

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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– A Participant in the DOE Metal Hydride Center of Excellence –

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Project ID #
ST18

Timeline

- Project start date: March 2005
 - Project end date*: Feb 2010
 - Percent complete*: 45%
- * Assumes support for Phases 1 and 2

Budget

• Total Project Funding:

<i>Phase One - 3 years:</i>	<i>\$1.65M</i>
– DOE Share:	\$1.20M
– Contractor Share:	\$0.45M
<i>Phase Two - 2 years:</i>	<i>\$1.1M</i>
– DOE Share:	\$0.8M
– Contractor Share:	\$0.3M

• Funding for FY07:

\$117K as of 4/10/07 (DOE),
\$150K (cost share)

Technical System Targets

	2007	2010
Gravimetric capacity:	4.5%	6%
Volumetric capacity:	0.036 kg/L	0.045 kg/L
Min/Max delivery temp:	-30/85°C	-40/85°C

Technical Barriers

- System weight and cost
- Large binding energies and slow H₂ sorption kinetics in light metal hydrides

Partners

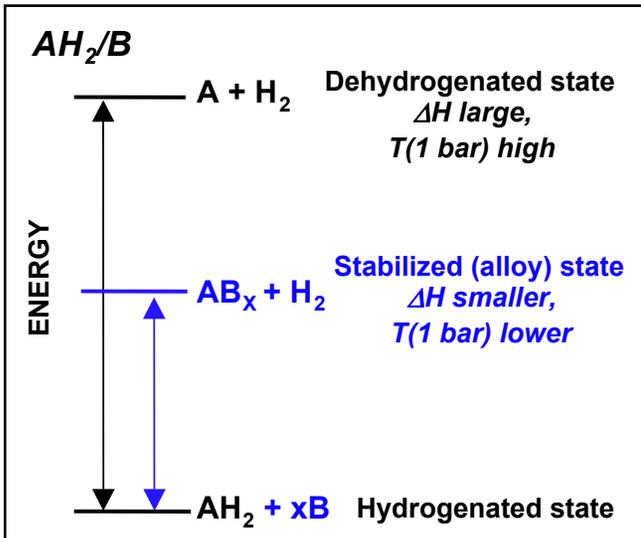
- Participant in DOE MHCoe
 - U. Pitt, CMU: modeling of new systems and kinetic barriers
 - Stanford: thin film systems
 - Caltech, JPL, U. Utah, Hawaii: scaffolds
 - Intematix: catalysis

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

2006/2007

- **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
- **To apply nano-engineering methods to address kinetics limitations**
 - Determine hydrogen exchange rates in nanoscale MgH_2/Si
 - Evaluate sorption kinetics and thermodynamics of LiBH_4 and Mg in carbon aerogel scaffolds
 - Assess capacity penalty for hydrides in scaffolds (can they be practical?)



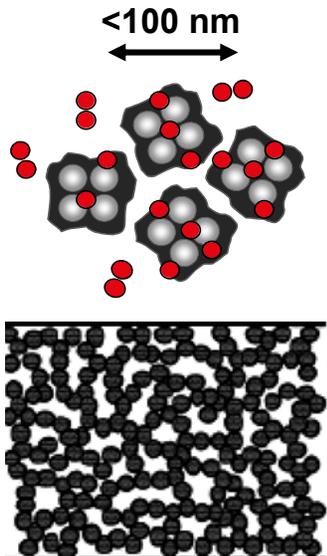
Hydride Destabilization

(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

- **Potential systems include: X = F, Cl, OH, O, S, Se, CO₃, Si, SO₄, Cu, Ge, & Ni**
 - 12 destabilization reactions identified and characterized using HSC modeling
 - H-capacities ranging from 5.4-9.6 wt.%, $T_{1 \text{ bar}}$ from -10°C to 430 °C
 - X = F, S, Se, CO₃ tested previously

- **In FY06/07, two new systems tested, X = Cl and Cu:**
 - $2\text{LiBH}_4 + \text{MgCl}_2 \leftrightarrow 2\text{LiCl} + \text{MgB}_2 + 4\text{H}_2$ (5.8 wt.%, $T_{1 \text{ bar}} = -10 \text{ °C}$)
No H₂ uptake from 2LiCl + MgB₂ at 150 bar, up to 250°C ($T_{1 \text{ bar}}$ too low)
 - $4\text{LiBH}_4 + \text{Mg}_2\text{Cu} \leftrightarrow 4\text{LiH} + 2\text{MgB}_2 + \text{Cu} + 6\text{H}_2$ (6.0 wt.%)
From 4LiBH₄ + Mg₂Cu, only trace MgB₂ formed (4LiBH₄ + Mg₂Cu did not react with each other)

- **Neither system is a good candidate for further work**
- **Results show kinetic limitations in destabilized systems**

- **Motivation: prototype system for nanoengineering, nearly ideal thermodynamics ($T_{1\text{bar}} \sim 50\text{ }^{\circ}\text{C}$)**
 - **Summary of effort to demonstrate reversibility**
 - **Catalysis** (tested bulk metals, nanoparticle metals, and oxides for effect on dehydrogenation and hydrogenation). All improved dehydrogenation (nano-Ni best).
No hydrogenation observed.
 - **Mechanical dispersion** (MgH₂ milled with excess Si to create dispersed nano-MgH₂). Onset of dehydrogenation decreased by up to 100°C.
No hydrogenation observed.
 - **Mg₂Si nanoparticles** (tested samples of nano-Mg₂Si formed using nano-Si precursors, self-propagating reactions, and chemical vapor synthesis (CVS)).
No hydrogenation observed.
 - **Mechano-chemistry** (milled Mg₂Si formed by powder metallurgy and mechanical synthesis in 50 bar of hydrogen, varied milling conditions and included catalysts).
No hydrogenation observed.
 - **Phase separation or passivation by hydrogen* prevents hydrogenation**
- * suggestion by Prof. Gabor Somorjai, (MHCoe/Berkeley Hydrogen Storage meeting 3/13/07)*

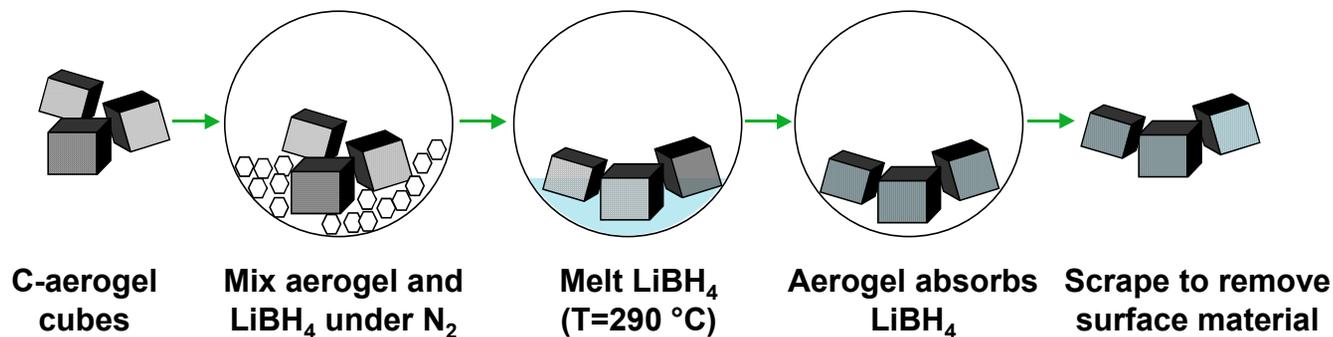
“No-Go” for continued work on MgH₂/Si system

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

- Initial work on LiBH_4 incorporated into carbon aerogels

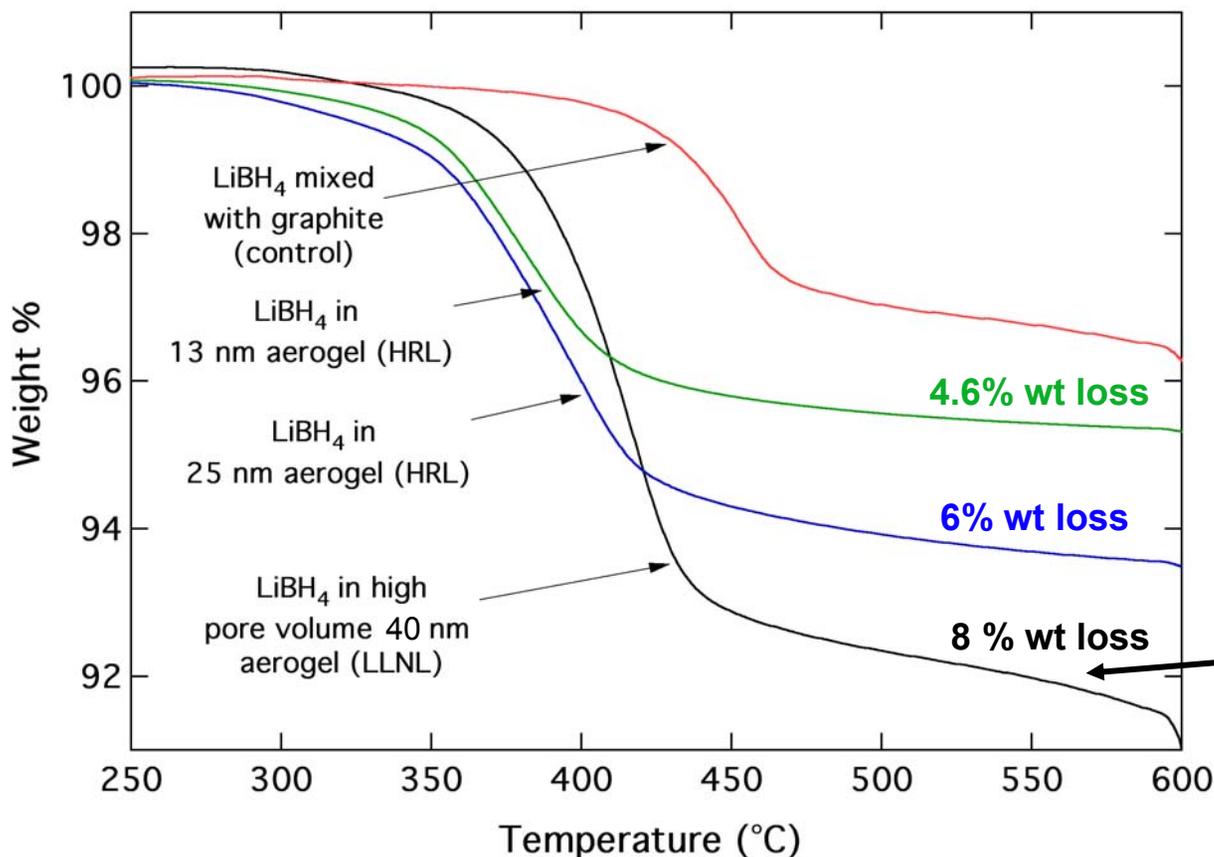
- Prototype complex hydride
- Slow kinetics
- Poor reversibility
- Synthesis (resorcinol/formaldehyde condensation)
- Pore sizes (5-25 nm) and volumes (1- 4 cm^3/g)
- Relatively chemically inert

- Aerogels filled with LiBH_4 ($\text{LiBH}_4@$ aerogel) by infiltration from melt:



80-90% of pore space filled with LiBH_4

TGA (10°C/min) for H₂ desorption: LiBH₄ → LiH + B + 1.5H₂ (13.6 wt %)



Capacity penalties for LiBH₄ in aerogel

13 nm (0.8 cm³/g) : 66%
 25 nm (1.3 cm³/g) : 56%
 40 nm (2.7 cm³/g)* : 40%
 Goal (>4 cm³/g) : < 25%

*provided by Ted Baumann, LLNL

**New data
 LLNL aerogel
 8 wt %
 0.072 kg/L H₂**

- Aerogel lowers dehydrogenation temperatures up to 70°C
- Capacity penalty reduced to 40% with high pore volume aerogel

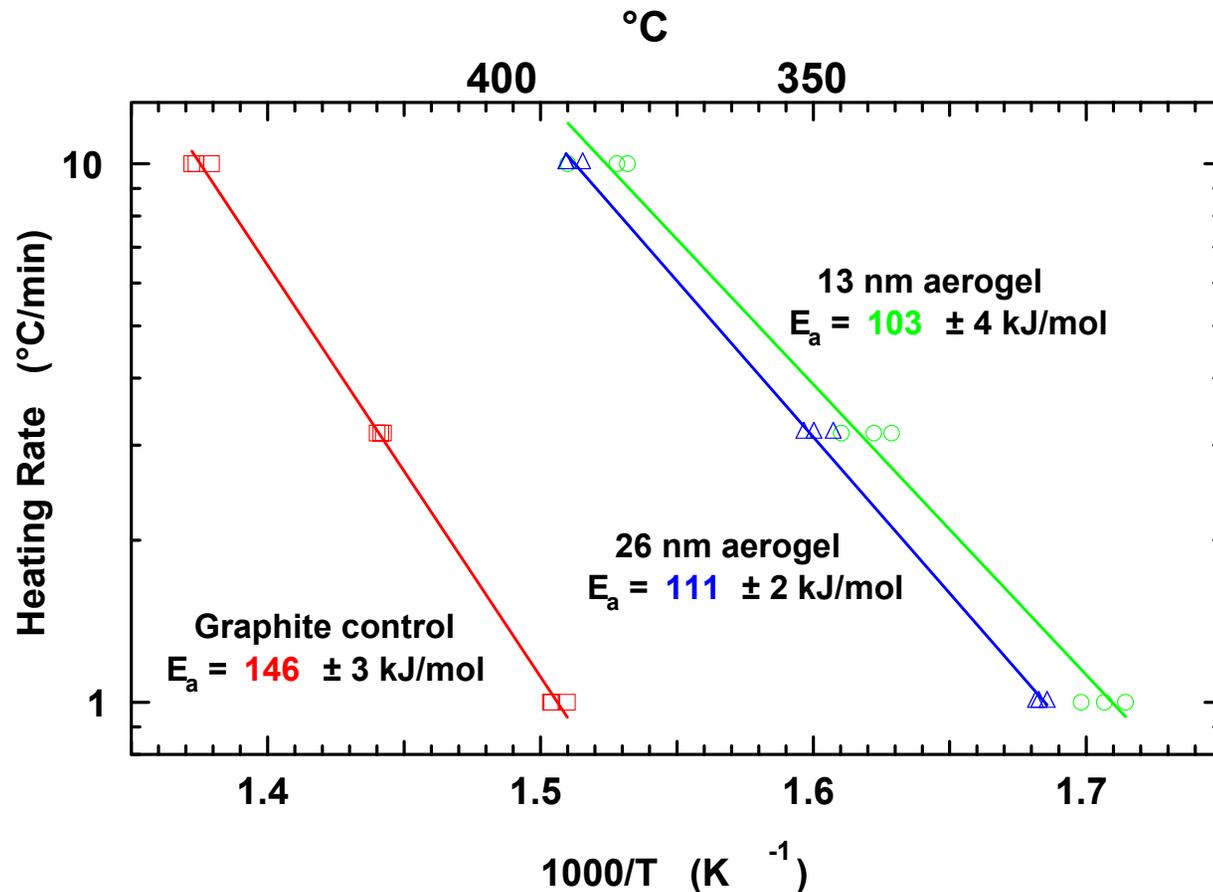
METHOD

Determine activation energy for dehydrogenation using Ozawa analysis:^{*}

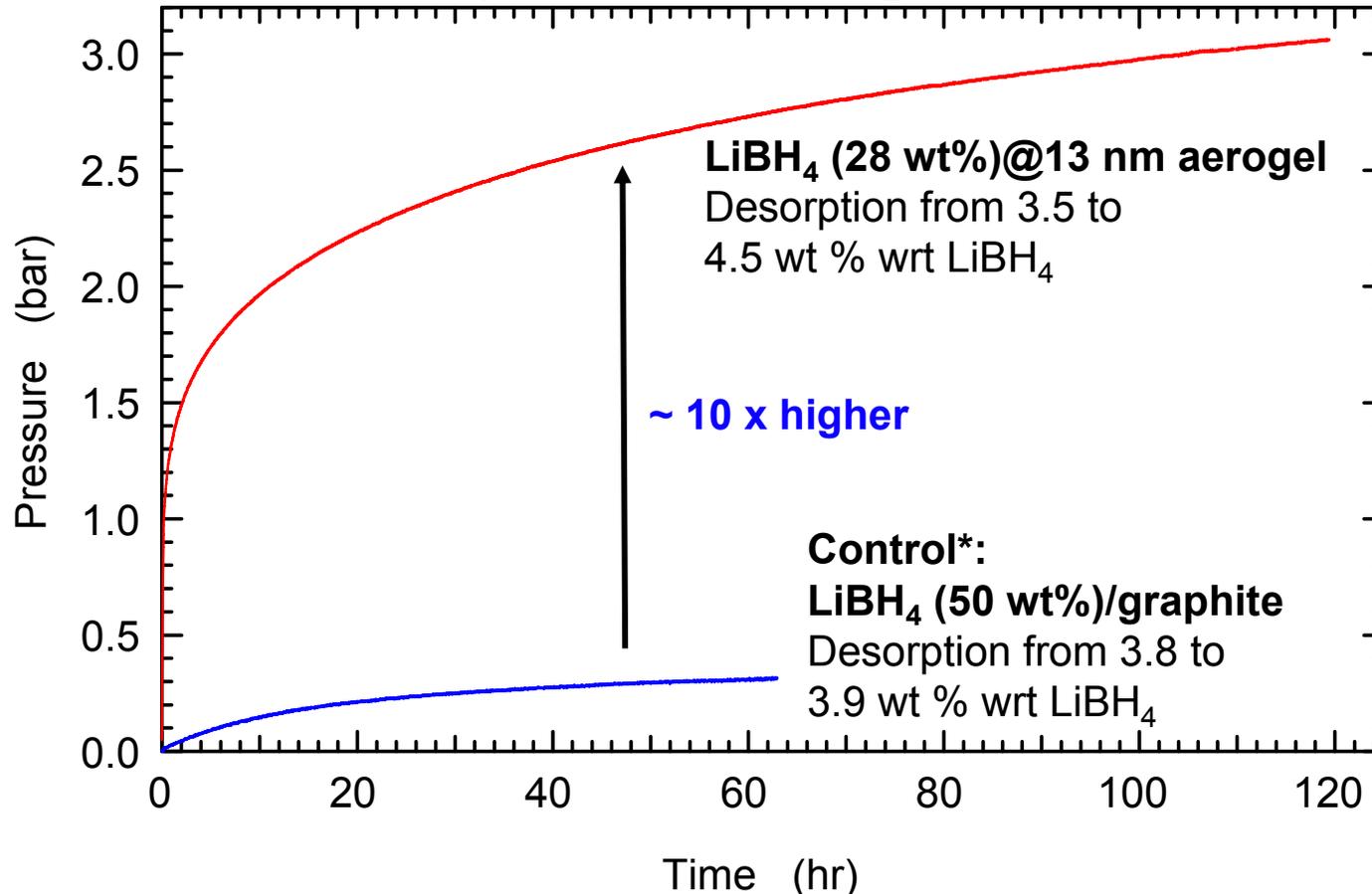
Heat samples at multiple ramp rates (b); measure transition temp (T). Fit data to:

$$\ln(b) = -E_a/(RT) + \text{constant}$$

^{*} Ozawa, T. *Bull. Chem. Soc. Jpn.* **38**, 1881 (1965).



- Activation energy for dehydrogenation is reduced in aerogel
- Reaction rate (Boltzmann factor) increases by ~ 1000x at 350 °C

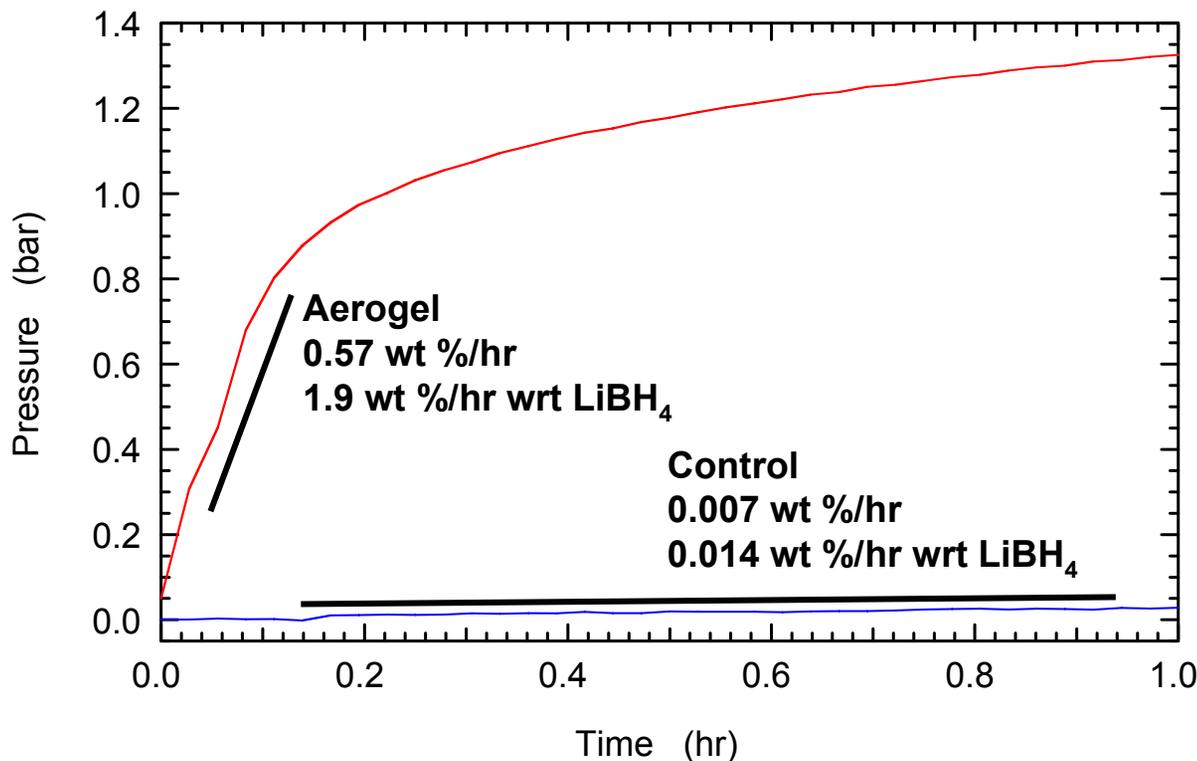


- Desorption rate accelerates if H₂ overpressure is removed
- Result suggests that the final pressures do represent equilibrium

* Could not obtain good data for neat LiBH₄

**Aerogel increases the equilibrium pressure of LiBH₄ by 10 times
(at ~ 4 wt % desorbed)**

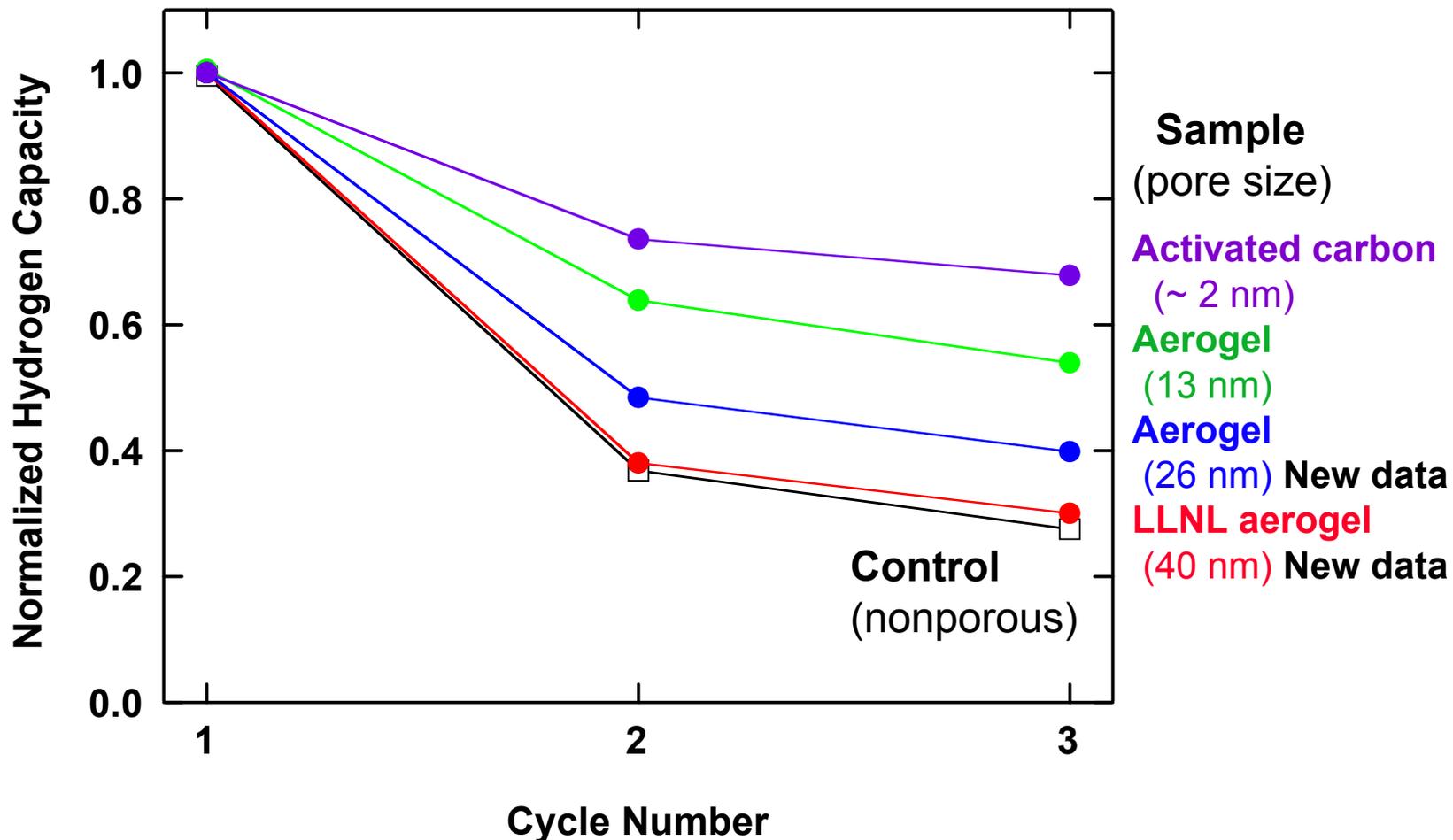
Initial portion (1 hr) of equilibrium curves



- After ~ 0.1 hr the desorption rate for the aerogel slows significantly due to the H₂ pressure
- Ratio of the initial desorption rates is 150
- Rate for control sample increases with dilution by graphite
- Initial desorption rate for aerogel sample may still be influenced by hydrogen pressure

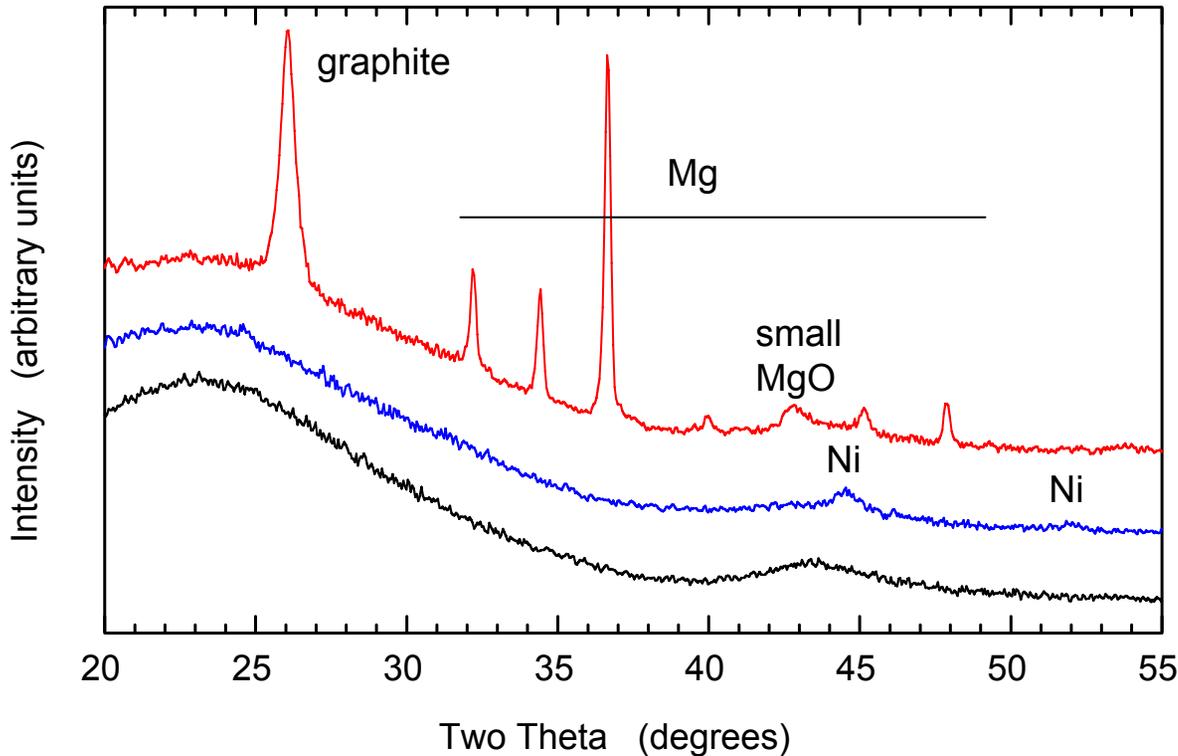
Incorporation of LiBH₄ into the aerogel significantly increases the dehydrogenation rate

Capacity from dehydrogenation (400 °C, 2 hr) after hydrogenation (100 bar H_2 , 400°C, 2 hr)



- Decreased pore size improves cycling
- Pore size of 40 nm shows bulk behavior

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



Oxidation in TGA indicates **Ni + Mg** sample contains 1.5 wt% Ni and 16 wt% Mg

Ni + Mg (900 °C, 60 hr)

Ni(NO₃)₂ (4% H₂, 500 °C, 6 hr)

No Ni, Mg (900 °C, 60 hr)

- Nickel “wetting layer” enables incorporation of Mg from melt
- Hydrogenation/dehydrogenation measurements in progress
- Significant step toward incorporating LiBH₄/MgH₂ in scaffold

New Destabilized Systems

- **Screened new LiBH_4/MgX systems, X = Cl and Cu** – Destabilization reactions not observed in these systems

Nanoparticles / $\text{MgH}_2\text{-Si}$

- **Reversibility (hydrogenation of Mg_2Si) not achieved** – tried catalysts, nanoparticles by direct synthesis and mechanical dispersion, and mechanically-induced hydrogenation
- **Made “No-Go” decision, Sept. 2006**

Nanoporous Scaffolds

- **Evaluated large pore volume carbon aerogel** – reduced capacity penalty for LiBH_4 to 40% (goal is 25%)
- **Measured equilibrium pressure of LiBH_4 in aerogel** – ~10x increase at 300°C
- **Compared rates of desorption**– aerogel potentially ~150x faster at 300°C
- **Incorporated Mg into carbon aerogel** – Ni used as wetting layer

New Destabilized Systems

- Explore additional $\text{LiBH}_4 + \text{MgX}$ reactions; determine influence of X on kinetics

Nanoporous Scaffolds

- Incorporate $\text{LiBH}_4/\text{MgH}_2$ destabilized system into carbon aerogel
 - Measure intrinsic dehydrogenation rates of $\text{LiBH}_4@\text{C}$ aerogel, i.e., at $P_{\text{H}_2} \rightarrow 0$
 - Test hydrogenation/dehydrogenation behavior of $\text{Mg}@\text{C}$ aerogel; Check U. Utrecht claims
 - Add LiBH_4 to $\text{Mg}@\text{C}$
 - Incorporate catalysts
 - Optimize aerogel materials (with T. Baumann, LLNL), processing, and catalysts (with Utah, Hawaii, and Intematix)

Destabilized System	Benchmark	2006 Status	2006/07 Progress	Future
MgH₂/Si 5.0 wt.%, 0.083 kg/L est. T _{1 bar} =30°C	<i>Prototype system</i> <2007 goal (including system penalty)	<ul style="list-style-type: none"> •Kinetics too slow •T (dehyd) >200°C •Hydrogenation not achieved 	<ul style="list-style-type: none"> •Reversibility still not observed •No-go decision Sept '06 	
LiBH₄ / MgH₂ @C aerogel 11.4 wt.%, 0.095 kg/L w/o aerogel, est. T _{1 bar} =170°C	Could meet 2010 system cap. goal (assuming 25% aerogel and 25% system penalties)	Lowered LiBH ₄ dehydrogenation temp by 70°C in C-scaffold	<ul style="list-style-type: none"> •Reduced capacity penalty to 40% •Measured 10x equilibrium pressure •Incorporated Mg into aerogel •Measured > 150x reaction rate 	<ul style="list-style-type: none"> •Incorporate full destabil. system in scaffold •Optimize scaffold
LiBH₄ / MgF₂ 7.6 wt%, est. T _{1 bar} =150°C	Could meet 2010 system cap. goal	Hydrogen uptake ~6.5% at 300-350°C Dehydrogenation 5.3% Not fully reversible		Candidate for incorporation into scaffold
LiBH₄ / MgS 8.0 wt%, est. T _{1 bar} =170°C	Could meet 2010 system cap. goal	Hydrogen uptake ~6% at 300°C Dehydrogenation 4.3% Not fully reversible		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=CO ₃ No destabilization	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