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HYDRIDE CHEMISTRY IN NANOPOROUS SCAFFOLDS

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Synopsis or Abbreviated Abstract

The effects of incorporating hydrogen storage materials into porous hosts are described.

Hydride Chemistry in Nanoporous Scaffolds

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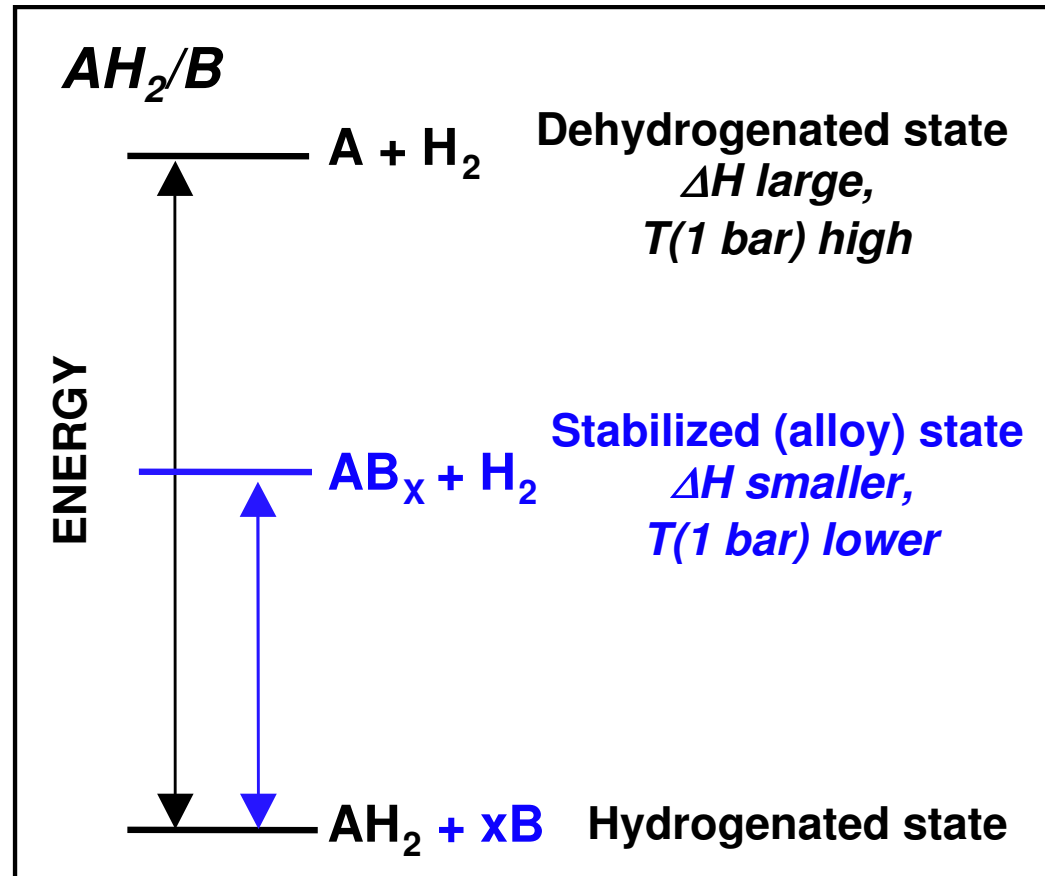
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Introduction and Outline

- Light element and complex hydrides (*such as LiH, MgH₂, AlH₃, LiAlH₄, LiBH₄, LiNH₂, NaAlH₄*) have high gravimetric and volumetric hydrogen capacities
 - (most) everything else is a problem...
 - Thermodynamics: *too stable or too unstable*
 - Kinetics: *slow kinetics and poor reversibility*
 - Material properties: *low thermal conductivity, large volume changes*
-

1. Formation of destabilized systems (**addresses thermodynamics**)
2. Nanoengineering using porous scaffolds (**addresses kinetics**)

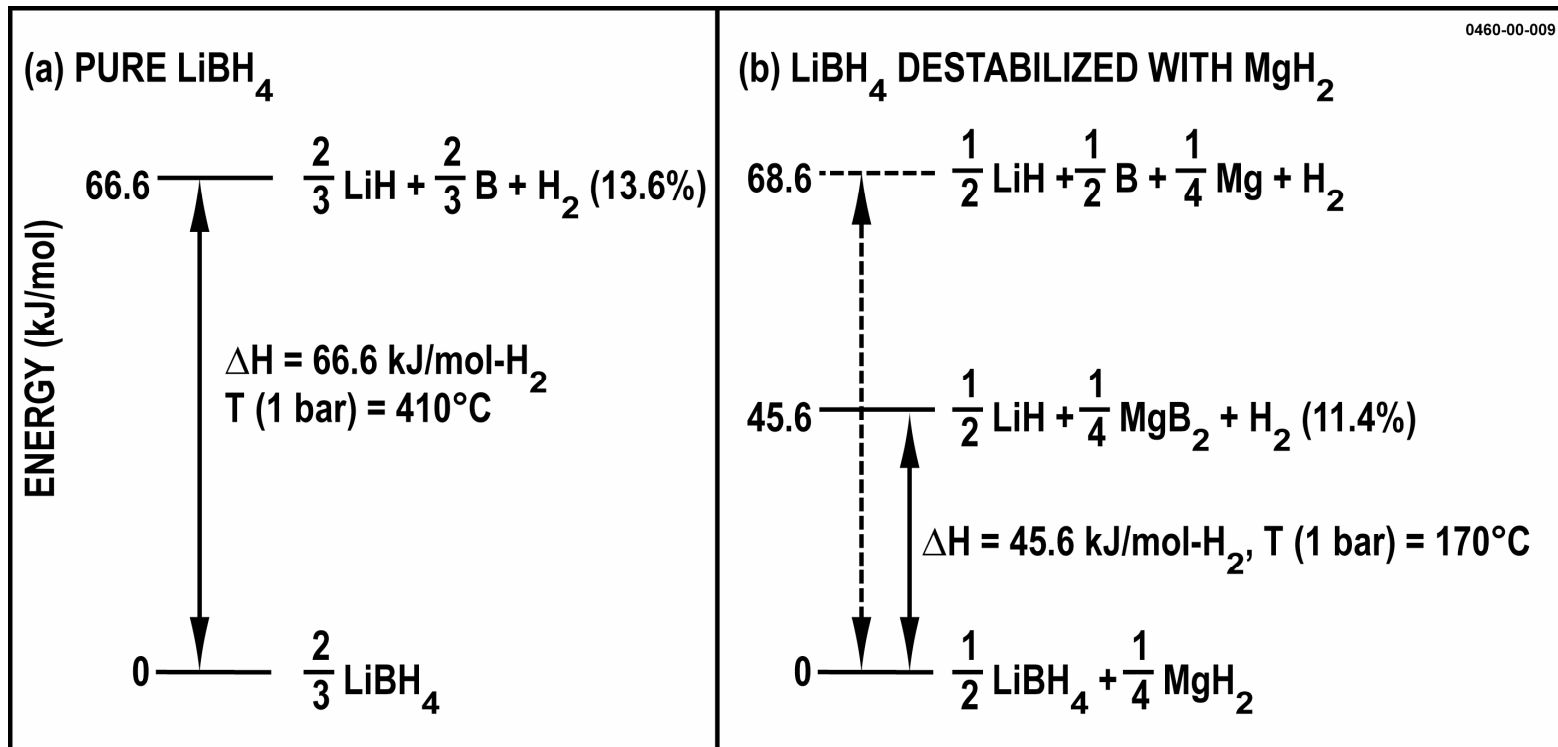
Destabilized Systems: General Approach*



- **Additive stabilizes dehydrogenated state, forming destabilized system**

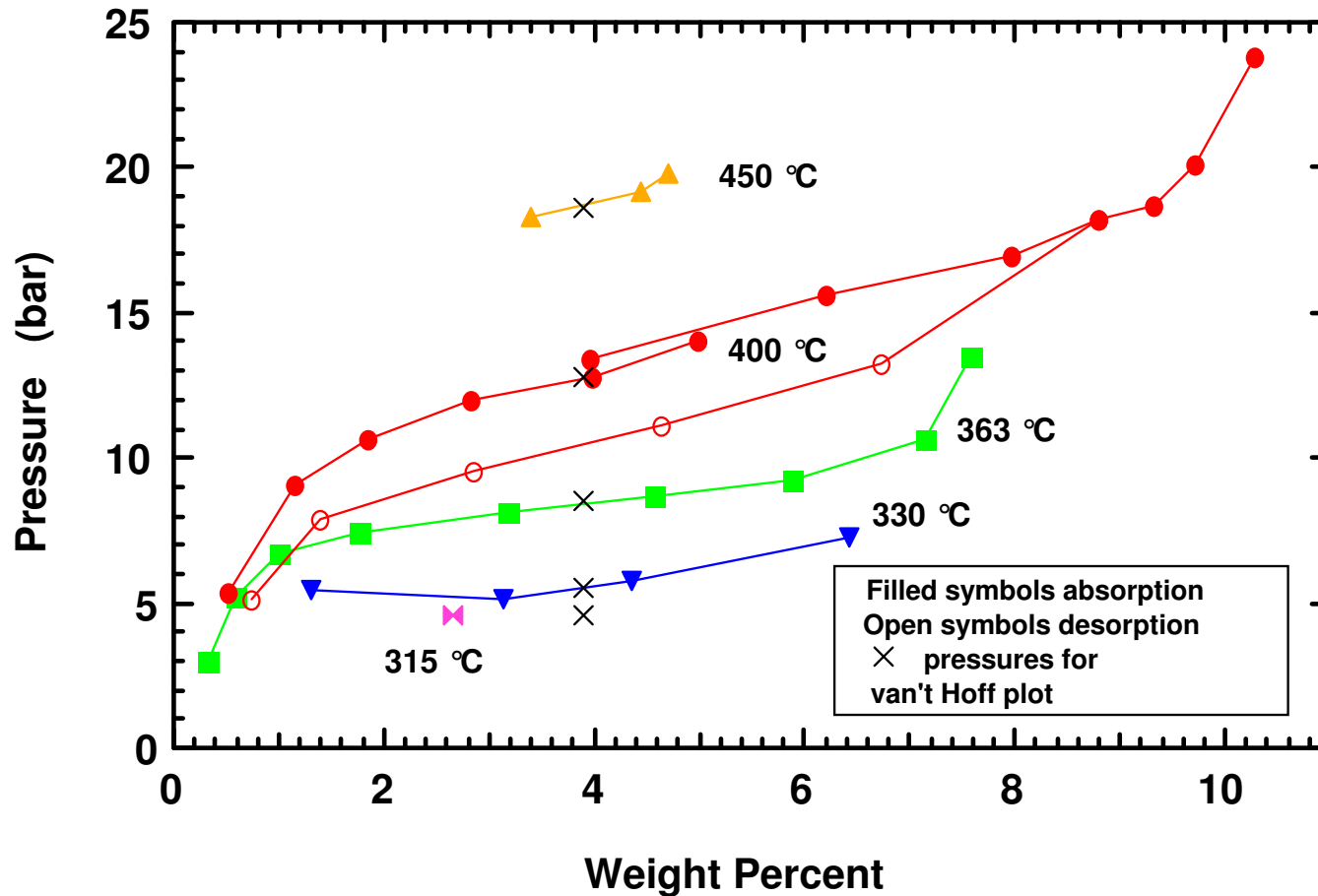
* Extends work on MgH_2/Cu (Reilly, 1967) to light/complex hydrides; recent computations propose >300 systems (Alapati et al, 2006)

LiBH₄/MgH₂ Destabilized Hydride System



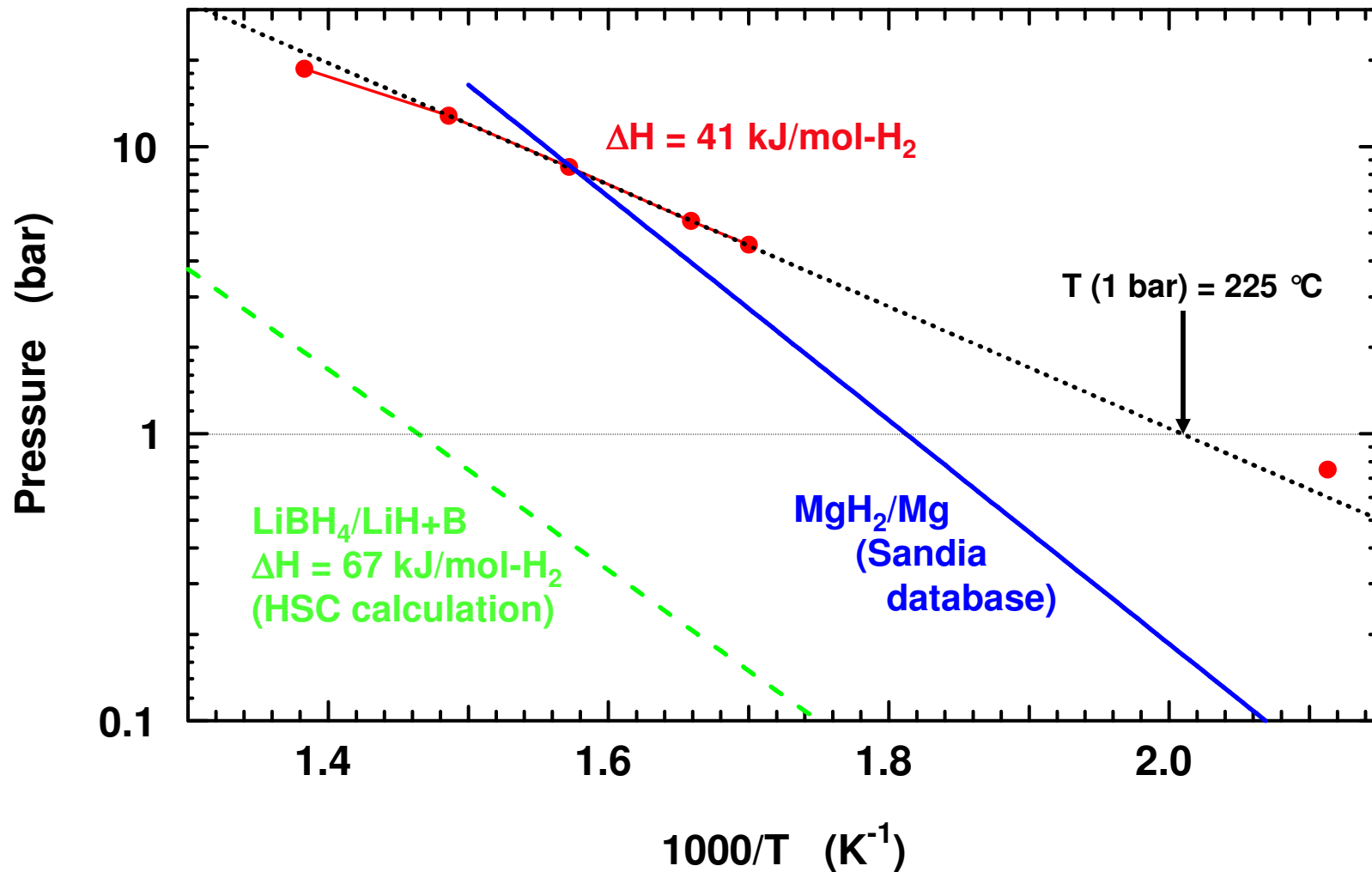
Formation of MgB₂ estimated to reduce T(1 bar) by ~ 240 °C

$\text{LiBH}_4/\text{MgH}_2 \leftrightarrow \text{LiH}/\text{MgB}_2$ Isotherms



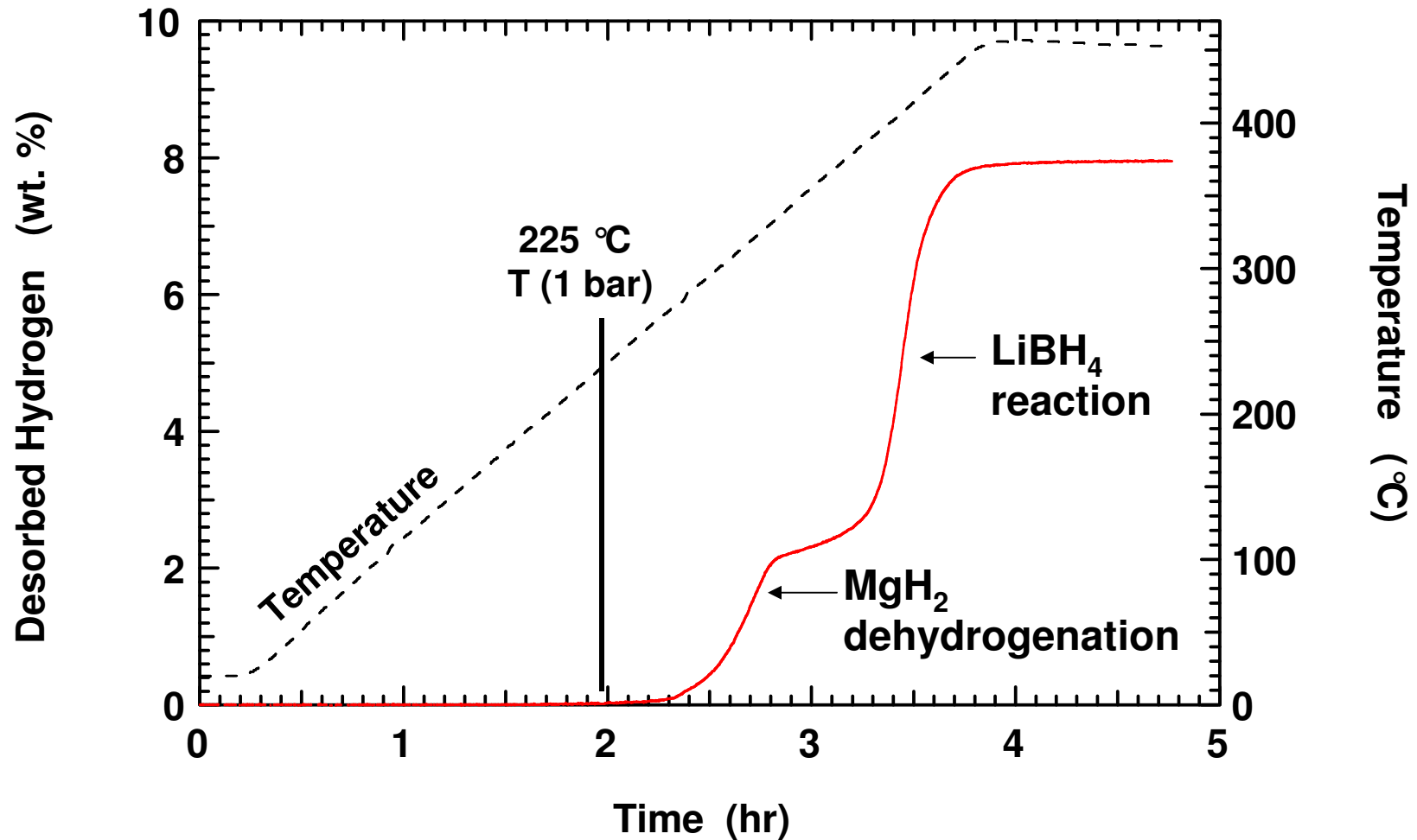
- XRD measurements confirm reaction scheme
- Sloping plateaus with capacities of 8 to 10 wt %
- Kinetics slow for $T < 350$ °C

$\text{LiBH}_4/\text{MgH}_2 \leftrightarrow \text{LiH}/\text{MgB}_2$: van't Hoff Behavior



- Equilibrium pressure increased by $\sim 10\text{x}$ compared to pure LiBH_4

Kinetics of $2\text{LiBH}_4 + \text{MgH}_2$ Dehydrogenation

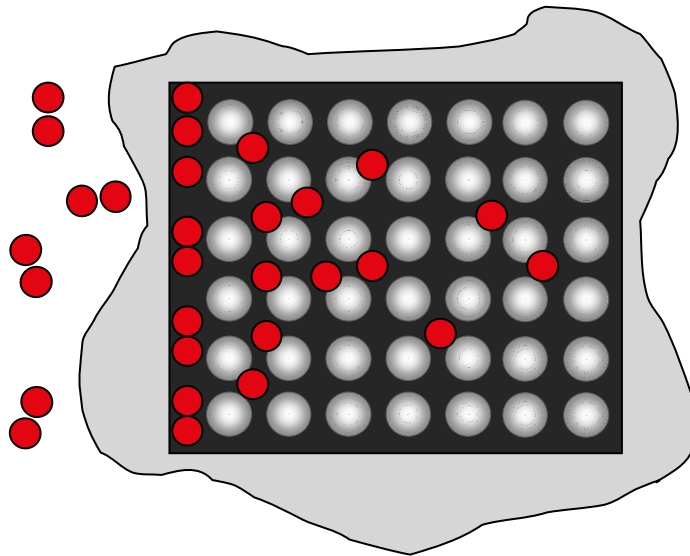


- MgH_2 and LiBH_4 reactions are not concerted
- Reaction temperatures \gg thermodynamic limit

Improve Kinetics using Nanoengineering

Enhance reaction rates by decreasing particle size

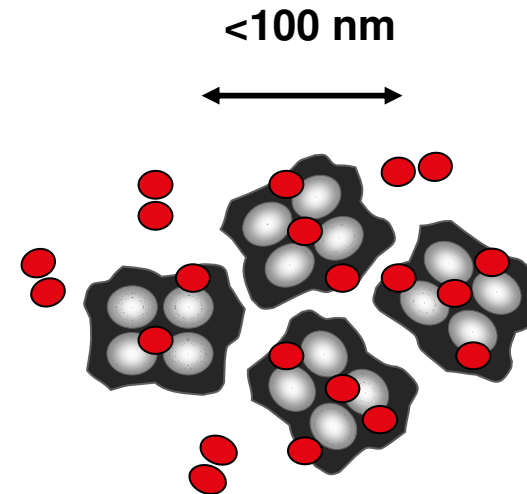
Bulk Hydride



Long H-diffusion distances in bulk material:

⇒ *slow*
hydrogen exchange rate

Nanoscale Hydride



Short H-diffusion distances in nanoparticles:

⇒ *fast*
hydrogen exchange rate

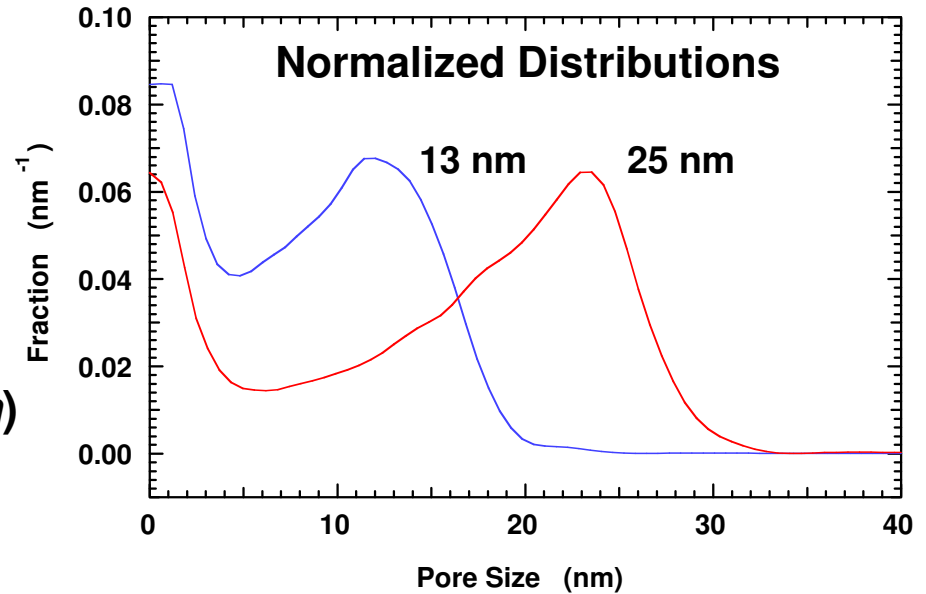
$$\tau \propto Dt/l^2$$

Porous Scaffolds for Nanoscale Hydrides

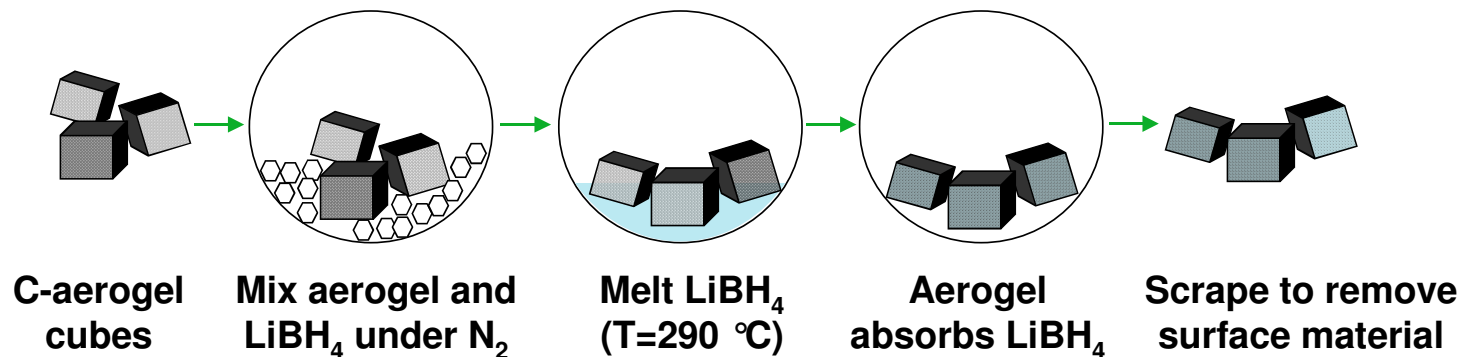
- **Interpenetrating network of pores**
 - wide range of pore sizes (*~1 to 50 nm*) and distributions
 - many scaffold materials (*C, SiO₂, Al₂O₃*) and surface chemistries
- **Scaffold serves as structure-directing agent for nanoscale hydride**
- **Hydride phase confined by pores** (*mitigates sintering and growth*)
- **Nanoscale confinement may alter thermodynamics**
- **Previous work:**
 - NaAlH₄ incorporated into carbon aerogels (*Schüth, 2003*)
 - NH₃BH₃ dehydrogenation in porous silica (*Gutowska, 2005*)
 - NaAlH₄ supported on carbon nanofibers (*de Jong, 2006*)
 - Mg incorporated into porous carbon (*de Jong, 2006*)
 - NH₃BH₃ dehydrogenation in carbon cryogel (*Feaver, 2007*)
- **Our work:**
 - LiBH₄, MgH₂, and NaAlH₄ incorporated into carbon aerogels

LiBH₄@Carbon Aerogels

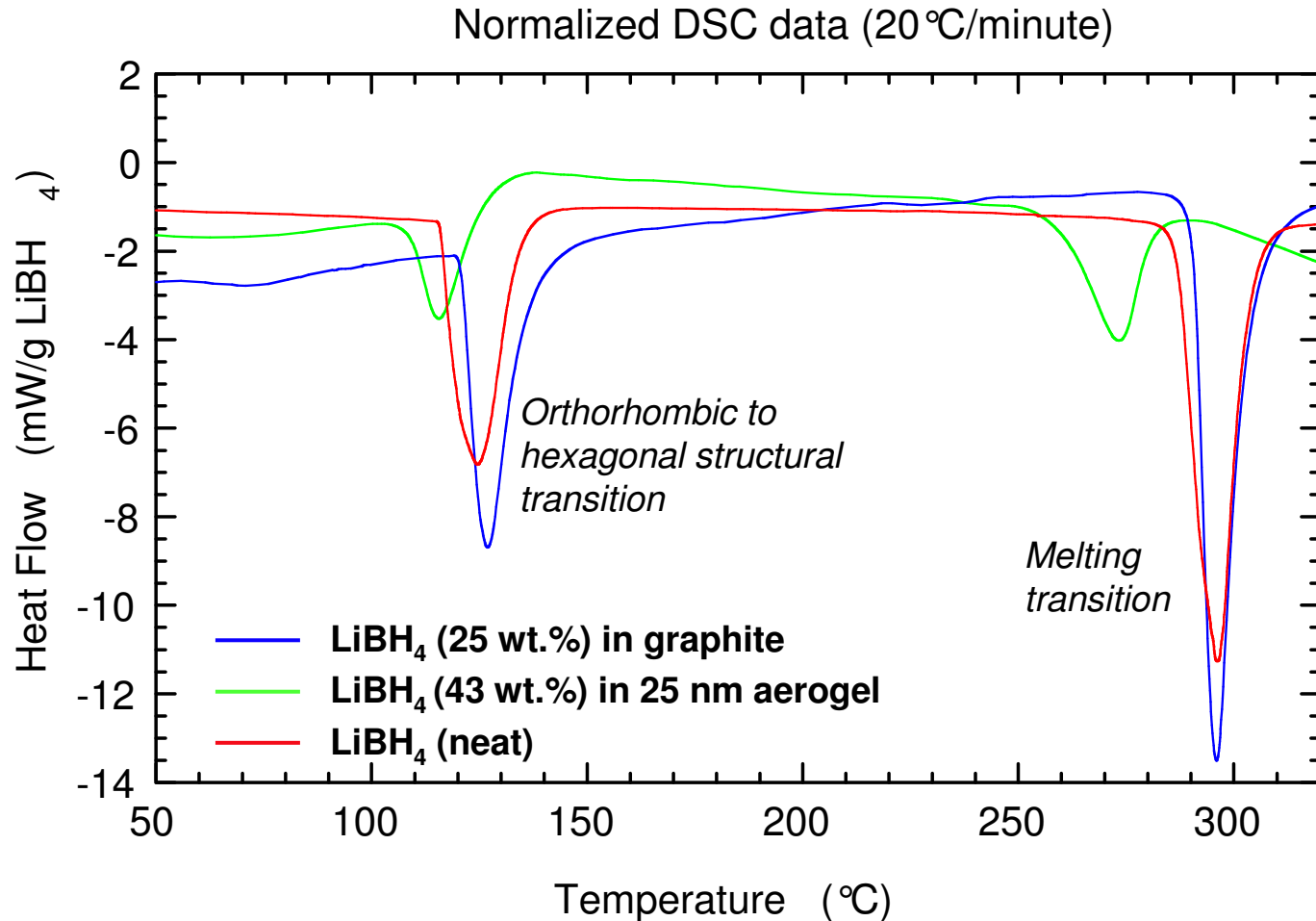
- HRL carbon aerogels:
 - 10 to 30 nm pores
 - 0.8 to 1.4 cm³/g pore volume
 - significant micropore fraction
- Loading with LiBH₄
 - 30 wt% (13 nm) to 50 wt% (25 nm)
 - 80 to 100 volume percent



Incorporate molten LiBH₄ into aerogel by “wicking” process

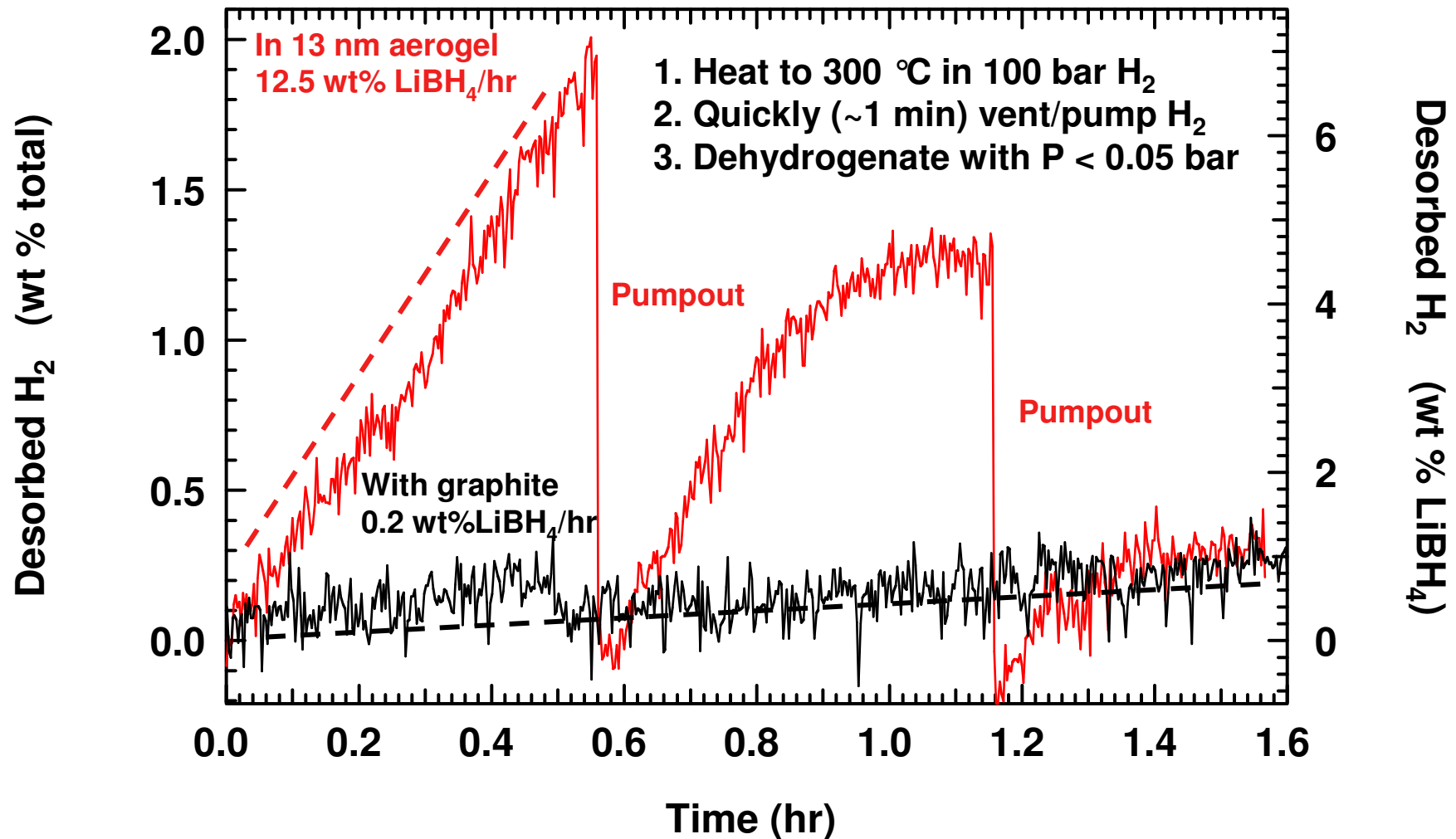


LiBH₄@Aerogel: Thermodynamic Changes



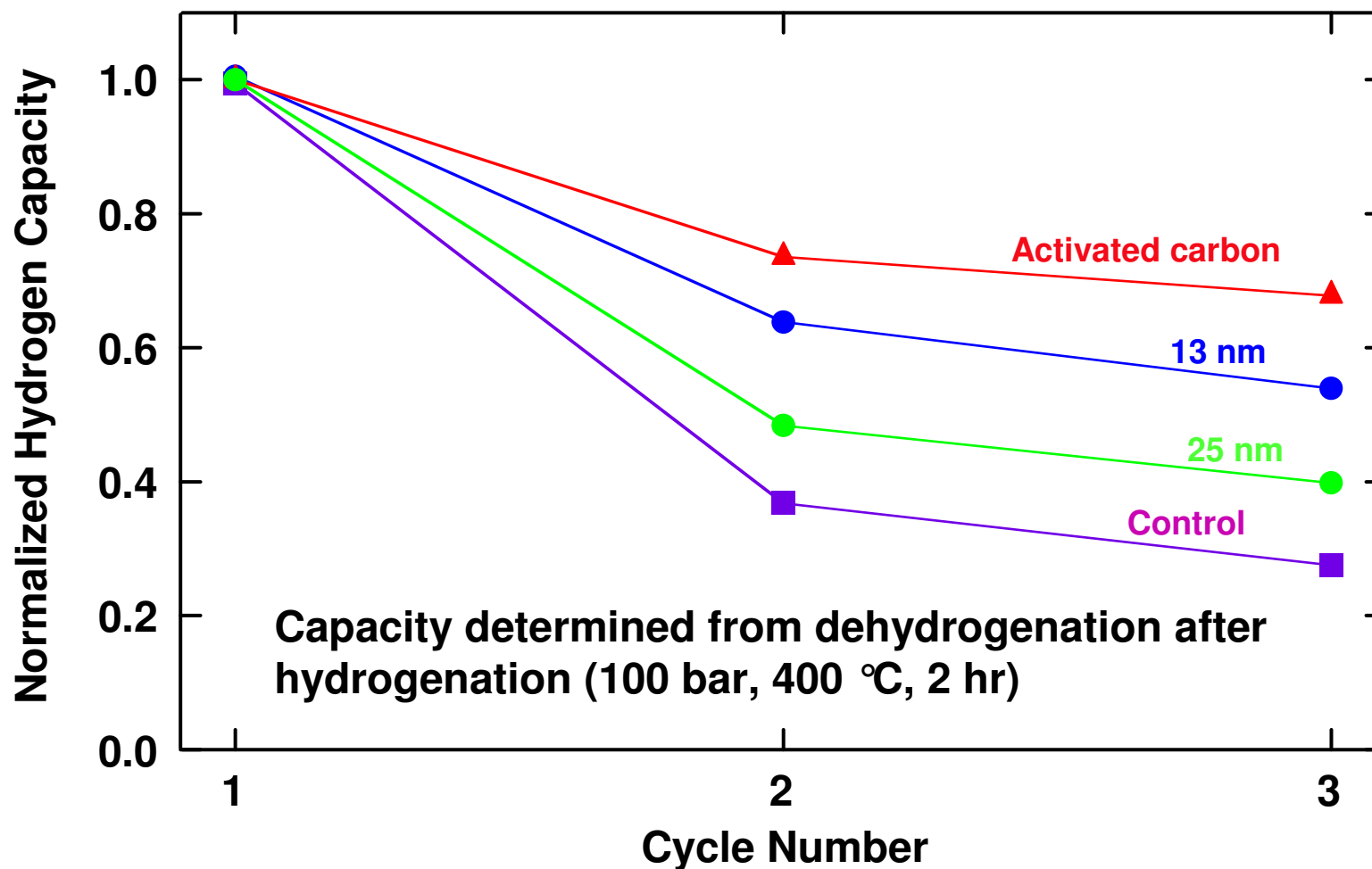
Significant reduction in transition temperatures and enthalpies
(well known for confined phases)

Dehydrogenation of LiBH₄@Carbon Aerogel



Rate for LiBH₄@ aerogel ~50x rate for LiBH₄/graphite control sample

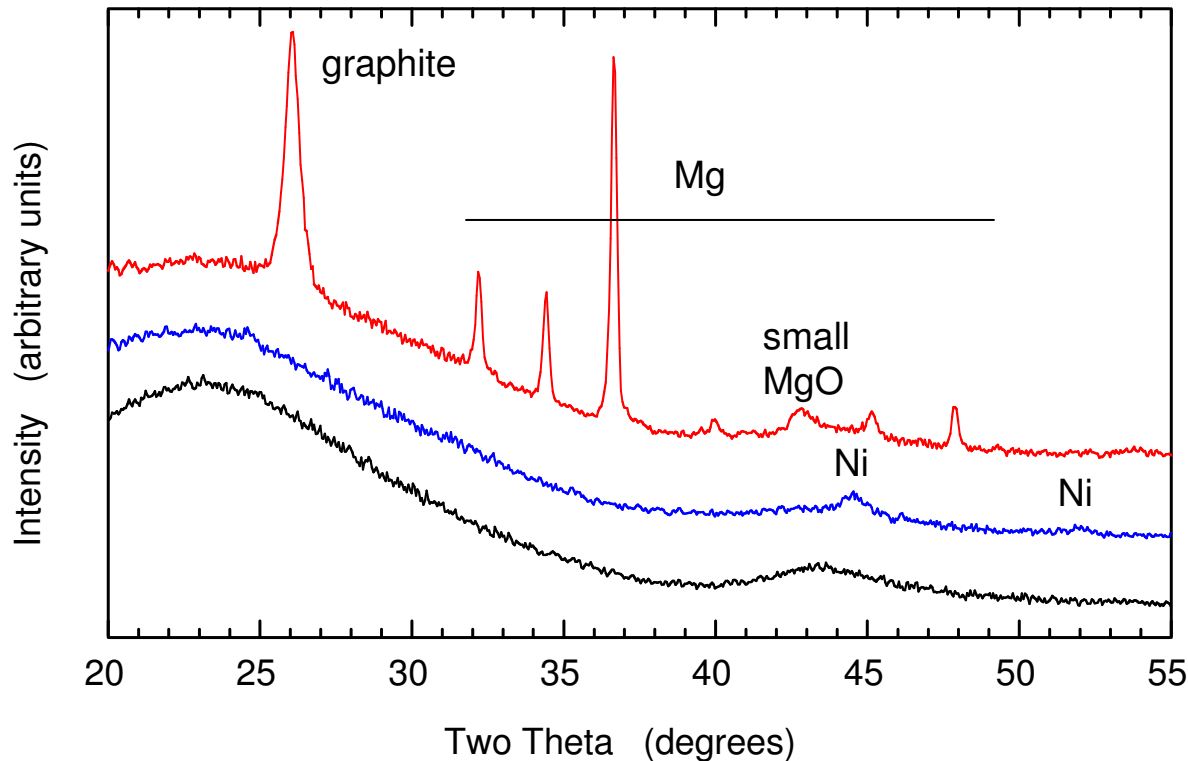
Reversibility of LiBH₄@Carbon Aerogel



- Reversibility still poor; however,
- Incorporation in aerogel improves reversible capacity

Incorporation of Mg into Carbon Aerogel

25 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

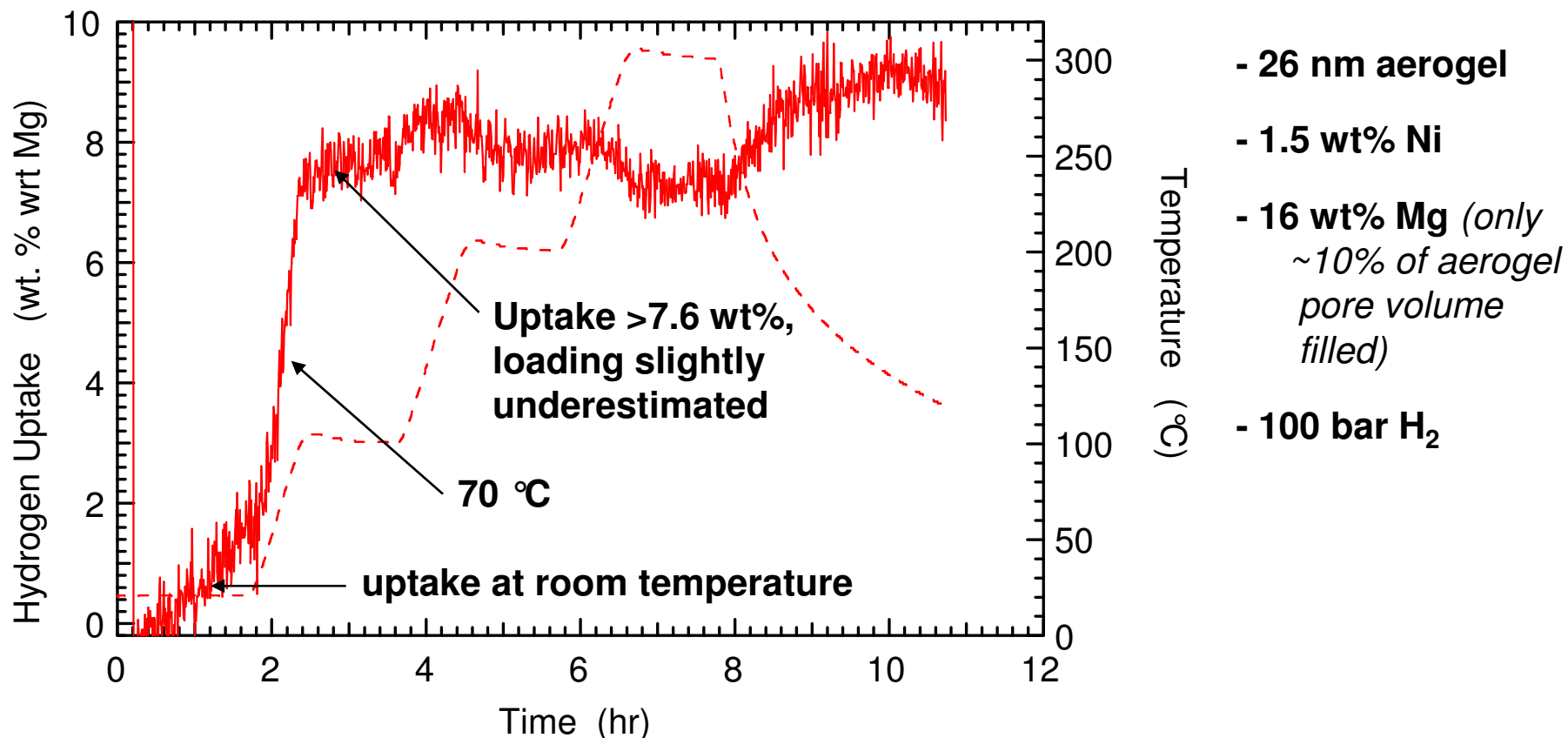
Ni + Mg (900 ° C, 60 hr)

Ni(NO₃)₂ (4%H₂, 500 ° C, 6 hr)

No Ni, Mg (900 ° C, 60 hr)

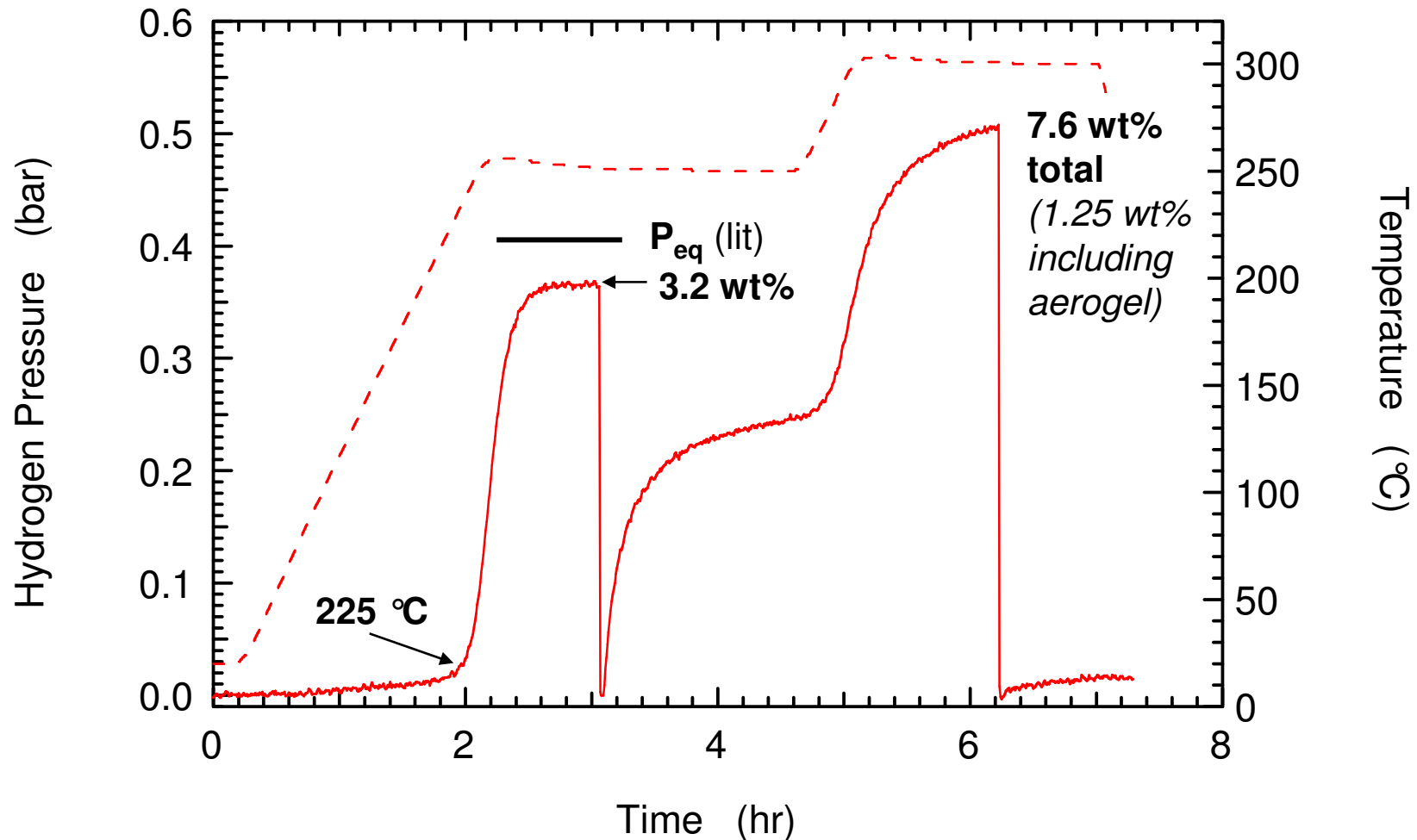
- Nickel “wetting layer” enables incorporation of Mg from melt
- Graphite peak indicates breakdown of aerogel structure

Hydrogenation of Mg@Carbon Aerogel



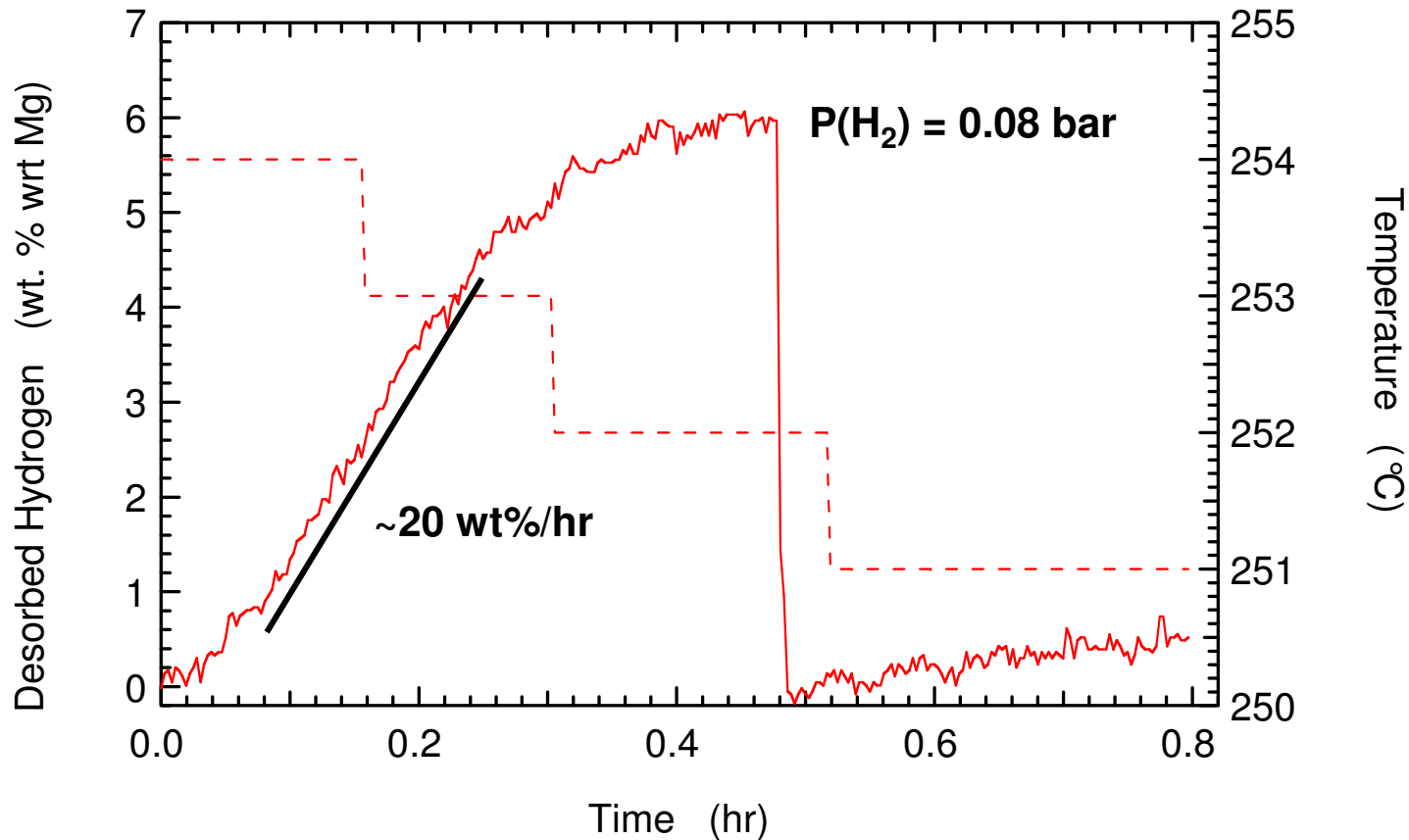
- Mg in aerogel can be fully hydrogenated
- Good hydrogenation kinetics on first cycle without activation
- No degradation on second cycle (*not shown*)

Dehydrogenation of Mg@Carbon Aerogel



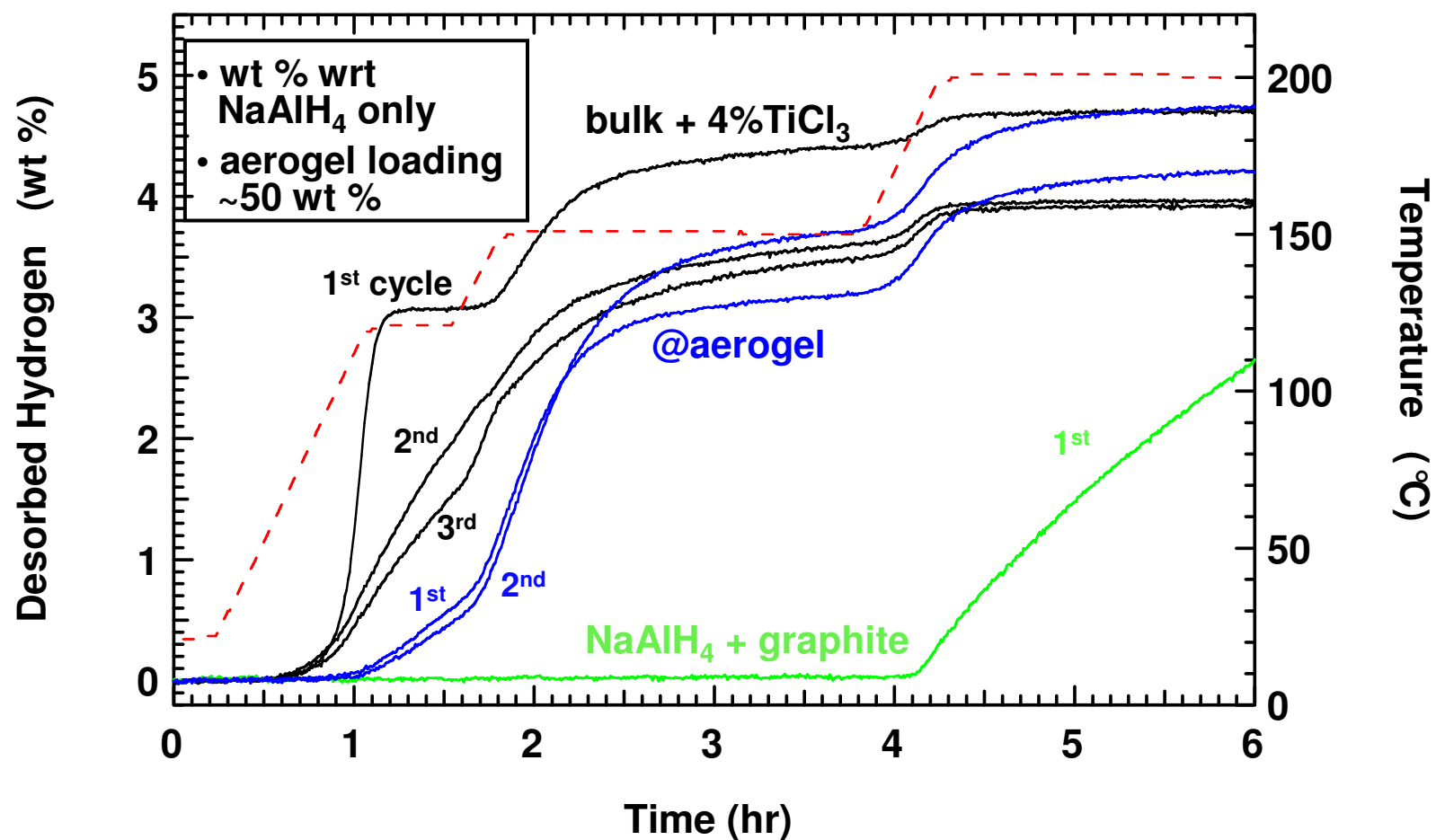
- MgH_2 in aerogel can be fully dehydrogenated
- $P_{eq}(250\text{ °C})$ equal to bulk value \Rightarrow no change in thermodynamics

Dehydrogenation of Mg@Carbon Aerogel



- Dehydrogenation rate at 250 °C comparable to rates in literature achieved by milling with catalysts (25 to 30 wt%/hr)

Dehydrogenation of NaAlH₄@Carbon Aerogel



- Aerogel enables cycling without catalyst

Summary & Outlook

- Formation of destabilized systems is an effective and versatile approach for addressing thermodynamics
 - $\text{LiBH}_4 + 0.5\text{MgH}_2$ can reversibly store ~ 10 wt% H_2 with T (1 bar) = ~ 225 °C
- Nanoporous scaffolds (carbon aerogels) enhance hydrogen storage kinetics
 - LiBH_4 : 12 wt%/hr dehydrogenation at 300 °C, *50x control sample*
improve reversibility from 37% to 73% (2nd cycle)
 - MgH_2 : 20 wt%/hr dehydrogenation at 250 °C, *similar to best milled samples*
 - NaAlH_4 : dehydrogenation at 120 °C, *similar to catalyzed sample*
improve reversibility from 0% to $\sim 90\%$ (2nd cycle)
- **Mechanisms** (*nanoscale dimensions, stress, surface/interface effects*) **unknown**
- **Parameters** (*scaffold material, pore size/distribution, surface chemistry*) **unexplored**

Acknowledgements

Collaborators

Channing Ahn (Caltech)

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DOE Metal Hydride Center of Excellence

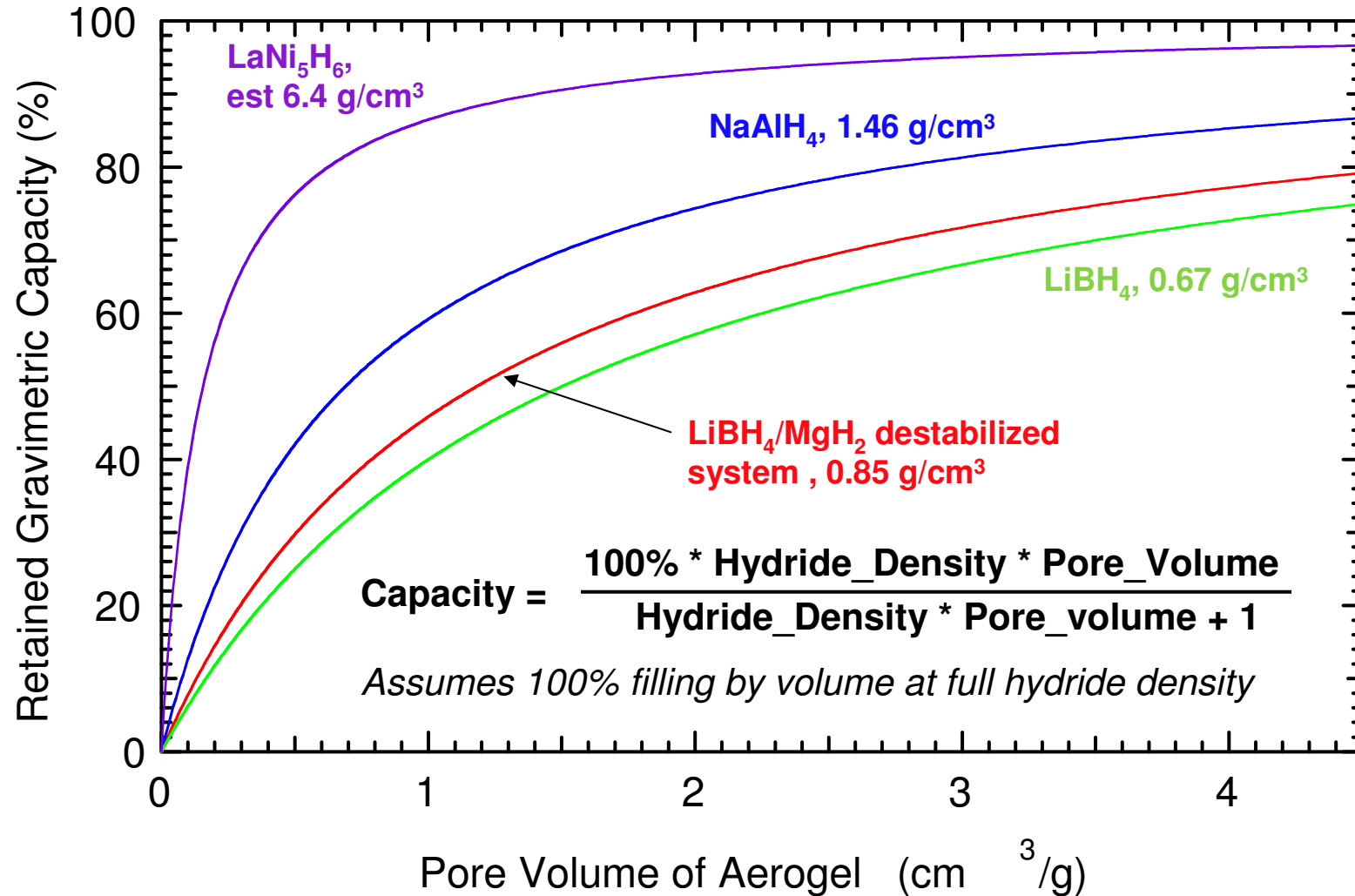
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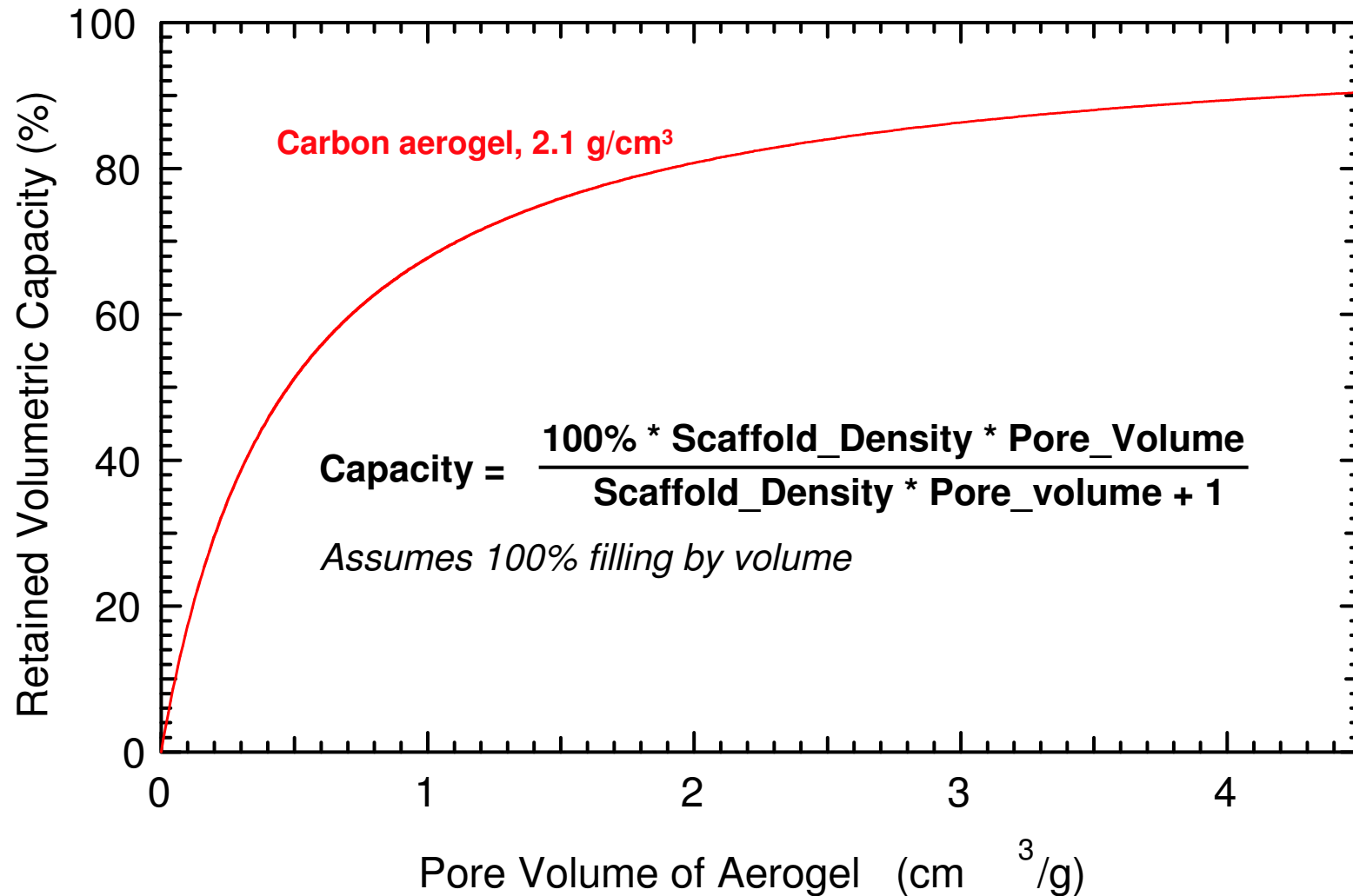
Back up slides

Retained Gravimetric Capacity with Scaffold



- Denser hydrides increase retained gravimetric capacity

Retained Volumetric Capacity with Scaffold



- Retained volumetric capacity depends on scaffold density