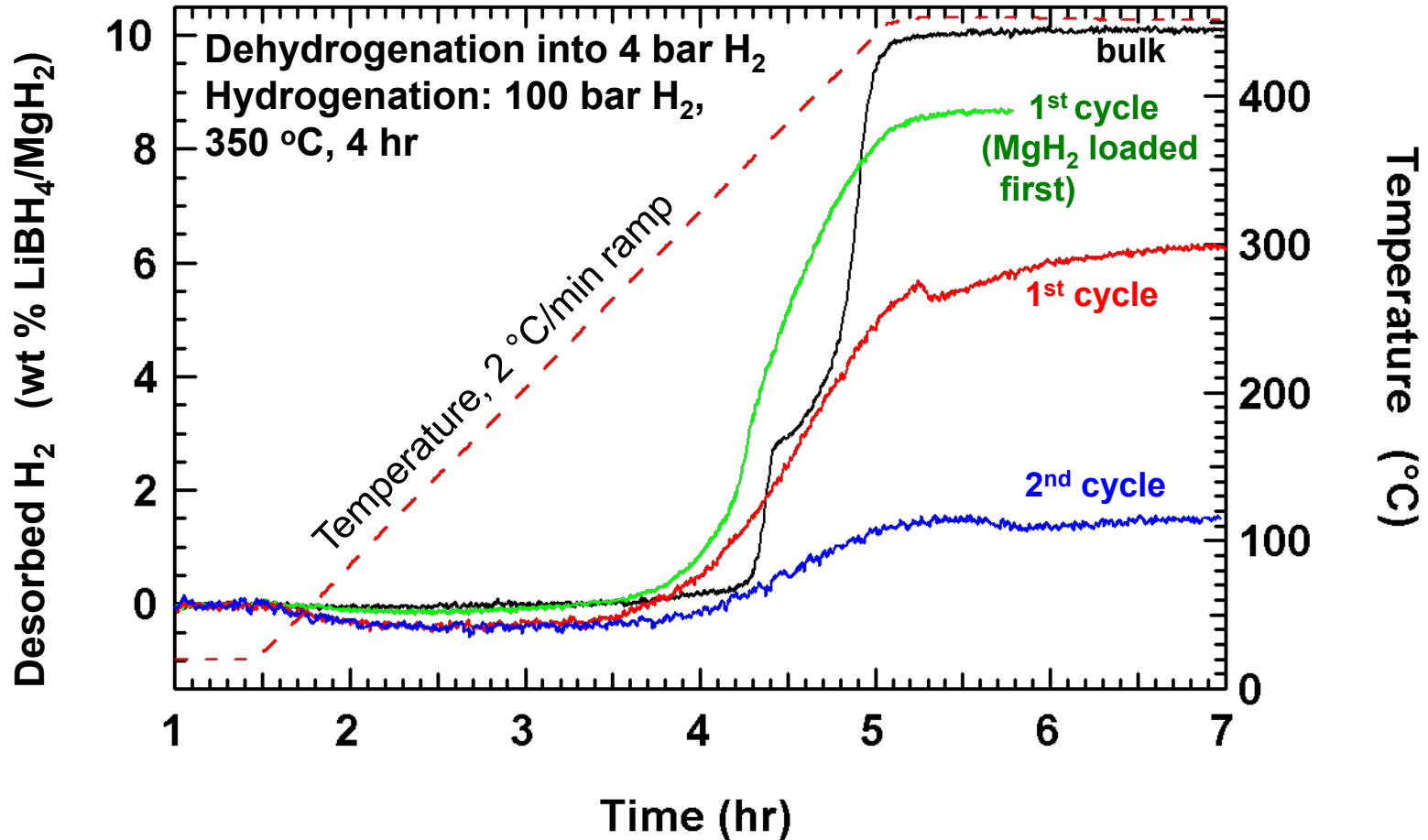
- Reaction temperature is lower than for bulk sample with catalyst
- Individual steps (if present) are not well resolved
- However, cycling is poor (sequential filling may lead to poor mixing in pores)

Pure components@aerogel scaled ( $0.25\text{MgH}_2 + 0.75\text{LiBH}_4$ ) to combined system



- Behavior is largely accounted for by individual components
- $\text{LiBH}_4$  and  $\text{MgH}_2$  do not appear to be mixed well within the pores  
(we are considering simultaneous incorporation)

*13 nm aerogel;  $\text{LiBH}_4$  incorporated at HRL, then  $\text{MgH}_2$  incorporated at U. Hawaii*

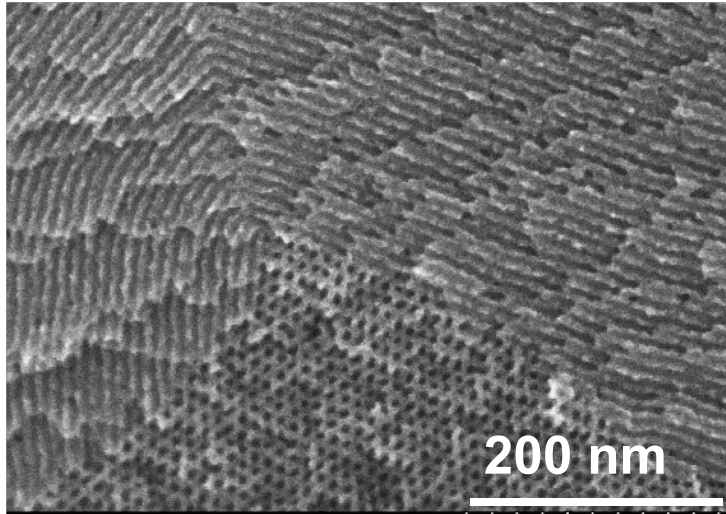


- 1<sup>st</sup> cycle capacity is low (may be due to sample handling, shipping to/from Hawaii)
- There is a large loss on the 2<sup>nd</sup> cycle (not understood)
- Only our 2<sup>nd</sup> try, we are working to perform the complete filling procedure at HRL

### 3. New Scaffold Structures

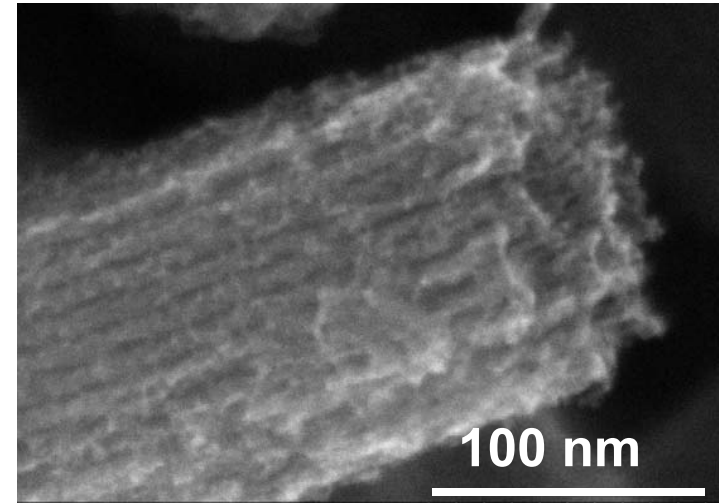
#### Mesoporous carbon from porous polymer

*Chem Mater., Lu et al., 20 5314 (2008)*



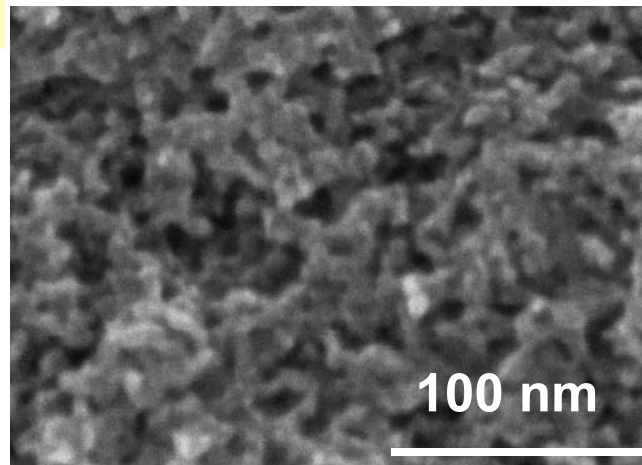
*Long, straight but not interconnected pores*

#### Mesoporous carbon by reverse casting from silica (T. Baumann, LLNL)

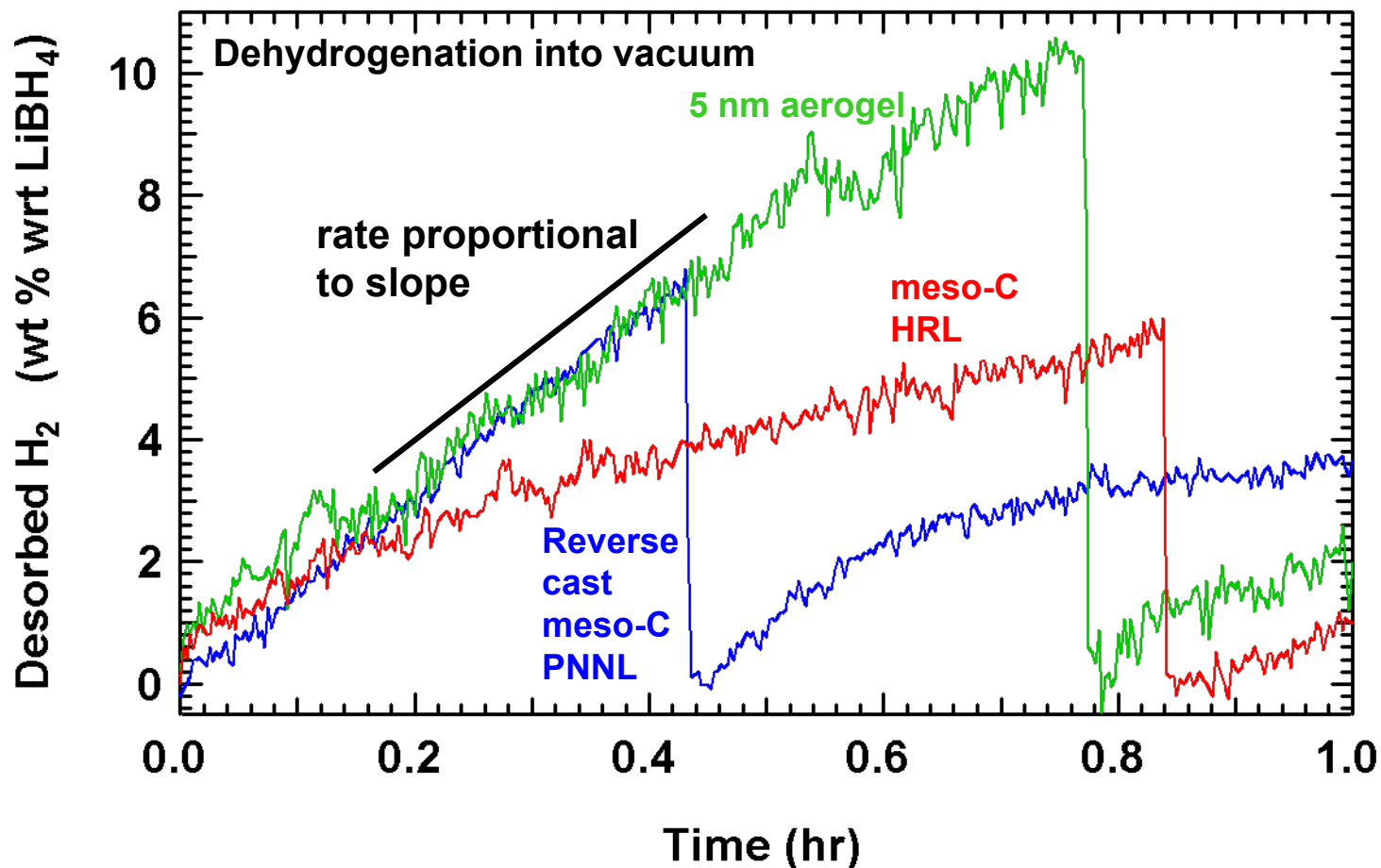


*Long, straight and interconnected pores*

#### Carbon aerogel



*Isotropic, 3-D, random pores*



- Rate for reverse cast meso-C from PNNL  $\approx$  rate for 5 nm aerogel
- Rate for HRL meso-C degrades quickly (*pores may be too long*)

## 1. Gravimetric and Volumetric Penalties

- Most aerogels:
  - $\sim 1 \text{ cm}^3/\text{g}$  for 5 to 10 nm pore sizes
  - up to  $> 4 \text{ cm}^3/\text{g}$  for pore sizes  $> 20 \text{ nm}$
- If kinetic improvements are sufficient, for penalties of  $< 25 \%$ , we will need:
  - $\sim 5$  to  $10 \text{ nm}$  pore sizes with  $> 3 \text{ cm}^3/\text{g}$  pore volume
- For  $10 \text{ nm}$  slit pores with two single graphene layers, the pore volume would be  $6.8 \text{ cm}^3/\text{g}$

**In 2008 LLNL achieved  $4.6 \text{ cm}^3/\text{g}$  with  $15 \text{ nm}$  pores, showing the possibility of meeting the goals**

## 2. Other issues

- Chemical stability, i.e.,  $\text{CH}_4$  formation from carbon scaffolds
- Mechanical stability over multiple cycles? (*Note: volume changes during cycling are contained within aerogel particles*)

**Continued advancement in porous carbon materials makes them both important research tools and potential practical solutions**

- **Center partners**

- **David Sholl (Georgia Tech) and Karl Johnson (U. Pitt):** HRL synthesized/tested LiBC based on their calculations; no hydrogenation observed at 100 bar
- **Bruce Clemens (Stanford):** determined diffusion lengths of hydrogen in hydride systems ( $Mg_2Si$  and  $MgH_2$ ) using thin films
- **Craig Jensen (Hawaii):** developed method for  $MgH_2$  incorporation into scaffolds using organic precursors
- **S-J Hwang (JPL):** NMR studies of ternary hydrides and scaffolds
- **Channing Ahn (Caltech):** TEM studies of scaffolds
- **Terry Udovic (NIST):** Neutron based characterization of scaffolds
- **Ewa Ronneboro (formerly Sandia) and Xia Tang (UTRC):** discussions on scaffolds; HRL supplied carbon aerogels
- **Zak Fang (Utah):** HRL measured equilibrium pressure of Ti doped  $MgH_2$

- **DOE partners**

- **Ted Baumann (LLNL):** provided porous carbon materials
- **Tom Autrey (PNNL):** provided mesoporous carbon
- **Leon Shaw (UConn):** collaborated on optimizing kinetics using milling, HRL validated UConn results



## New Destabilized Systems

- **Complete investigation of the  $\text{MgNi}_x\text{B}_2$  system (Milestone: Sept 09)**
  - Fully establish reaction(s)
  - Measure isotherms
- **Search for other ternary systems with high capacity and low reaction temperatures**

## Nanoporous Scaffolds

- **Optimize  $\text{LiBH}_4/\text{MgH}_2$  in scaffolds**
  - Understand and address poor cycling
  - Incorporate  $\text{LiBH}_4$  and  $\text{MgH}_2$  simultaneously
  - Incorporate catalysts
- **Carbon scaffolds**
  - Continue to study influence of pore size and distribution
  - Perform further characterization of mesoporous carbon
  - Elucidate mechanism of kinetic enhancement

## New Destabilized Systems

- Investigated  $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  system
  - Observed first kinetically destabilized system
  - Confirmed the formation of ternary borides
  - Synthesized ternary borides and observed their hydrogenation

## Nanoporous Scaffolds

- Incorporated  $\text{LiBH}_4/\text{MgH}_2$  destabilized system into scaffold
  - Observed lower dehydrogenation temperature but with poor cycling
  - Tentatively assigned poor cycling to poor mixing of components
- Investigated effect of scaffold on hydrogen exchange reaction rate
  - Developed synthetic capability of mesoporous carbon at HRL
  - Observed effect of pore architecture on reaction rate

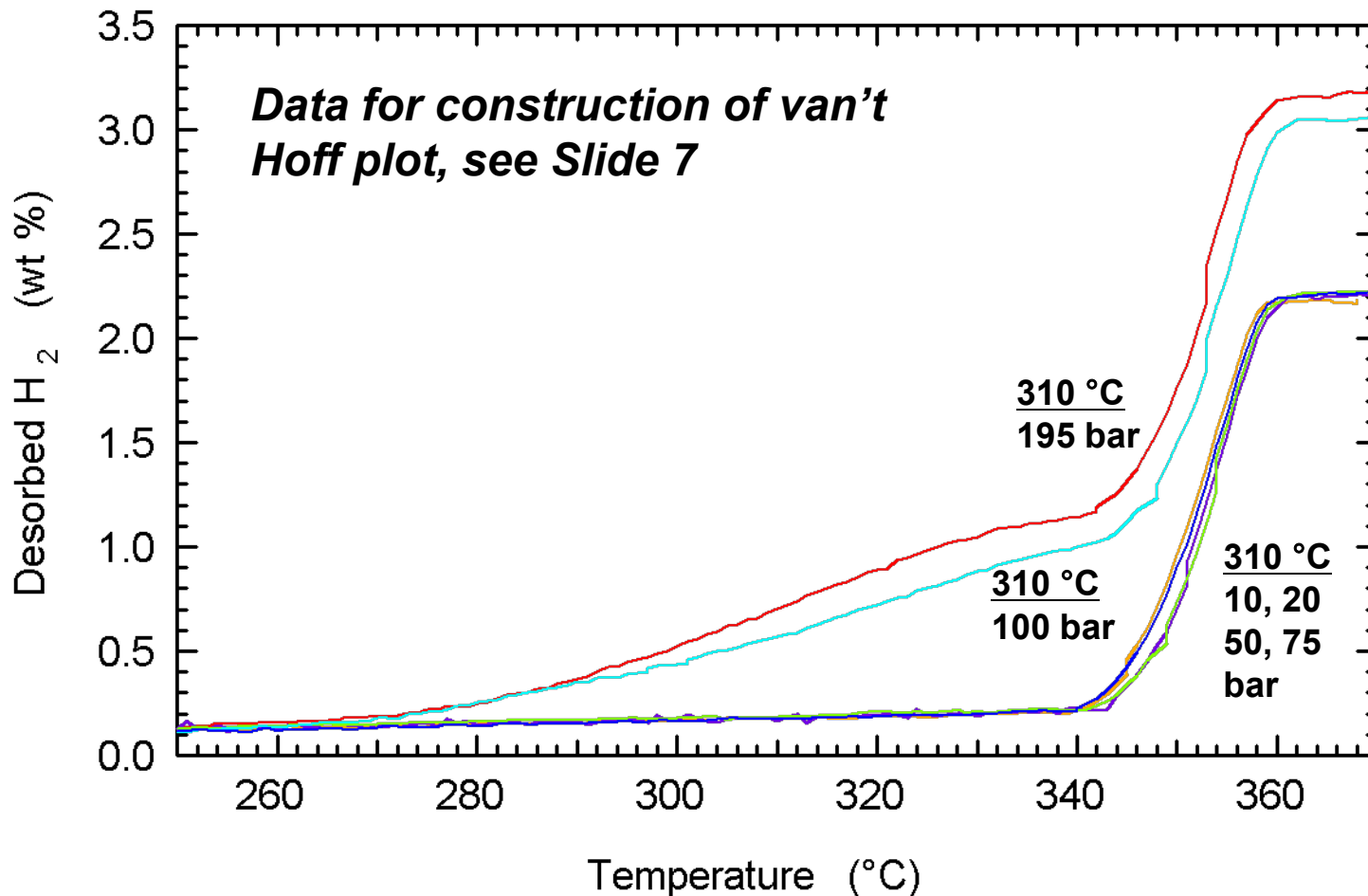
# Supplemental Slides

# Program Direction

## – By System –

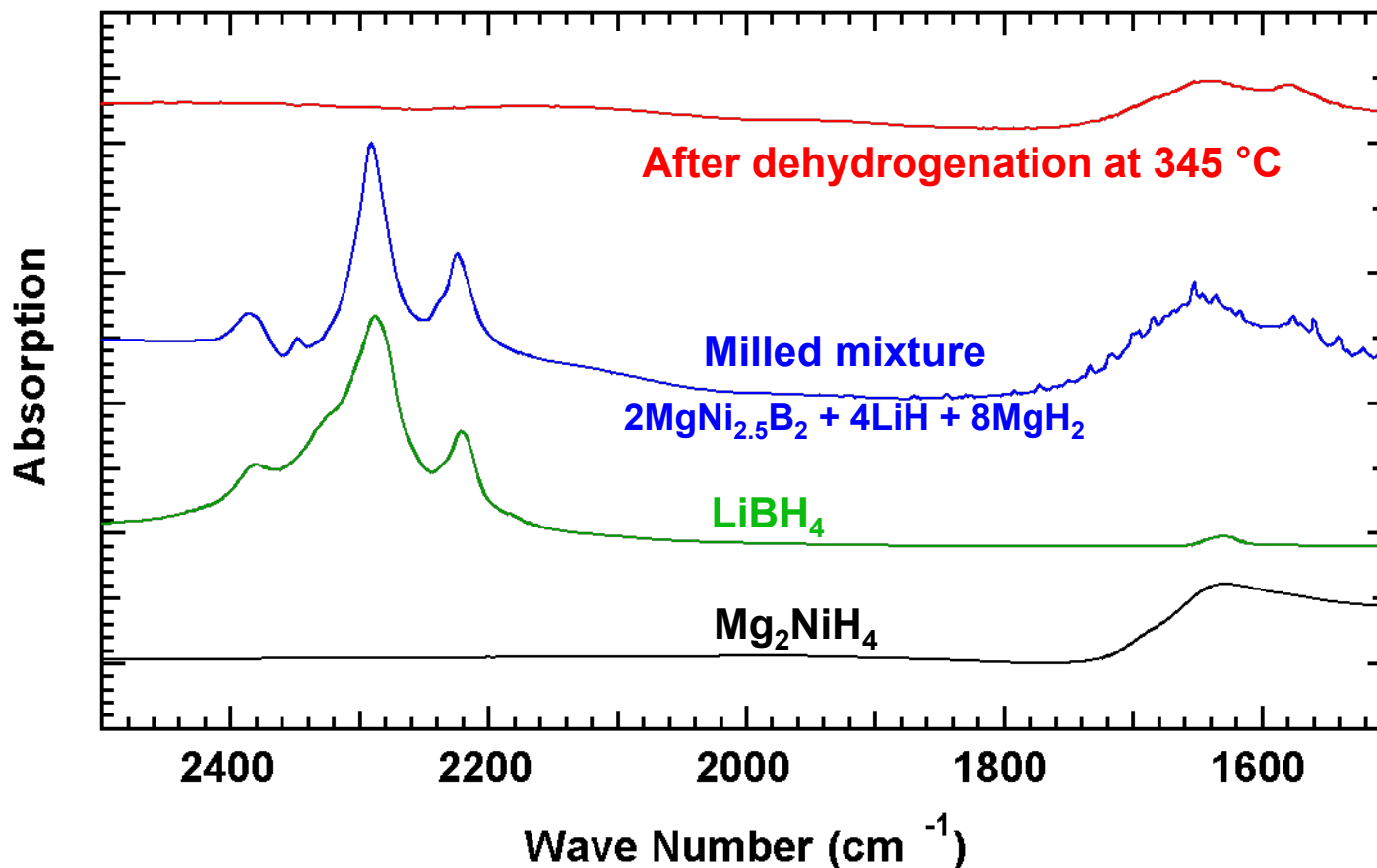
Destabilized System	Benchmark	2008 Status	2008/09 Progress	Future
<b>LiBH<sub>4</sub> / MgH<sub>2</sub></b> <b>@C aerogel</b> 11.4 wt.%, 0.095 kg/L w/o aerogel, est. T <sub>1 bar</sub> =170°C	Could meet 2010 system weight and volume capacity goals (assuming 25% aerogel and additional 25% system penalties)	<ul style="list-style-type: none"> <li>•Reduced capacity penalty to 40%</li> <li>•Measured 10x equilibrium pressure of bulk</li> <li>•Incorporated Mg into aerogel</li> <li>•Measured &gt; 150x reaction rate</li> </ul>	<ul style="list-style-type: none"> <li>•Incorporated complete destabilized system into aerogel</li> <li>•Reaction temperature lowered but with degradation</li> <li>•Mesoporous carbon synthesized and shows promise for improved kinetics</li> </ul>	<ul style="list-style-type: none"> <li>•Incorporate LiBH<sub>4</sub> and MgH<sub>2</sub> into aerogel simultaneously</li> <li>•Further optimize pore architecture and surface chemistry for maximum kinetic benefit</li> </ul>
<b>LiBH<sub>4</sub> / Mg<sub>2</sub>NiH<sub>4</sub></b> 8.3 wt%, est. T <sub>1 bar</sub> =150°C	Could meet 2010 system capacity goal (but only small system penalty)	<ul style="list-style-type: none"> <li>•Reversible capacity of ~6.5% at 350°C</li> <li>•Slight degradation observed</li> </ul>	<ul style="list-style-type: none"> <li>•Measured T<sub>1 bar</sub> of 65°C for low temperature step</li> <li>•Hydrogenation of ternary boride confirmed</li> </ul>	<ul style="list-style-type: none"> <li>•Candidate for incorporation into scaffold</li> <li>•Candidate for catalyst screening</li> </ul>
<b>LiBH<sub>4</sub> / MgF<sub>2</sub></b> 7.6 wt%, est. T <sub>1 bar</sub> =150°C	Could meet 2010 system capacity goal (but only small system penalty)			Candidate for incorporation into scaffold
<b>Other LiBH<sub>4</sub> / MgX</b> 4-10 wt.%, est. T <sub>1 bar</sub> : -10 to 430°C	Could meet 2007 goal (including moderate system penalty)	Sorption meas.: X=Cl, Cu No destabilization		<ul style="list-style-type: none"> <li>•Test new destabil. agents, X=O, OH, Ni</li> <li>•Use nano-engineering to improve kinetics</li> </ul>

*Dehydrogenation after hydrogenation at indicated pressure and temperature*



- At 310 °C, the  $P_{eq}$  for the low temperature step is between 75 and 100 bar
- At 280 °C,  $P_{eq}$  is between 50 and 75 bar (*data not shown*)

*Ex-situ FTIR spectra, refer to Slide 6*



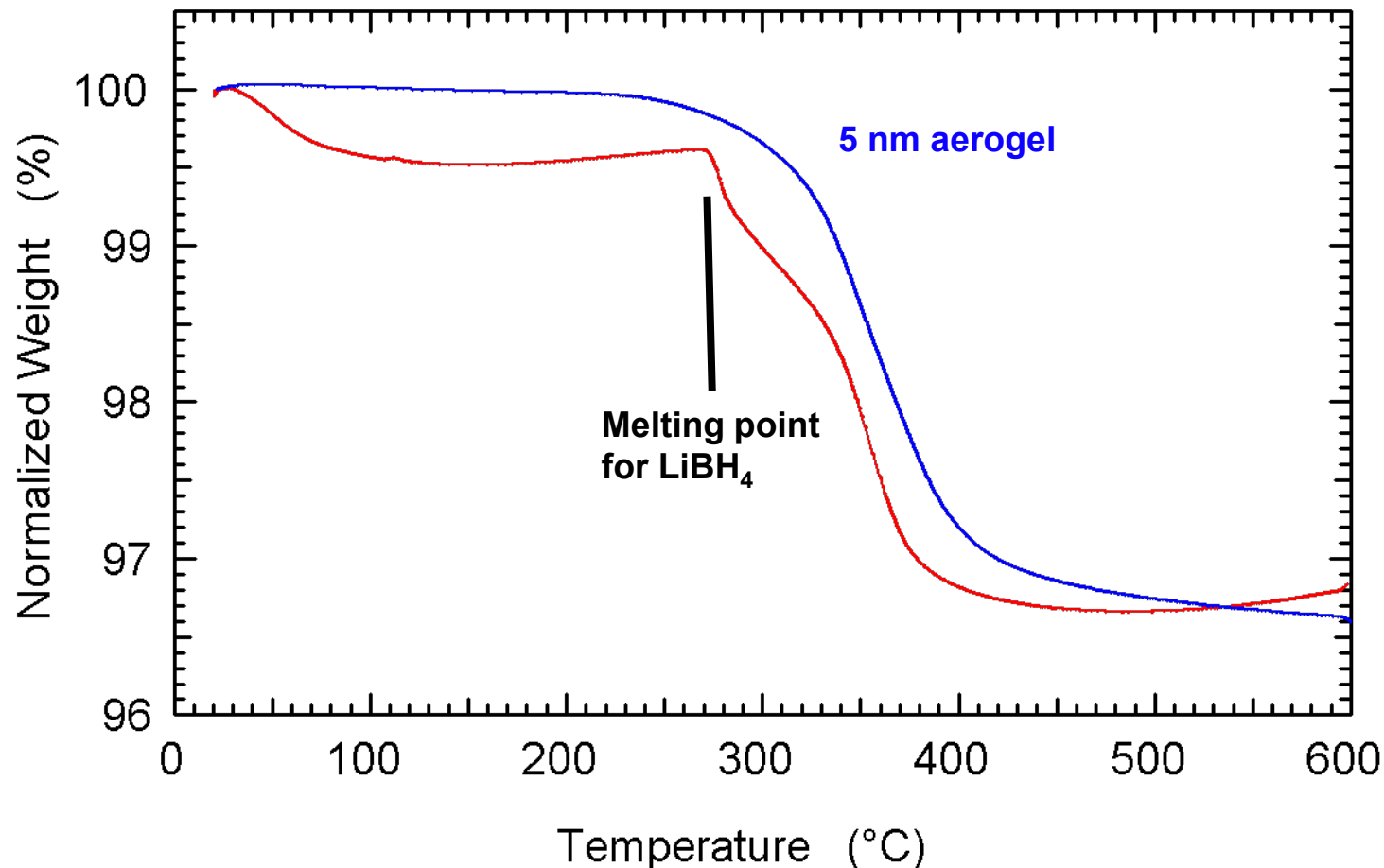
- $\text{LiBH}_4$  is largely reacted by 345 °C
- Supports Rxn:  $4\text{LiBH}_4 + 5\text{Mg}_2\text{NiH}_4 = 2\text{MgNi}_{2.5}\text{B}_2 + 4\text{LiH} + 8\text{MgH}_2 + 2.5 \text{ wt\% H}_2$

**$\text{Mg}_2\text{NiH}_4$  kinetically destabilizes  $\text{LiBH}_4$**

Refer to Slide 13

Sample	Mode pore size (nm)	Total pore volume (cm <sup>3</sup> /g)	Micropore volume (cm <sup>3</sup> /g)
HRL 5 nm aerogel	6	0.50	0.13
HRL mesoporous carbon	6	0.57	0.13
LLNL reverse cast mesoporous carbon	4	1.35	0.03

*Dehydrogenation of  $\text{LiBH}_4$  following incorporation from melt*



- First sample to show significant dehydrogenation at melting point
- Weight loss slightly lower than expected indicating some decomposition during incorporation ( $H_2$  overpressure may be needed)