

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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Project ID #
ST065

Timeline

- Project start date: March 2005
- Project end date: Feb 2010
- Percent complete: 100%

Budget

- **Total Project Funding:**

Phase I and II: \$ 2.75M

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

- **Funding received in FY10:**

\$ 0 K

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
- Caltech, JPL, NIST: scaffolds characterization

- **DOE collaborations:**

- LLNL: carbon scaffold synthesis
- Washington Univ. : scaffold NMR

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

2009/2010

1. Complete characterization of LiBH_4/MgX , X = Ni destabilized system

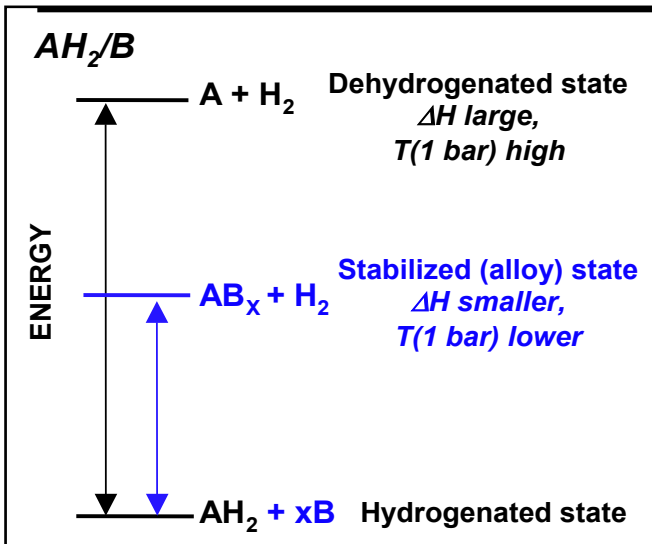
- Determine thermodynamic destabilization (ΔH and ΔS)
- Determine reaction path (is new reaction path accessible in mixture?)
- Addresses Barriers A, C, and E.

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

- Increase hydrogen exchange rate through nanoengineering
- Achieve and characterize intimate mixture within pores of aerogel
- Addresses Barriers C and E

3. Improve kinetics of LiBH_4/MgX , X = F destabilized system

- Increase hydrogen exchange rate using catalysts and processing (milling)
- Addresses Barriers C and E



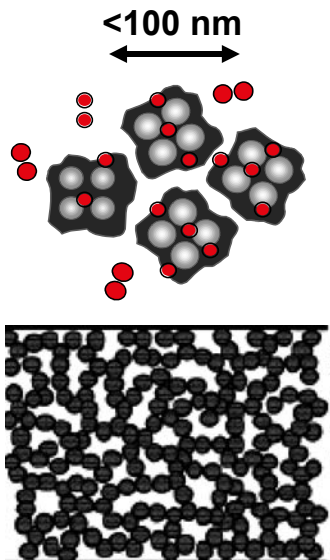
Hydride Destabilization

(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*

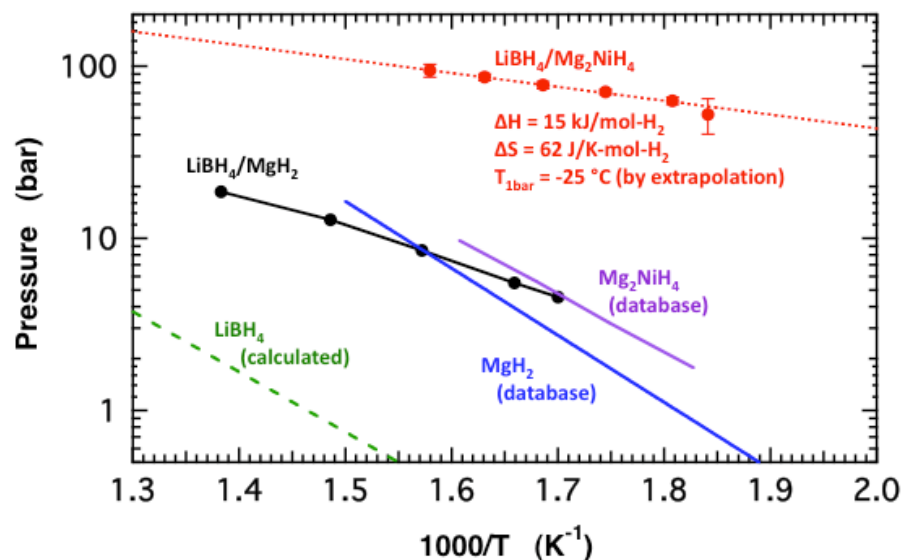
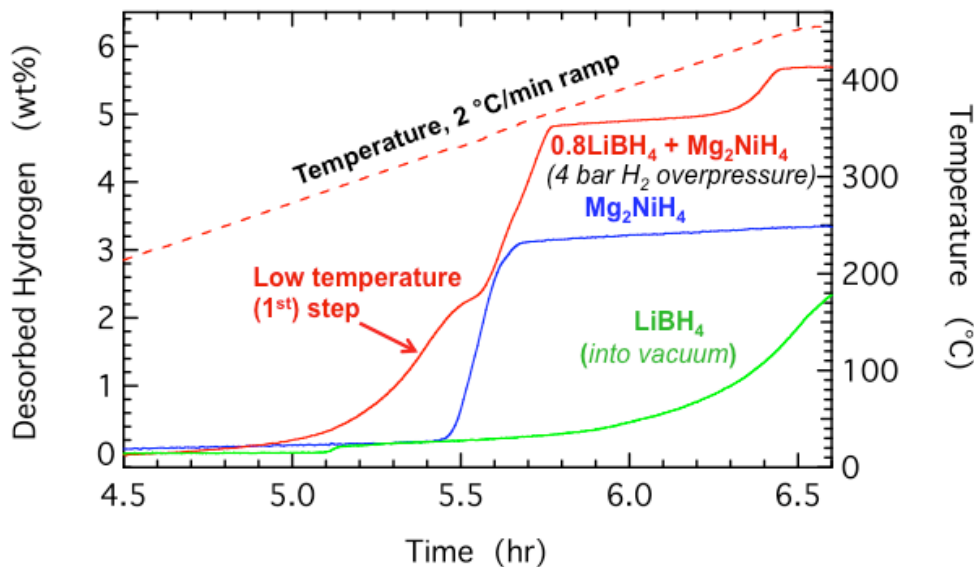
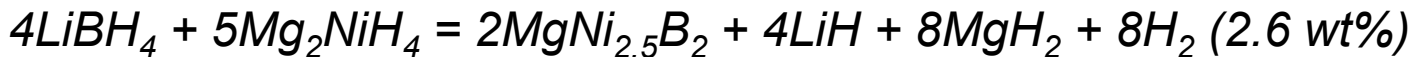
Enhanced reaction rate and improved cycling

Status as of March 2009:

- Observed low temperature step for the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system; hydrogenation of ternary boride confirmed
- Achieved sequential incorporation of LiBH_4 and MgH_2 into carbon aerogel; cycling poor, unidentified peak in NMR
- $\text{LiBH}_4/\text{MgF}_2$ destabilized system only partially reversible

Month/Year	Milestone or Go/No-Go Decision
Sept-09	Milestone: Complete investigation of ternary boride system. Completed characterization of the Mg-Ni-B system

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

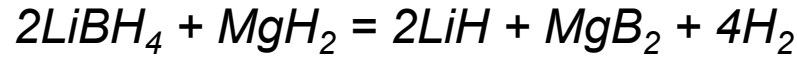


- For mixture, a 1st dehydrogenation step occurs at temperatures lower than either component. This indicates first example of kinetic coupling (*ie*, opening of a new reaction pathway)
- Kinetics are better than $\text{LiBH}_4/\text{MgH}_2$ (possibly due to catalytic nature of Ni in $[\text{NiH}_4]^{2-}$ anion)
- Reaction produces $\text{MgNi}_{2.5}\text{B}_2$ (example of a reversible ternary boride, many others may exist)
- $P_{\text{eq}} \sim 10x P_{\text{eq}}$ for $\text{LiBH}_4/\text{MgH}_2$ system (sufficient for PEM system)
- ΔH is low (due to stability of $\text{MgNi}_{2.5}\text{B}_2$, calc. $\Delta H_f = -323 \text{ kJ/mol}$)
- ΔS is low (possibly due to two complex hydrides in hydrogenated state)
- Stable cycling of 10 cycles but capacity is low

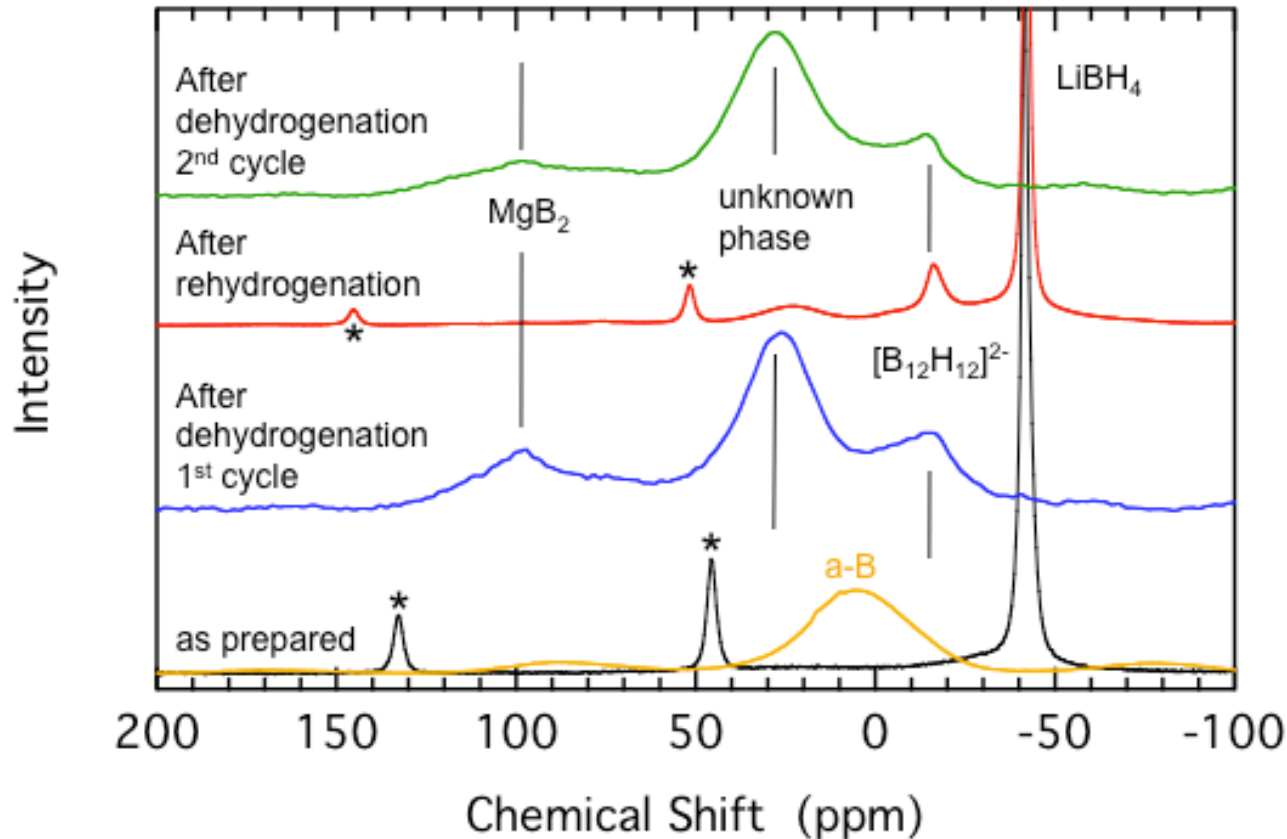
Summary of attempts to achieve well mixed 2:1 $\text{LiBH}_4:\text{MgH}_2$ in aerogel

1. **Sequential** incorporation – MgH_2 then LiBH_4 or vice versa:
 - improved kinetics on 1st cycle
 - however, poor coupling (*little MgB_2 with unidentified phase*) and poor cycling
2. **Sequential** incorporation – LiBH_4 followed by complete dehydrogenation (at 670 ° C) then MgH_2 :
 - low capacity (~ 4 wt%) and poor cycling
3. **Simultaneous** incorporation – ($\text{LiBH}_4 + \text{Bu}_2\text{Mg}$)/DEE (diethyl ether) hydrogenated at 170 °C in 55 bar H_2 :
 - significant reaction of LiBH_4 with DEE (*from NMR*)
 - $\text{LiBH}_4:\text{MgH}_2 > 2.5$ (*could not control ratio*)
4. **Simultaneous** incorporation – ($\text{LiBH}_4 + \text{Bu}_2\text{Mg}$)/DEE followed by evaporation of DEE, then hydrogenation at 170 °C in 55 bar H_2 :
 - $\text{LiBH}_4:\text{MgH}_2 = 0.01$ (*evaporation excluded LiBH_4 from aerogel*)
5. **Simultaneous** incorporation – ($\text{LiBH}_4 + \text{Bu}_2\text{Mg}$)/DEE followed by freezing and evaporation of DEE during warming, then hydrogenation at 170 °C in 55 bar H_2 :
 - $\text{LiBH}_4:\text{MgH}_2 = 1.61$ (*sample currently being tested*)

- **Sequential incorporation leads to poor mixing**
- **For simultaneous incorporation, transition from soluble to insoluble species must be subtly controlled (*to achieve proper composition*)**

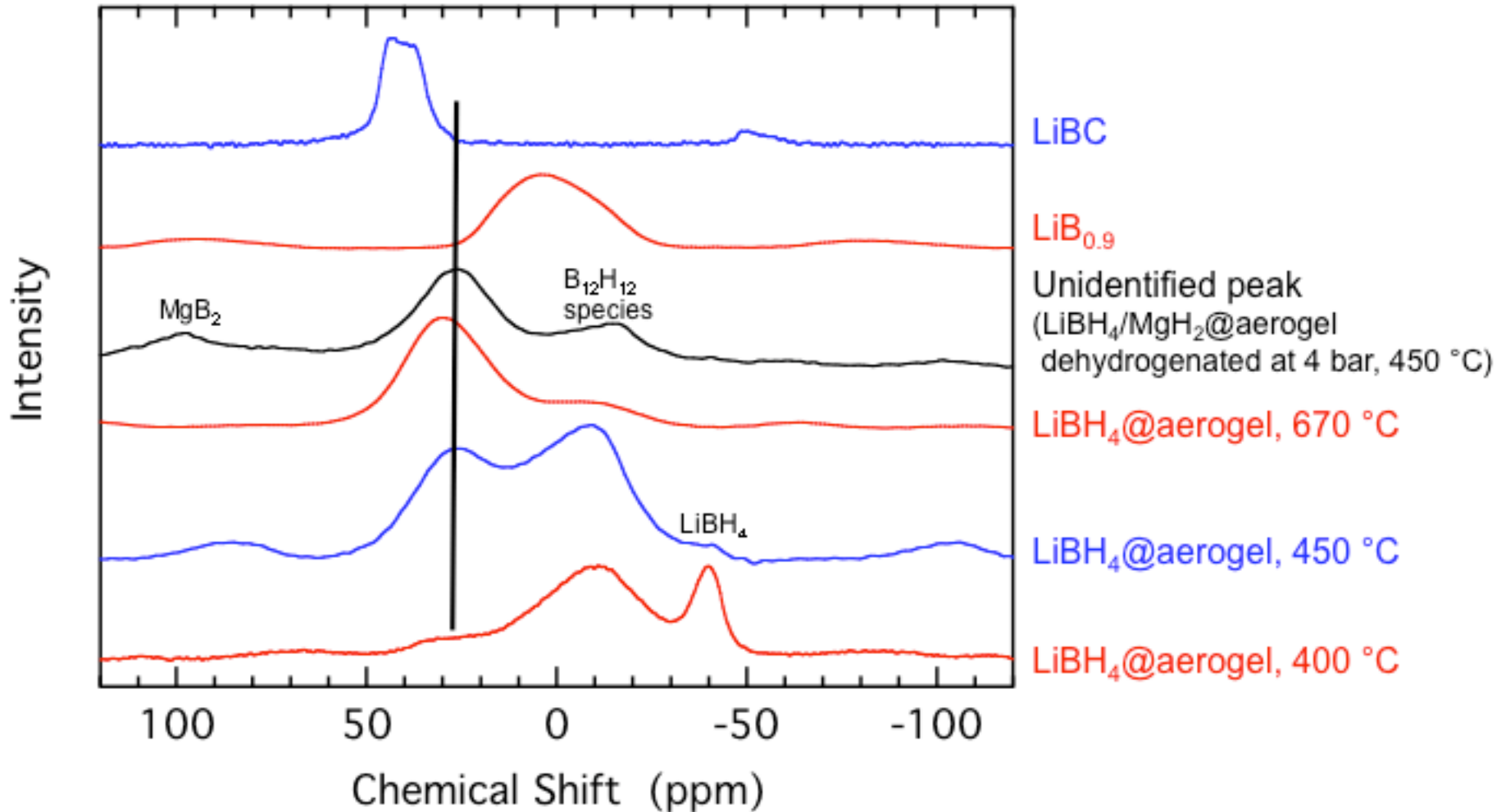


Sequential incorporation, LiBH_4 1st



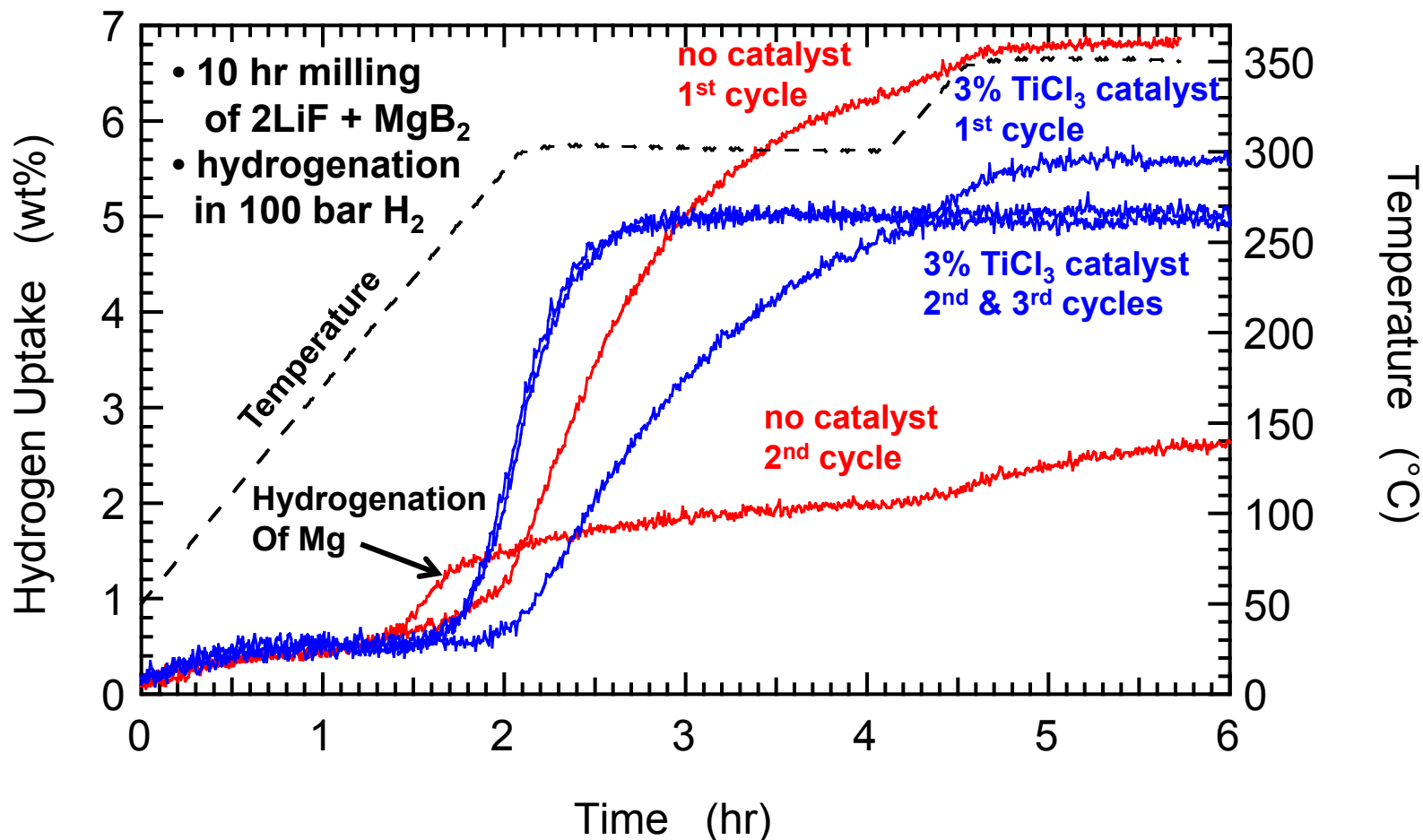
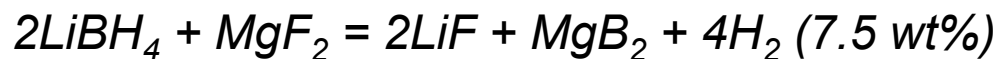
- Dehydrogenation produces some MgB_2
- However, major product is unidentified phase at ~ 30 ppm
- Amount of MgB_2 is reduced on 2nd cycle (*consistent with reduced capacity*)

Identification of New Phase



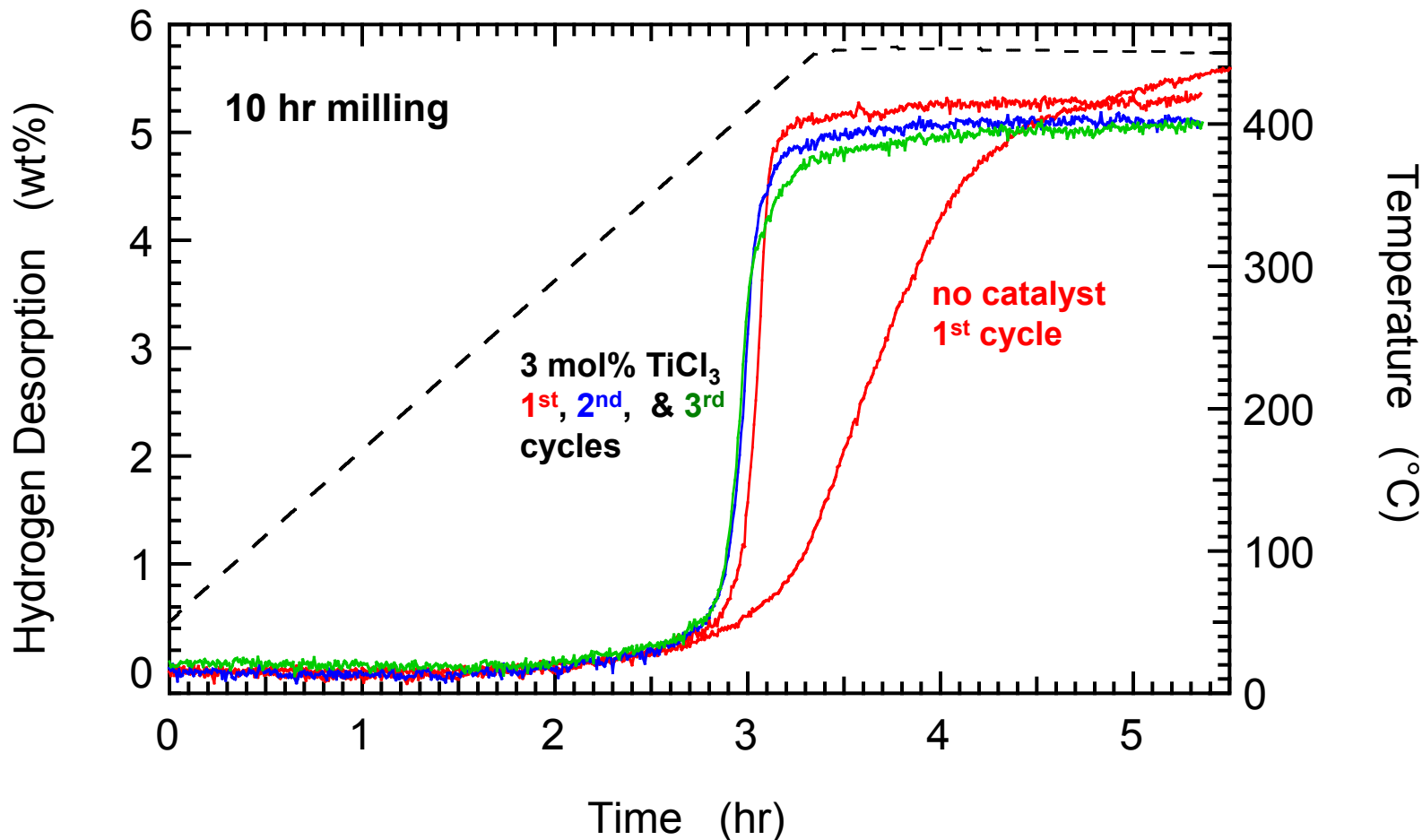
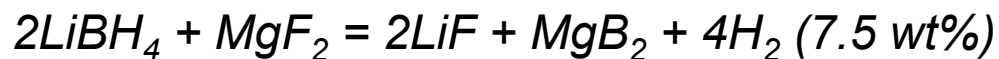
- New phase formation does not require Mg, indicative of poor mixing
- Appears associated with LiBH_4 /aerogel interaction during dehydrogenation

3. $\text{LiBH}_4/\text{MgF}_2$ System: Hydrogenation



- On 1st cycle, kinetics are good without catalyst
- On 2nd cycle Mg feature indicates poor reversibility during dehydrogenation
- Addition of 3% TiCl_3 improves kinetics

LiBH₄/MgF₂ System: Dehydrogenation



- Combination of extended milling and catalyst enables full reversibility

- **Center partners**
 - David Sholl (Georgia Tech) and Karl Johnson (U. Pitt): performed calculations of Li-Mg-Ni-B system
 - S-J Hwang (JPL): NMR studies of ternary hydrides and scaffolds
 - Jason Zan (JPL): preparation of $\text{LiB}_{12}\text{H}_{12}/\text{MgH}_2$ samples for Sieverts testing
- **DOE partners**
 - Ted Baumann (LLNL): provided porous carbon materials
 - Mark Conradi (Wash U): characterized $\text{LiBH}_4@$ aerogel samples with NMR

Destabilized Systems

- **Further work on transition metal complex hydride anion systems**
 - Test other transition metal complex hydrides (*eg, Mg₂FeH₆, Mg₂CoH₅, etc.*)
 - Test other transition metal ternary borides (*MgTmB_x*) for reversible hydrogenation activity
 - Search (*experimental/computational*) for new ternary (*or higher*) borides
- **Study effect of solid/solid interface on kinetics**
 - Characterize interfacial area and structure (*including effects of additives and processing*)
 - Correlate area and structure with kinetics
 - Determine interface energies computationally (*correlate with kinetics*)

Nanoporous Scaffolds

- **Continue work on LiBH₄/MgH₂ system in scaffolds**
 - Optimize simultaneous incorporation techniques (*achieve intimate mixing in pores*)
 - Incorporate catalysts (*to further improve kinetics*)
 - Vary scaffold structure (*beyond aerogels*)
- **Elucidate mechanism of kinetic enhancement**
 - Understand nature/origin of fast diffusing species (*seen with NMR*)
 - Determine nature of scaffold hydride interactions (*effects of surface chemistry*)
- **Search for thermodynamic effects in sub 2 nm pore scaffolds**

New Destabilized Systems

- **Completed work on $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system**
 - **System is kinetically coupled** (*reaction proceeds through new pathway enabled by mixture*)
 - **ΔH ($= 15 \text{ kJ/mol-H}_2$) and ΔS ($= 62 \text{ J/K-mol-H}_2$) are the lowest reported so far for a reversible system; this is very advantageous for practical systems**
 - **This system demonstrates that the full benefits of destabilized systems** (*improved thermodynamics and new reaction paths*) can be realized
- **Demonstrated complete reversibility in $\text{LiBH}_4/\text{MgF}_2$ system**
 - **Combination of extended milling** (*10 hr*) and catalyst (*3% TiCl_3*) enabled full reversibility

Nanoporous Scaffolds

- **Progress on simultaneous incorporation of $\text{LiBH}_4/\text{MgH}_2$ into aerogel**
 - **Determined that achieving good mixing necessitates carefully controlling the soluble to insoluble species transition**
 - **The new ^{11}B species observed by NMR** (*at 30 ppm*) involves a Li-B-C phase and does not require Mg

Supplemental Slides

Destabilized System	Benchmark	2009 Status	2009/10 Progress	Future
<p>LiBH₄ / MgH₂ @C aerogel 11.4 wt.%, 0.095 kg/L w/o aerogel, est. T_{1 bar}=170° C</p>	<p>Could meet 2015 system weight and volume capacity goals (assuming 25% aerogel and additional 25% system penalties)</p>	<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"> •Explored various approaches to incorporate LiBH₄ and MgH₂ into aerogel simultaneously and sequentially 	<ul style="list-style-type: none"> •Optimize loading and composition •Complete characterization of hydrogen exchange kinetics •Incorporate catalysts; optimize scaffold
<p>LiBH₄ / Mg₂NiH₄ 8.3 wt%, est. T_{1 bar}=150° C</p>	<p>Could meet 2015 system capacity goal (but only small system penalty)</p>	<ul style="list-style-type: none"> •Measured T_{1bar} of 65°C for low temperature step •Hydrogenation of ternary boride confirmed 	<ul style="list-style-type: none"> •Completed thermodynamic characterization; found low ΔH of 15 kJ/mol and low ΔS of 62 J/K-mol 	<ul style="list-style-type: none"> •Candidate for incorporation into scaffold •Candidate for catalyst screening •Search for other ternary hydrides with higher capacities
<p>LiBH₄ / MgF₂ 7.6 wt%, est. T_{1 bar}=150° C</p>	<p>Could meet 2015 system capacity goal (but only small system penalty)</p>	<ul style="list-style-type: none"> •Partially reversible with degradation 	<ul style="list-style-type: none"> •Combination of extended milling and addition of catalysts lead to a fully reversible, stable cycling system 	<ul style="list-style-type: none"> •Candidate for incorporation into scaffold