

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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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 LiBH_4/MgX , $\text{X} = \text{Ni}$ destabilized hydride system

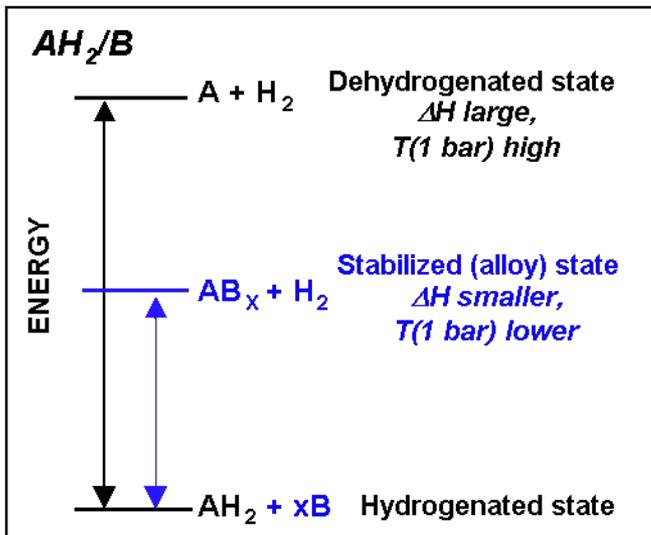
- New destabilized hydride system with reversible theoretical capacity of 8.3% (6.5% observed) and lower temperature than $\text{X} = \text{H}_2$ for hydrogen exchange
- Addresses Barriers A, C, and E.

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 ΔH

Destabilization results in lower ΔH and $T_{1 \text{ bar}}$

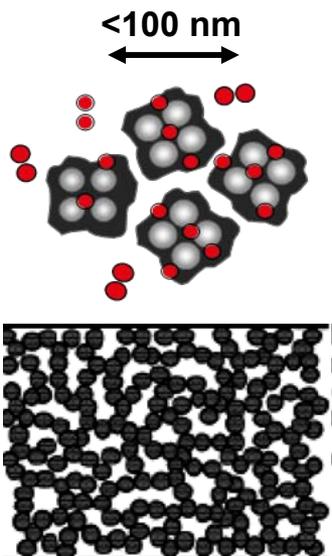
Nano-engineering

(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



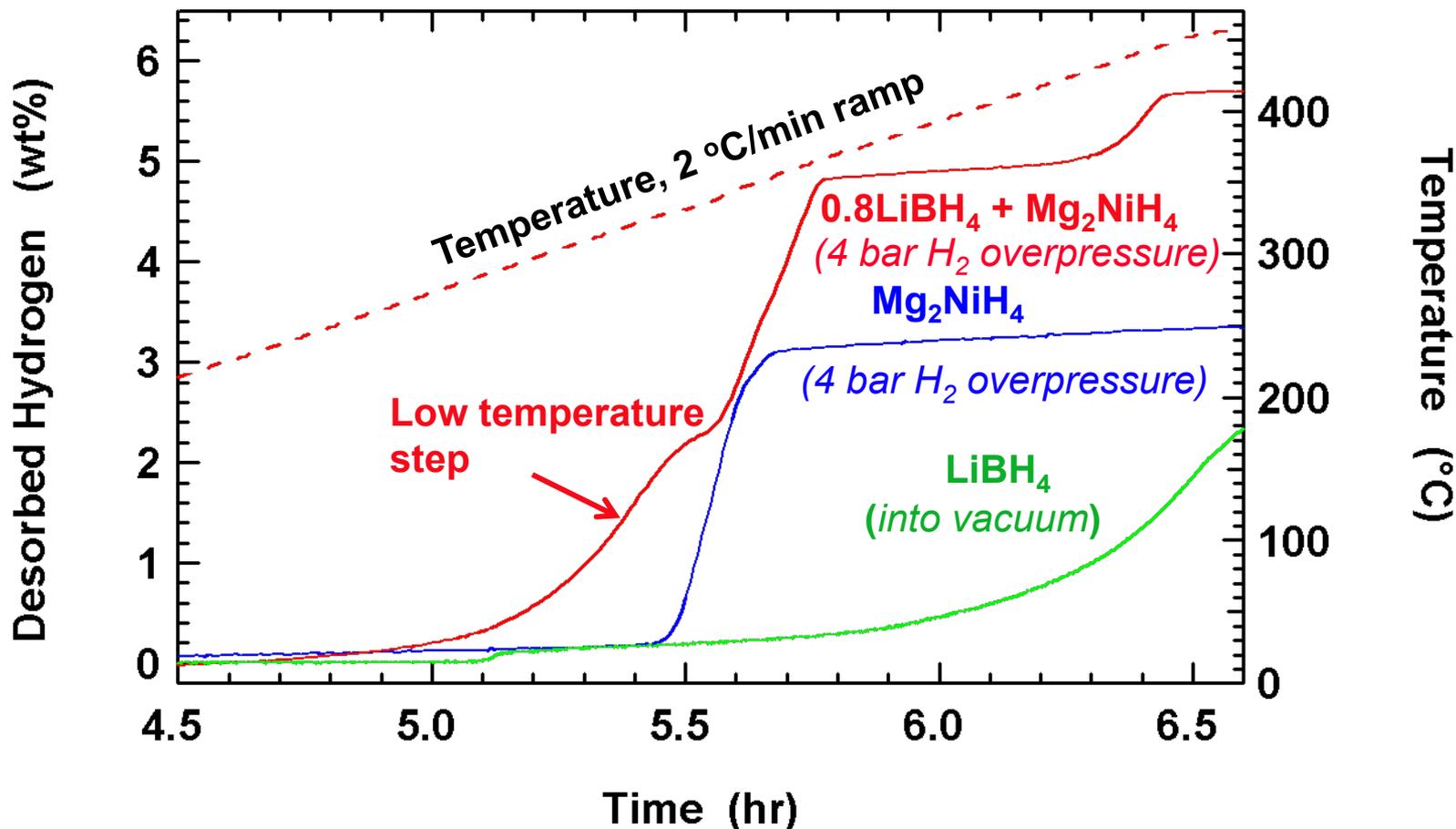
From Petricevic, et al., Carbon 39, 857 (2001)

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 LiBH_4 in carbon aerogel
- Incorporated Mg into Ni loaded carbon aerogel through melting

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

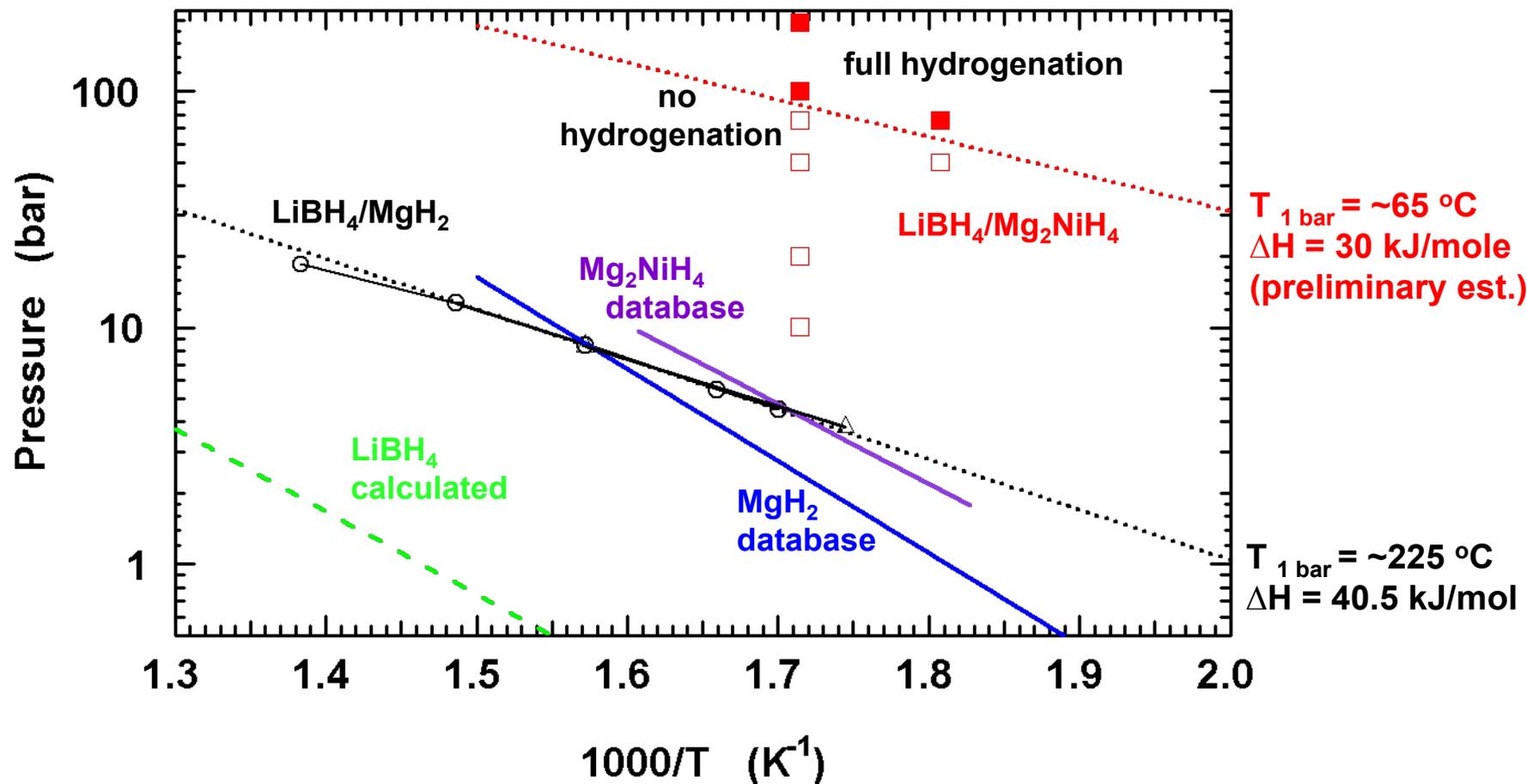
1. $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ Destabilized System



- IR spectra shows complete consumption of LiBH_4 by 345°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 Mg_2NiH_4 or LiBH_4 individually

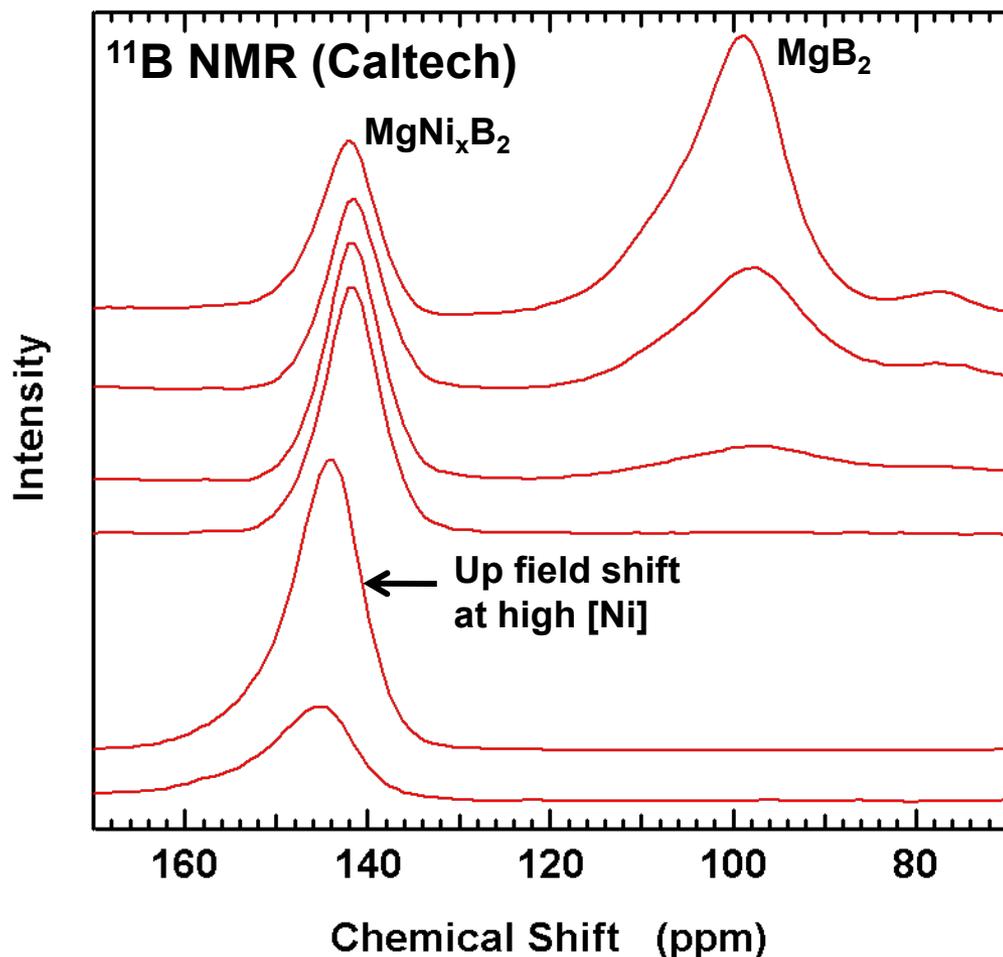
First example of *kinetically* destabilized system

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*)

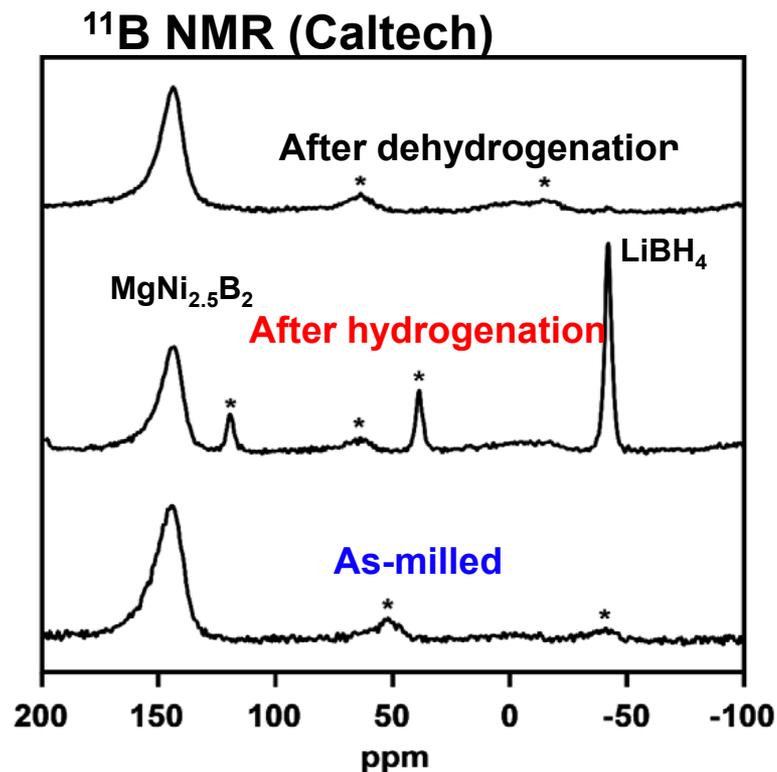
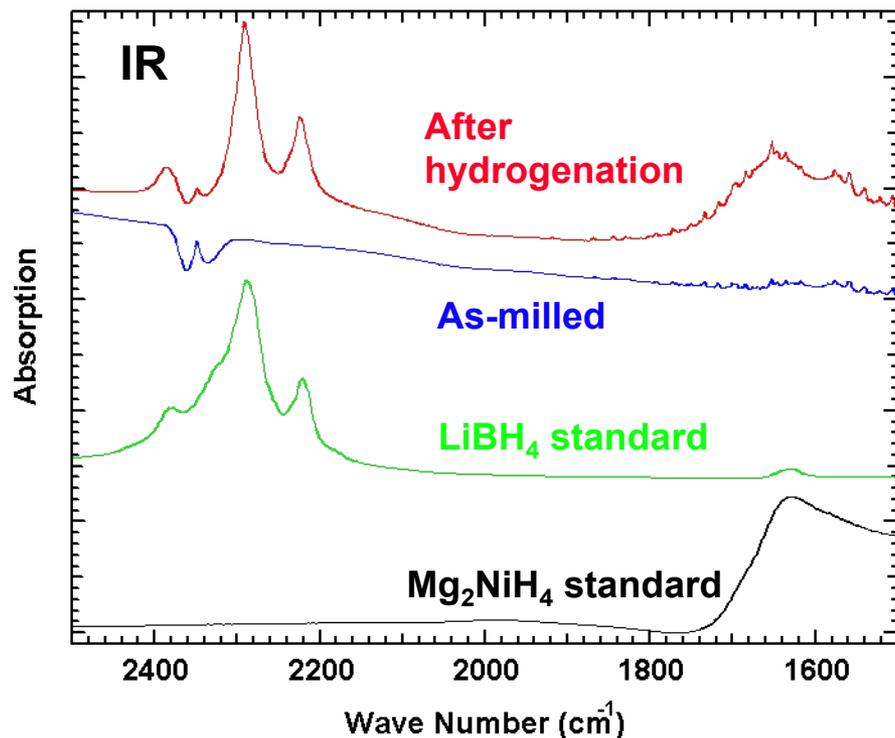
Alloys synthesized from milled mixtures of $\text{MgB}_2 + x\text{Ni}$, sintered at 800°C , 24 hr



Ni composition	Approximate actual composition
$x = 0.5$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 2\text{MgB}_2$
$x = 0.75$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 1\text{MgB}_2$
$x = 1.0$	$\text{MgNi}_{\sim 1.5}\text{B}_2 + \sim 0.5\text{MgB}_2$
$x = 2.0$	MgNi_2B_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 ~ 1.5 to ~ 3

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

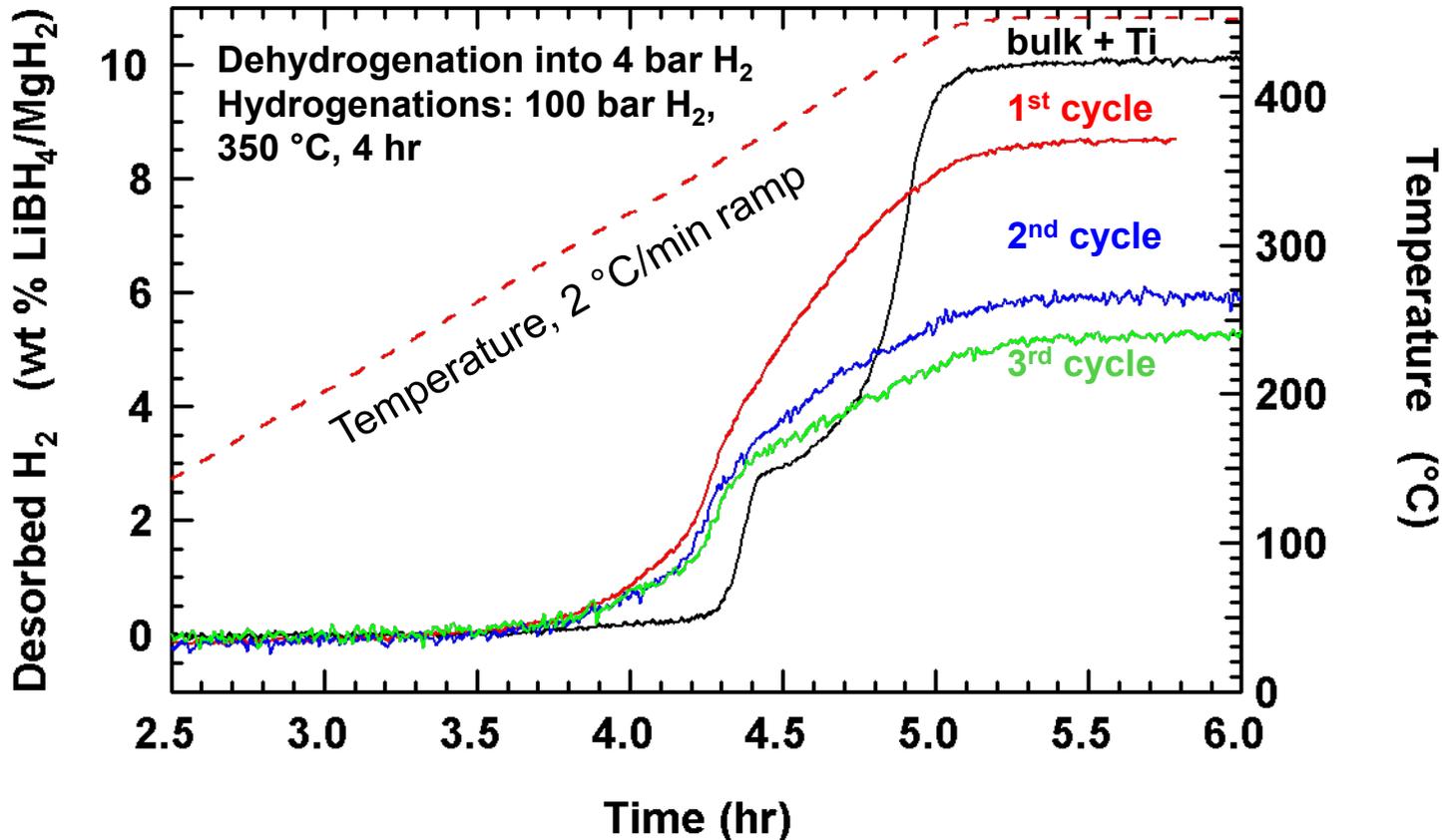


- Ternary boride ($x = 2.5$) can be hydrogenated partially (~30%)
- Only boride other than MgB_2 that readily reacts with hydrogen

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

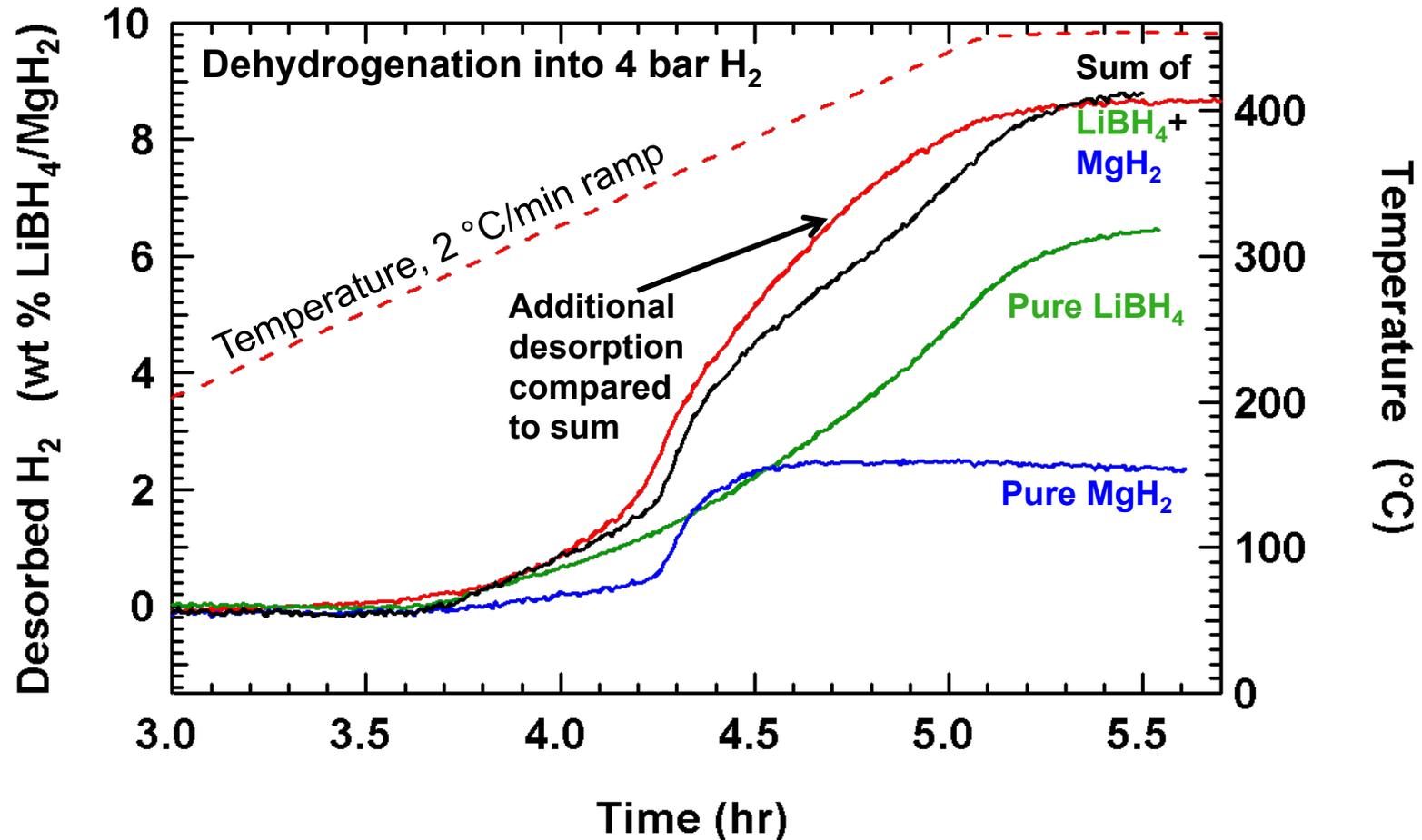
2. LiBH₄/MgH₂ System in Carbon Aerogel

MgH₂ incorporated 1st at U. Hawaii from Bu₂Mg, then LiBH₄ at HRL
Overall composition is 2 LiBH₄ + MgH₂ in aerogel at a loading of 25 wt%



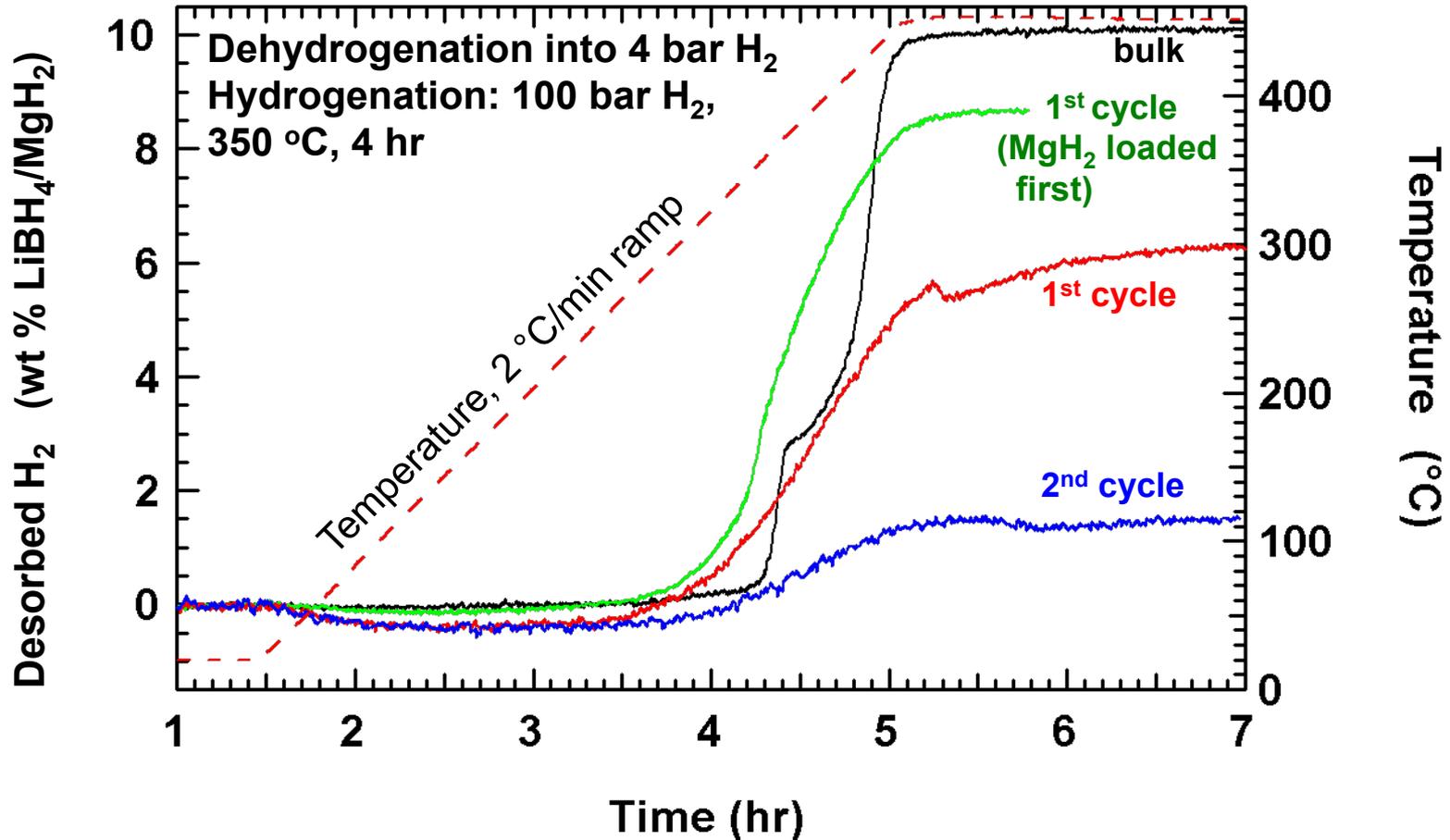
- Reaction temperature is lower than for bulk sample with catalyst
- Individual steps (if present) are not well resolved
- However, cycling is poor (sequential filling may lead to poor mixing in pores)

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
- LiBH_4 and MgH_2 do not appear to be mixed well within the pores
(we are considering simultaneous incorporation)

13 nm aerogel; LiBH₄ incorporated at HRL, then MgH₂ incorporated at U. Hawaii

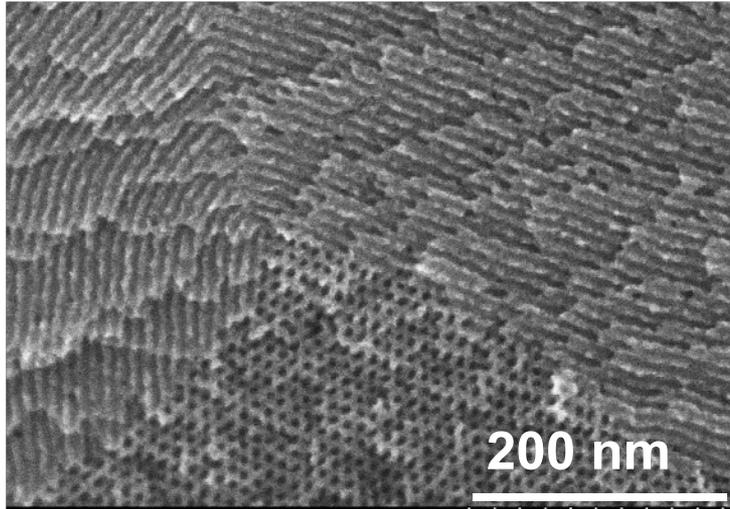


- 1st cycle capacity is low (may be due to sample handling, shipping to/from Hawaii)
- There is a large loss on the 2nd cycle (not understood)
- Only our 2nd try, we are working to perform the complete filling procedure at HRL

3. New Scaffold Structures

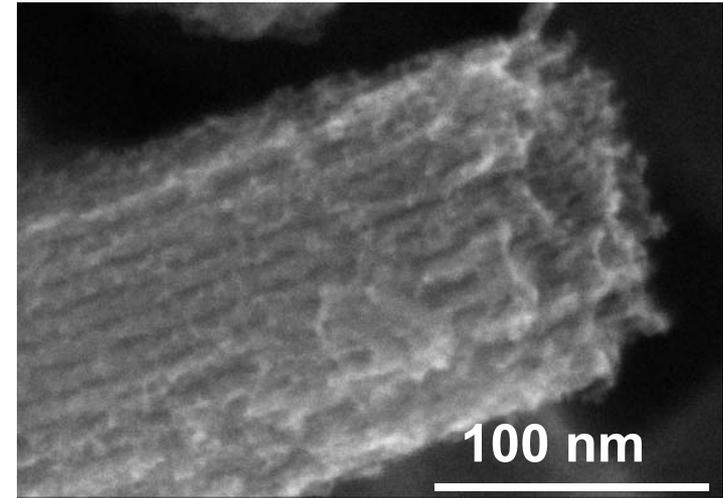
Mesoporous carbon from porous polymer

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



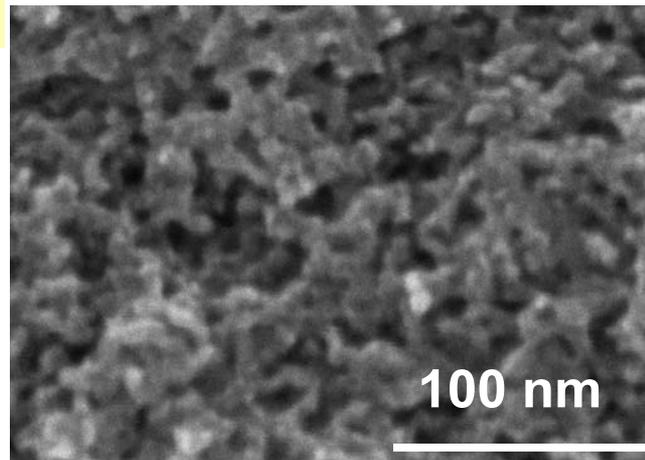
Long, straight but not interconnected pores

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

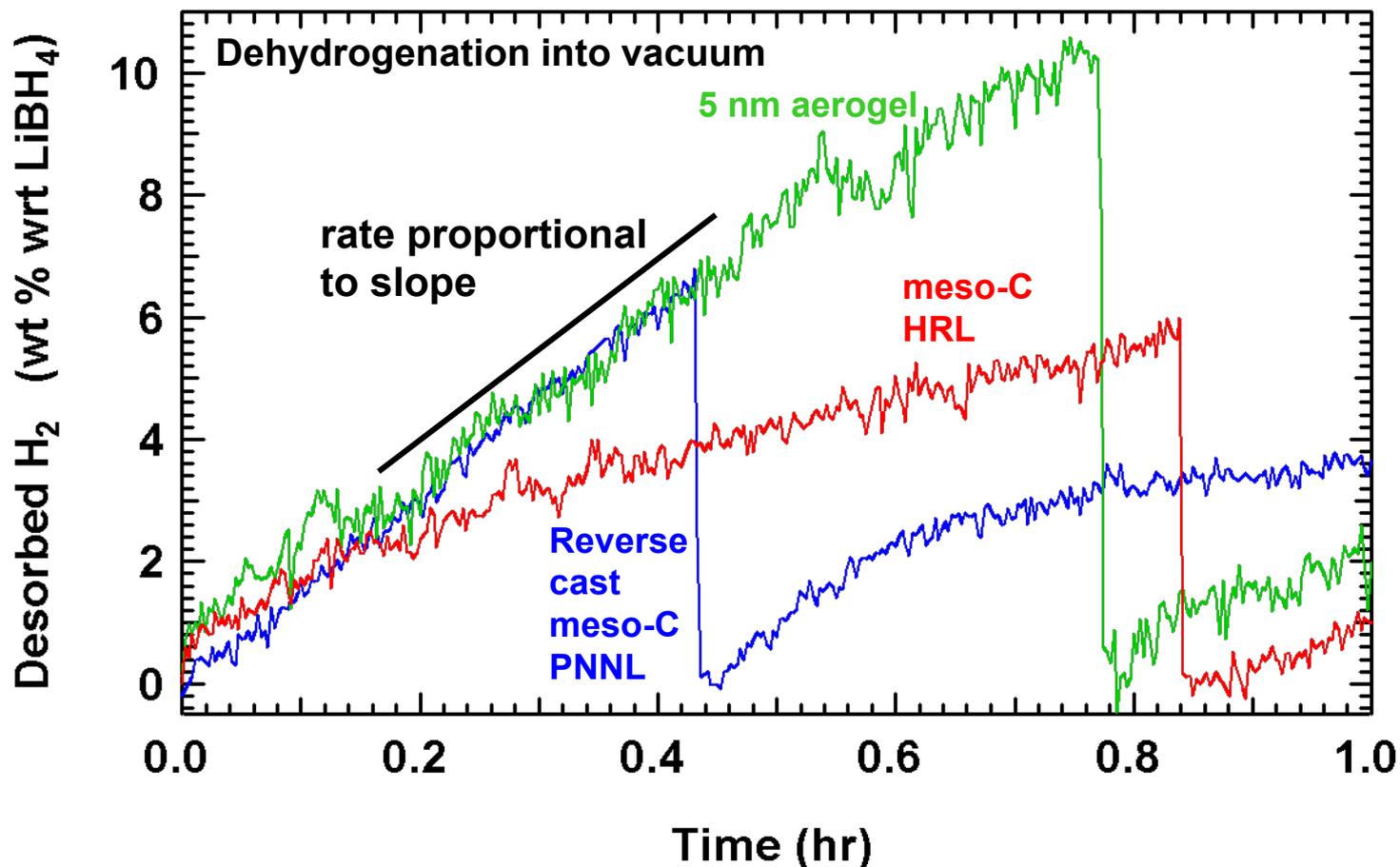


Long, straight and interconnected pores

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:
 - ~ 5 to 10 nm pore sizes with $> 3 \text{ cm}^3/\text{g}$ pore volume
- For 10 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 nm pores, showing the possibility of meeting the goals

2. Other issues

- Chemical stability, i.e., 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 MgNi_xB_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 LiBH_4 and 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

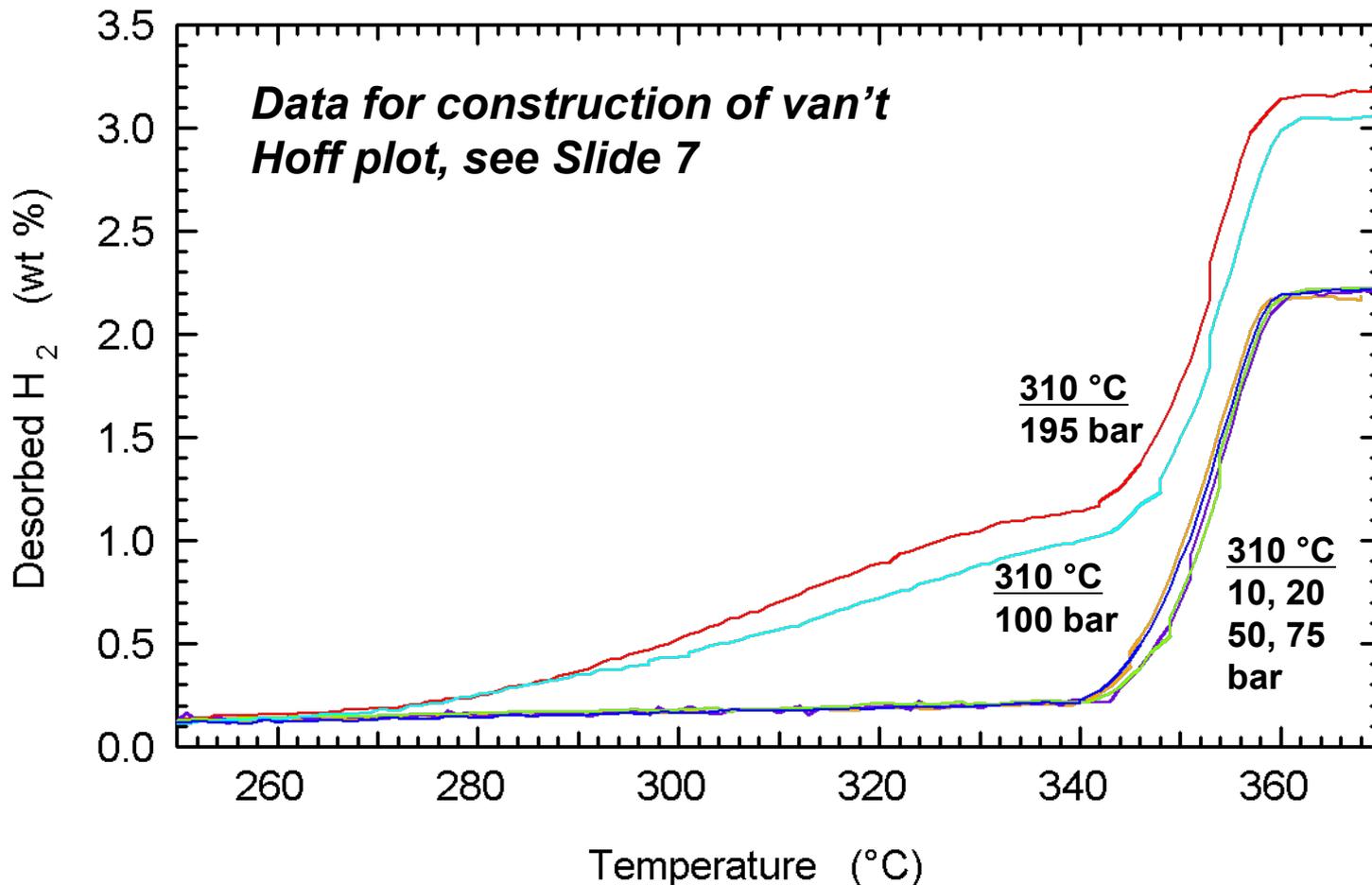
Nanoporous Scaffolds

- 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

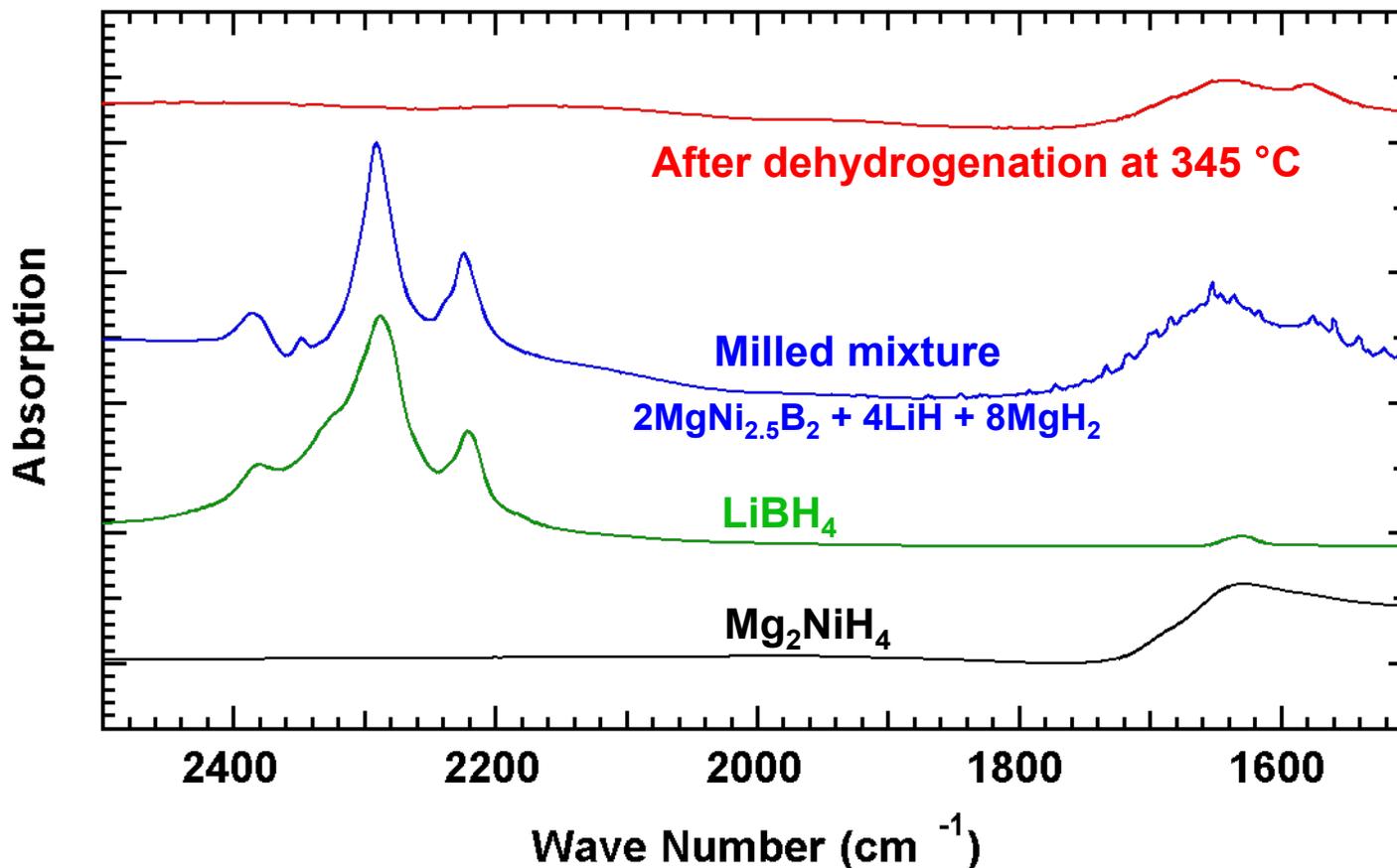
Destabilized System	Benchmark	2008 Status	2008/09 Progress	Future
LiBH₄ / MgH₂ @C aerogel 11.4 wt.%, 0.095 kg/L w/o aerogel, est. T _{1 bar} =170°C	Could meet 2010 system weight and volume capacity goals (assuming 25% aerogel and additional 25% system penalties)	<ul style="list-style-type: none"> •Reduced capacity penalty to 40% •Measured 10x equilibrium pressure of bulk •Incorporated Mg into aerogel •Measured > 150x reaction rate 	<ul style="list-style-type: none"> •Incorporated complete destabilized system into aerogel •Reaction temperature lowered but with degradation •Mesoporous carbon synthesized and shows promise for improved kinetics 	<ul style="list-style-type: none"> •Incorporate LiBH₄ and MgH₂ into aerogel simultaneously •Further optimize pore architecture and surface chemistry for maximum kinetic benefit
LiBH₄ / Mg₂NiH₄ 8.3 wt%, est. T _{1 bar} =150°C	Could meet 2010 system capacity goal (but only small system penalty)	<ul style="list-style-type: none"> •Reversible capacity of ~6.5% at 350°C •Slight degradation observed 	<ul style="list-style-type: none"> •Measured T_{1 bar} of 65°C for low temperature step •Hydrogenation of ternary boride confirmed 	<ul style="list-style-type: none"> •Candidate for incorporation into scaffold •Candidate for catalyst screening
LiBH₄ / MgF₂ 7.6 wt%, est. T _{1 bar} =150°C	Could meet 2010 system capacity goal (but only small system penalty)			Candidate for incorporation into scaffold
Other LiBH₄ / MgX 4-10 wt.%, est. T _{1 bar} : -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"> •Test new destabil. agents, X=O, OH, Ni •Use nano-engineering to improve kinetics

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



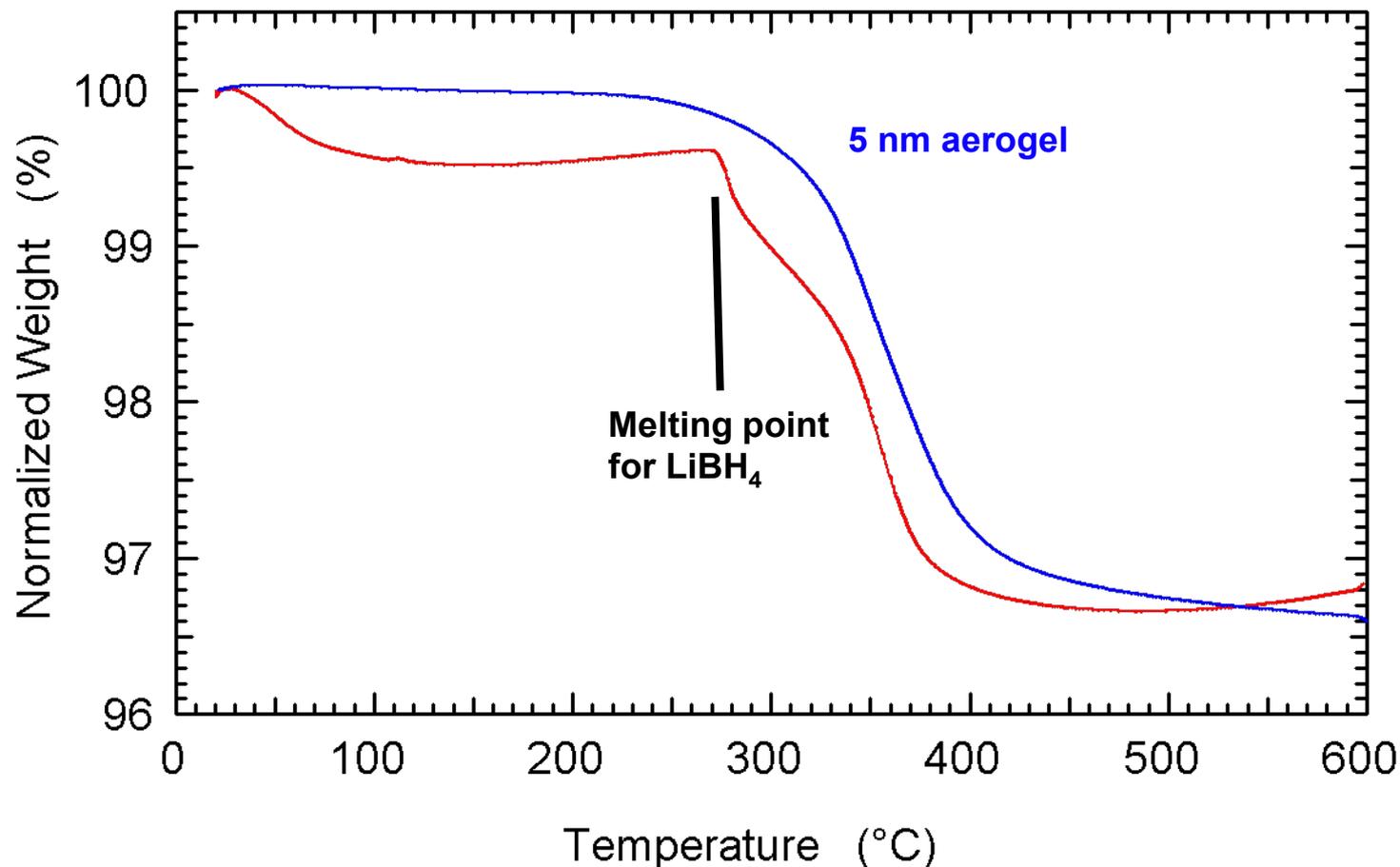
- LiBH_4 is largely reacted by 345 °C
- Supports Rxn: $4\text{LiBH}_4 + 5\text{Mg}_2\text{NiH}_4 = 2\text{MgNi}_{2.5}\text{B}_2 + 4\text{LiH} + 8\text{MgH}_2 + 2.5 \text{ wt\% H}_2$

Mg_2NiH_4 kinetically destabilizes LiBH_4

Refer to Slide 13

Sample	Mode pore size (nm)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /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 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)