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 # ST16

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: March 2005
- Project end date*: Feb 2010
- Percent complete*: 25%

** Assume support for Phases 1 and 2*

Budget

- **Total Project Funding:**

  Phase One - 3 years: *$1.65M*
  - DOE Share: $1.20M
  - Contractor Share: $0.45M

  Phase Two - 2 years: *$1.1M*
  - DOE Share: $0.8M
  - Contractor Share: $0.3M

- **Funding for FY06:**

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

Technical 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 H_2 sorption kinetics in light metal hydrides

Partners

- Participant in DOE MHCoE – collaborations with partners on synthesis, modeling, and advanced characterization
- Coordinator of MHCoE sub-team on destabilized hydrides – sub-team comprises 10 organizations in MHCoE

Objectives

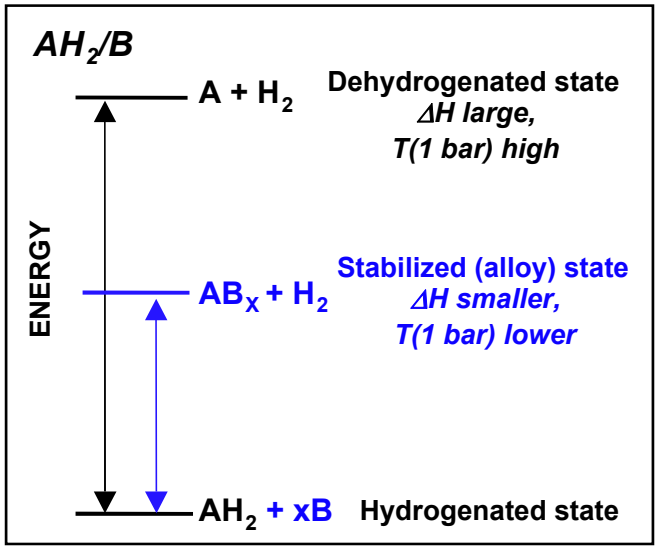
Overall

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

2005/2006

- **To identify and test new high capacity Li- and Mg-based destabilized hydrides**
  - Screen candidate $LiBH_4$ + MgX destabilized systems and evaluate energetics and kinetics
  - Down-select systems for additional work
- **To apply nano-engineering methods to address kinetics limitations**
  - Develop solid state approaches for efficient synthesis of nanoscale reactants
  - Assess hydrogen exchange rates in nanoscale MgH_2/Si and destabilized complex hydrides
  - Evaluate sorption kinetics of reversible metal hydrides in nanoporous scaffold hosts

Approach:
– *Hydride Destabilization and Nano-engineering* –



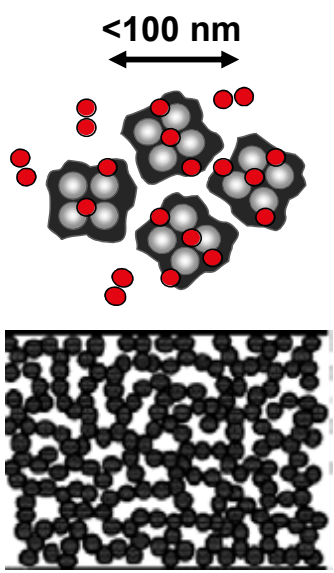
Hydride Destabilization

(addresses thermodynamics challenge)

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 $T_{1\ bar}$



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

Nano-engineering

(addresses kinetics challenge)

Decrease diffusion distances, nanoporous scaffolding

- Short H diffusion distance in nanoparticles: *fast exchange*
- More efficient catalysis pathways
- Nanoparticles, encapsulated as needed to mitigate sintering
- Nano-scaffolds as hosts for nanostructured hydrides:
  ⇒ *structure- directing agents, mitigate particle agglomeration*

Enhanced reaction rate and improved cycling

New Destabilized Systems
– $LiBH_4$ + MgX –

- **Potential systems include: X = F, Cl, OH, O, S, Se, CO_3, Si, SO_4, Cu, Ge, & Ni**
  - 12 destabilization reactions identified and characterized using HSC modeling
  - H-capacities ranging from 5.4-9.6 wt.%, $T_{1\ bar}$ from -10°C to 430°C
- **Partial reversibility demonstrated in three systems:**
  - $2LiBH_4 + MgF_2 \leftrightarrow 2LiF + MgB_2 + 4H_2$ (7.6 wt.%, $T_{1\ bar}$ =150°C)

    H_2 uptake ~6.5% at 300-350°C; dehydrogenation 5.3%
  - $2LiBH_4 + MgS \leftrightarrow Li_2S + MgB_2 + 4H_2$ (8.0 wt.%, $T_{1\ bar}$ =170°C))

    H_2 uptake ~6% at 350°C; dehydrogenation ~4.3%; 2nd cycle uptake <4%
  - $2LiBH_4 + MgSe \leftrightarrow Li_2Se + MgB_2 + 4H_2$ (5.4 wt.%, $T_{1\ bar}$ =70°C)

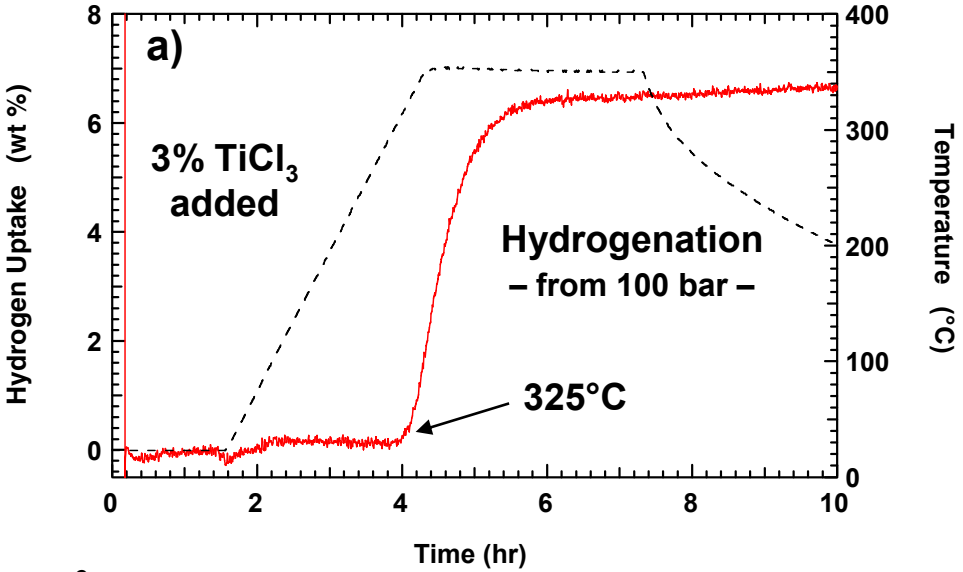
    H_2 uptake ~4.5% at 350°C; dehydrogenation ~3.3%

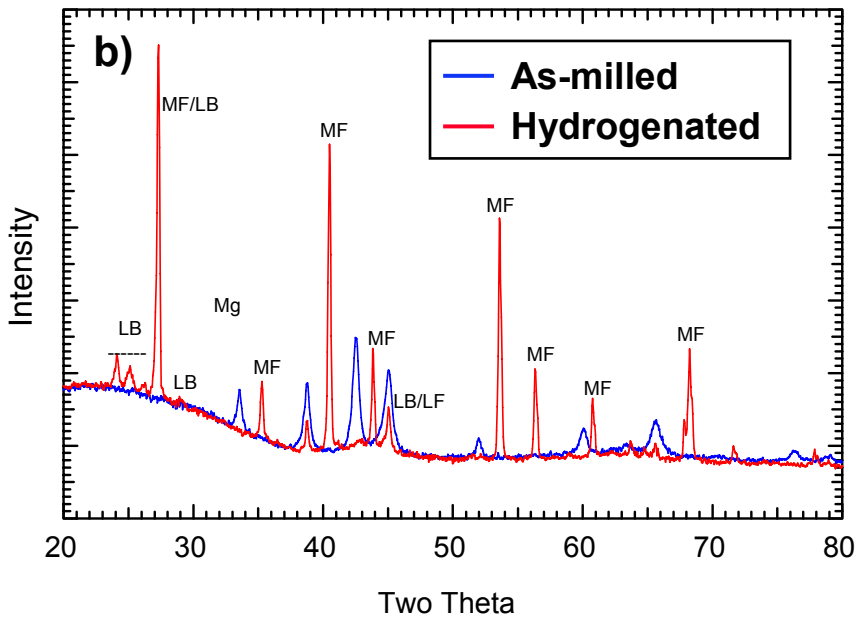
- ***Results show that destabilization is a promising approach for overcoming thermodynamics limitations in light-metal systems***
- ***However, exptl temps >> equil temps ⇒ all systems kinetically limited***

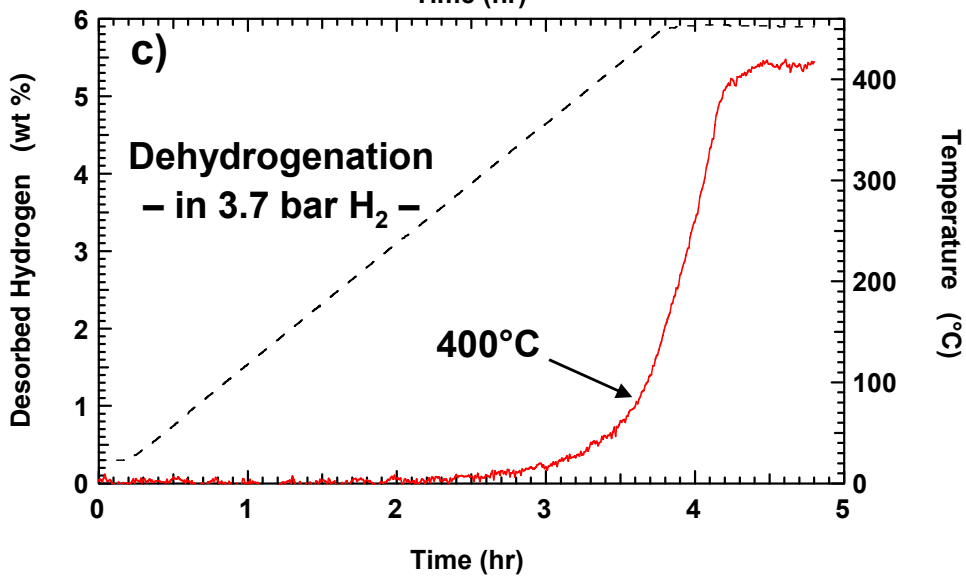
New Destabilized System

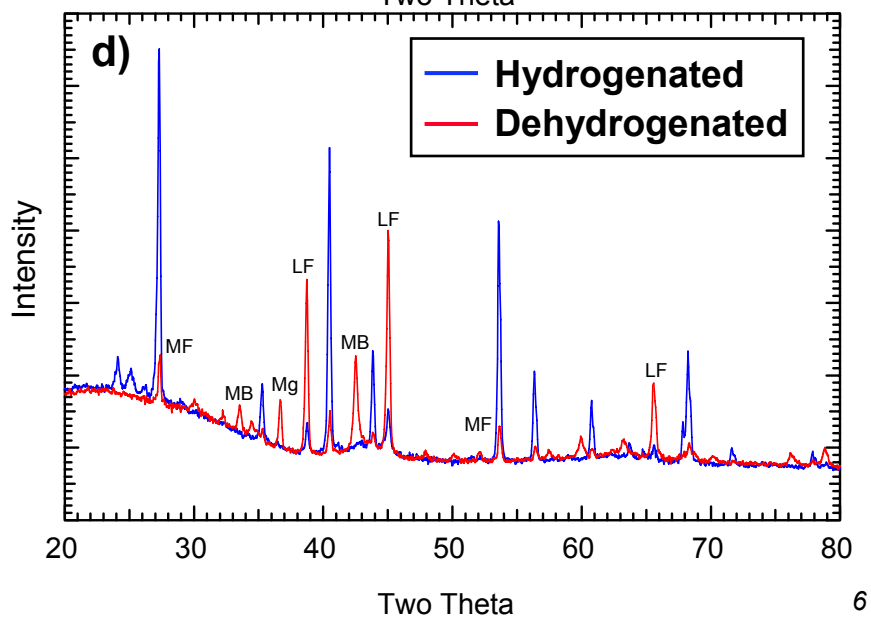
$2LiBH_4 + MgF_2 \leftrightarrow 2LiF + MgB_2 + 4H_2$ (7.6%)

Starting point: LiF + MgB_2

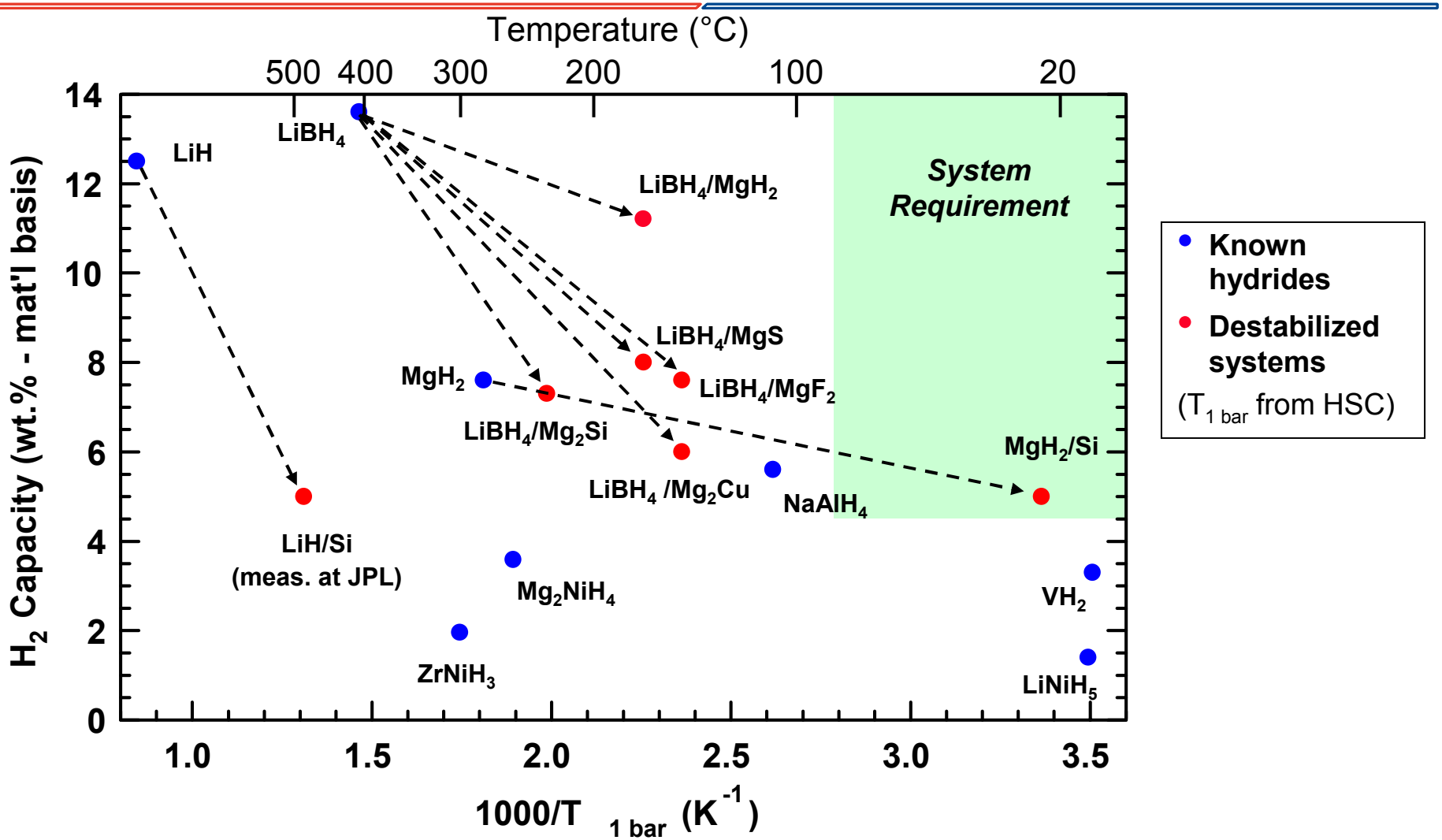








Summary of Destabilized Systems



- ***Destabilization provides pathway to reaching system targets***
- ***Kinetics issues dominate as temperatures are reduced***

MgH_2/Si

– *Enhancing Kinetics and Reversibility* –

$$2MgH_2 + 1/2Si \rightarrow Mg_2Si + 2H_2$$

- **Destabilized system ⇒ 5 wt.%, 0.083 kg/L; $T_{1\ bar} \approx 30°C$**
- **However, slow kinetics; reversibility not demonstrated**

Approaches in 2005/06 to overcome slow kinetics:

$$2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$$

Synthesis

- **Nanoparticle reactions**
- **Powder metallurgy synthesis**
- **Self-propagating reactions**
- **Synthesis in Sieverts (vacuum)**

Processing

- **Dilution milling**
- **Milling in H_2 overpressure**
- **nano-catalysts**

⇒

Characterization

H_2 desorption and hydrogenation rates
(TGA, Sieverts)

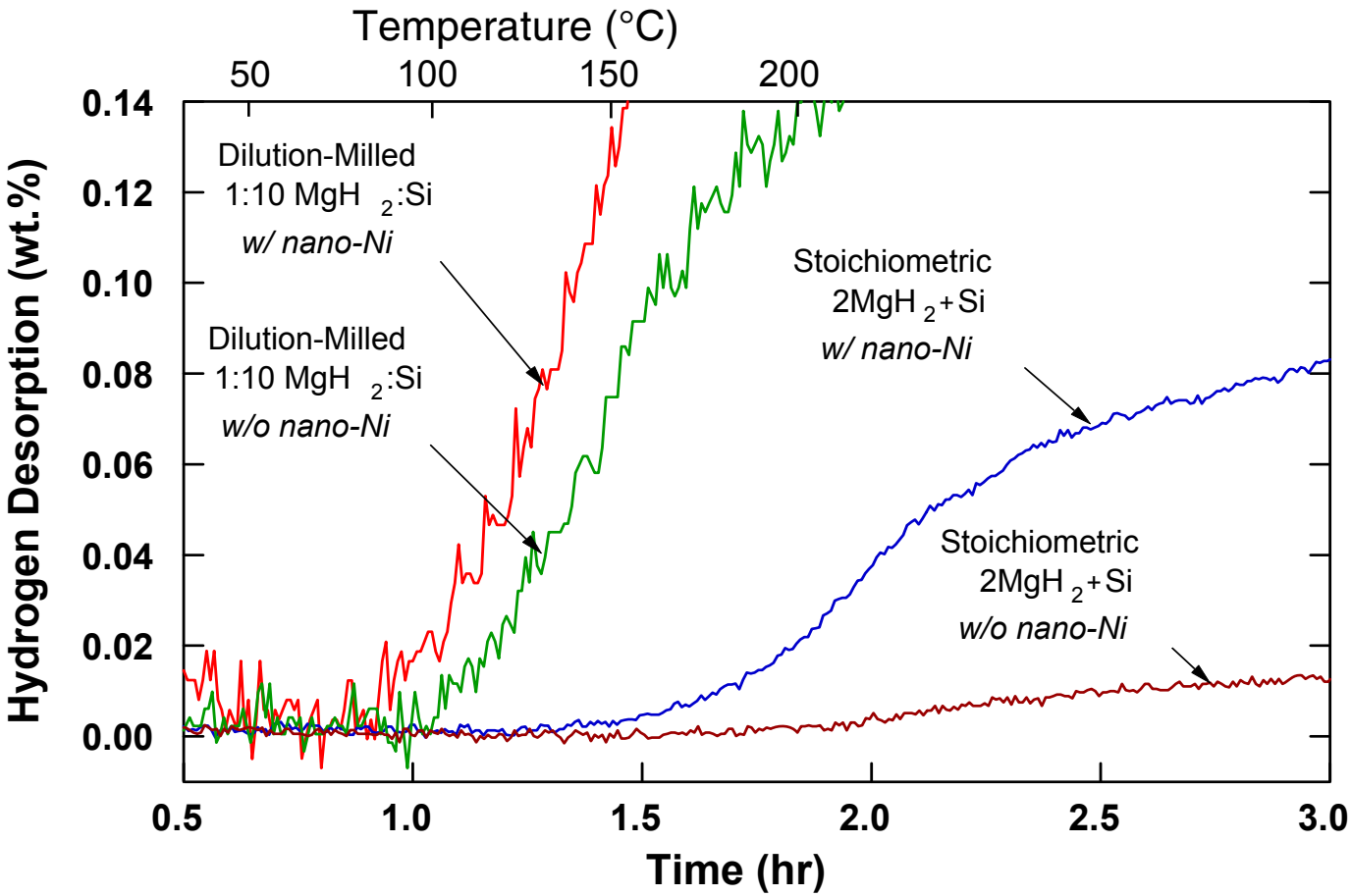
Structure and composition
(XRD, NMR, TEM)

Additional collaborations with MHCoE partners on modeling, synthesis, catalysis and characterization

Dilution Milling and Nano-Ni Catalyst

– *Effect on H_2 Desorption in MgH_2/Si* –

$$2MgH_2 + 1/2Si \rightarrow Mg_2Si + 2H_2$$



Onset temp. for H_2 desorption

(1:10 is MgH_2:Si ratio during ball-milling)

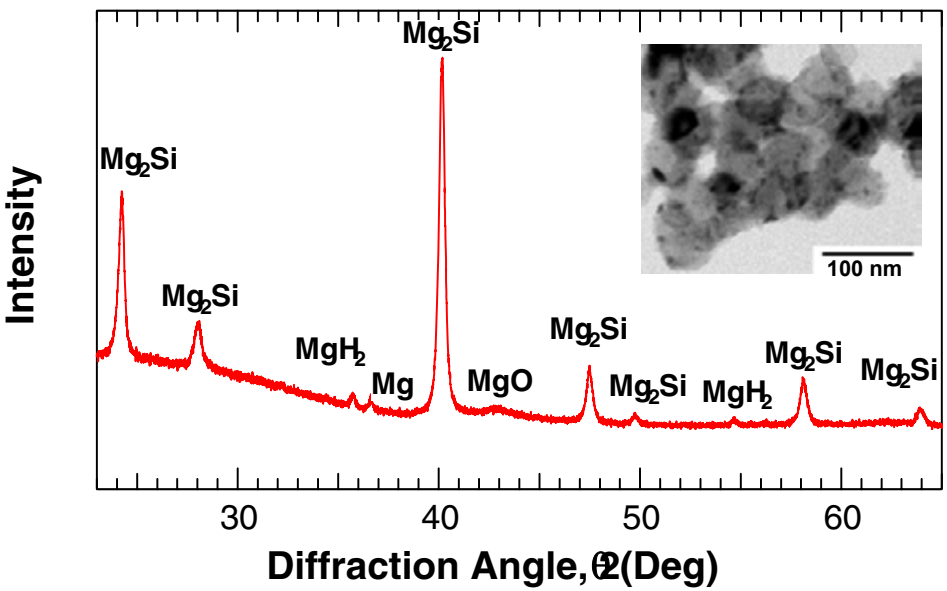
1:10 w/ Ni	**85°C**
1:10 w/o Ni	**100°C**
Stoich. w/ Ni	**140°C**
Stoich. w/o Ni	**200°C**

- ***Dehydrogenation rate improved by dilution milling and nano-Ni catalyst***
- ***Dilution milling demonstrates utility of nanoparticles for improving kinetics***

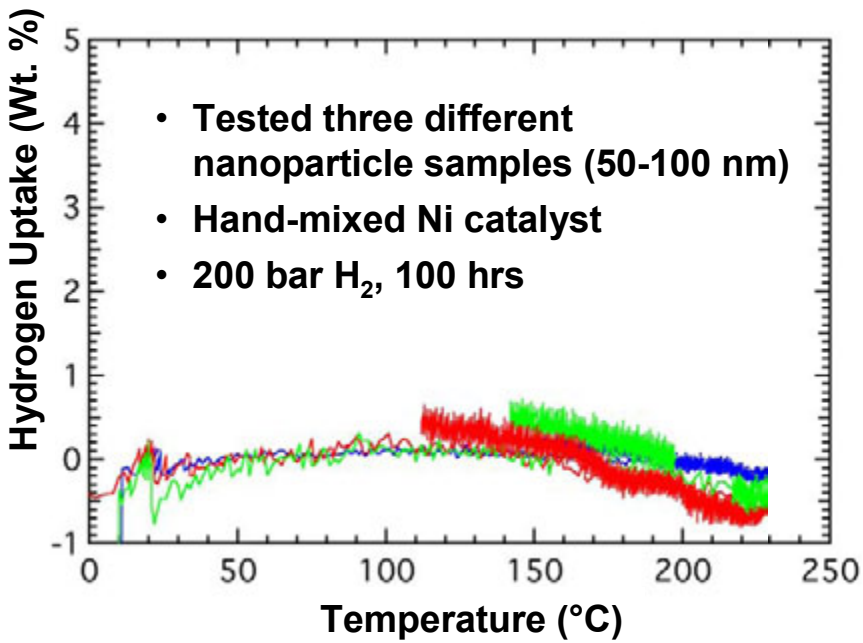
Mg_2Si Nanoparticle Synthesis and Testing
– *Solid State Reaction from Si Nanoparticles* –

$$Si(nano) + 2Mg \Rightarrow Mg_2Si(nano)$$

- Use nano-Si to define nanoscale morphology
- Use different reactive Mg sources to retain nanoscale morphology



Mg_2Si formation evident from XRD; particle size confirmed by TEM

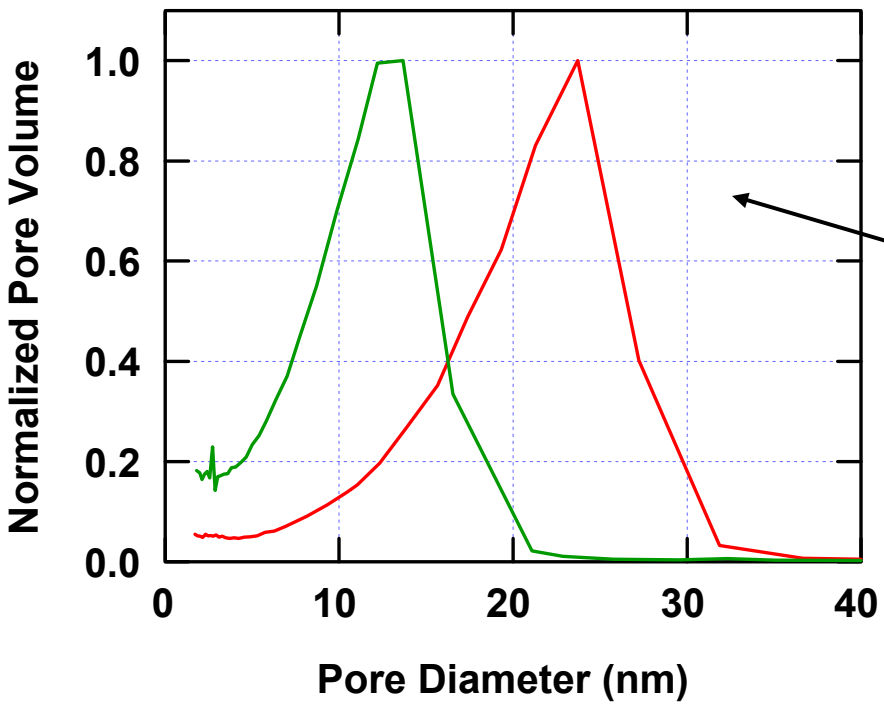


No hydrogenation observed

Successful hydrogenation may require smaller particles (<50 nm), reduced surface oxide, better catalyst incorporation

Reversible Hydrides in Porous Scaffolds

- **Porous scaffolds are effective structure-directing agents for forming nano-structured hydrides**
- **Improve kinetics* by limiting particle size and reducing diffusion distances**
- ***This work:*** **explore effect of C-aerogel scaffolds on sorption properties of reversible hydrides*** $\Rightarrow$ ***Initial studies using $LiBH_4$*** *(basis for destabilized systems)*

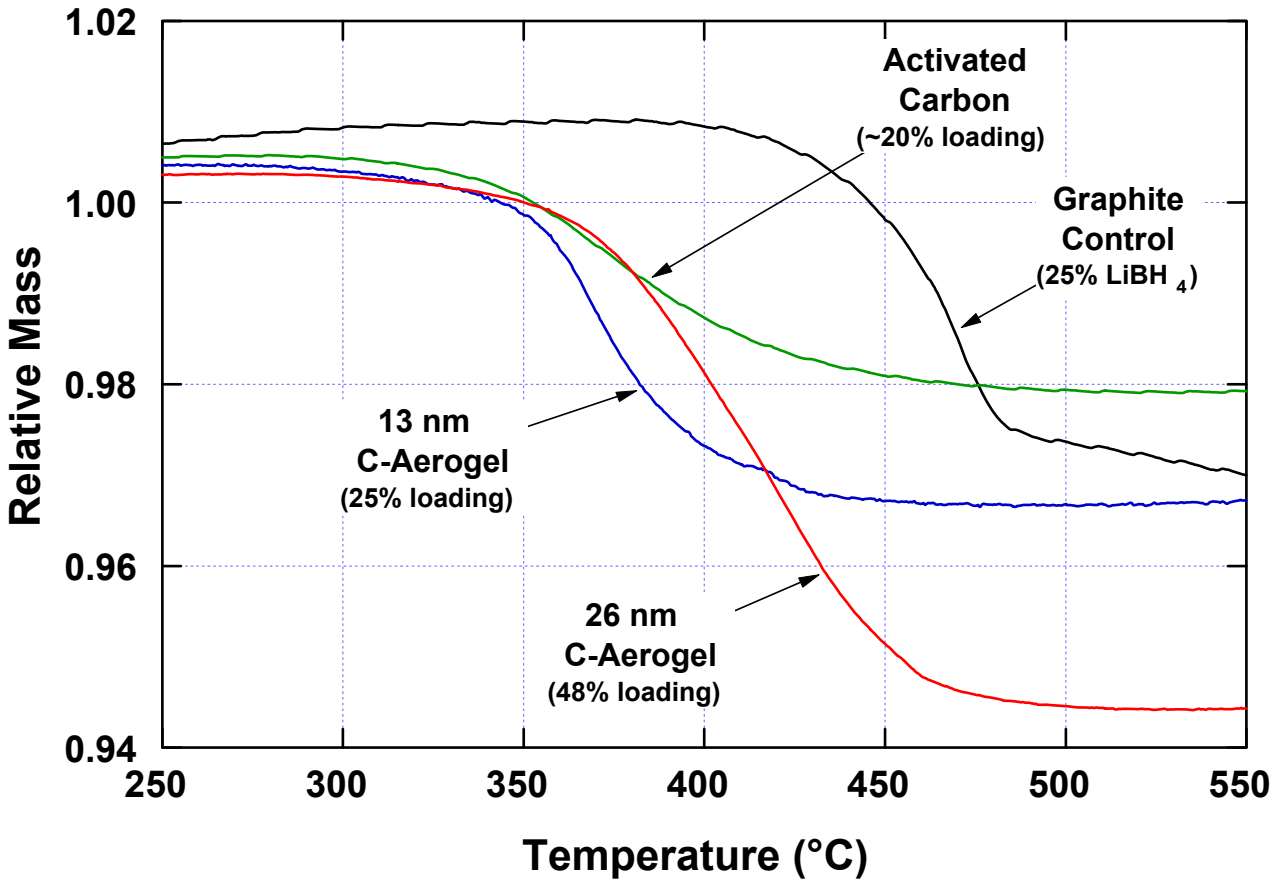


- $LiBH_4$ ($\rightarrow$ LiH + B + 1.5H_2) has high capacity (13.6 wt.%), but slow kinetics, and poor reversibility
- C-aerogels: 10 to 30 nm pores, 0.80 to 1.38 cm^3/g pore volume
- $LiBH_4$ incorporated from melt (25 to 50 wt.% loadings) into aerogel cubes (scraped to remove external material)
- Also investigated activated-C (<2 nm pores) and graphite (non-porous control)

*** Demonstrated for NH_3BH_3 in silica by Gutowska *et al.* (*Angew. Chem. Int. Ed.* 2005, *44,* 3578)**

Incorporation in Scaffold Reduces Dehydrogenation Temperature

TGA (10°C/min) for H_2 desorption: $LiBH_4 \rightarrow LiH + B + 1.5H_2$



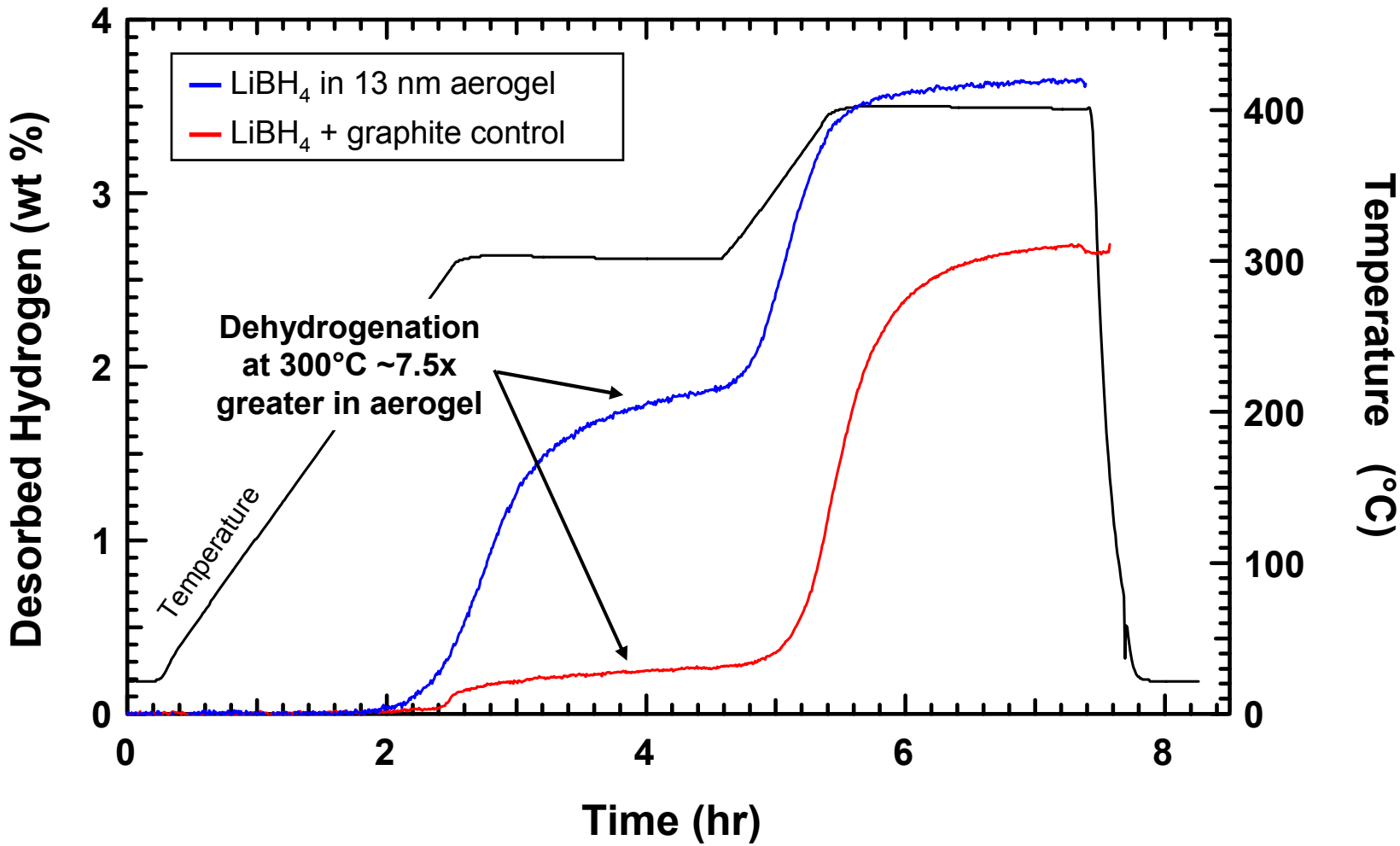
Capacity penalty using scaffolds
(depends on pore volume and densities)

Gravimetric: ≥ 25%

Volumetric: ≥ 13%

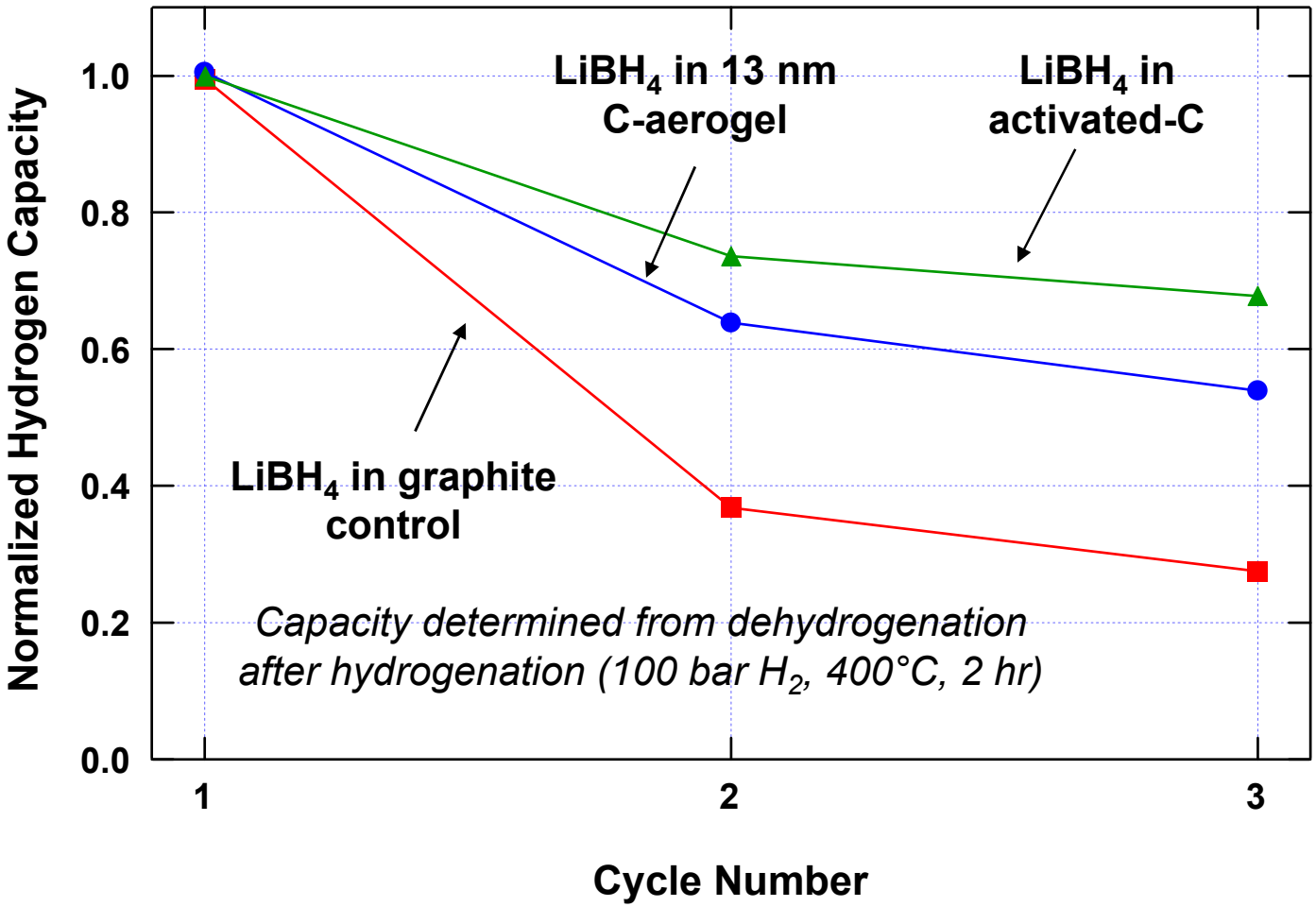
- ***Faster kinetics in scaffolds – lowers reaction temperature up to 100°C***
- ***Dehydrogenation temperature depends on pore size***

Enhanced Dehydrogenation Rate in in $LiBH_4$/C-aerogel



- ***Nanoporous scaffold significantly improves dehydrogenation rate***
- ***Increased pore volume will result in higher capacity***

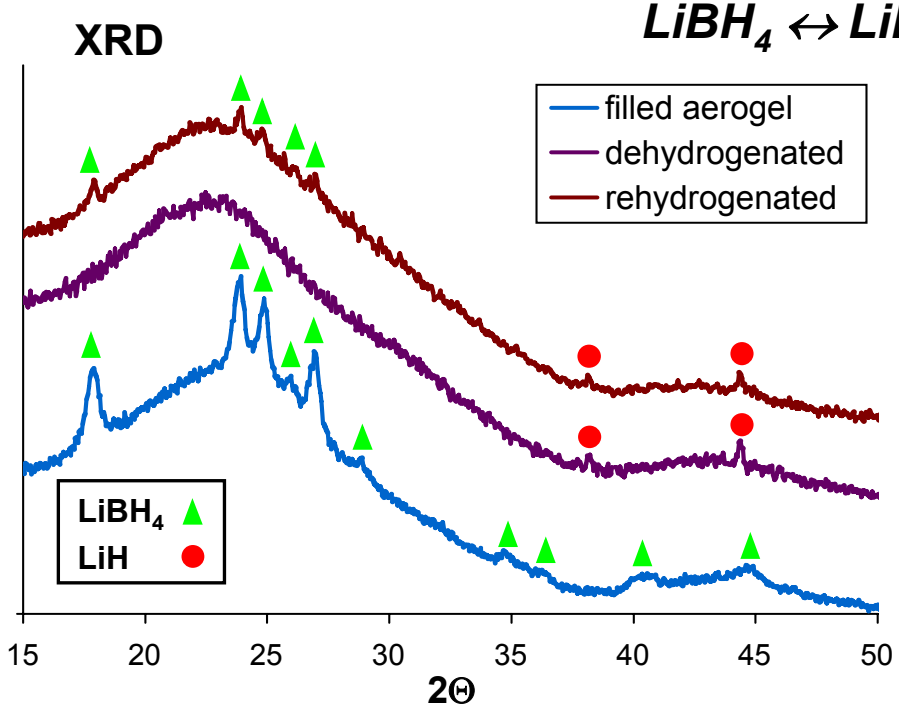
Confinement of $LiBH_4$ in Nanoporous Host Improves Cycling

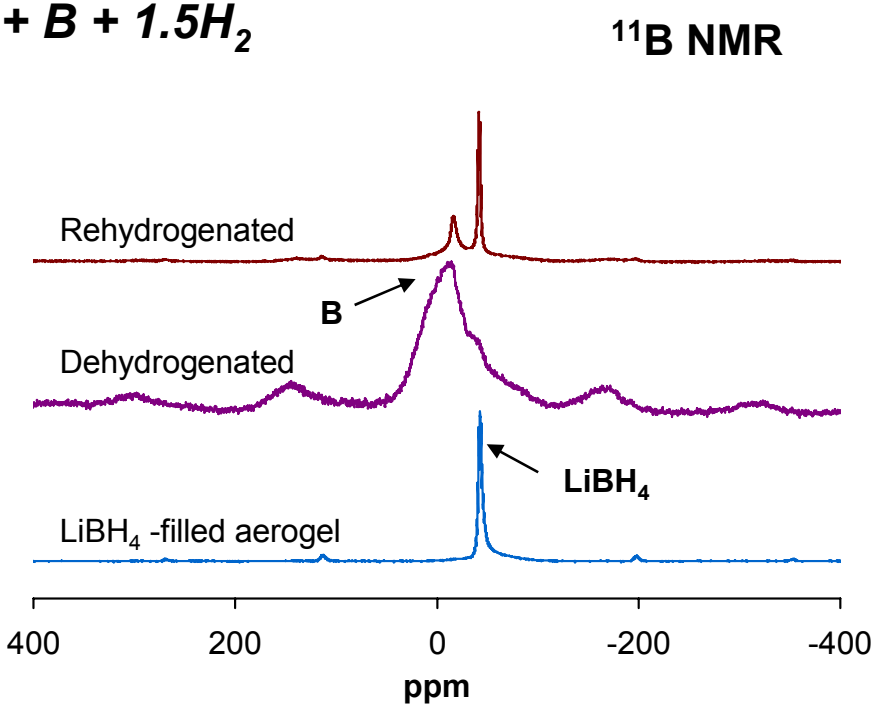


- ***Enhanced cycling capacity in nanoporous scaffolds***
- ***Diminished capacity with increased cycling***

Diminished Cycling Capacity Due to Non-reactive LiH and B in Aerogel

$$LiBH_4 \leftrightarrow LiH + B + 1.5H_2$$





- Only LiH in dehydrogenated sample
- Both LiH and $LiBH_4$ after rehydrogenation
- Peak broadening at high angles – strain?

- Not all LiH and B transforms back to $LiBH_4$
- No apparent interaction with scaffold
- Pore size may affect max. size of LiH and B

- ***Non-reactive B and LiH identified by XRD and NMR***
- ***Partial reversibility of $LiBH_4$ in aerogel - corroborates volumetric data***

Summary

– *FY 2005/06* –

New Destabilized Systems

- **Destabilization shown to be a practical method for overcoming thermo. limitations**
- **Reversibility measured in several new systems:** $LiBH_4$/MgX (X= F_2,S, Se)
  However, temperatures, capacity and reversibility do not meet goals
- **Additional reactions identified; new systems being explored by theory group**

Nanoparticles / MgH_2-Si

- **Synthesized nano-Mg_2Si using nanoscale Si precursors and self-propagating rxns**
- **Conducted systematic milling study** – varied milling conditions, sample dilution, composition, H_2 overpressure, Ni and Pd catalyst incorporation
- **Dilution milling and nano-catalyst dramatically improve dehydrogenation kinetics**
- **No reversibility (hydrogenation) observed thus far –** Reversibility also not seen by other MHCoE partners (Stanford, Sandia, Hawaii, Intematix)

Nanoporous Scaffolds

- **$LiBH_4$ in C-aerogel result in faster sorption kinetics; smaller pores yield lower temps**
- **Small length scales may prevent large LiH and B particles from forming – improves cycling capacity**

Future Work
– *FY2006/07* –

New Systems

- Explore additional $LiBH_4$+MgX reactions
- Investigate new Li-Si-N systems

Nanoparticles / MgH_2-Si

- Use smaller particles with narrow size distribution
- Reduce surface oxide
- Test improved catalysts and other alloying agents

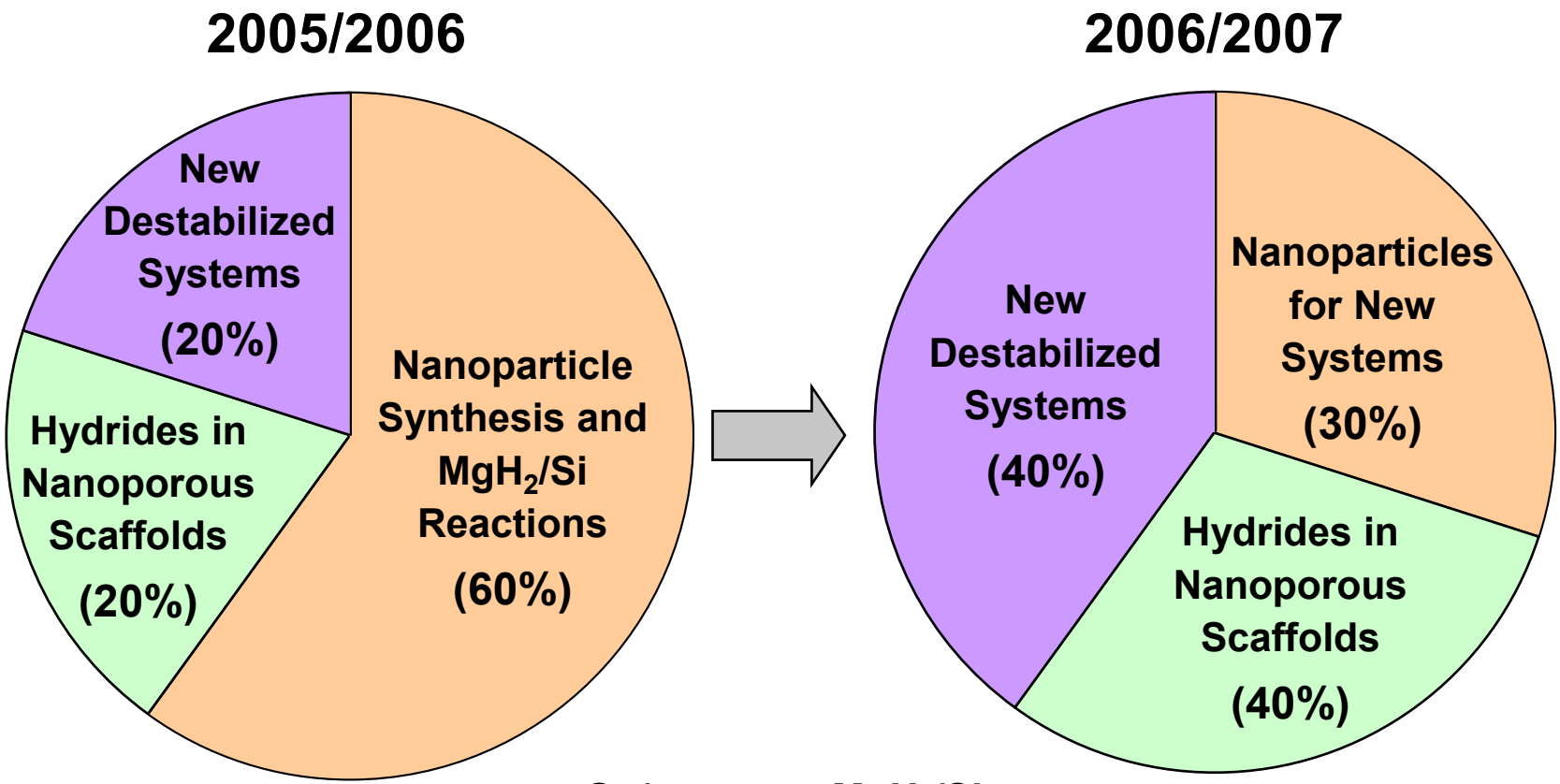
Nanoporous Scaffolds

- Incorporate destabilizing agents and catalysts
- Increase pore volume (to increase capacity)
- Explore other nanoporous materials

Program Direction
– By System –

Destabilized System	Benchmark	2005 Status	2005/06 Progress	Future
MgH_2/Si 5.0 wt.%, 0.083 kg/L est. $T_{1\ bar}$=30°C	*Prototype system* <2007 goal (including system penalty)	• Kinetics too slow T (dehyd) >200°C • Hydrogenation not achieved	• Lowered dehydr. temp by >100°C • Reversibility still not observed	• Complete nanoparticle study for reversibility • Go/no-go Sept '06
$LiBH_4$ / MgH_2 11.4 wt.%, 0.095 kg/L est. $T_{1\ bar}$=170°C	Could meet 2010 system cap. goal (assuming 50% system penalty)	• Kinetics too slow T (dehyd) ~400°C • $T_{1\ bar}$ too high	Lowered $LiBH_4$ dehydrogenation temp by 100°C (in C-scaffold)	• Incorporate full destab. system in scaffold • Optimize scaffold
$LiBH_4$ / MgX 4-10 wt.%, est. $T_{1\ bar}$: -10 to 430°C	Could meet 2007 goal (including moderate system penalty)	New untested systems	• Sorption meas.: X=F, S, Se, CO_3 • F, S, Se partially reversible – slow kinetics	• Test new destab. agents, and Li-Si-N systems • Use nano-engineering to improve kinetics

Program Emphasis
– 2005/06 and 2006/07 –

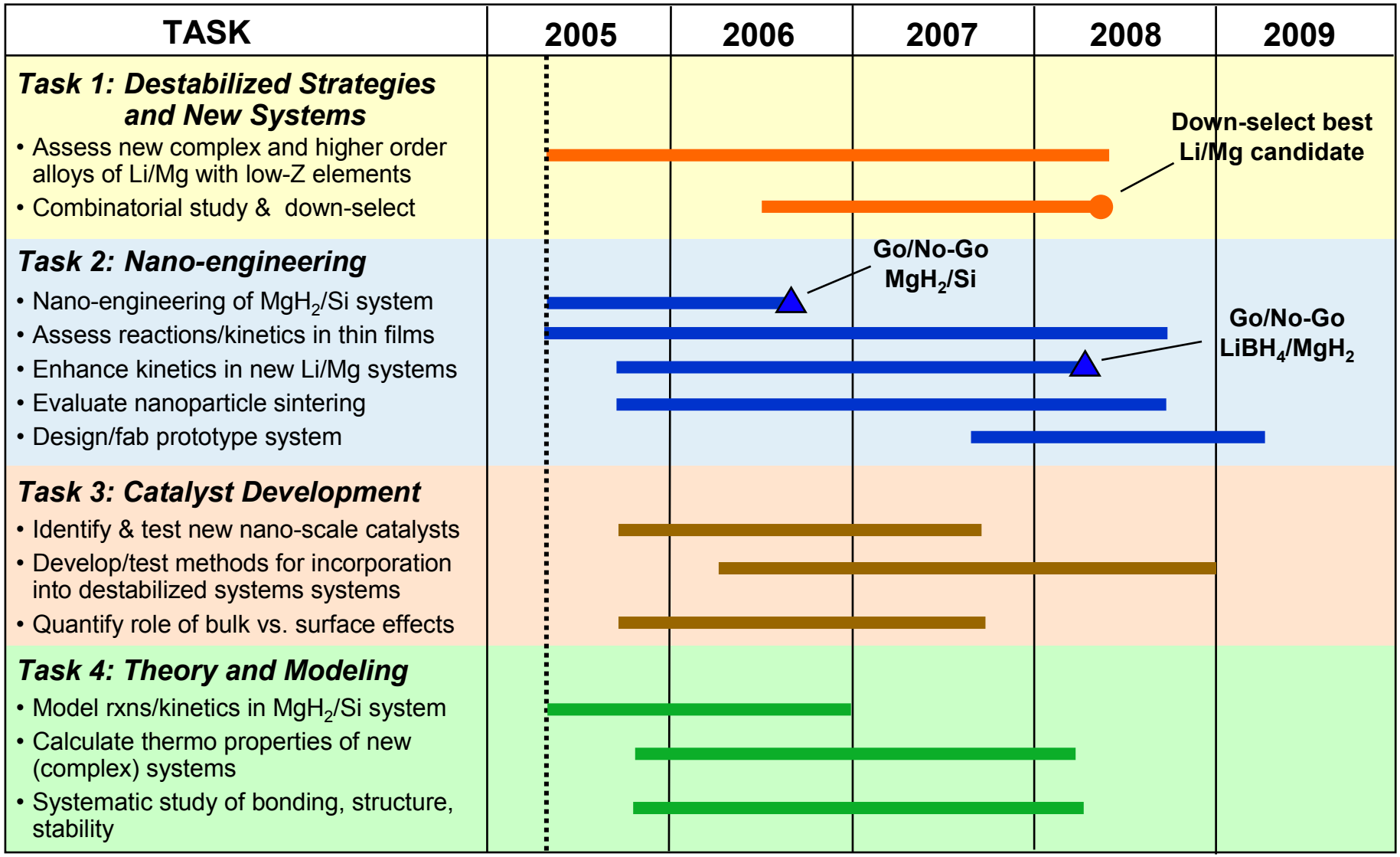


Go/no-go on MgH_2/Si system Sept '06

Increased emphasis in 2006/07 on new destabilized systems and hydrides in nanoporous scaffolds

Destabilized Hydrides Sub-Team

– *Summary of Program Plans* –



Back-up Slides

Destabilized Hydrides
– *Sub-Team Tasks and Collaborations* –

Task 1. Destabilized Hydride Strategies and New Systems

- Assess new complex and higher order alloys of Li/Mg with low-Z elements *(HRL)*
- Conduct combinatorial study; down-select best systems *(Intematix, HRL, JPL)*

Task 2. Nano-engineering for Improved Kinetics

- Nano-engineering & sorption kinetics in MgH_2/Si (*HRL, Caltech, SNL, Utah, UH)*
- Assess reactions/kinetics in thin film model systems (*Stanford, HRL)*
- Enhance kinetics in new Li/Mg systems *(HRL, Stanford, NIST, UIUC, Utah, NIST)*
- Evaluate nanoparticle sintering; develop mitigation strategies *(HRL)*

Task 3. Catalysts for Destabilized Hydrides

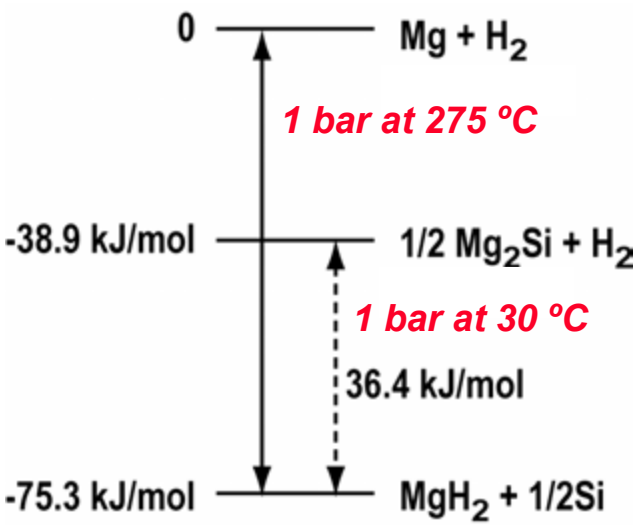
- Identify/test new nano-scale catalysts *(Intematix, UH, HRL)*
- Develop methods for incorporation into destabilized systems *(Intematix, UH, HRL)*
- Quantify role of bulk vs. surface catalytic effects *(Stanford, HRL)*

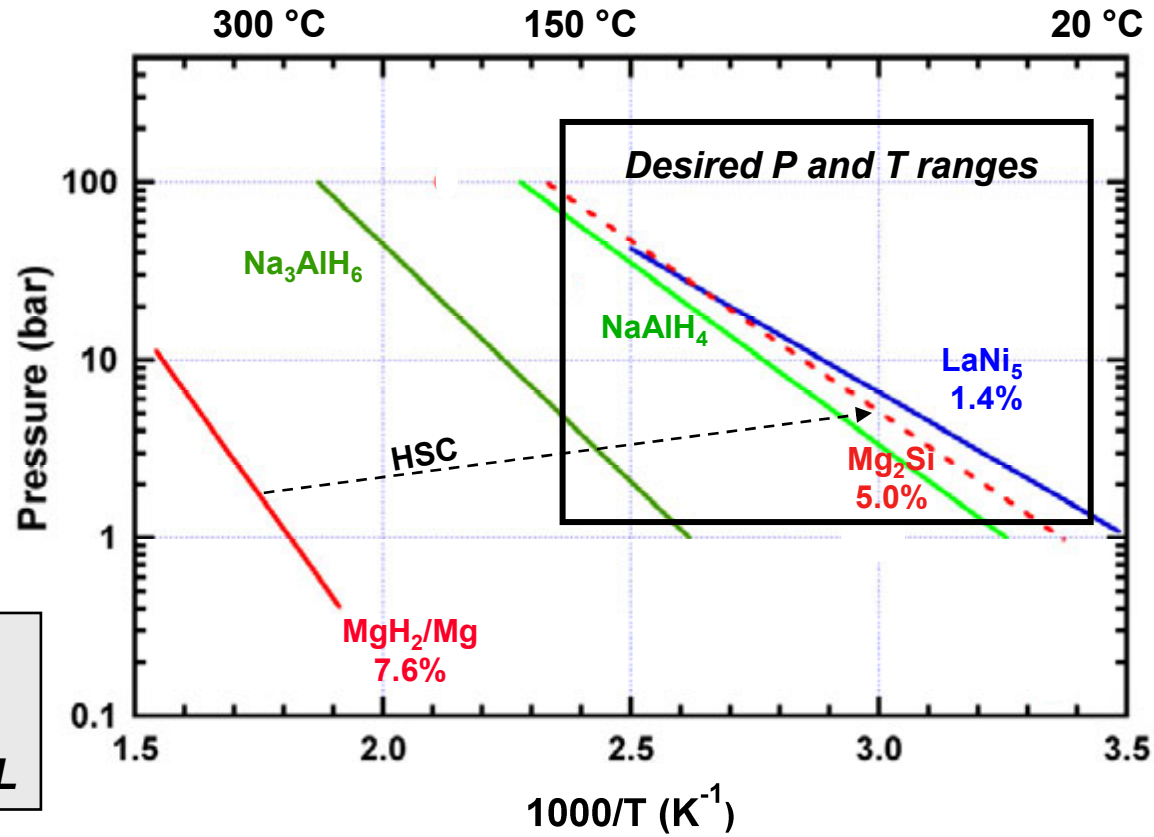
Task 4. Theory and Modeling

- Model reactions/kinetics in MgH_2/Si (*Pitt/CMU)*
- Calculate thermo properties of new (complex) systems (*Pitt/CMU, UIUC, NIST)*
- Systematic study of bonding, structure, stability *(UIUC)*

MgH_2 / Si

– *Prototype Destabilized Hydride System* –





Mg_2Si:

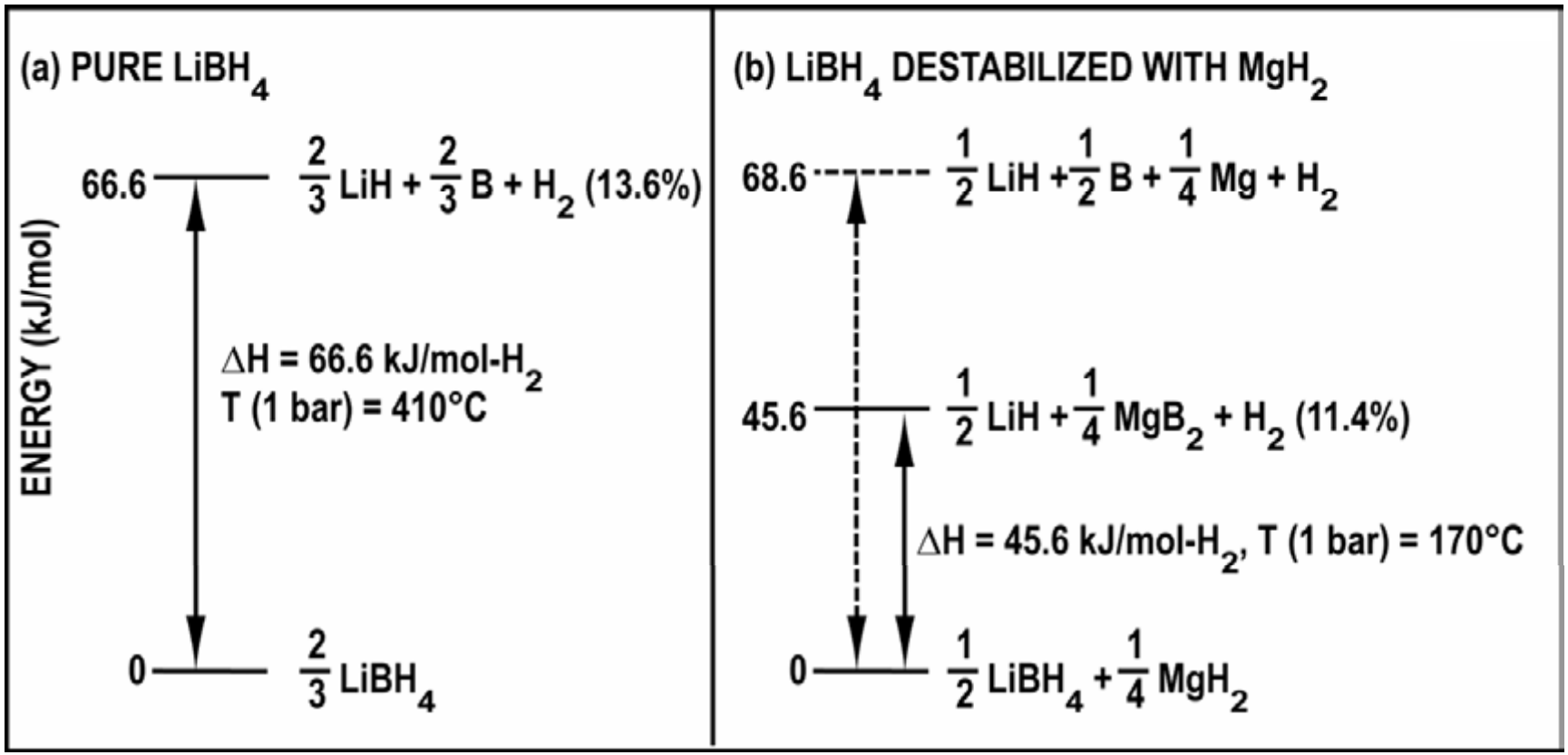
Gravimetric Capacity: 5%

Volumetric Capacity: 0.083 kg/L

- **Thermodynamic calculations predict behavior in desired P,T range**
- **However, reversibility not yet achieved – nano-engineering approaches being pursued to overcome kinetic barriers**

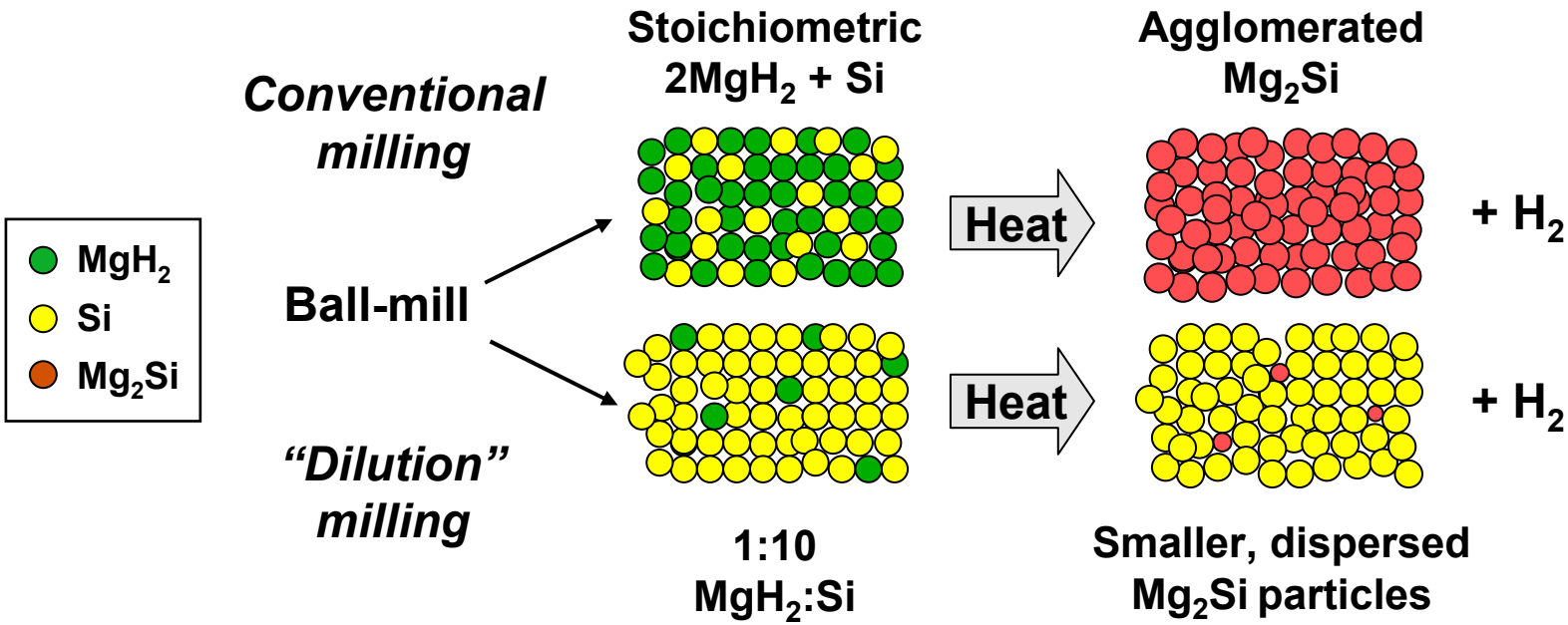
Background: $LiBH_4$ / MgH_2

– (11.4 wt. % and 0.095 kg/L) –



Formation of MgB_2 estimated to reduce $T_{1\ bar}$ by ~ 240 °C

"Dilution Milling" for Formation of Dispersed Reactants

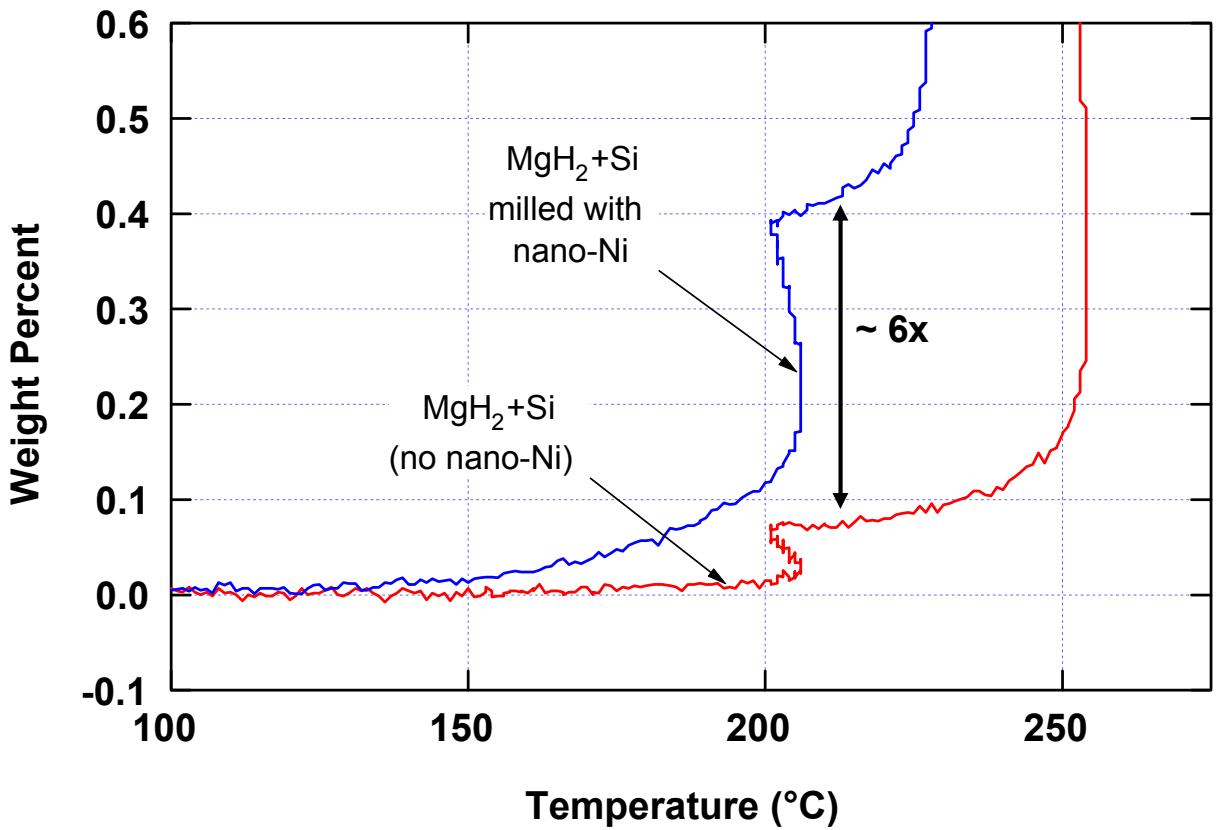


Dilution of MgH_2 in excess Si yields dispersed Mg_2Si particles without agglomeration

Straightforward method to test H_2 exchange kinetics in isolated particles

Effect of Nano-Ni Catalyst on Dehydrogenation of MgH_2/Si

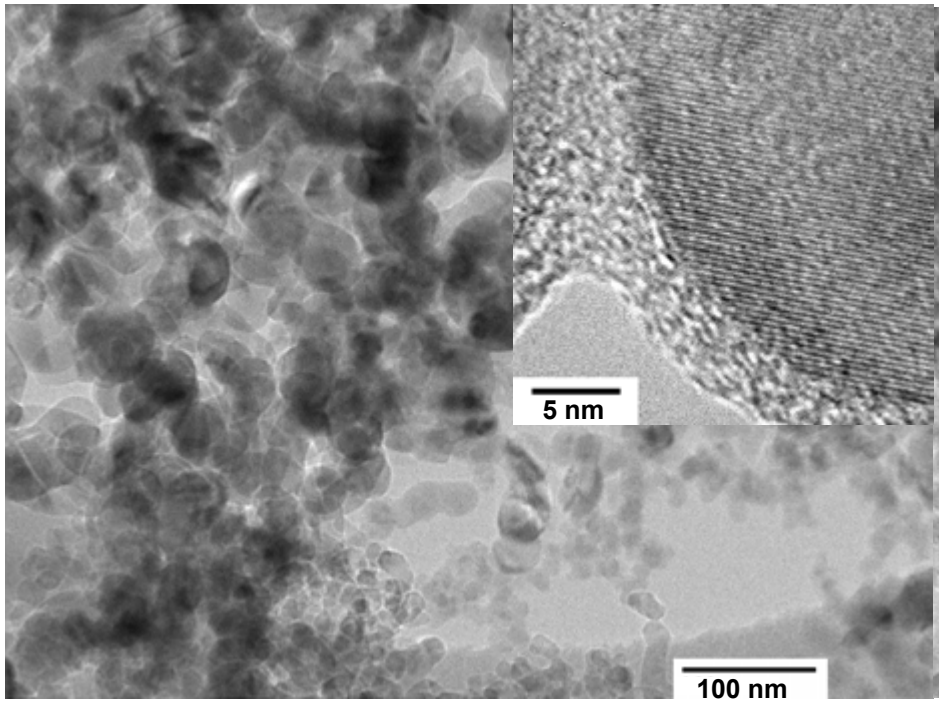
- Samples milled 5 hrs @ 400 rpm; 1 sample milled additional 5 mins with nano-Ni (50nm)
- MgH_2 dehydrogenation in Sieverts apparatus; 2°/min temp ramp; dwell at 200°C



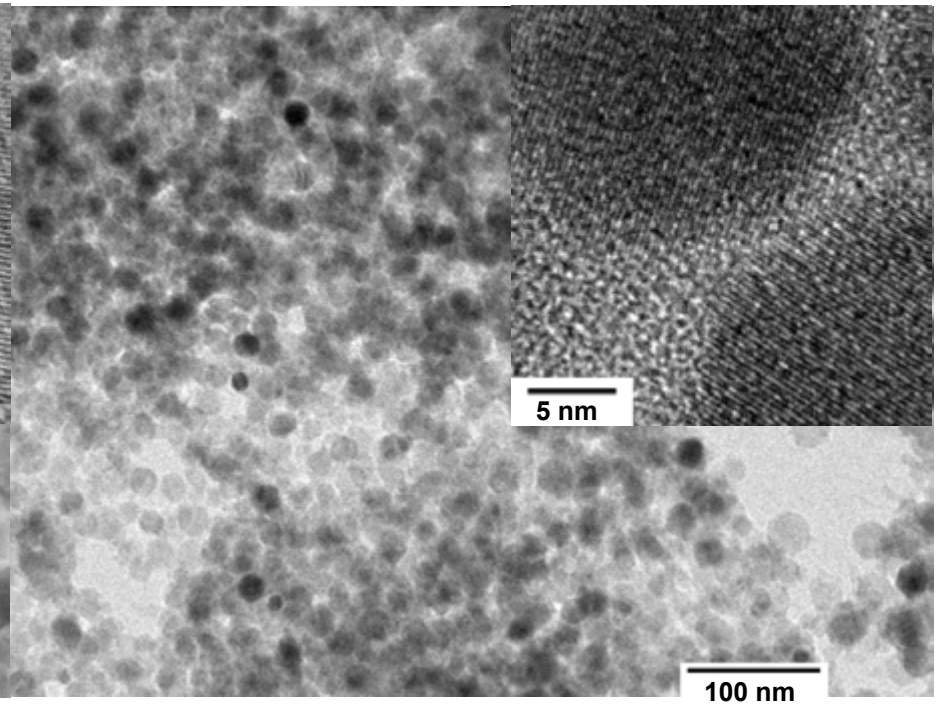
Amount of desorbed H_2 from MgH_2 increases by ~6x with addition of nano-Ni catalyst during milling

Si Nanoparticle Synthesis and Characterization by TEM

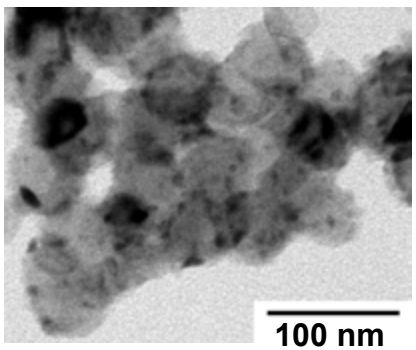
"5 nm" Si starting material (Meliorum, Inc.)



Si nanoparticles formed by gas condensation (Caltech)



After reaction with MgH_2 to form Mg_2Si

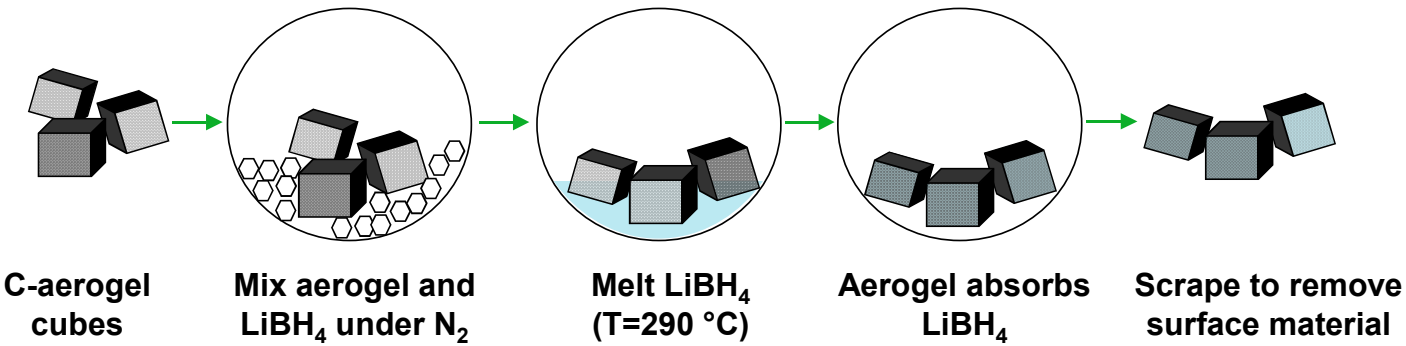


Gas phase condensation produces generally smaller particles with narrower size distribution

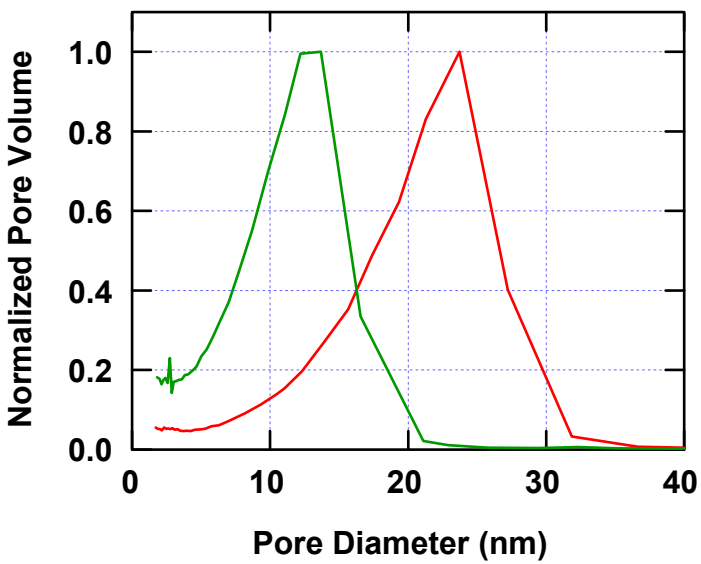
⇒ *Promising as nano-Mg_2Si precursor*

Aerogel Synthesis and $LiBH_4$ Incorporation

- Carbon aerogel synthesized by resorcinol + formaldehyde condensation
- Aerogel filled with $LiBH_4$ by infiltration from melt:



Aerogel Pore Size Distributions



- Pore sizes approx. 13 and 25 nm
- Pore volumes: 0.80 to 1.38 cm^3/g (0.33 to 0.57 cm^3 carbon/cm^3 free space)
- 80-90% of pore space filled with $LiBH_4$
- Contains up to 45 wt.% $LiBH_4$ (pore size dependent)
- Also investigated activated-C (<2 nm pores) and graphite (non-porous control)

Presentations and Publications
– 2005/2006 –

Presentations to date:

J.J. Vajo, "Destabilization of Strongly Bound Hydrides for Hydrogen Storage Applications" (invited presentation) Gordon Research Conference Hydrogen-Metal Systems Waterville, ME, (July 10-15, 2005).

G.L. Olson, J.J. Vajo, A.F. Gross, T. M. Salguero, S.L. Skeith, and B. M. Clemens, *"Nanostructure Engineering for Improved Reaction Rates in Destabilized Hydrides"* (poster presentation) Gordon Research Conference Hydrogen-Metal Systems Waterville, ME, (July 10-15, 2005).

G.L. Olson and J.J. Vajo "*Destabilized Hydrides"* presentation to FreedomCAR Hydrogen Storage Tech Team (1/12/2006).

A. F. Gross, J.J. Vajo, S.L. Skeith, and G.L Olson, "*Enhanced Hydrogen Storage Properties of Metal Hydrides using Nanoporous Carbon Scaffolds"* at American Chemical Society Meeting, Atlanta, GA (March 27-31, 2006).

J.J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, and G. L. Olson, "Kinetics and Thermodynamics of Destabilized Hydride Systems" (invited presentation) Materials Research Society Spring Meeting, San Francisco, CA (April 17-21, 2006).

Upcoming Presentations:

J.J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, and G. L. Olson "*Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems"* (Invited presentation), International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications, Lahaina, Maui, Hawaii (Oct. 1-6, 2006).

Publications (planned for 2006)

J.J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, and G. L. Olson "*Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems"* (to be submitted to J. Alloys and Compounds – special proceedings issue for MH2006 Conference) (Oct. 1-6, 2006).

A.F. Gross, J.J. Vajo, S.L. Skeith, and G.L Olson, *"Reversible Hydrides in Nanoporous Scaffolds"* (in preparation).

G.L. Olson, J.J. Vajo, A.F. Gross, S.L. Skeith, R. Cumberland, and C. C. Ahn, *"Enhanced Reaction Kinetics in Nanostructured MgH_2/Si"* (planned).

Critical Problems and Issues

- **A destabilized system that meets all of the DOE thermodynamics requirements has not yet been identified**
  - System capacity remains problematic (i.e., a 50% system penalty would require an 18% grav. capacity material to meet 2015 goal – a path to a such a material is unclear)
  - Although calculations show acceptable $T_{1\ bar}$ values are possible – not yet experimentally confirmed
- **Kinetics in light metal hydrides are prohibitively slow**
  - Our approach relies on nano-engineering to reduce diffusion distances and improve reaction rates
  - At this point we are uncertain if this approach will enable us to meet DOE goals for delivery temperature and refueling rates
- **Sintering/agglomeration of nanoparticles could be a serious problem (reduced H_2 exchange rates)**
  - Scaffolds show promise for enhancing kinetics; may also mitigate sintering
  - However, scaffolds also introduce a capacity penalty – can penalty be reduced to acceptable levels? – high pore volume scaffolds needed