



# **Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage**

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**Project ID #  
ST30**

## Timeline

- Project start date: March 2005
- Project end date: Feb 2010
- Percent complete: 60%

## Budget

- **Total Project Funding:**

*Phase I - 3 years: \$1.65M*

- DOE Share: \$1.20M
- Contractor Share: \$0.45M

*Phase II - 2 years: \$1.1M*

- DOE Share: \$0.8M
- Contractor Share: \$0.3M

- **Funding for FY08:**

\$350K as of 4/1/07 (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
- Caltech, JPL, Hawaii, NIST: scaffolds
- Intematix: catalysis

- **DOE collaborations:**

- Drexel, LLNL, PNNL: carbon scaffolds

- **International collaboration**

- Norway IFE: synchrotron XRD

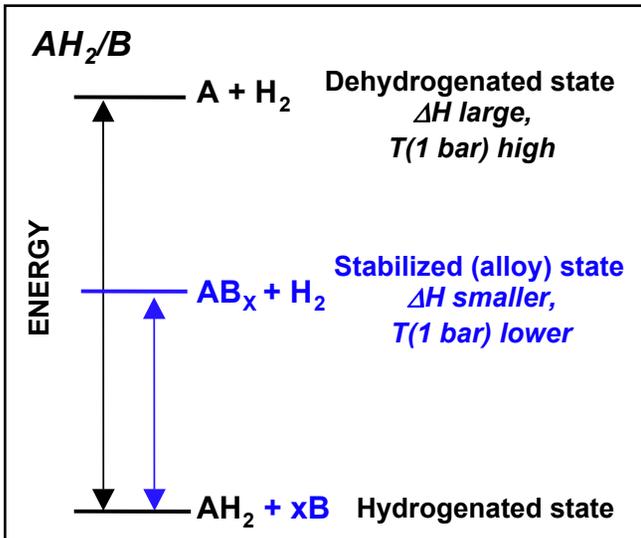
## Overall

**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**

## 2007/2008

- **To identify and test new high capacity Li- and Mg-based destabilized hydrides**
  - Screen candidate  $\text{LiBH}_4 + \text{MgX}$  destabilized systems and evaluate energetics and kinetics
  - Down-select systems for additional work
- **Evaluate sorption kinetics and thermodynamics of  $\text{LiBH}_4$  and Mg in carbon aerogel scaffolds**
  - Investigate effects of pore size and pore size distribution on reaction rates of  $\text{LiBH}_4$
  - Incorporate Mg into the aerogel and measure its kinetics

Month/Year	Milestone or Go/No-Go Decision
June-07	<p><b>Milestone: Incorporate Mg into carbon aerogel.</b> Facilitated Mg incorporation with Ni or Cu as a wetting layer. Continue to improve process to reduce aerogel destruction and increase Mg loading.</p>
Sept-07	<p><b>Milestone: Complete screening of LiBH<sub>4</sub>+MgX system and down select for further studies.</b> Tested X=Si and Ni and found Ni system to be reversible with promising kinetics; work to continue on this system.</p>
Sept-08	<p><b>Milestone: Incorporate the LiBH<sub>4</sub>/MgH<sub>2</sub> destabilized system into nanoscale scaffold.</b> Successfully incorporated LiBH<sub>4</sub> and MgH<sub>2</sub> separately. Working to encapsulate the combined system. Measure hydrogen sorption thermodynamics and kinetics; incorporate catalysts into the system and investigate their effect on reaction rate.</p>



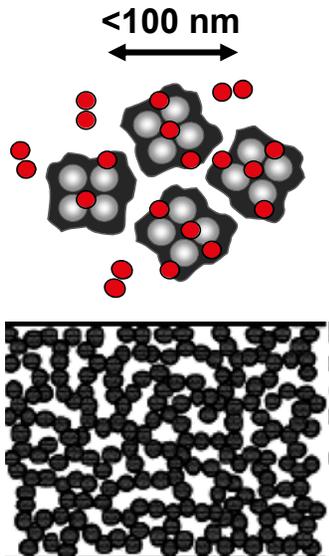
### Hydride Destabilization

(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**

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

- **Potential systems include: X = F, Cl, OH, O, S, Se, CO<sub>3</sub>, Si, SO<sub>4</sub>, Cu, Ge, & Ni**

- 12 destabilization reactions identified and characterized using HSC modeling software
- H-capacities ranging from 5.4-9.6 wt.%,  $T_{1 \text{ bar}}$  from -10°C to 430 °C
- X = F, S, Se, CO<sub>3</sub>, Cl, and Cu tested previously

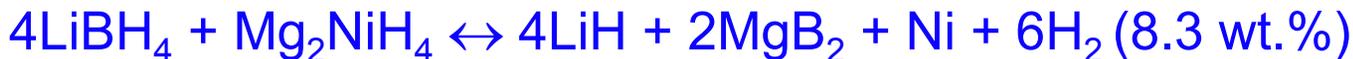
- **In FY07/08, two new systems tested, X = Si and Ni:**



4LiH + 2MgB<sub>2</sub> + Si absorbs 5.5 wt % H<sub>2</sub> at 150 bar, 350°C

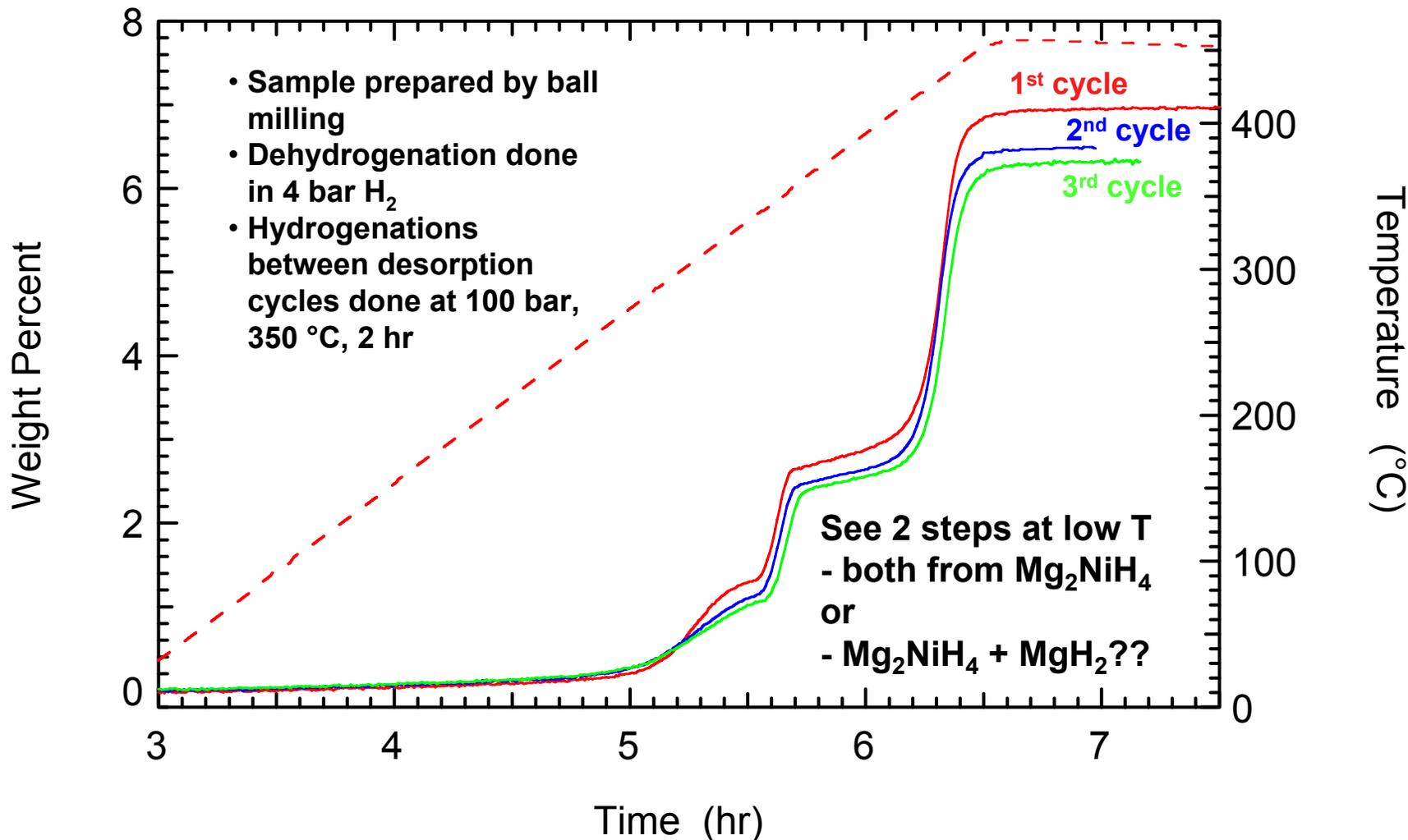
Hydrogenation forms LiBH<sub>4</sub> and Mg<sub>2</sub>Si

However upon dehydrogenation Mg<sub>2</sub>Si does not react



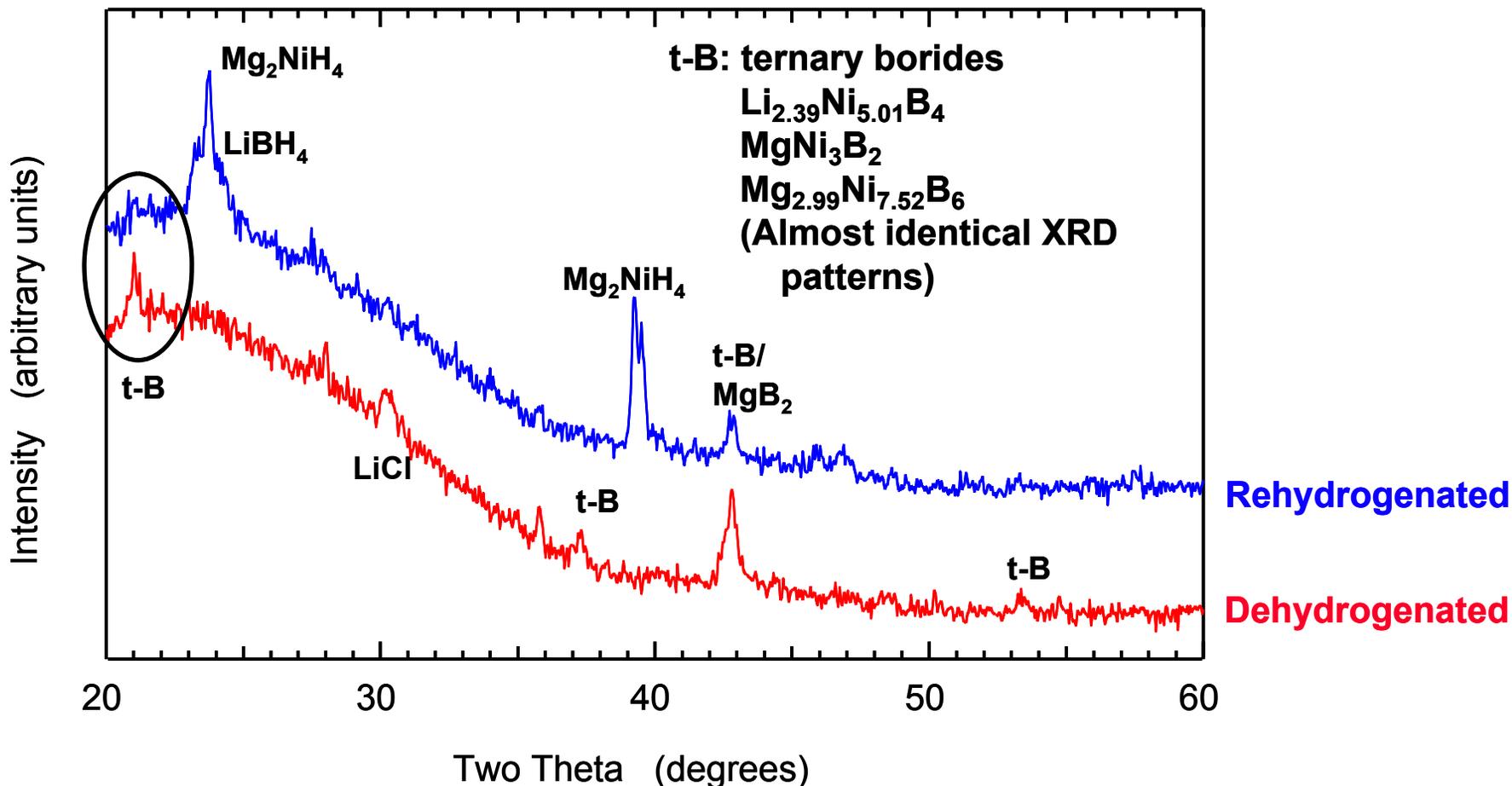
System cycles forming ternary boride(s) -- see following slides

**Results for LiBH<sub>4</sub>/Mg<sub>2</sub>Ni may indicate new class of systems**

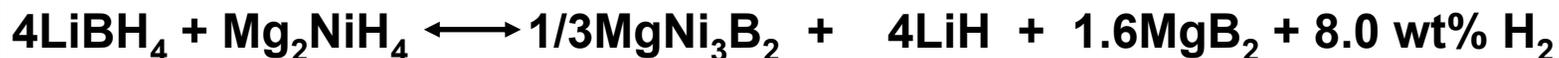


**System cycles at ~ 6.5 wt % with some degradation**

# XRD after Cycling



- $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  appears to have formed upon hydrogenation
- Ternary borides formed upon dehydrogenation; appear to cycle
- Further characterization (FTIR, NMR) required

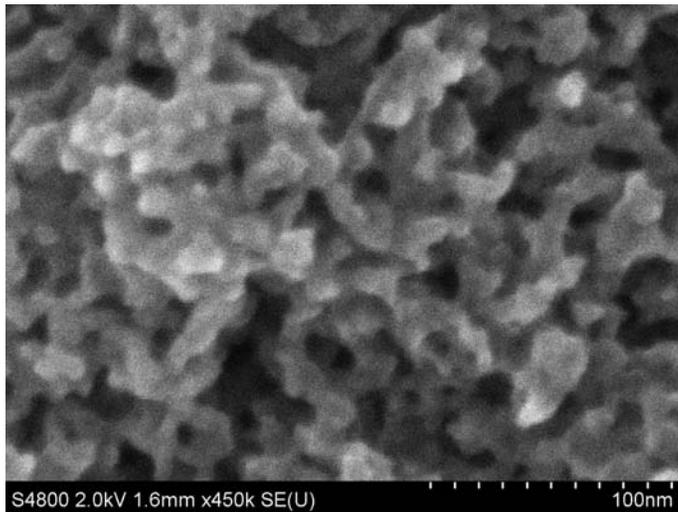


- Three ternary borides have XRD patterns consistent with our observations
- Further work to characterize reaction with NMR is planned
- Suggests computational and experimental efforts to search for other Li(Mg)-transition metal borides

## Motivation:

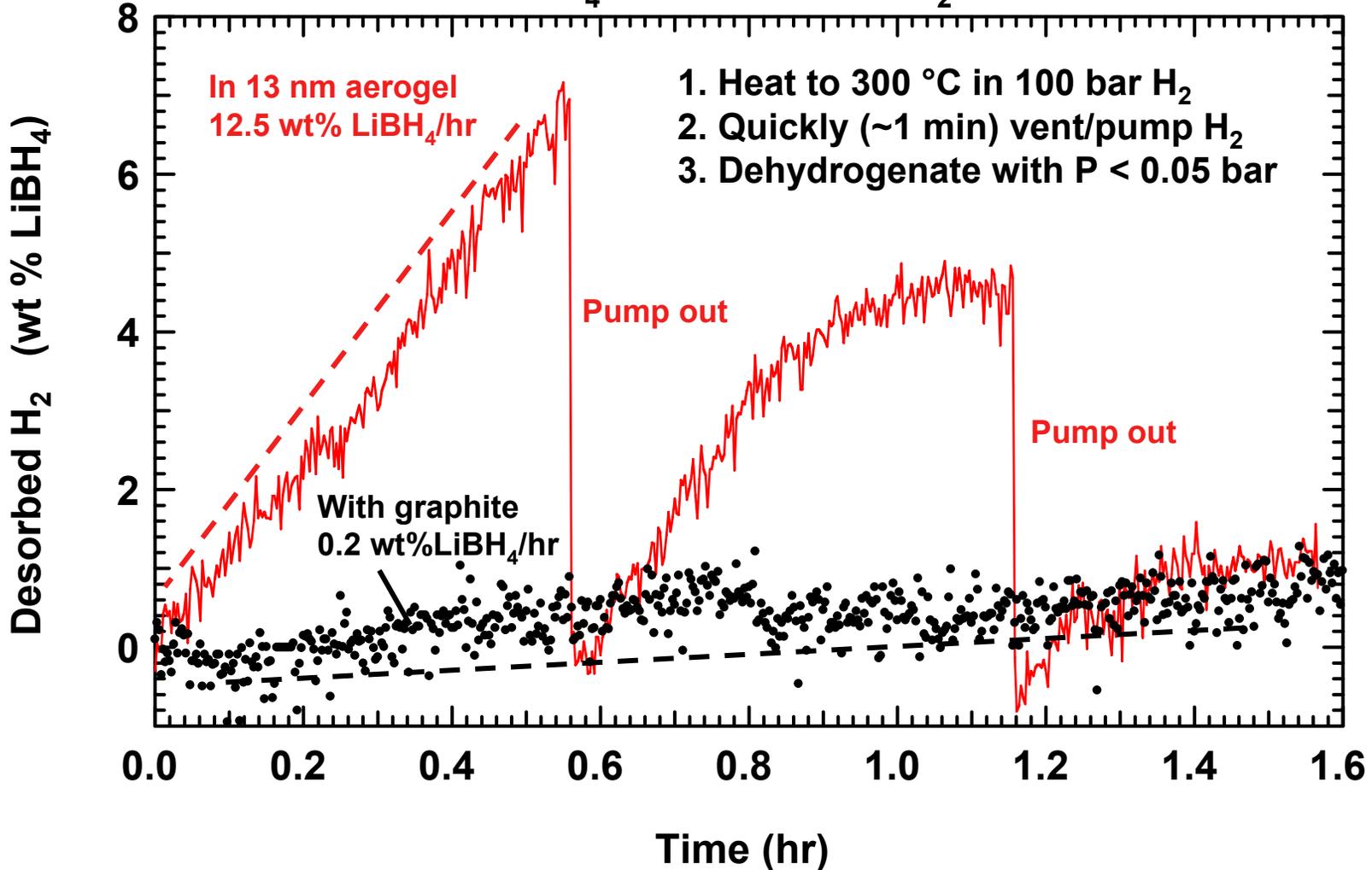
- Scaffolds are effective structure-directing agents for nanoscale hydrides
- Kinetics improved by limiting particle size and diffusion distances
- Thermodynamic changes possible through surface/interface energy effects

Initial work demonstrated feasibility using  $\text{LiBH}_4$  incorporated into carbon aerogels (in collaboration with T. Baumann, LLNL)



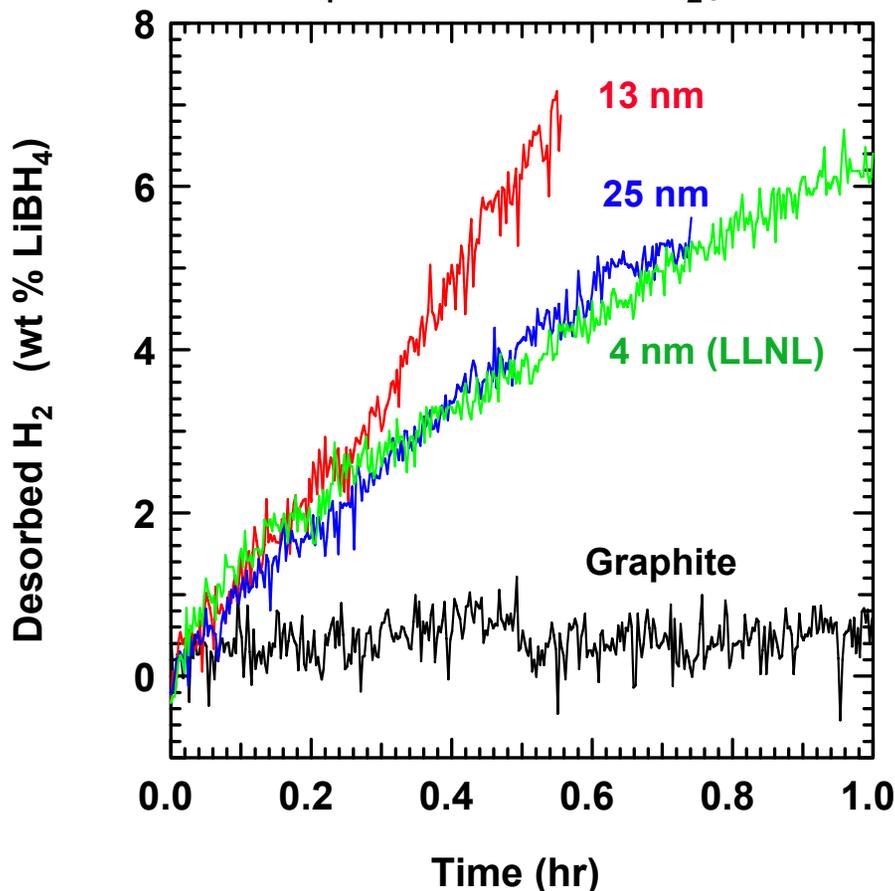
## Current Effort:

- *optimize pore size and pore size distribution*
- *incorporate Mg into aerogels*
- *incorporate full  $\text{LiBH}_4/\text{MgH}_2$  destabilized system into aerogel*

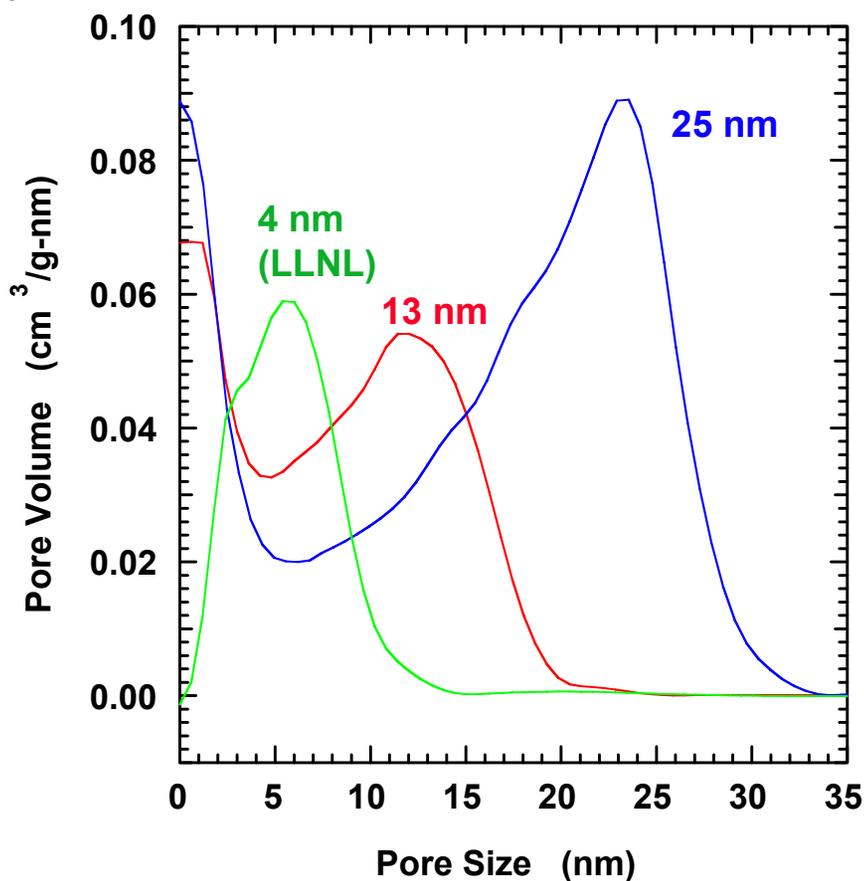


Rate for LiBH<sub>4</sub>@aerogel ~60X rate for LiBH<sub>4</sub>/graphite control sample

TGA:  $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 1.5\text{H}_2$  (13.6 wt %)

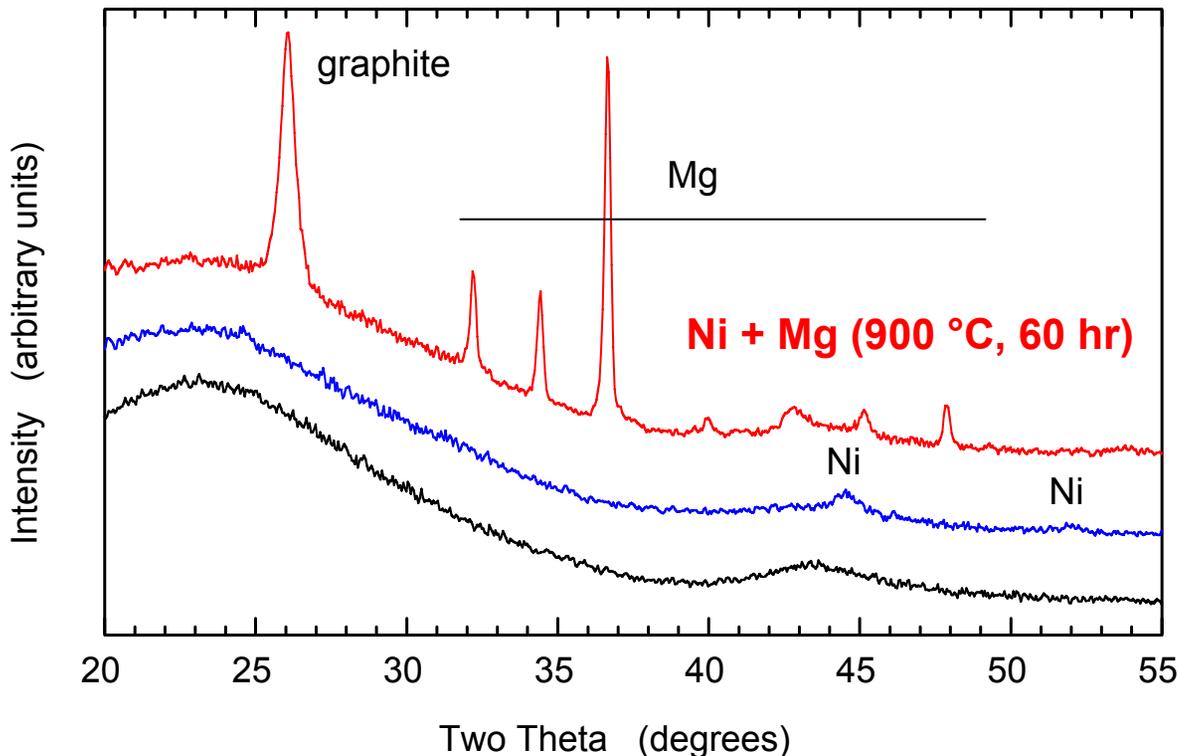


Pore size distributions

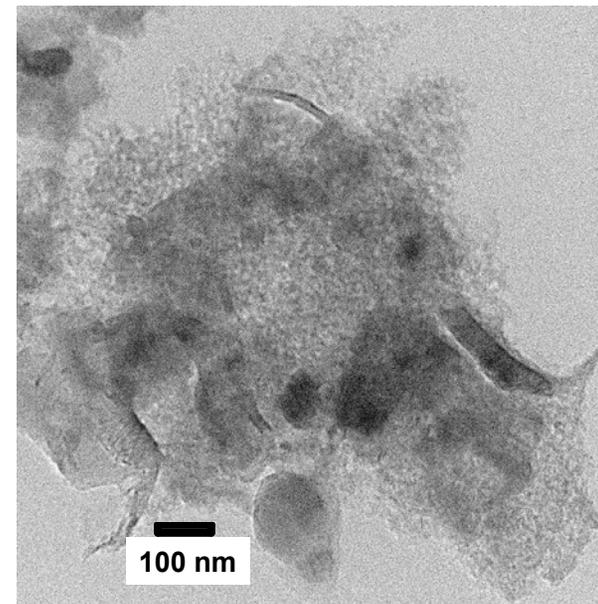


- Rate for 13 nm > 25 nm, indicates influence of pore size
- Relatively slow rate for 4 nm indicates requirement for access

26 nm average pore size ( $1.3 \text{ cm}^3/\text{g}$ ) carbon aerogel



TEM (C. C. Ahn, Caltech)



**Aerogel Degradation:**

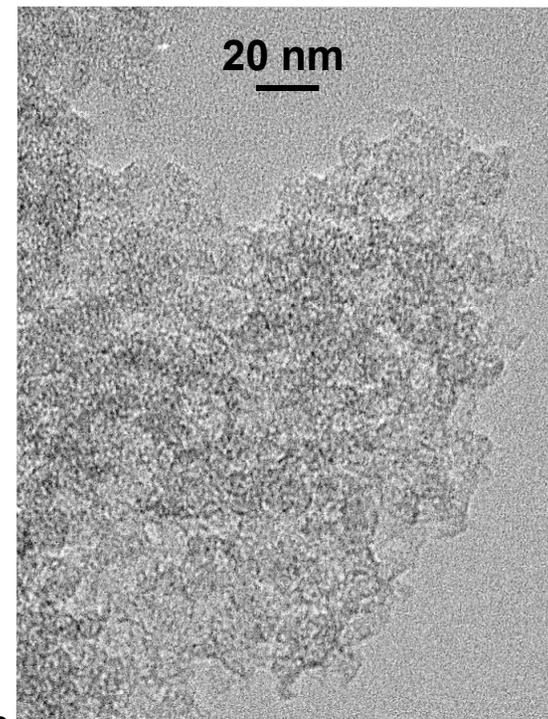
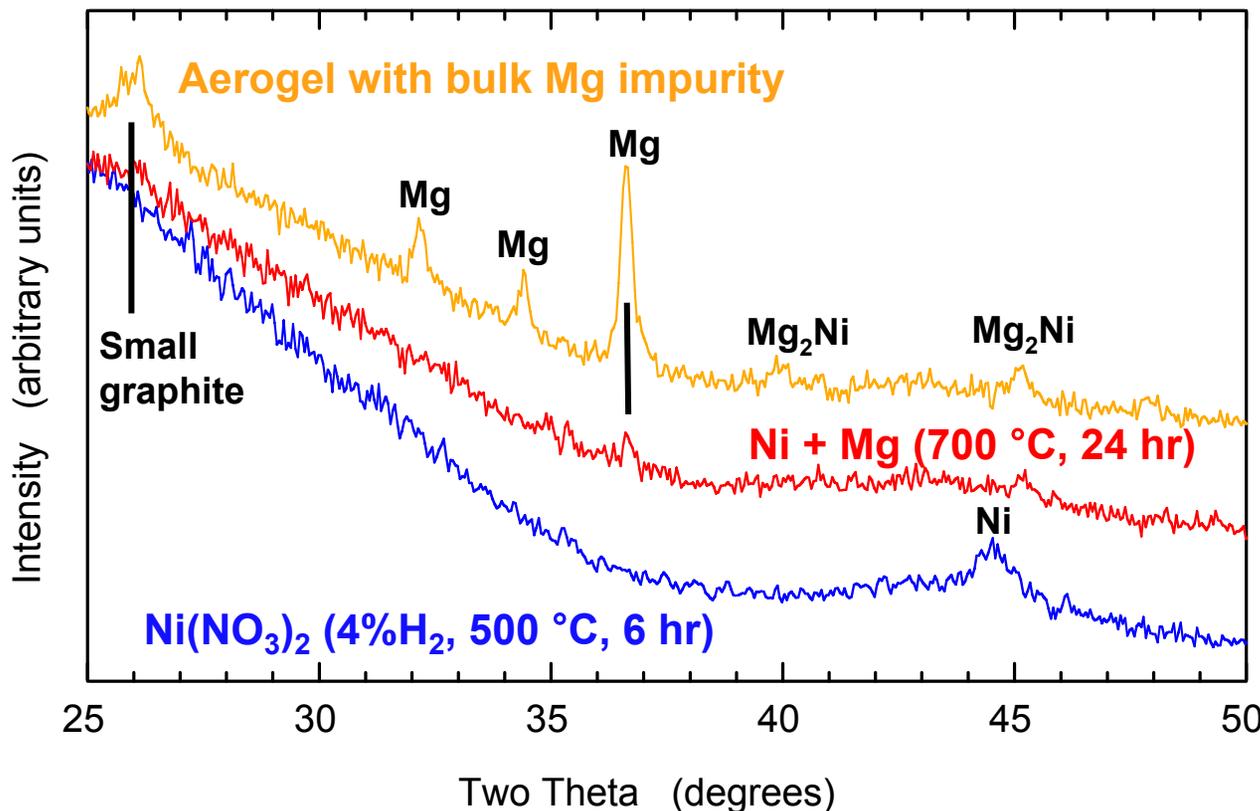
- Graphitic regions and Mg particles

- Nickel “wetting layer” enables incorporation of Mg from melt
- However, 900 °C is too high to preserve aerogel structure
- Lower temperatures needed



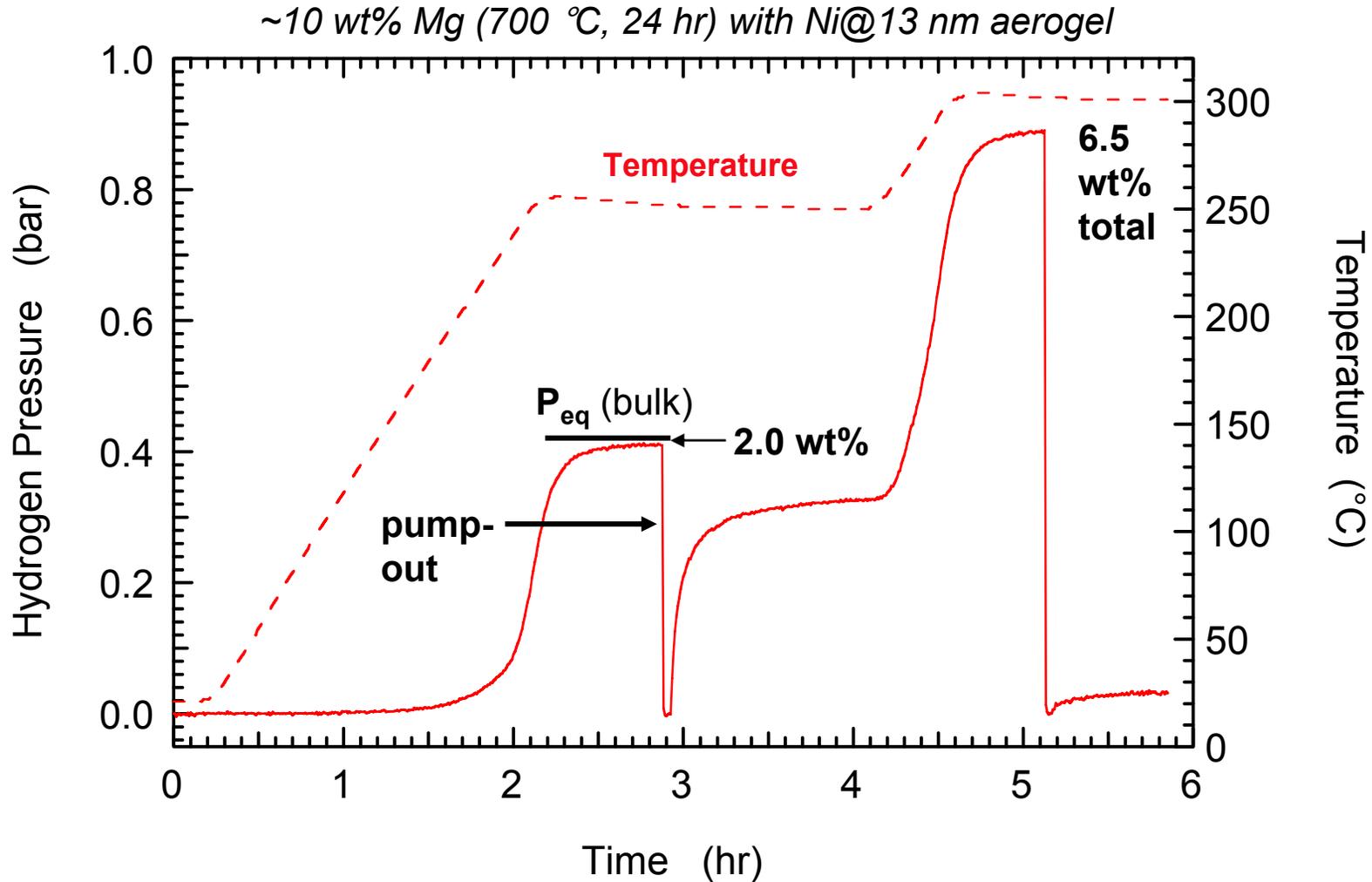
TEM (C. C. Ahn, Caltech)

13 nm average pore size ( $1.3 \text{ cm}^3/\text{g}$ ) carbon aerogel



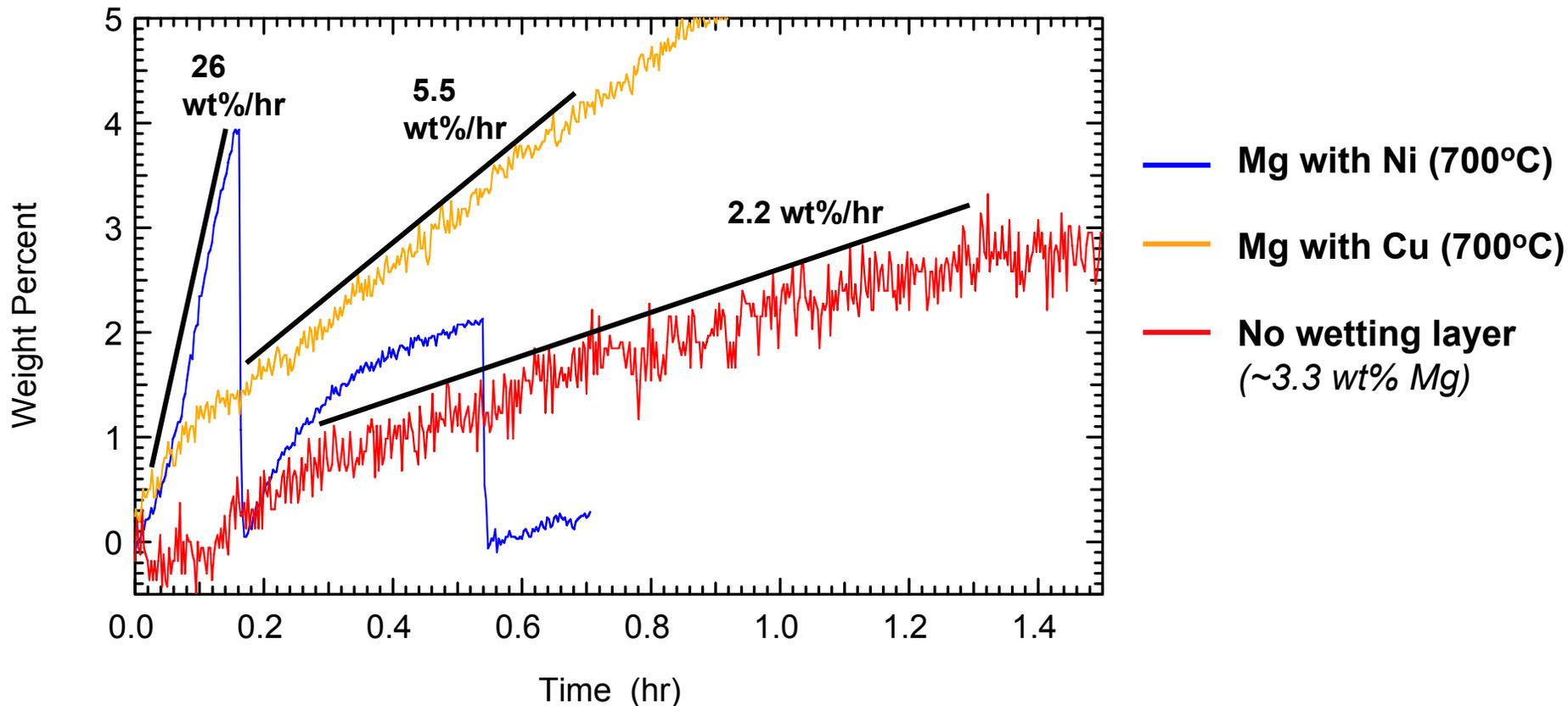
No change in aerogel

- Lower temperature (700 °C vs. 900 °C) reduces aerogel break down
- Cube samples contain bulk Mg impurity



- MgH<sub>2</sub> in aerogel can be fully dehydrogenated ✓
- $P_{eq}$ (250 °C) equal to bulk value, no change in thermodynamics

*Isothermal desorption at 250 °C (~10 wt% Mg@13 nm aerogel)*



- Ni & Cu wetting layers catalyze dehydrogenation
- Rate without wetting layer still higher than (uncatalyzed) milled  $MgH_2$

## 1. Gravimetric and Volumetric Penalties

- **Current 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, then will need:**
  - $\sim 5 \text{ to } 10 \text{ nm}$  pore sizes with  $> 3 \text{ cm}^3/\text{g}$  pore volume

**This is difficult but not impossible** (*requires thinner scaffold walls which will exacerbate mechanical stability issues*)

## 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*)

**Aerogels are a useful research tool for studying nanoscale effects.  
Practical use will require advances in the aerogels themselves**

## New Destabilized Systems

- Further characterize the  $\text{LiBH}_4/\text{Mg}_2\text{Ni}$  reaction
- Explore oxide-based destabilized reactions  
Ex:  $6\text{LiBH}_4 + \text{B}_2\text{O}_3 \rightleftharpoons 3\text{Li}_2\text{O} + 8\text{B} + 12\text{H}_2$  (12.0%)

## Nanoporous Scaffolds

- Continue to work towards incorporating full  $\text{LiBH}_4/\text{MgH}_2$  destabilized system into carbon aerogel
  - Complete work on Mg incorporation (*evaluate U Hawaii samples*)
  - Add  $\text{LiBH}_4$  to selected Mg@aerogel samples (*test full system*)
  - Continue to understand effects of pore size and pore size distribution
  - Optimize aerogel materials for pore size and volume

## New Destabilized Systems

- **Screened new  $\text{LiBH}_4/\text{MgX}$  systems, X = Si and Ni**
  - Observed new Ni based destabilized system with reversible capacity of  $\sim 6.5\%$
  - Observed the formation of ternary borides, pointing to potential new direction of discovery

## Nanoporous Scaffolds

- **Quantified rates for  $\text{LiBH}_4$  dehydrogenation in aerogel:**
  - at  $300^\circ\text{C}$ , rate in aerogel is 60X rate for control sample
- **Incorporated Mg into aerogel at reduced temperature to minimize degradation of aerogel (in progress)**
- **Measured dehydrogenation rates for Mg@aerogel**
  - with Ni wetting layer/catalyst, the rate at  $250^\circ\text{C}$  comparable to best catalyzed bulk samples
- **Began to understand effects of pore size and pore size distribution**
  - smaller pores lower reaction temperatures; hydrogen access is important

# Program Direction

## – By System –

Destabilized System	Benchmark	2007 Status	2007/08 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 25% system penalties)	Lowered LiBH <sub>4</sub> dehydrogenation temp by 70°C in C-scaffold	<ul style="list-style-type: none"> <li>•Reduced capacity penalty to 40%</li> <li>•Measured 10x equilibrium pressure</li> <li>•Incorporated Mg into aerogel</li> <li>•Measured &gt; 150x reaction rate</li> </ul>	<ul style="list-style-type: none"> <li>•Incorporate full destabil. system in scaffold</li> <li>•Optimize scaffold</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)	Reversible capacity of ~6.5% at 350°C Slight degradation observed		Candidate for incorporation into scaffold
<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)	Hydrogen uptake ~6.5% at 300-350°C Dehydrogenation 5.3% Not fully reversible		Candidate for incorporation into scaffold
<b>LiBH<sub>4</sub> / MgS</b> 8.0 wt%, est. T <sub>1 bar</sub> =170°C	Could meet 2010 system capacity goal (but only small system penalty)	Hydrogen uptake ~6% at 300°C Dehydrogenation 4.3% Not fully reversible		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=CO <sub>3</sub> No destabilization	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>