

R&D – 10971

HYDRIDE CHEMISTRY IN NANOPOROUS SCAFFOLDS

J. VAJO
A. GROSS
HRL Laboratories, LLC

R. STEPHENS
Chemical & Environmental Sciences Lab

T. SALGUERO
S. VAN ATTA
P. LIU
HRL Laboratories, LLC



PUBLICATION

GM RESEARCH & DEVELOPMENT CENTER

17 SEPTEMBER 2007

Hydride Chemistry in Nanoporous Scaffolds

J. Vajo
A. Gross
HRL Laboratories, LLC

R. Stephens
Chemical & Environmental Sciences Lab

T. Salguero
S. Van Atta
P. Liu,
HRL Laboratories, LLC

Synopsis or Abbreviated Abstract

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

Hydride Chemistry in Nanoporous Scaffolds

John J. Vajo*, Adam F. Gross*

Robert D. Stephens**

Tina T. Salguero*, Sky L. Van Atta*, Ping Liu*

* HRL Laboratories, LLC

** General Motors Research and Development Center

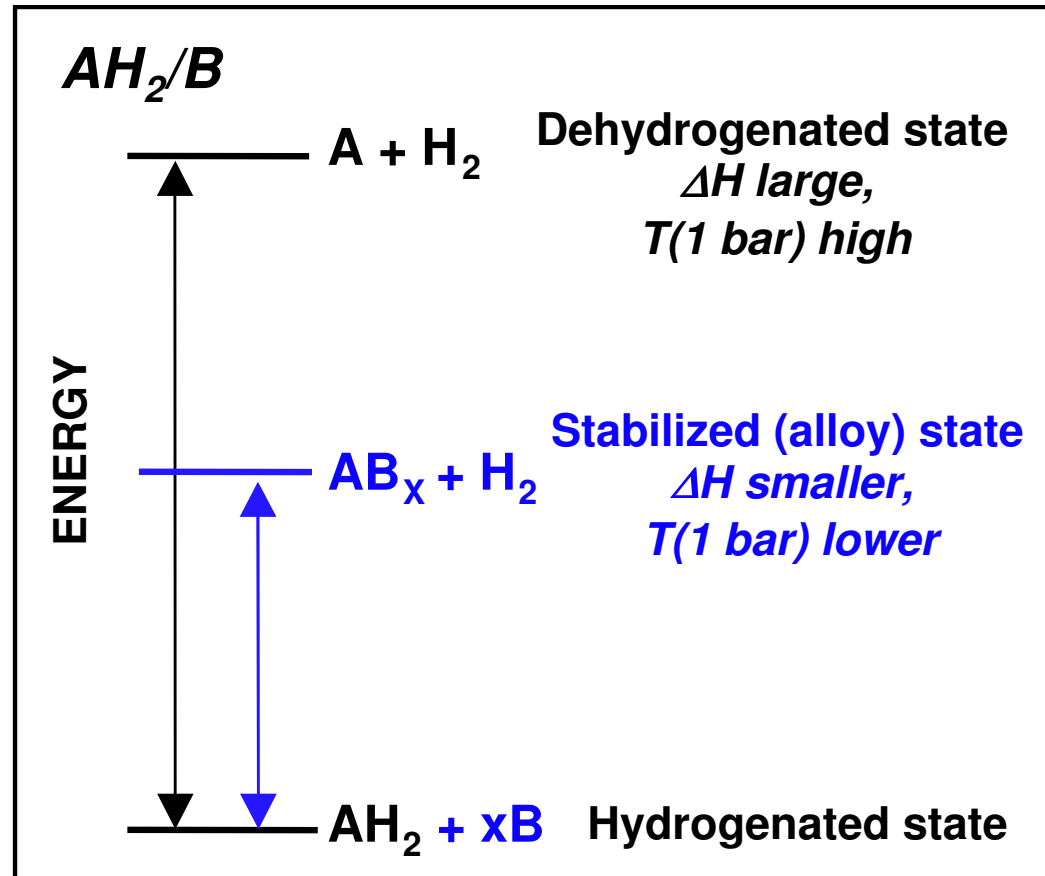
November 2007

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**)

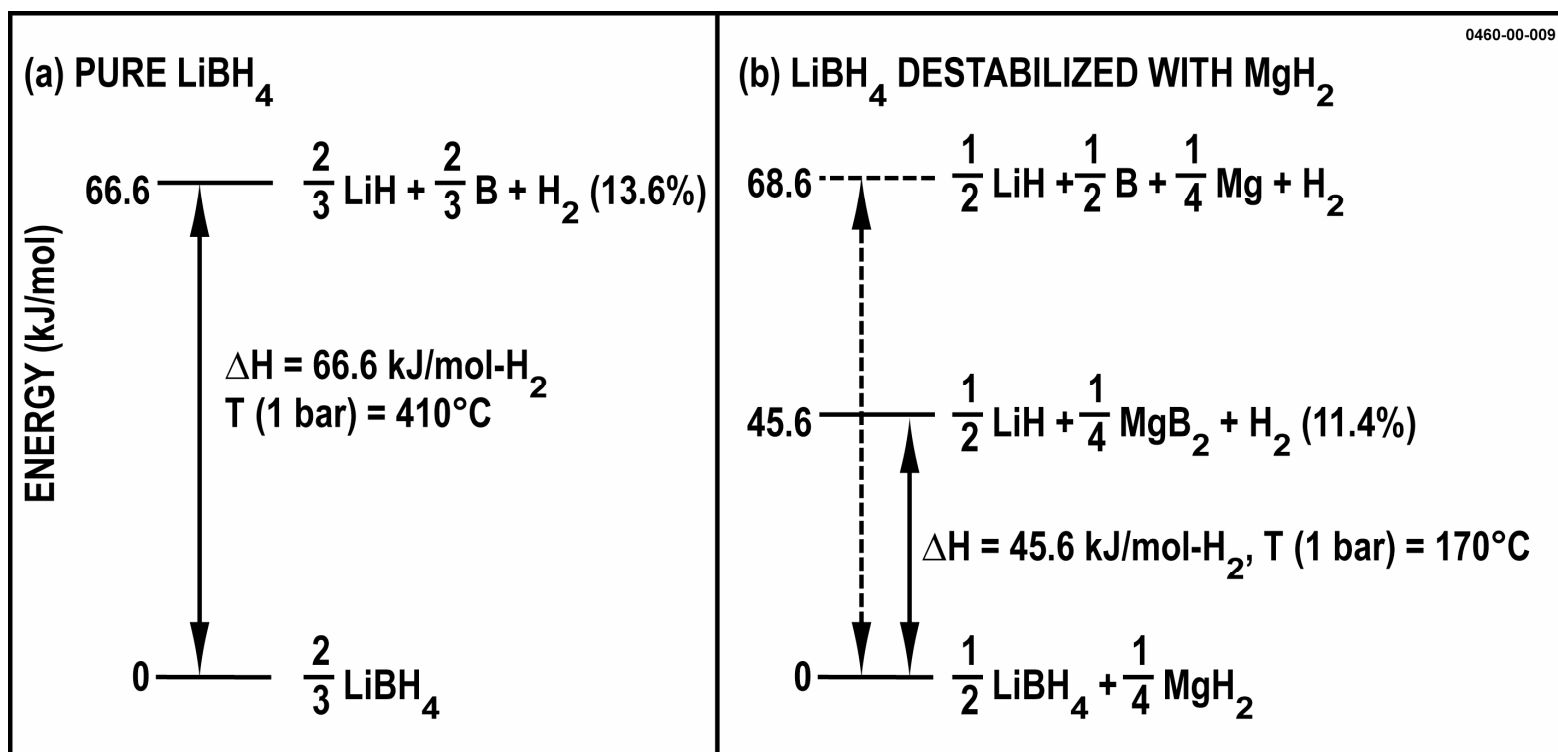
Destabilized Systems: General Approach*



- Additive stabilizes dehydrogenated state, forming destabilized system

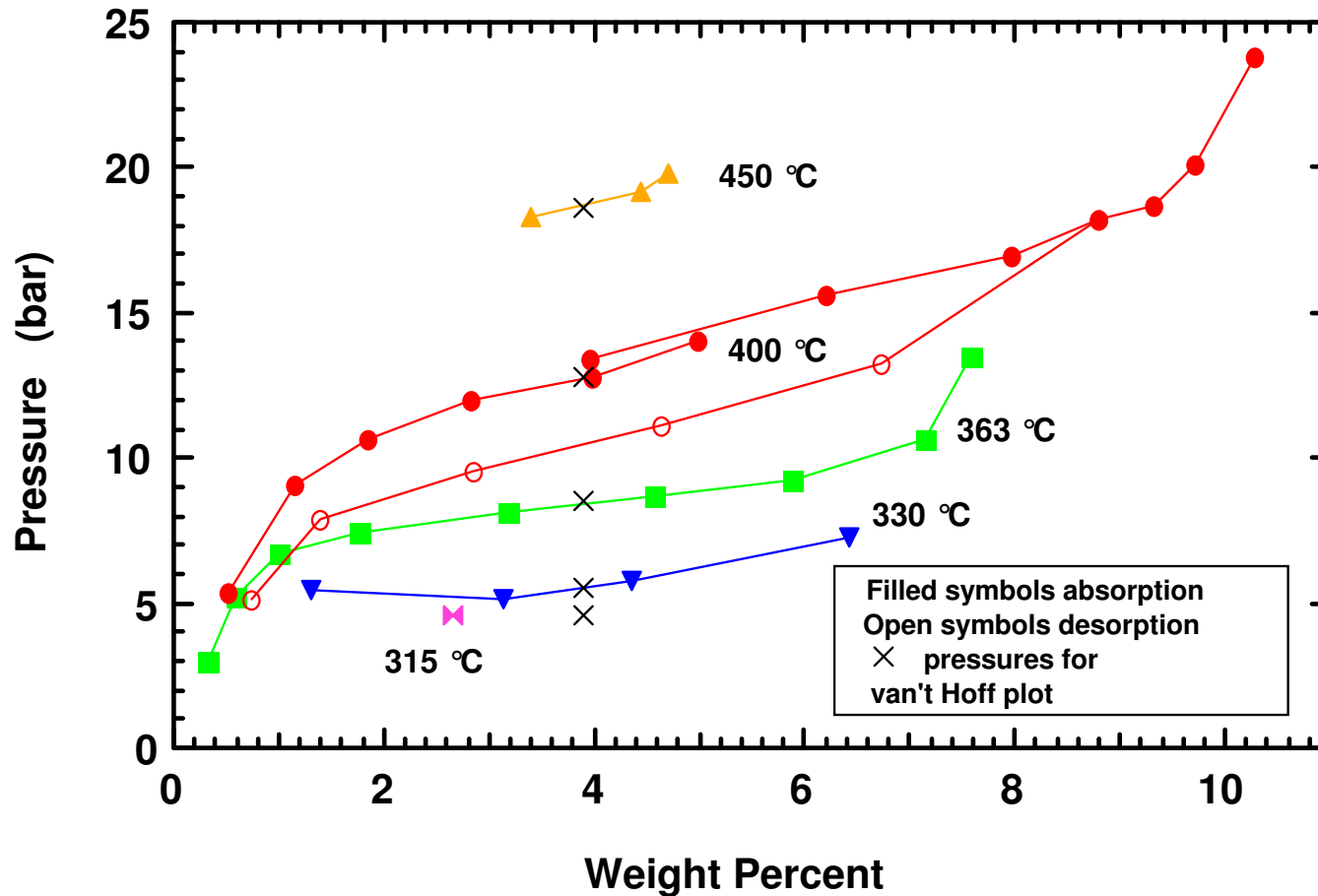
* Extends work on MgH_2/Cu (Reilly, 1967) to light/complex hydrides; recent computations propose >300 systems (Alapati et al, 2006)

LiBH₄/MgH₂ Destabilized Hydride System



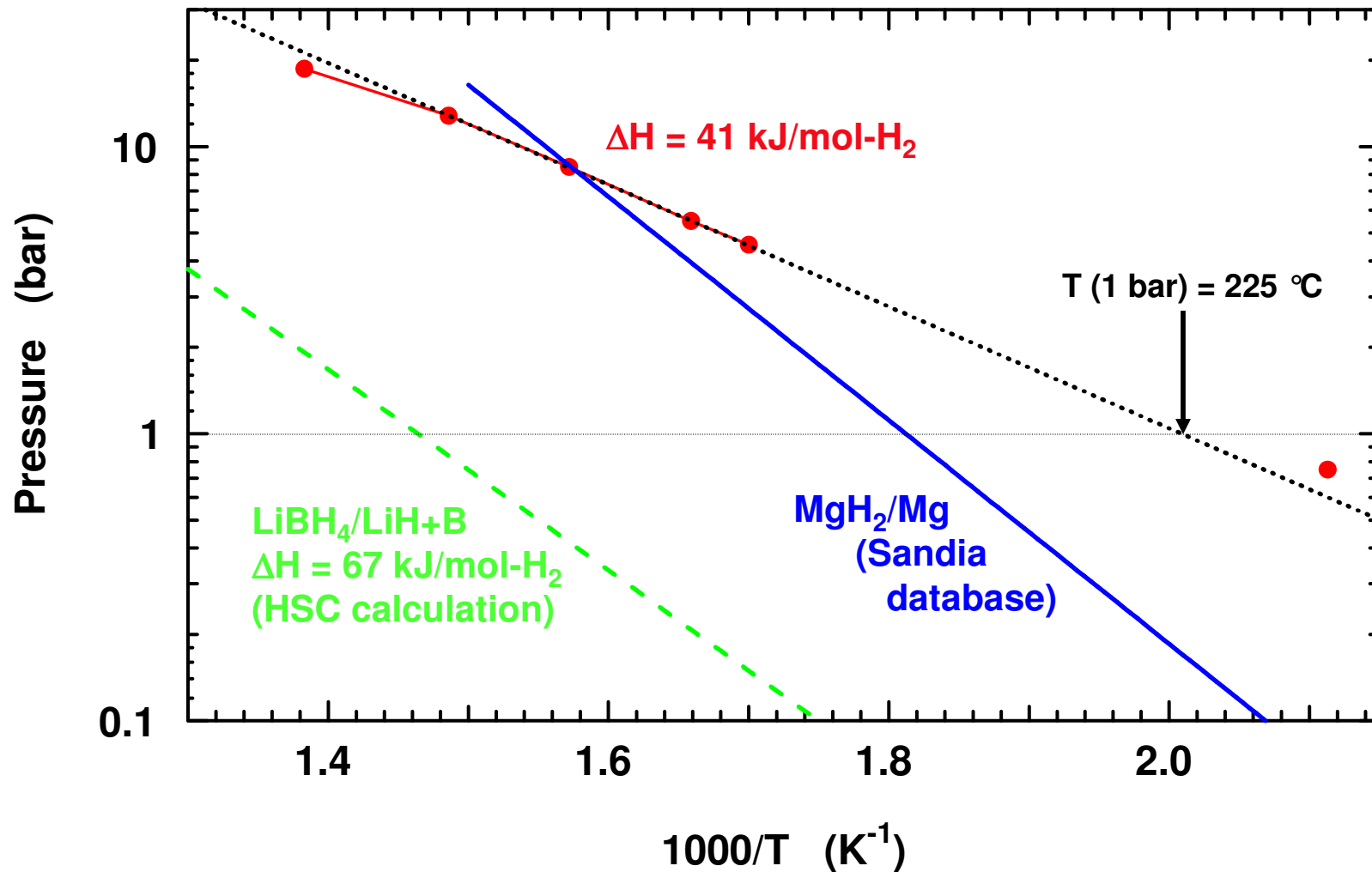
Formation of MgB₂ estimated to reduce T(1 bar) by ~ 240 °C

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



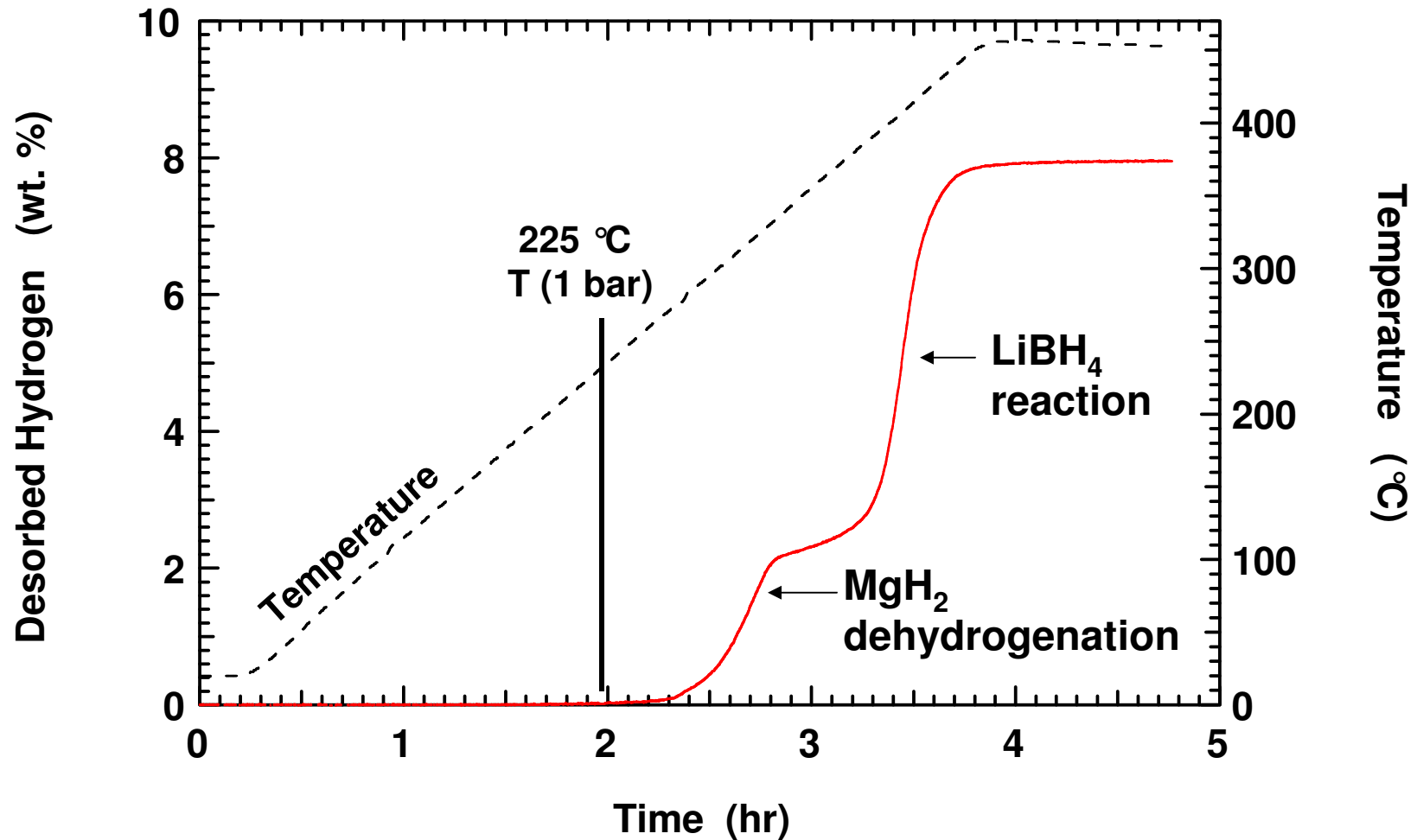
- XRD measurements confirm reaction scheme
- Sloping plateaus with capacities of 8 to 10 wt %
- Kinetics slow for $T < 350$ °C

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

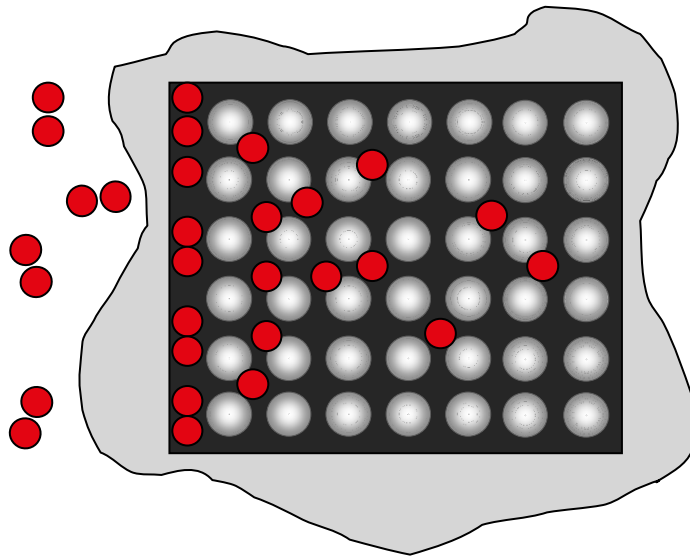


- MgH_2 and LiBH_4 reactions are not concerted
- Reaction temperatures \gg thermodynamic limit

Improve Kinetics using Nanoengineering

Enhance reaction rates by decreasing particle size

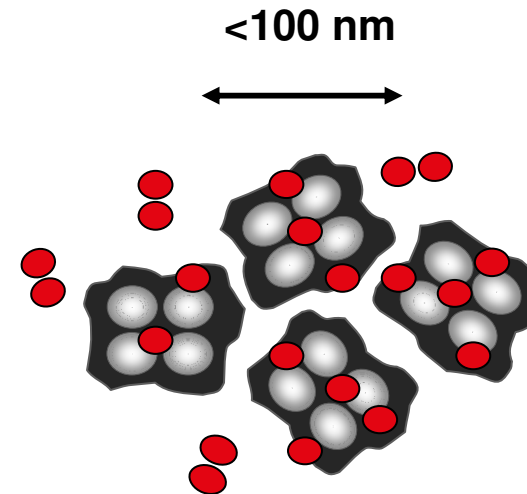
Bulk Hydride



Long H-diffusion distances in bulk material:

⇒ *slow*
hydrogen exchange rate

Nanoscale Hydride



Short H-diffusion distances in nanoparticles:

⇒ *fast*
hydrogen exchange rate

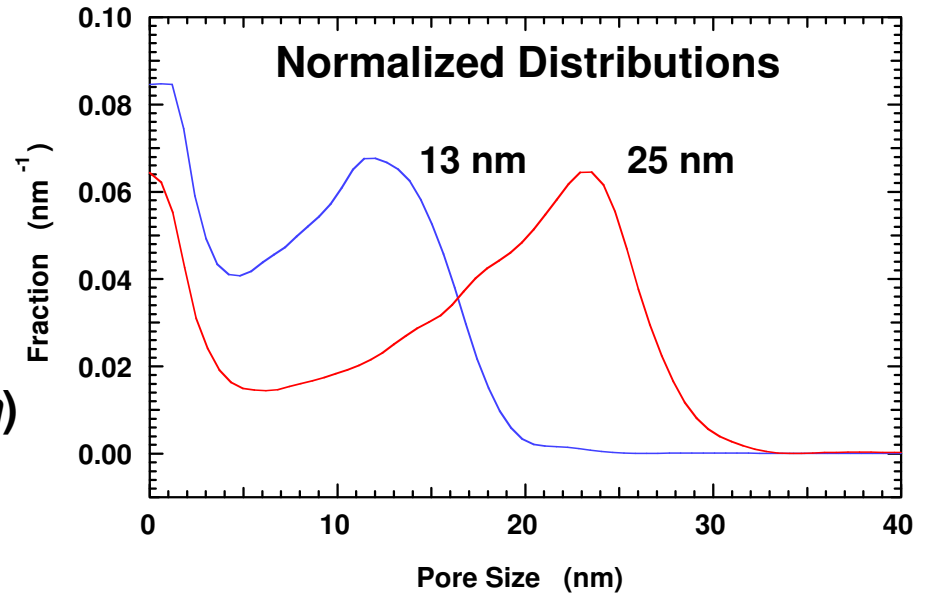
$$\tau \propto Dt/l^2$$

Porous Scaffolds for Nanoscale Hydrides

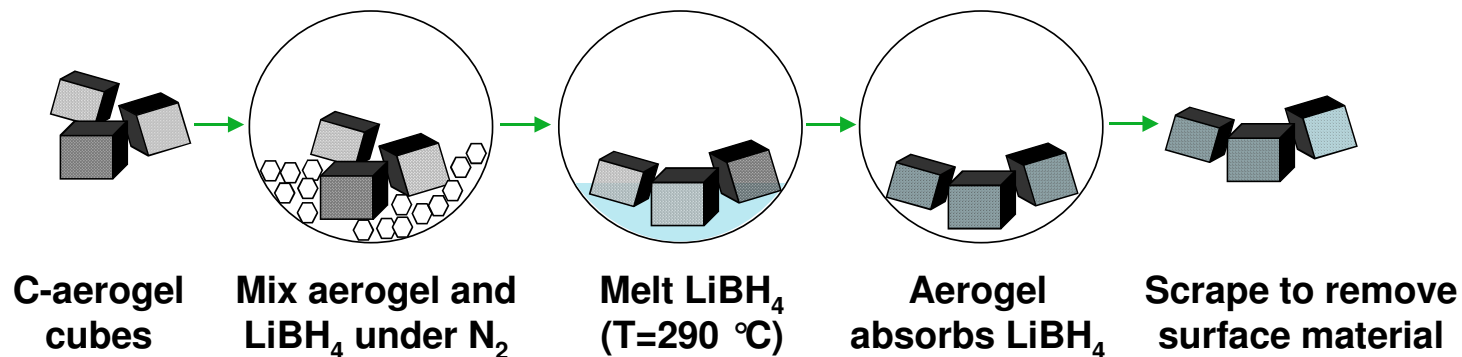
- **Interpenetrating network of pores**
 - wide range of pore sizes (*~1 to 50 nm*) and distributions
 - many scaffold materials (*C, SiO₂, Al₂O₃*) and surface chemistries
- **Scaffold serves as structure-directing agent for nanoscale hydride**
- **Hydride phase confined by pores** (*mitigates sintering 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

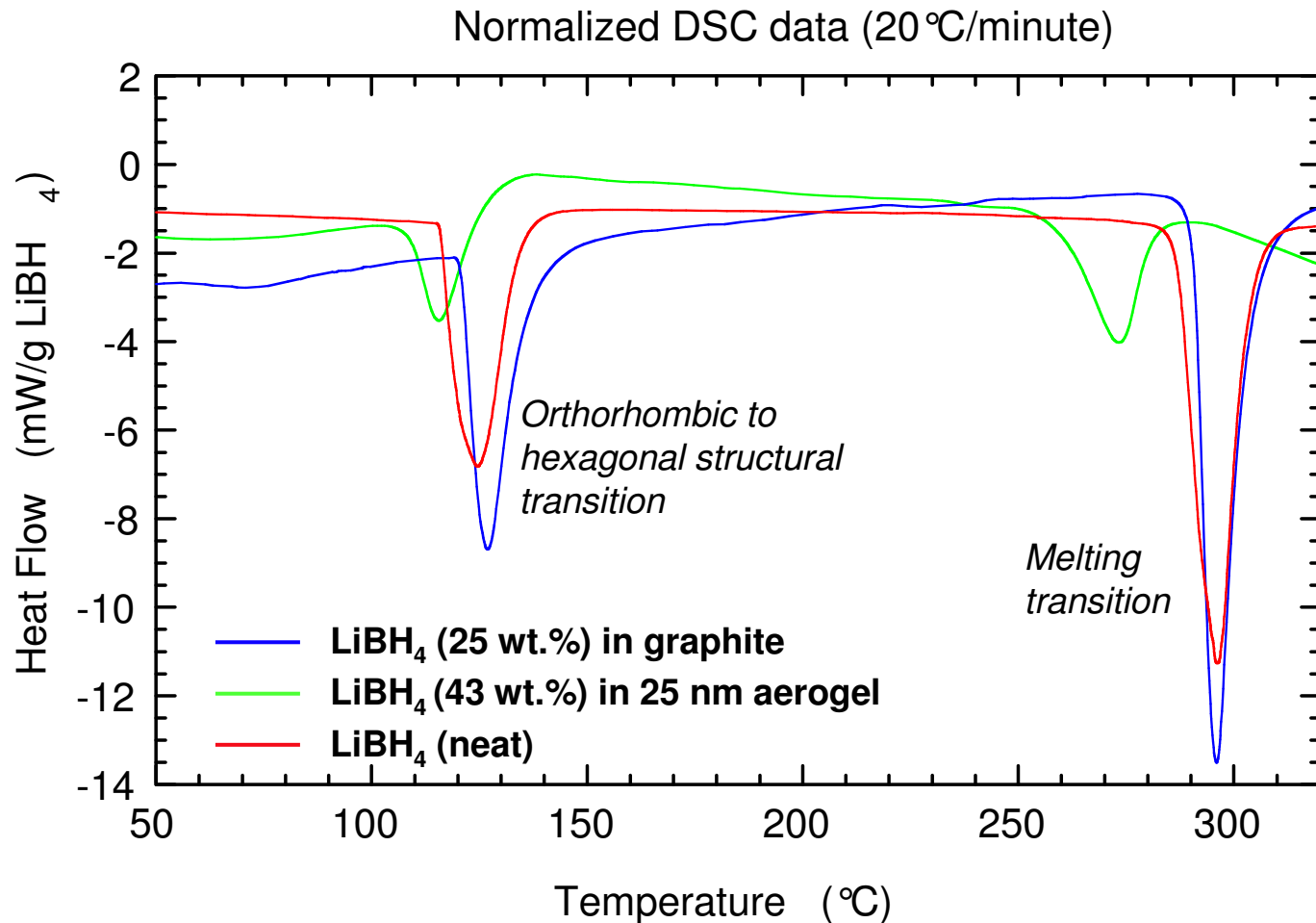
- HRL carbon aerogels:
 - 10 to 30 nm pores
 - 0.8 to 1.4 cm³/g pore volume
 - significant micropore fraction
- Loading with LiBH₄
 - 30 wt% (13 nm) to 50 wt% (25 nm)
 - 80 to 100 volume percent



Incorporate molten LiBH₄ into aerogel by “wicking” process

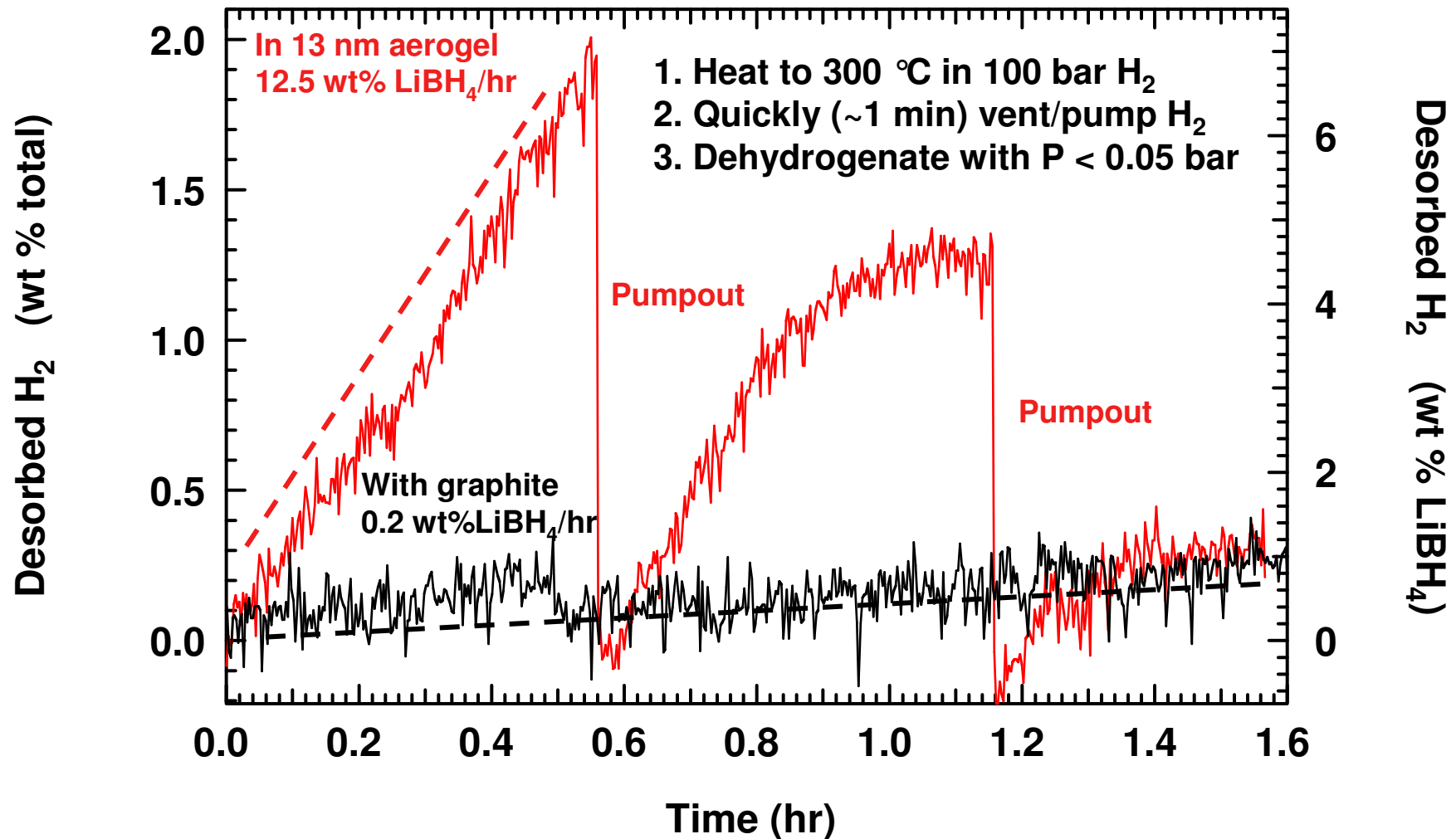


LiBH₄@Aerogel: Thermodynamic Changes



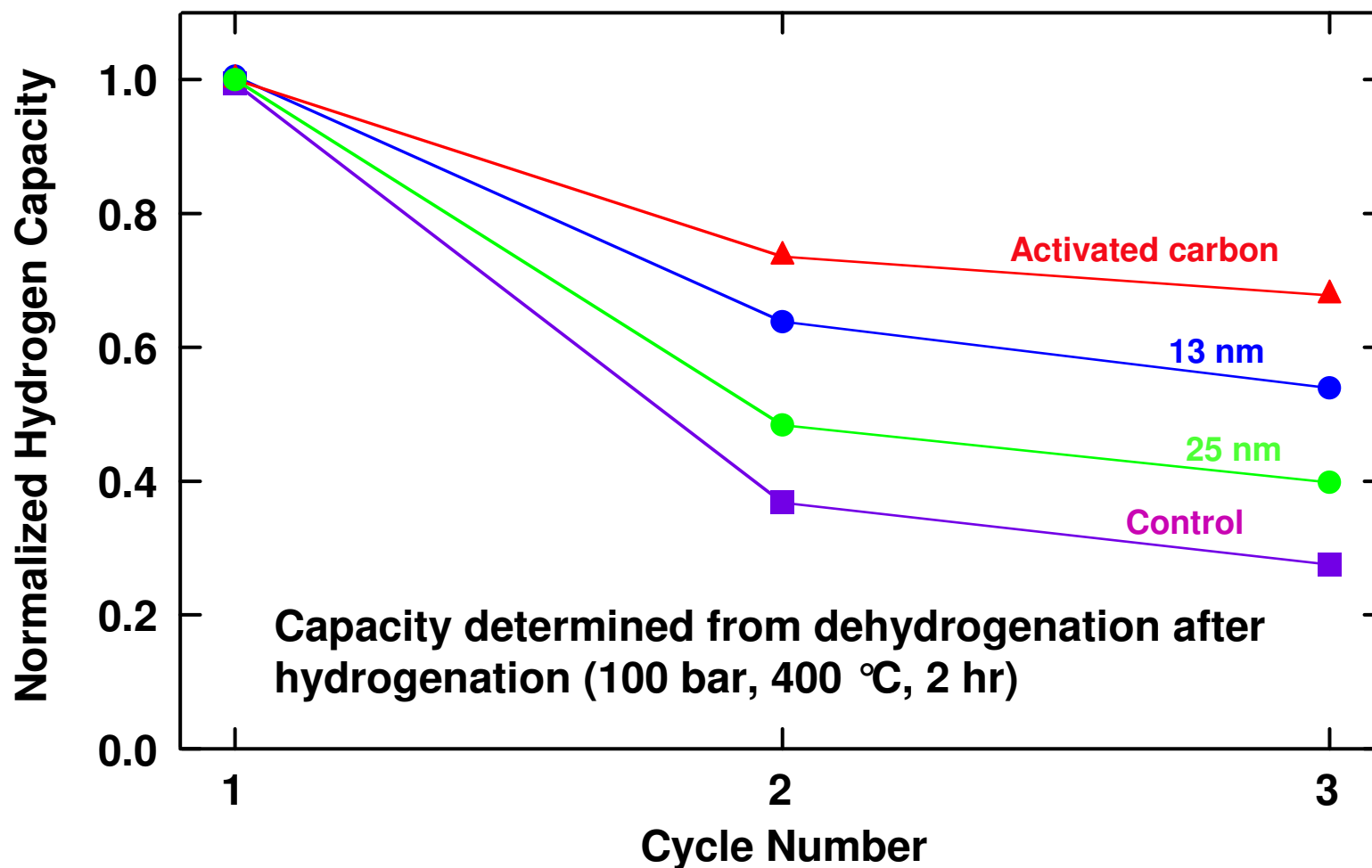
Significant reduction in transition temperatures and enthalpies
(well known for confined phases)

Dehydrogenation of LiBH₄@Carbon Aerogel



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

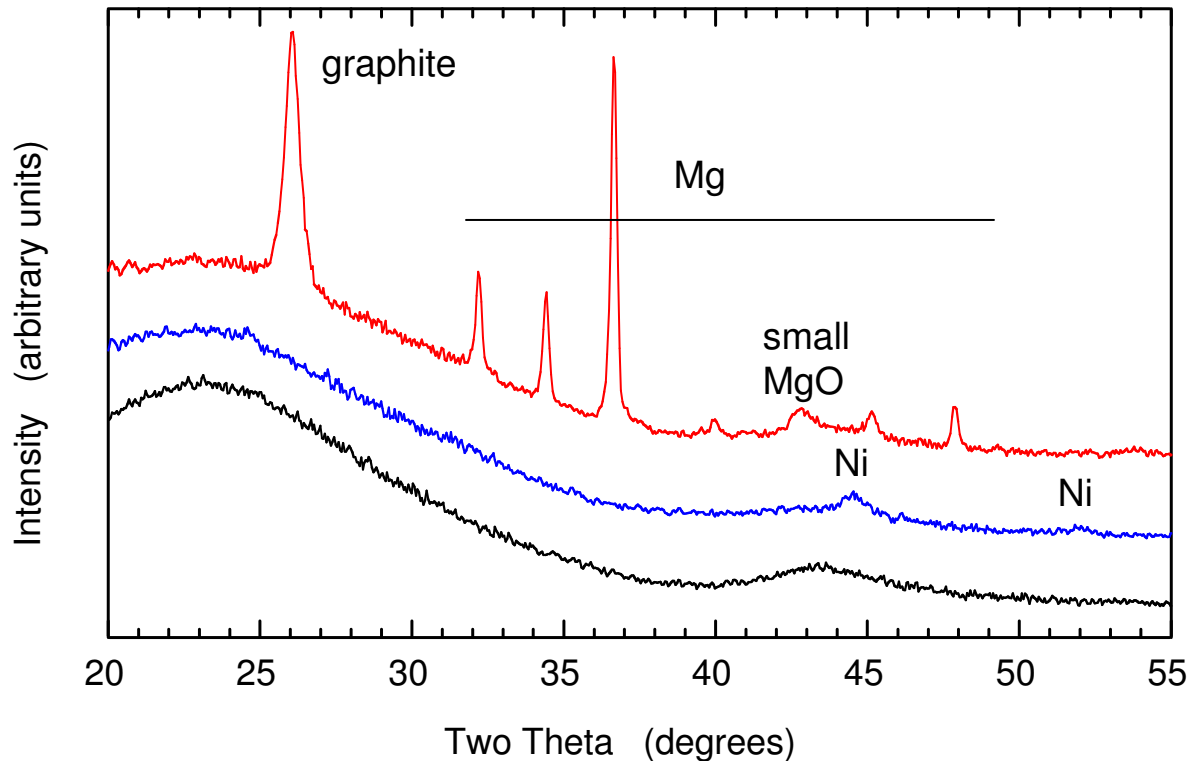
Reversibility of LiBH₄@Carbon Aerogel



- 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

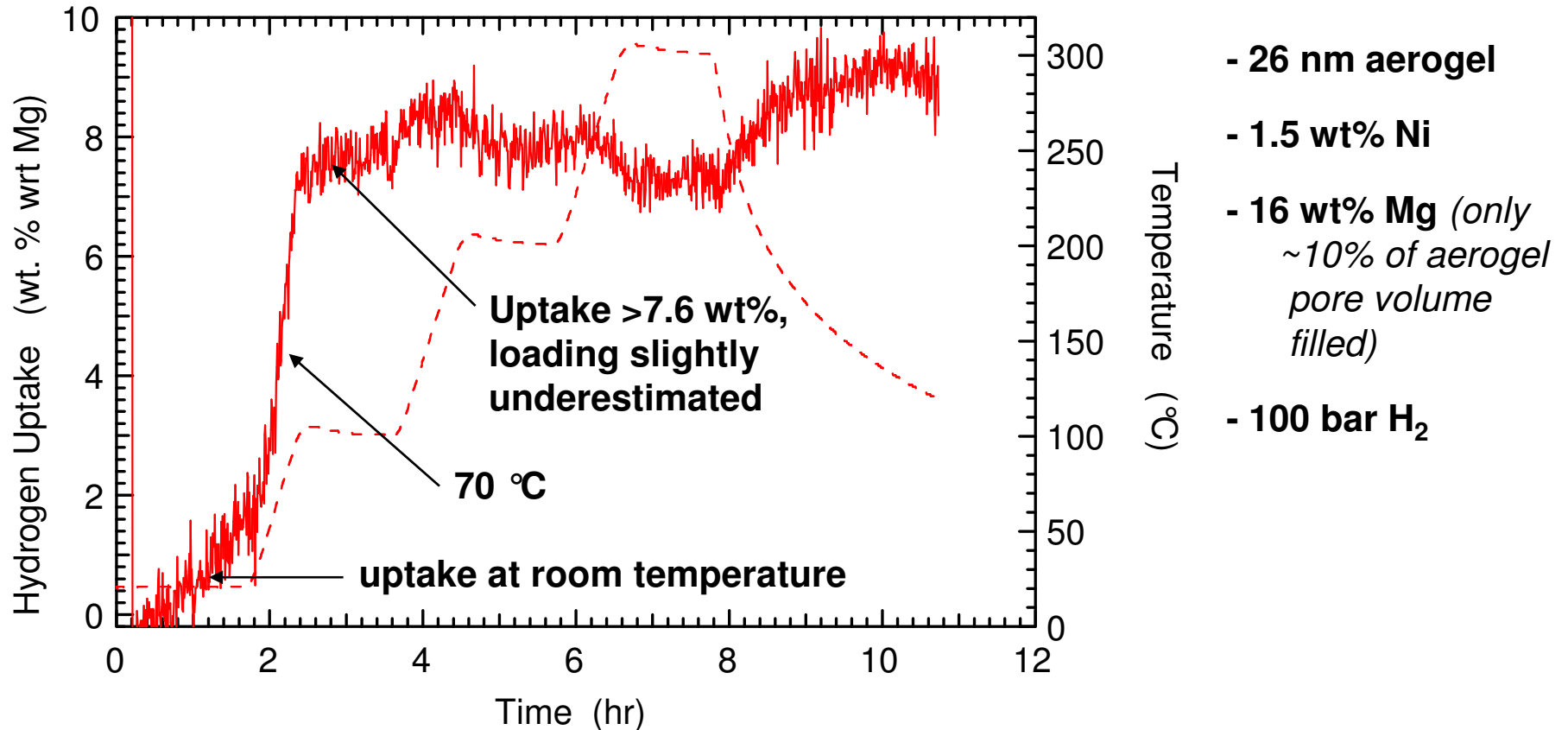
Ni + Mg (900 ° C, 60 hr)

Ni(NO₃)₂ (4%H₂, 500 ° C, 6 hr)

No Ni, Mg (900 ° C, 60 hr)

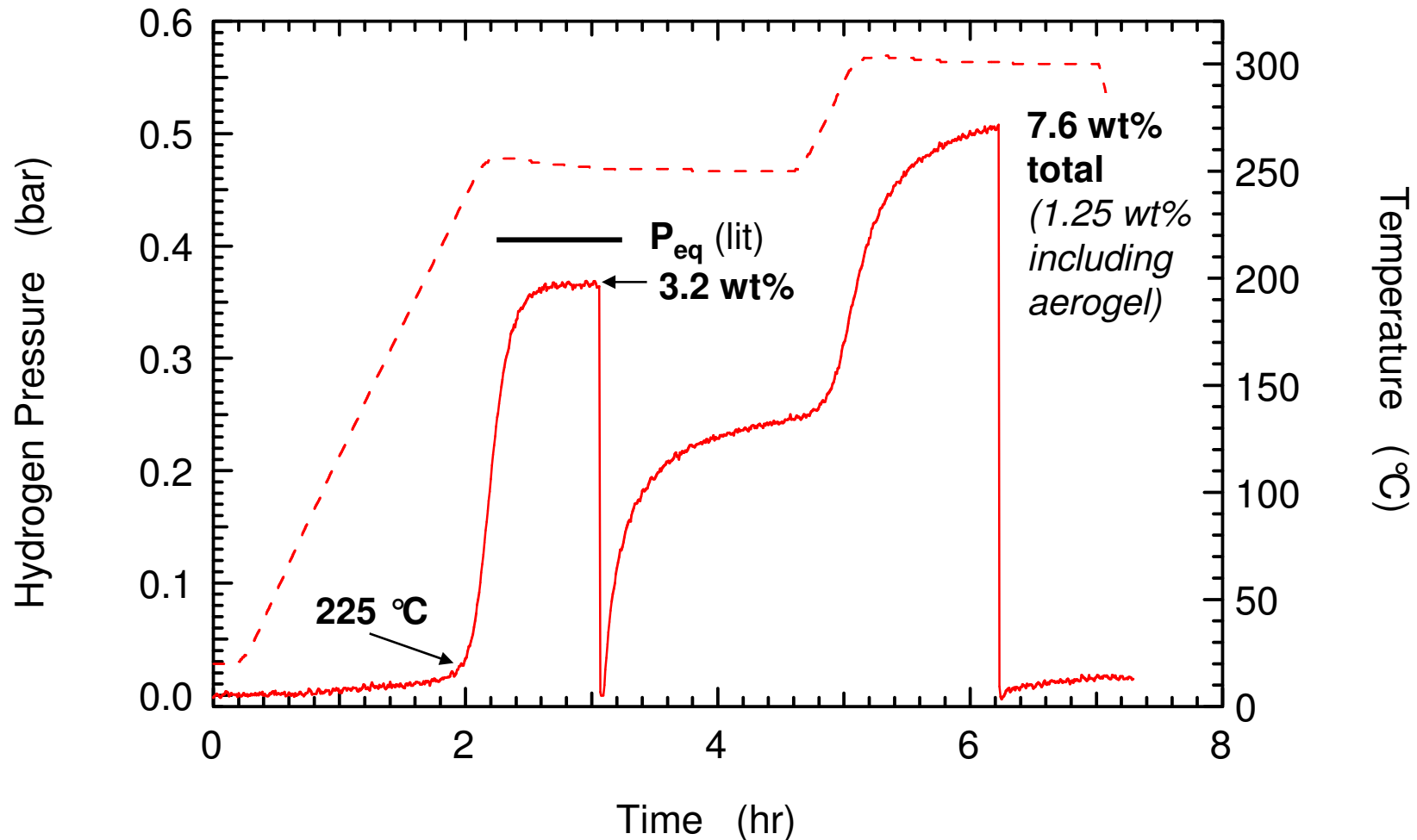
- Nickel “wetting layer” enables incorporation of Mg from melt
- Graphite peak indicates breakdown of aerogel structure

Hydrogenation of Mg@Carbon Aerogel



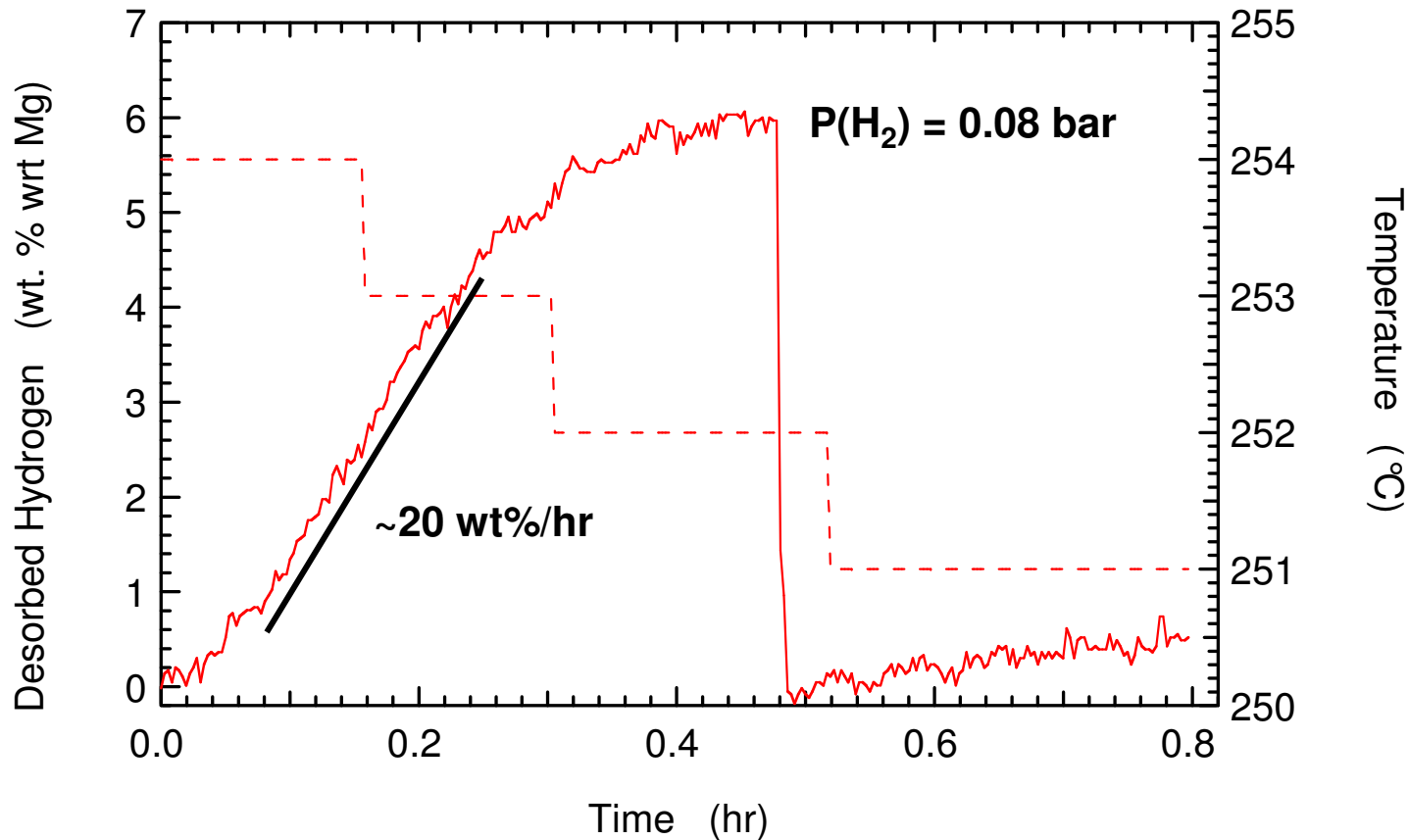
- Mg in aerogel can be fully hydrogenated
- Good hydrogenation kinetics on first cycle without activation
- No degradation on second cycle (*not shown*)

Dehydrogenation of Mg@Carbon Aerogel



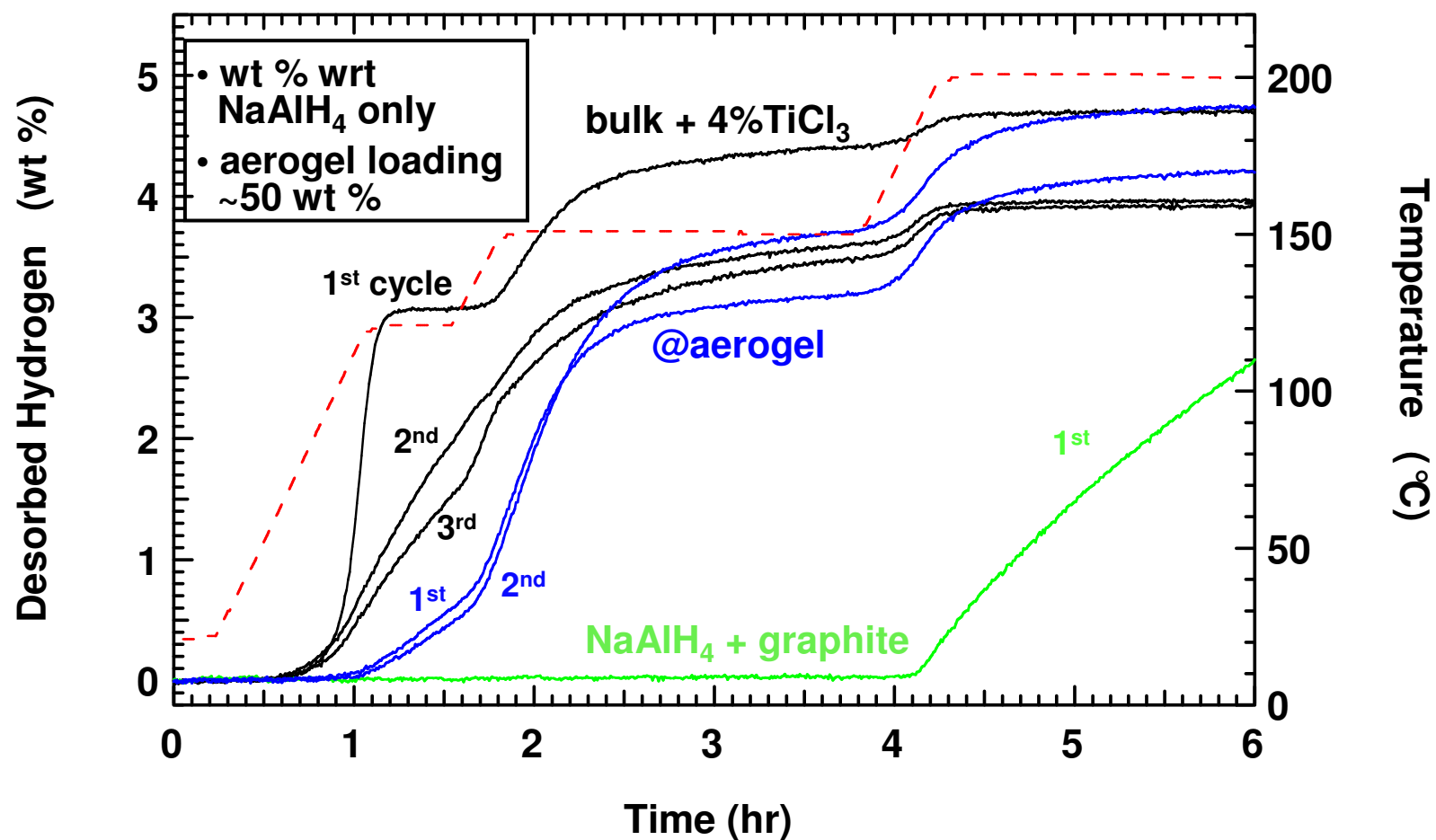
- MgH_2 in aerogel can be fully dehydrogenated
- $P_{eq}(250\text{ °C})$ equal to bulk value \Rightarrow no change in thermodynamics

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)

Robert Bowman Jr. (JPL)

DOE Metal Hydride Center of Excellence

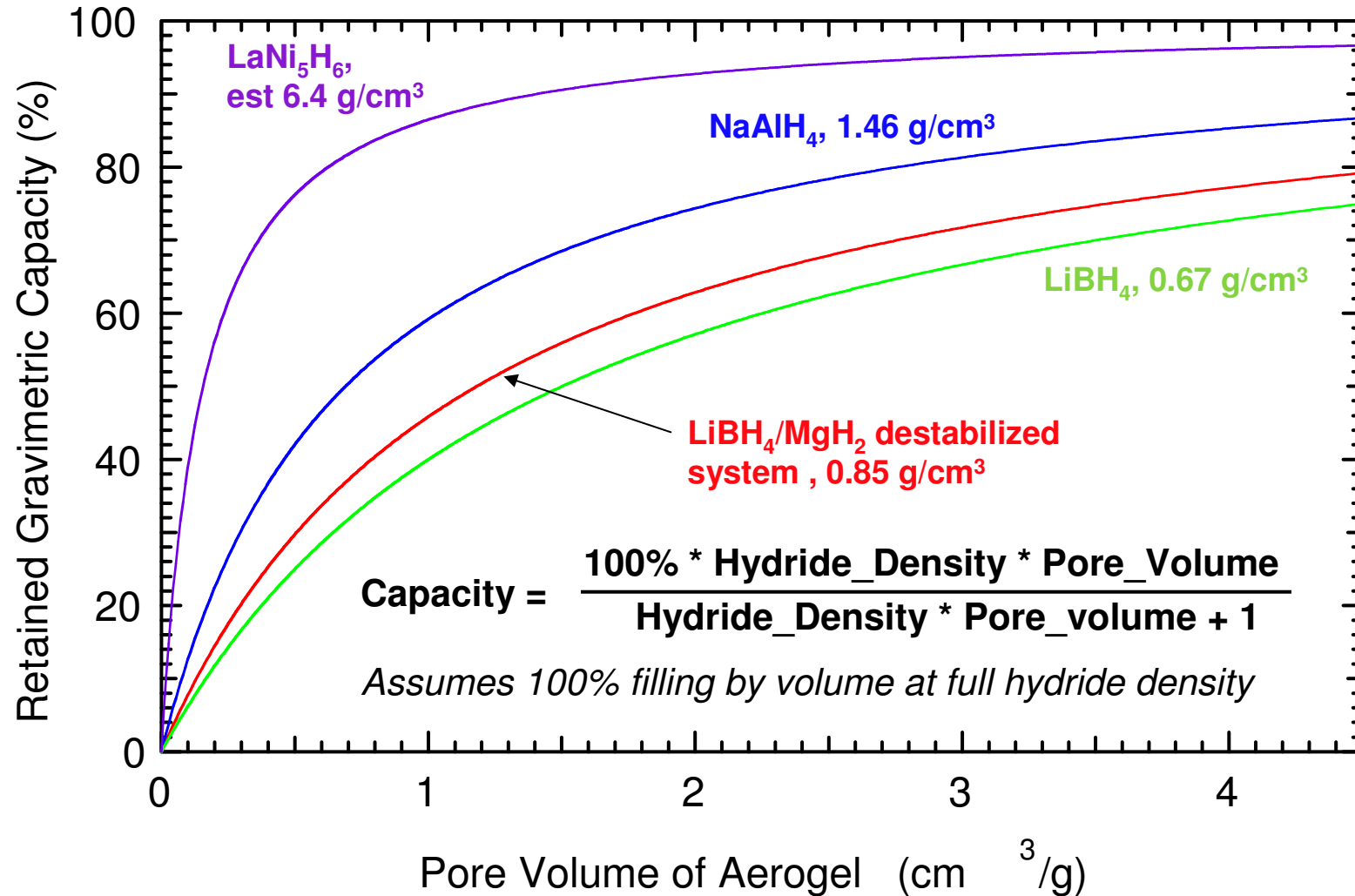
Funding

General Motors Corporation

United States Department of Energy

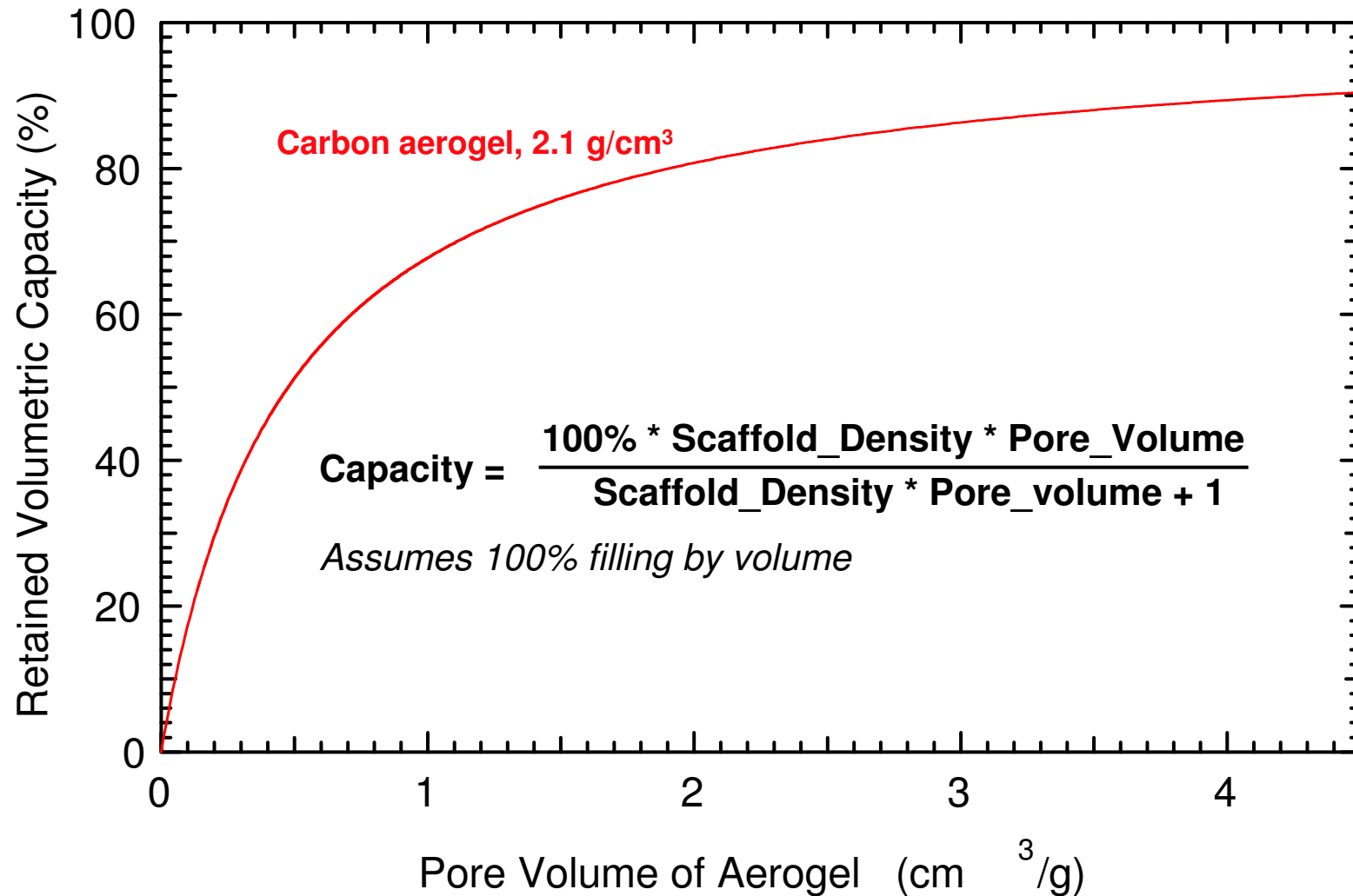
Back up slides

Retained Gravimetric Capacity with Scaffold



- Denser hydrides increase retained gravimetric capacity

Retained Volumetric Capacity with Scaffold



- Retained volumetric capacity depends on scaffold density