Hydrogen Storage

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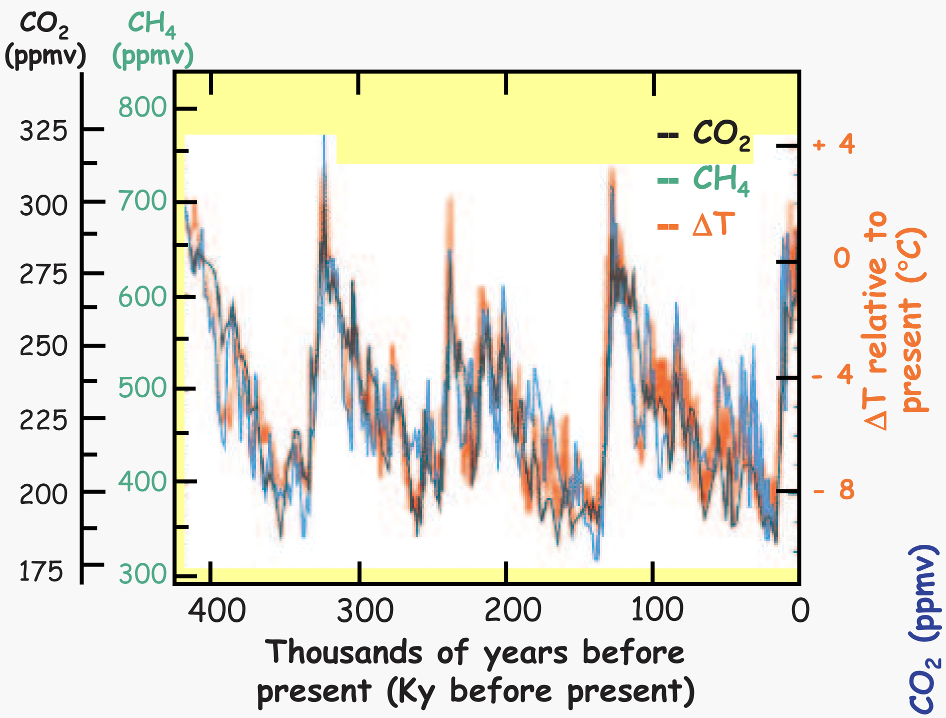
Outline

- Why hydrogen economy?
- Hydrogen storage requirements/challenges
- Ways to store hydrogen
- Nanoscale effects on hydrogen storage

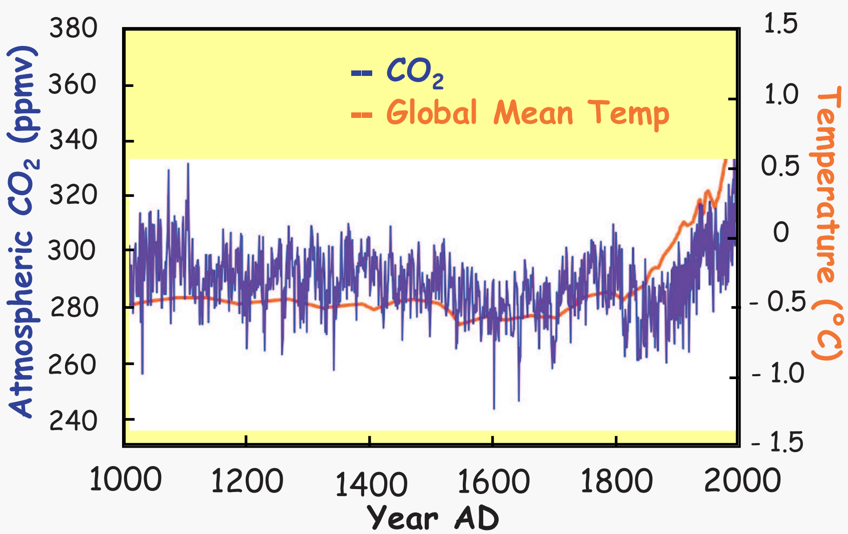
Energy Challenges: Climate Change



Relaxation times

50% of CO_2 pulse to disappear: 50 - 200 years

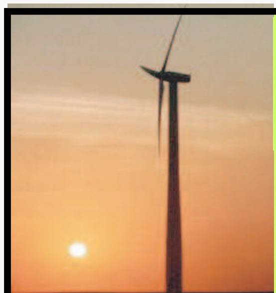
transport of CO_2 or heat to deep ocean: 100 - 200 years

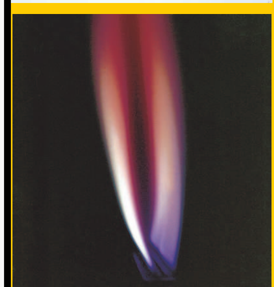


Intergovernmental Panel on Climate Change, 2001
http://www.ipcc.ch

Hydrogen Economy

Production





Biomass

Hydro
Wind
Solar

Nuclear

Oil

Coal

Natural Gas

With Carbon Sequestration

Storage

Storage is Bottleneck

HIGH EFFICIENCY & RELIABILITY

ZERO/NEAR ZERO EMISSIONS

Use

Transportation

Distributed Generation

From Patrovic & Milliken (2003) and *James Wang*
Sandia National Laboratories

Hydrogen: A National Initiative

"Tonight I'm proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles… With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom, so that the first car driven by a child born today could be powered by hydrogen, and pollution-free."

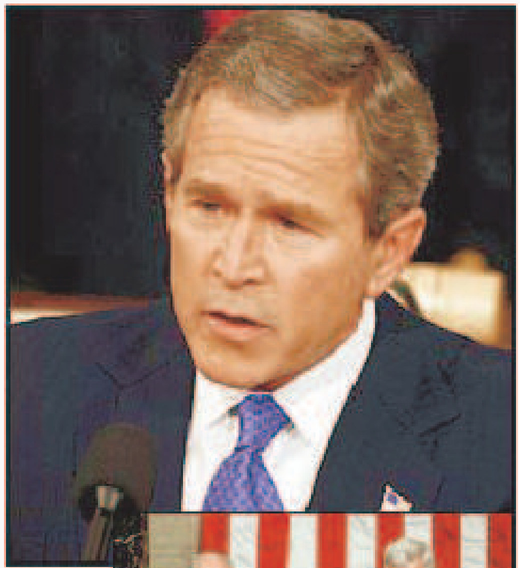
President Bush, State-of the-Union Address, January 28, 2003

"America is addicted to oil, which is often imported from unstable parts of the world,"

"The best way to break this addiction is through technology.."

"..better batteries for hybrid and electric cars, and in pollution-free cars that run on hydrogen'

President Bush, State-of the-Union Address, January 31, 2006



Ways to Store Hydrogen

- Compressed gas
- Liquid hydrogen
- Condensed state

Key Issues

- Volumetric density
- Gravimetric density
- Kinetics
- Heat transfer
- Efficiency
- Reversibility
- Operation temperature

How large of a gas tank do you want?

Volume Comparisons for 4 kg Vehicular H_2 Storage

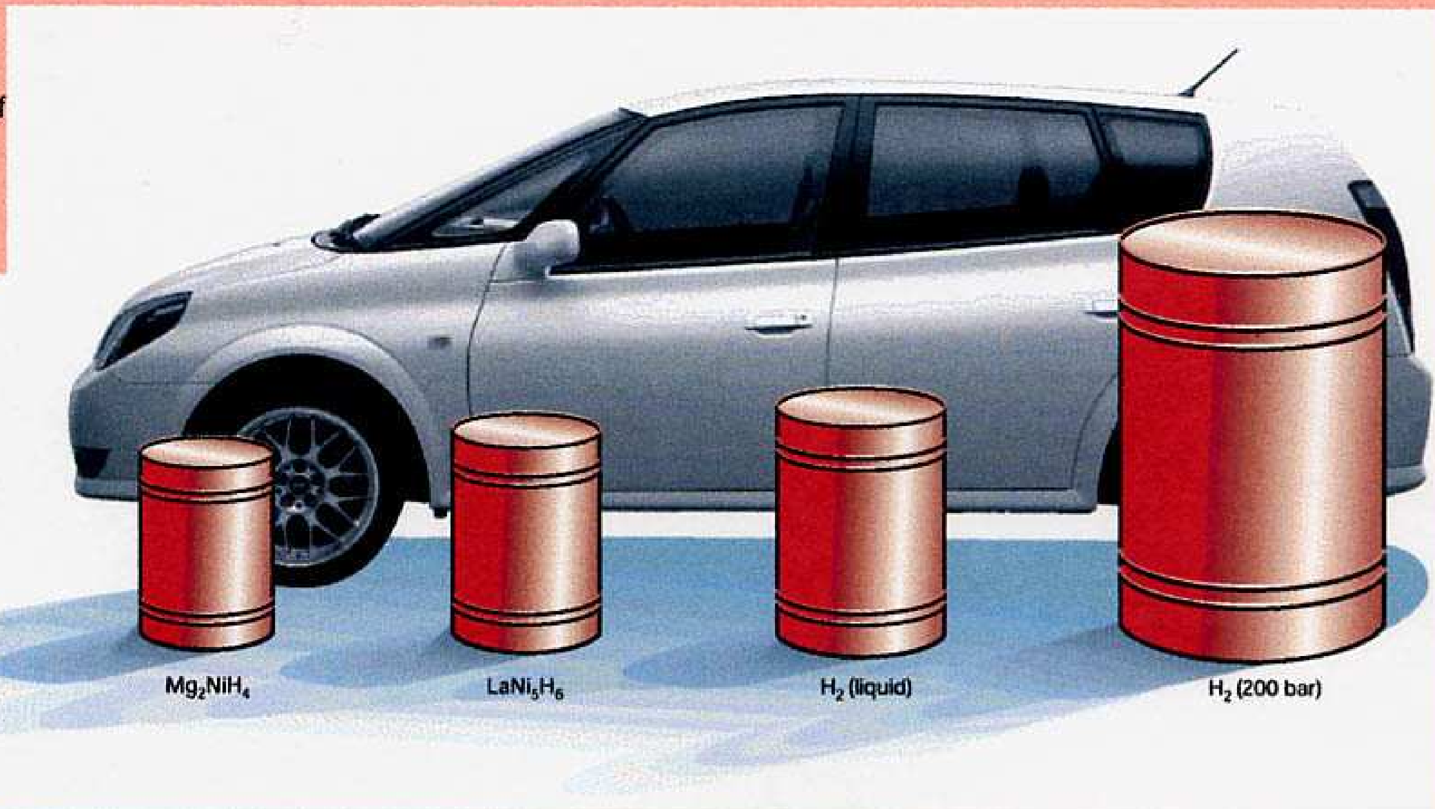


Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

Schlapbach & Züttel, Nature, 15 Nov. 2001

DOE Targets

Table 1 FreedomCAR Hydrogen Storage System Targets

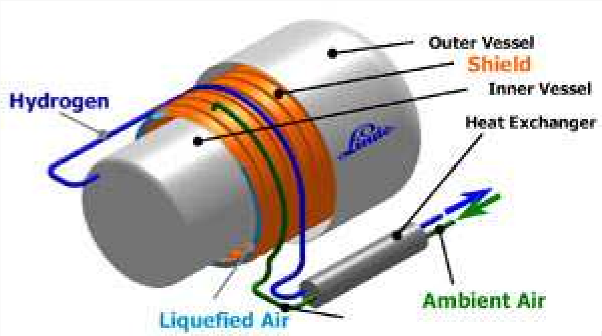
Targeted Factor	2005	2010	2015
Specific energy (MJ/kg)	5.4	7.2	10.8
Hydrogen (wt%)	4.5	6.0	9.0
Energy density (MJ/L)	4.3	5.4	9.72
System cost ($/kg/system)	9	6	3
Operating temperature (°C)	-20/50	-20/50	-20/50
Cycle life-time (absorption/desorption cycles)	500	1,000	1,500
Flow rate (g/s)	3	4	5
Delivery pressure (bar)	2.5	2.5	2.5
Transient response (s)	0.5	0.5	0.5
Refueling rate (kg H_2/min)	0.5	1.5	2.0

[a] Source: Milliken (2003).

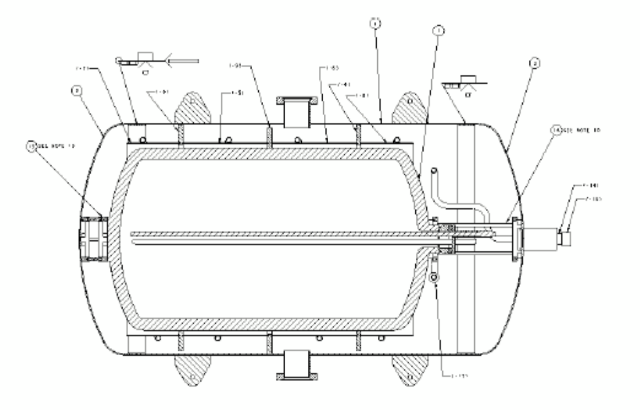
Compressed Hydrogen Gas

- **Type IV all-composite tanks are available at 5000 psi (350 bar)**
- **10,000 psi tanks being developed**

Liquid Hydrogen Storage



Linde Tank, GM



From Patrovic & Milliken (2003)

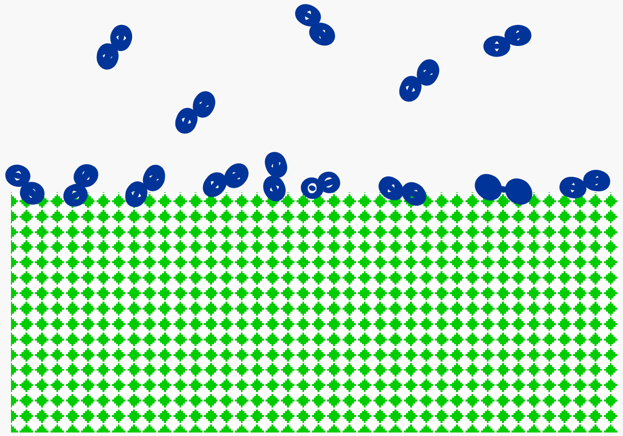
- Equilibrium temperature at 1 bar for liquid hydrogen is ~20 K.
- Estimated storage densities[1]

Berry (1998)	4.4 MJ/liter
Dillon (1997)	4.2 MJ/liter
Klos (1998)	5.6 MJ/liter

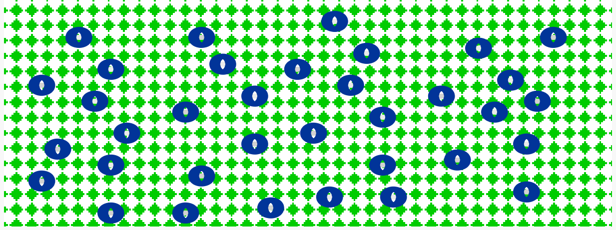
- Issues with this approach are:
  - dormancy
  - energy cost of liquifaction.

[1] J. Pettersson and O Hjortsberg, KFB-Meddelande 1999:27

Hydrogen Storage in Condensed States

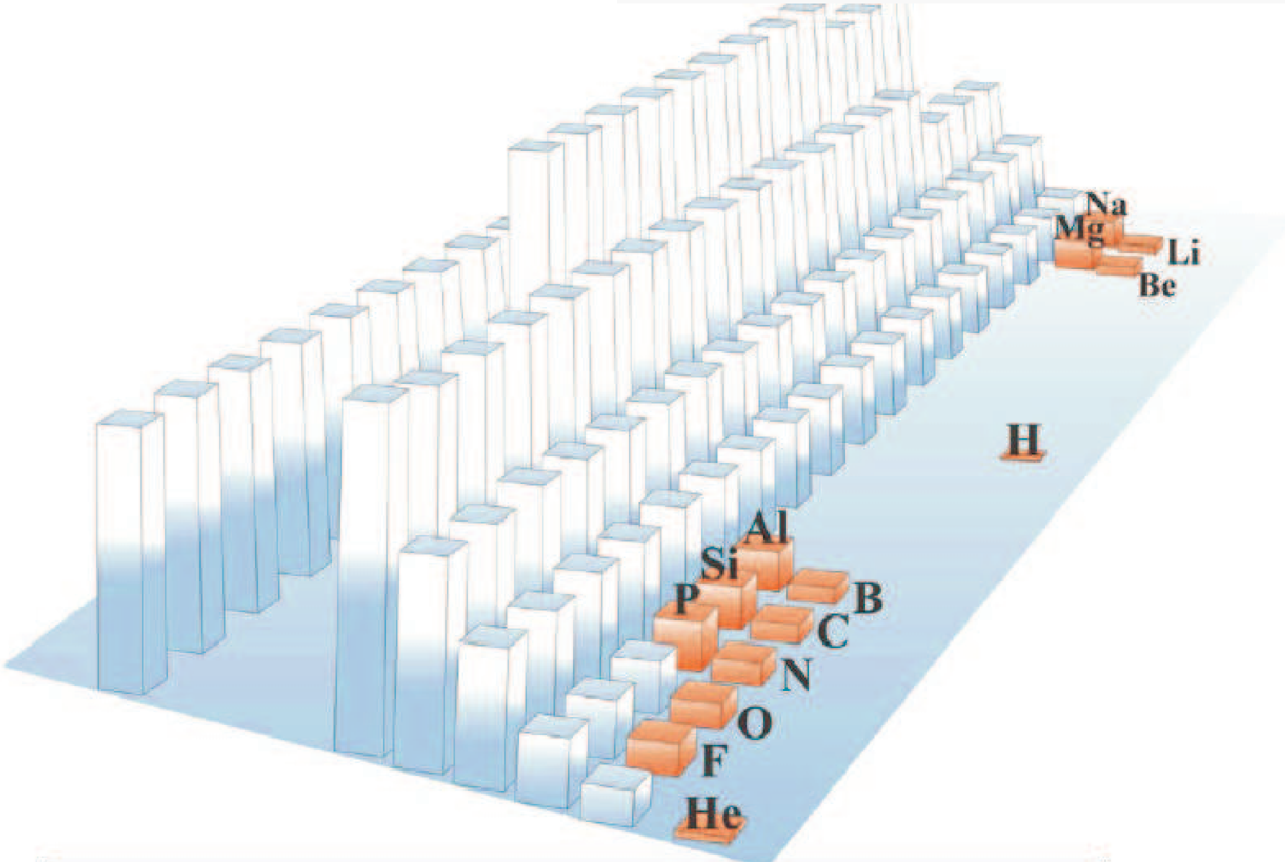


Physisorption
Adsorption on Surface



Chemisorption
Absorption into Matter

Potential Elements

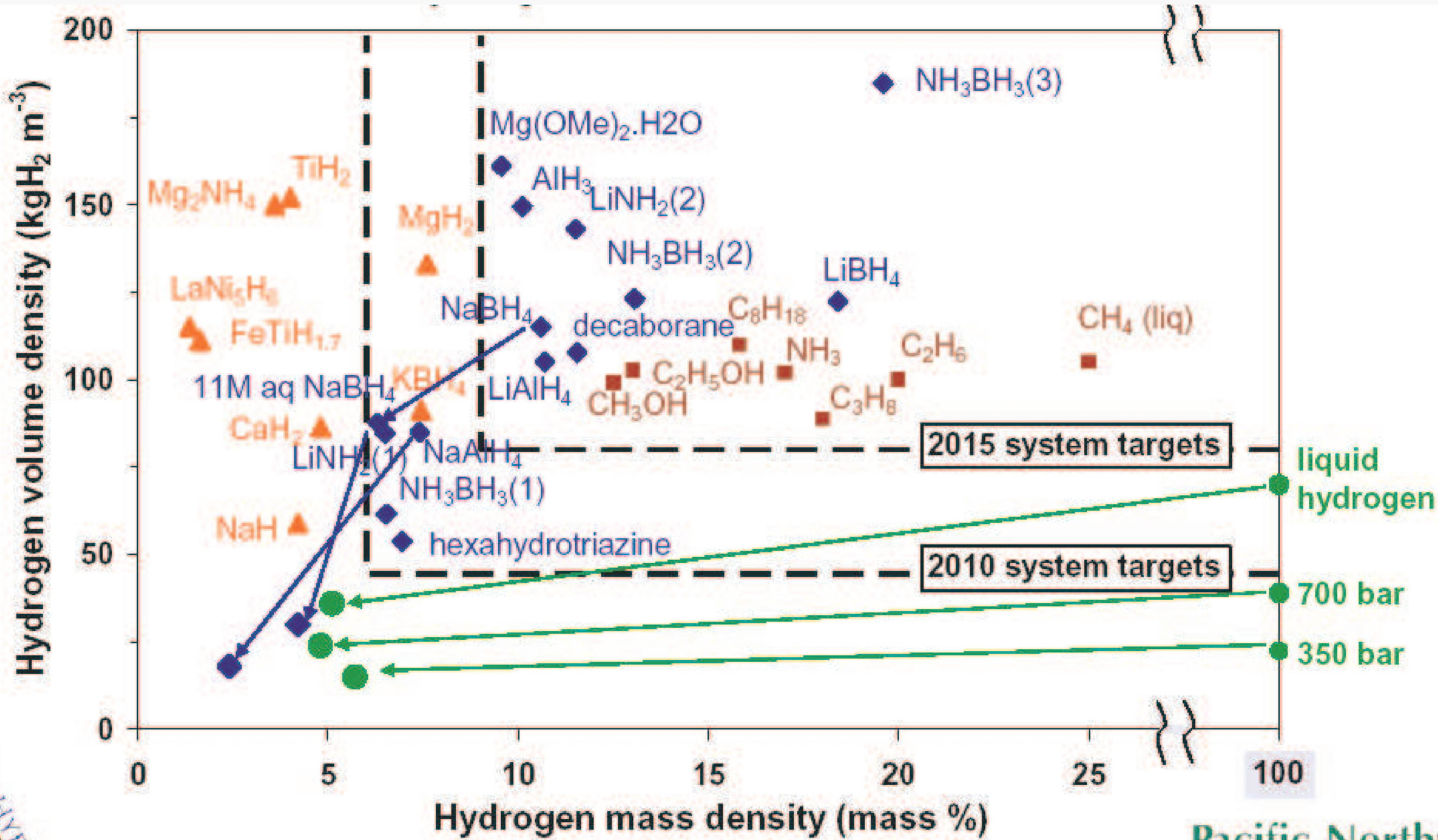


Element choices to store H limited
Li, Be, B, C, N, O, Na, Mg, Al, Si, P, S

CHEMICAL HYDROGEN STORAGE

March 2004
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Hydrogen Density of Materials

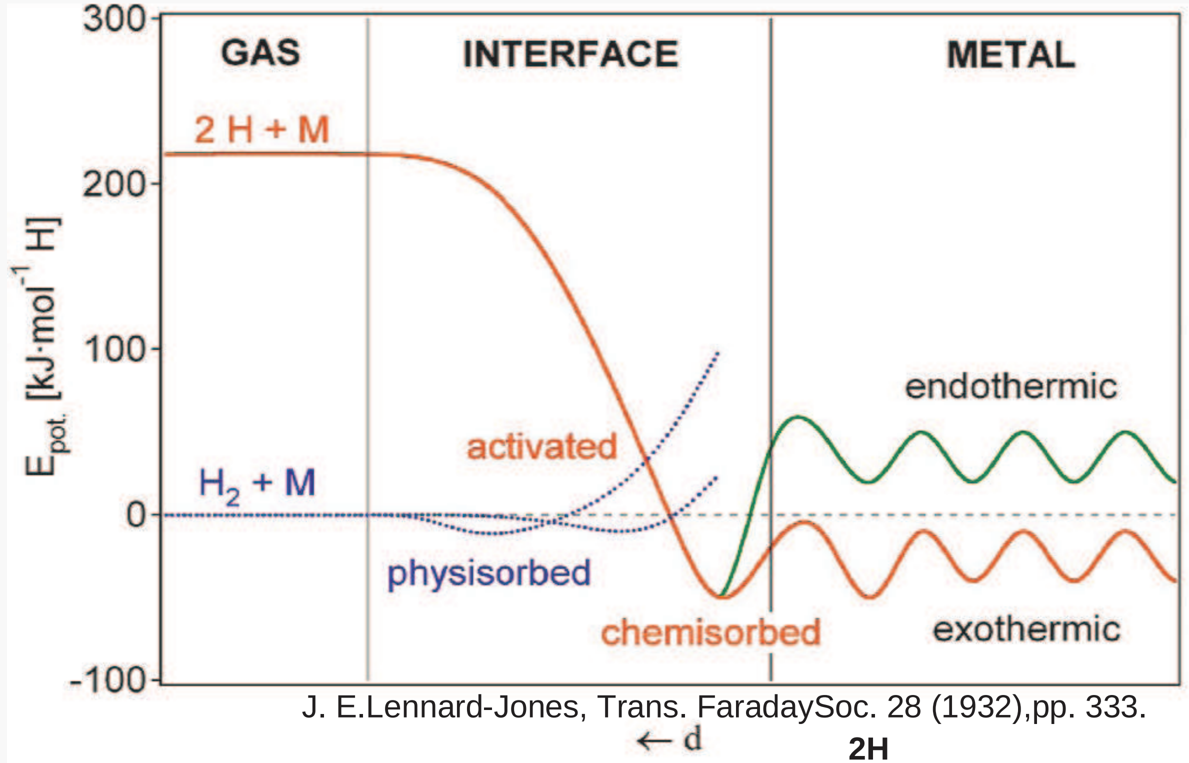


Targets are for total system weight

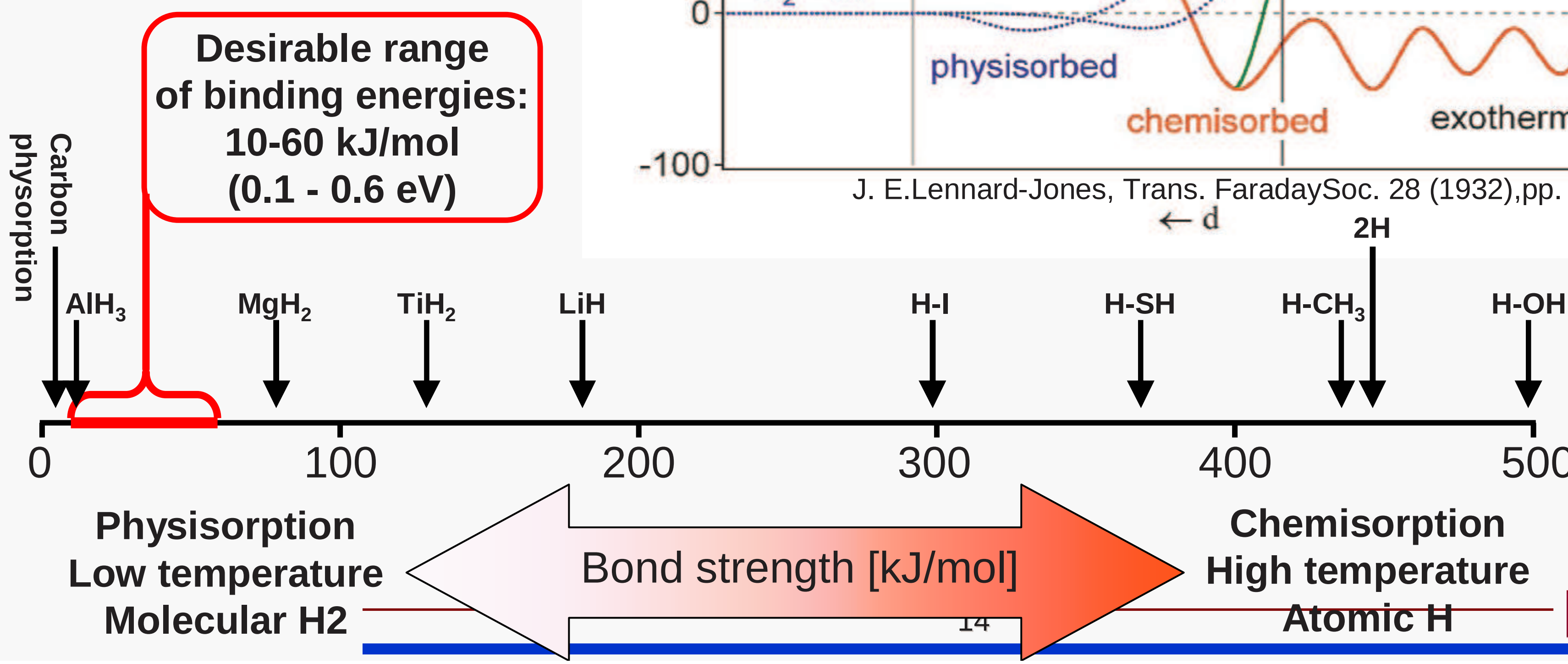
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Desired binding energy range

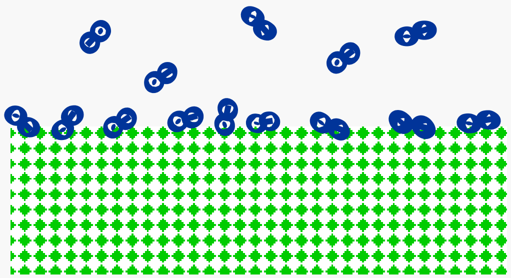
Potential energy for molecular and atomic hydrogen absorption



J. E.Lennard-Jones, Trans. FaradaySoc. 28 (1932),pp. 333.



Physisorption

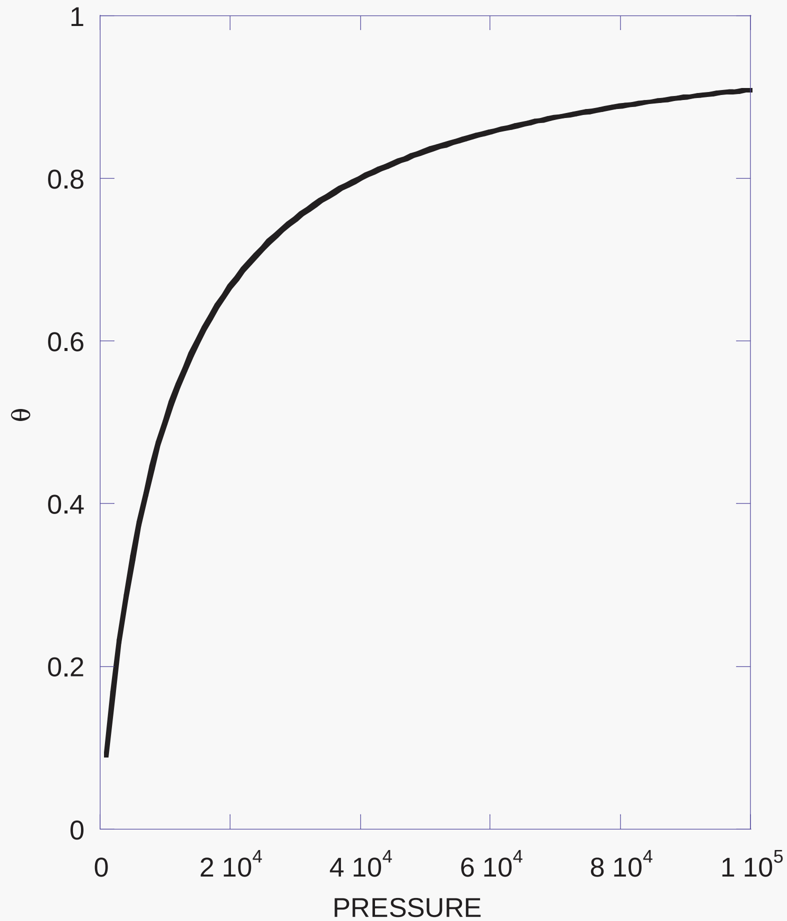


- **Langmuir Isotherm**

$$\theta = \frac{Kp}{1 + Kp}$$

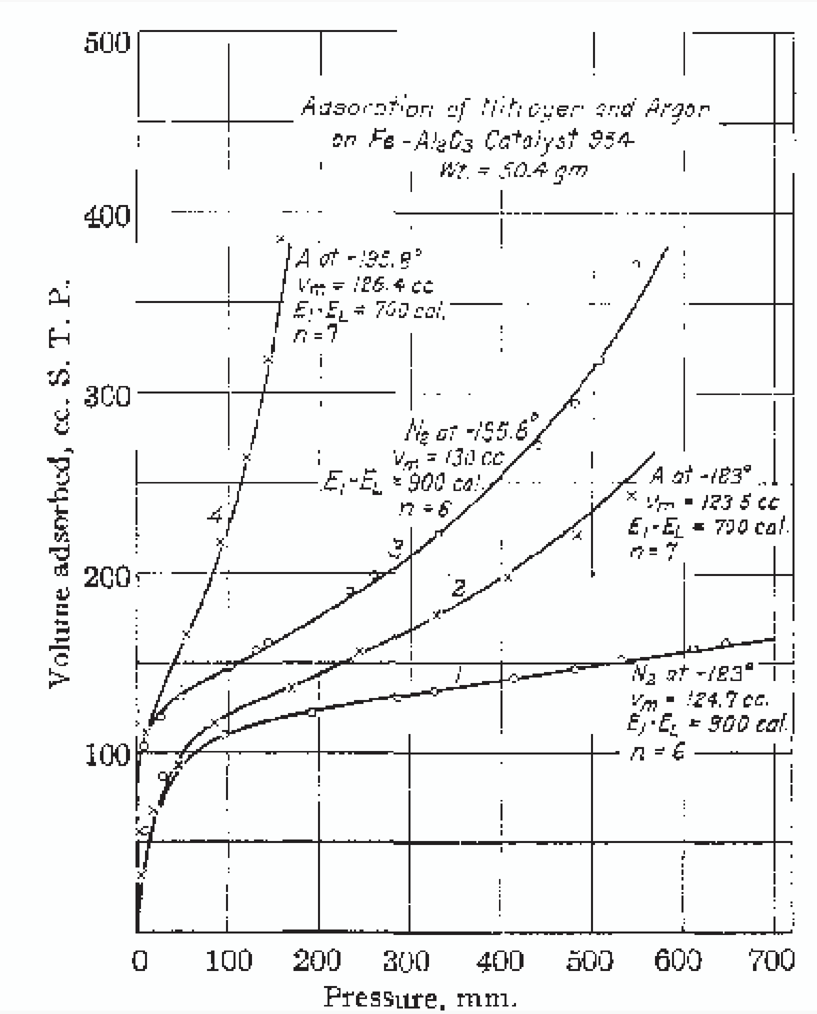
$$\theta = \frac{\text{Molecules Adsorbed}}{\text{Number of Adsorption Site}}$$

$$K \propto T^{-1/2} \exp\left(\frac{\varepsilon}{k_B T}\right)$$



Assumption: Monolayer coverage

Physisorption



S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309

Multilayer coverage

BET Area

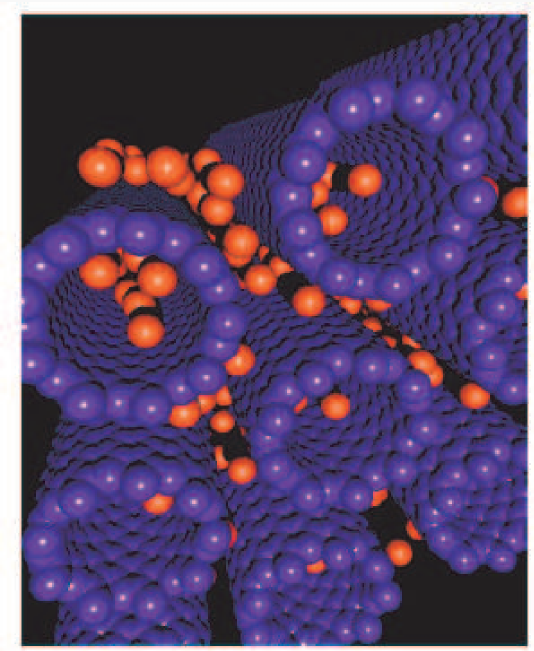
$$A_{sp} = \frac{V_m N_A \sigma}{22,414}$$

V_m cm^3/g at STP

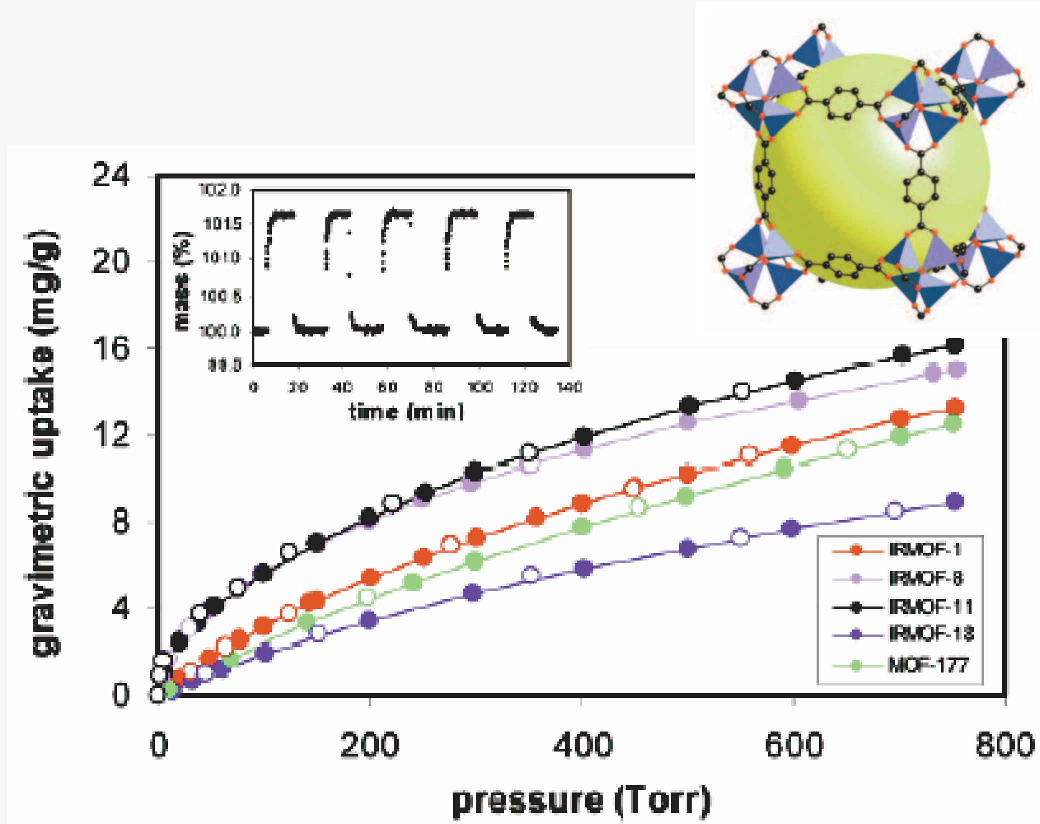
Research Directions

- Increasing surface area
- Increasing binding energy

Increasing Surface Area



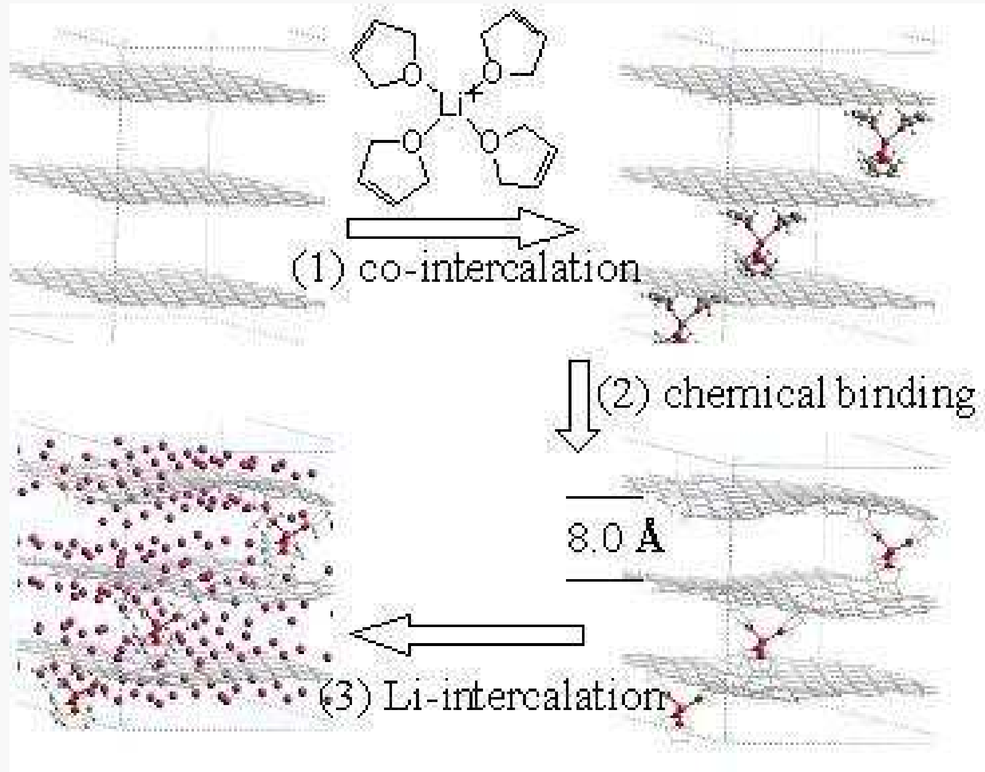
Johnson, Chem. & Eng. News, 2002

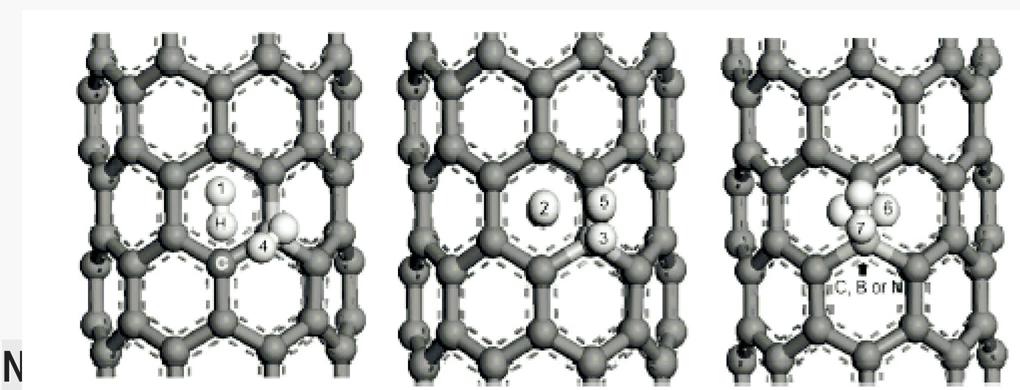


MOF: Rosi et al., Science, 2003
Roswell et al., JACS, 2004

Increasing Binding Energy

http://www.wag.caltech.edu/fuelcells/index.html





Boron Doping of CNT,
Z. Zhou et al., Carbon, 44, 939, 2006

Chemisorption

HYDRIDES

Metal hydrides

MgH_2, AlH_3

$XAlH_4$, XBH_4

$-NH_2$, $=NH$

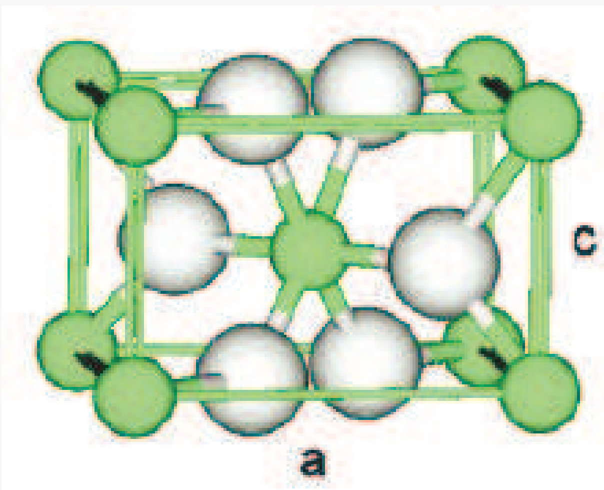
$H^{\delta+}$ and $H^{\delta-}$

Material	H_2 [mass%]	T_{dec} [°C] 1 bar
$LaNi_5H_6$	1.49	15
$TiMn_{1.5}H_{2.5}$	1.76	
$FeTiH_2$	1.86	-10
ZrH_2	2.16	
$TiCr_{1.8}H_{3.5}$	2.43	
Mg_2NiH_4	3.62	300
VH_2	3.81	-10,
TiH_2	3.98	780
NaH	4.20	430
CaH_2	4.79	1000
Li_2NH + LiH	5.50	600
$LiNH_2$ + LiH	6.50	300
$NaAlH_4$	7.46	30, 120
MgH_2	7.66	320
AlH_3	10.07	<RT
$LiAlH_4$	10.62	-93
$NaBH_4$	10.66	620
LiH	12.86	900
$Al(BH_4)_3$	16.90	<100
NH_3	17.75	-32
$LiBH_4$	18.51	230

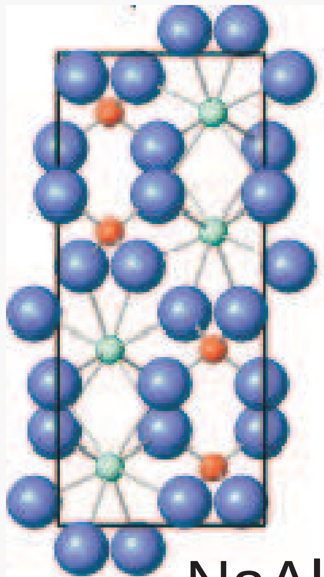
A. Zuttel

Classification

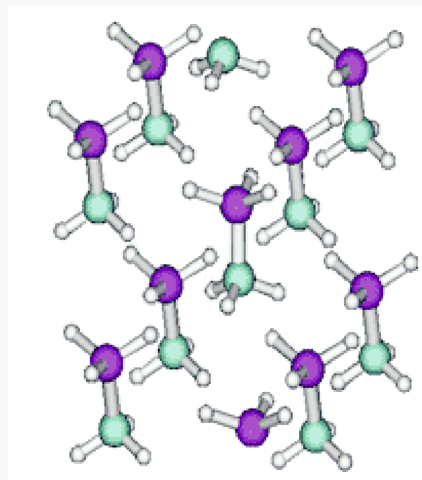
- Metal hydrides: MgH_2
- Complex hydrides: $NaAlH_4$
- Chemical hydrides: LiBH4, NH_3BH_3



MgH_2



$NaAlH_4$



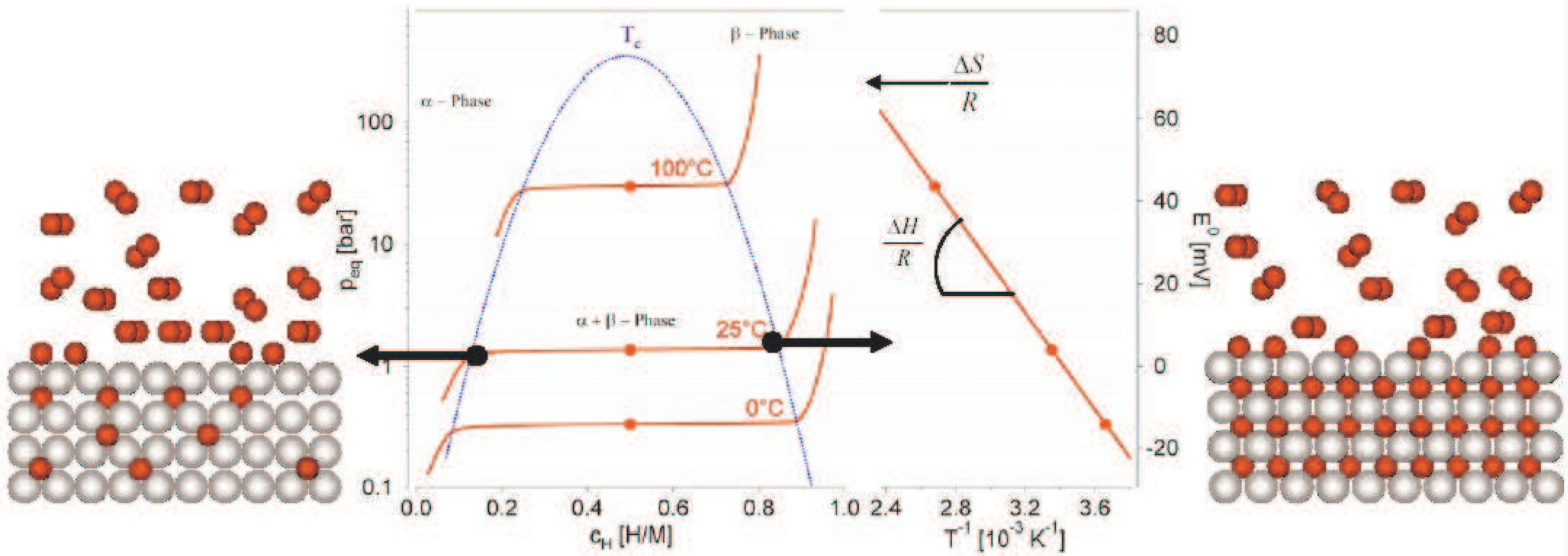
NH_3BH_3

The Hydrogen Bottleneck

	DOE goal (2015)	Metal hydride	Chemical hydride
Storage wt. %	9%	✓	✓
Storage vol. %	81 kg/m^3	✓	✓
Reversibility (cycle)	1500 cycles	Limited	✗
System storage cost	$2/kWh	$50/kWh	$18/kWh
Fueling time (reaction kinetics)	30 s/kg-H_2	✗ (too slow)	✗
Operating temperature	-40 - 60 °C	✗ (too high)	✓
Operating pressure	<100 atm.	✓	✓

JoAnn Milliken (2002)

PcT Relation



$$\ln\left(\frac{p}{p_0}\right) = \frac{\Delta H^0}{R \cdot T} - \frac{\Delta S^0}{R}$$

α-Phase: Solid Solution

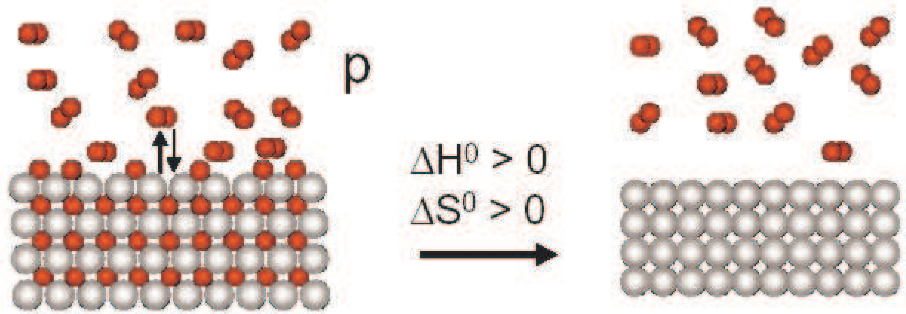
β-Phase: Hydride Phase

MH_x $(0 < x < 0.1)$

MH_x $x = \{1, 2, 3, \ldots\}$

From A. Zuttel

Thermodynamics



$x\,MH_{2/x} \longrightarrow x\,M + H_2$

Equilibrium $\Delta G = 0$

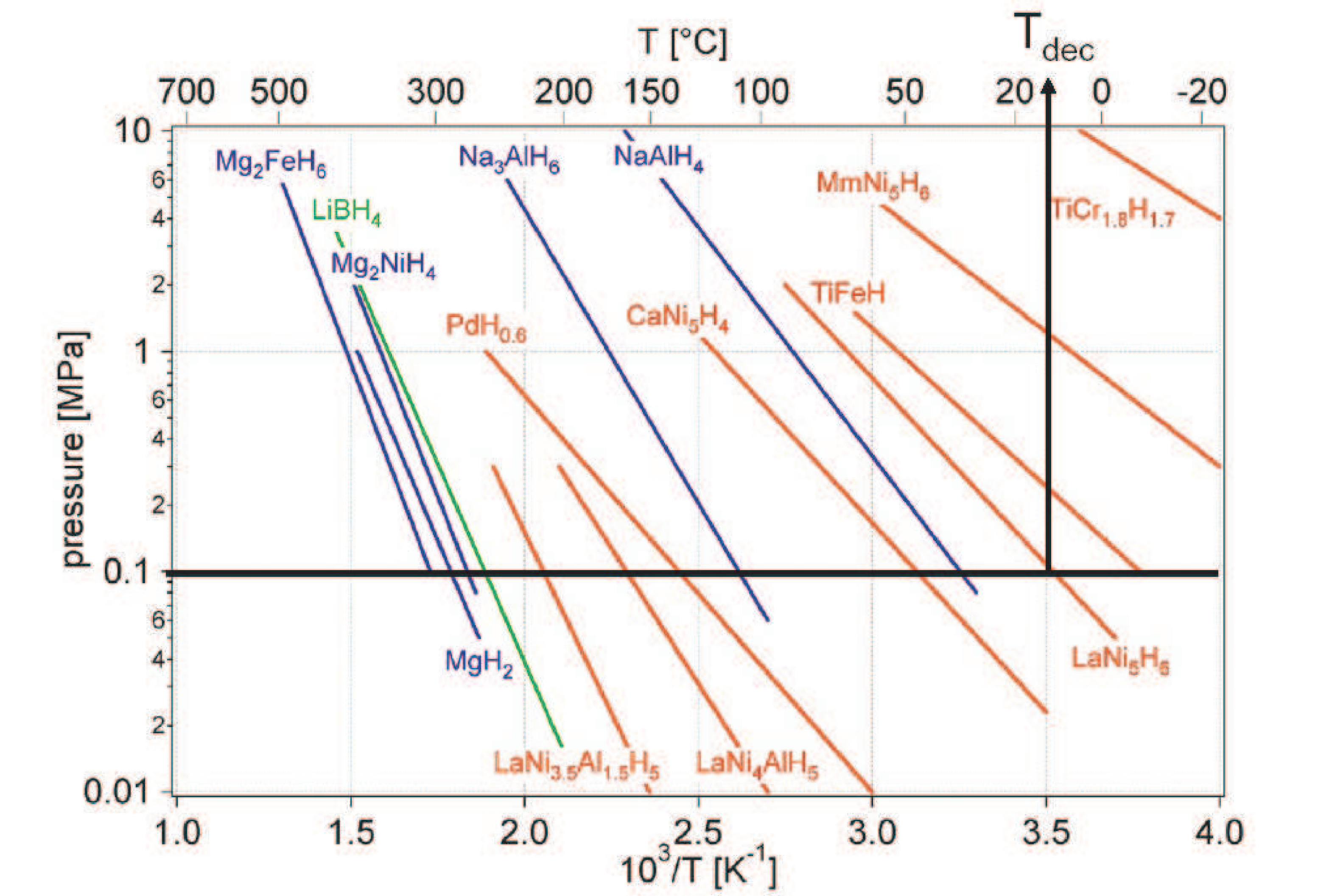
$$\Delta G = 0 = \Delta G^0 + R \cdot T \cdot \ln\left(\frac{p}{p_0}\right)$$

$$\Delta G^0 = -R \cdot T \cdot \ln\left(\frac{p}{p_0}\right) = \Delta H^0 - T \cdot \Delta S^0$$ Van't Hoff equation

$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

for $p = p_0$ $\quad T_{dec} = \dfrac{\Delta H^0}{\Delta S^0}$ decomposition temperature

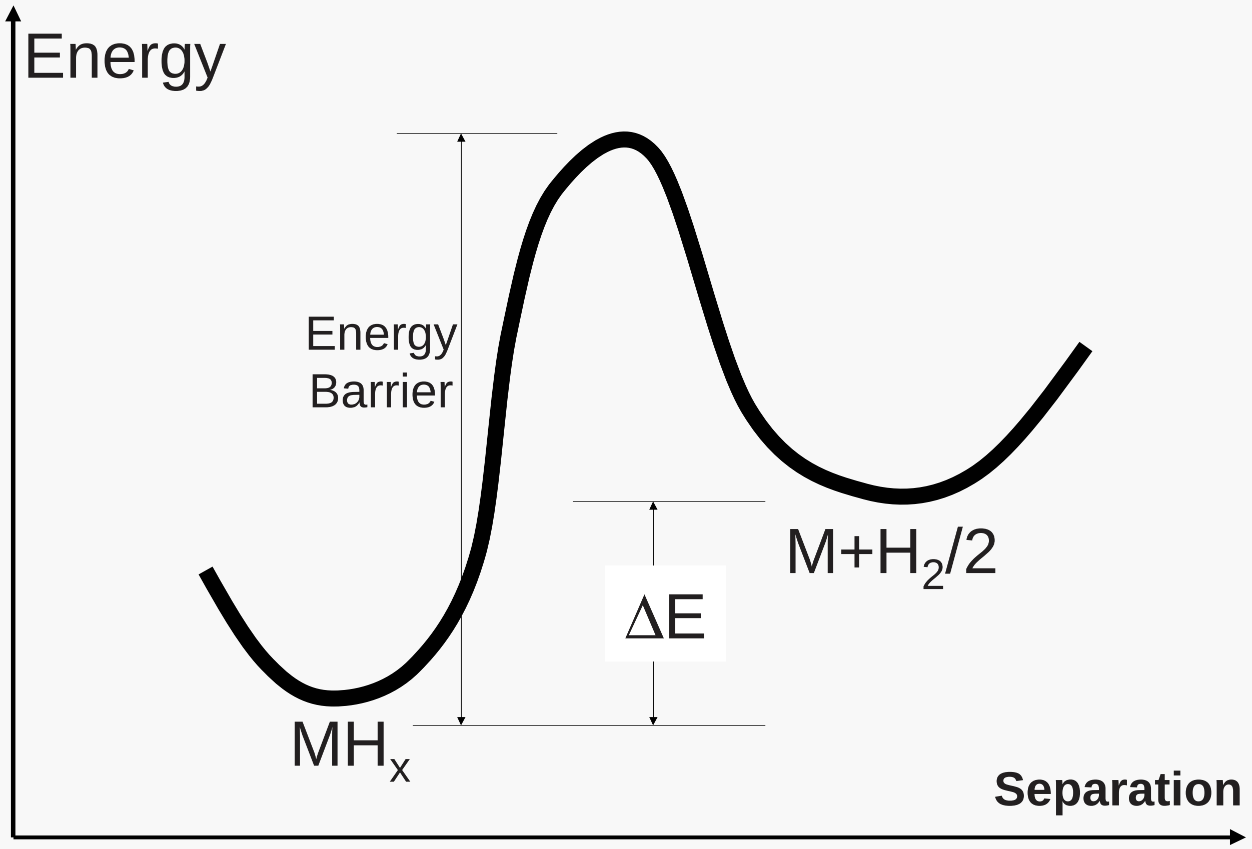
Stability of Hydrides



Thermodynamic Equilibrium

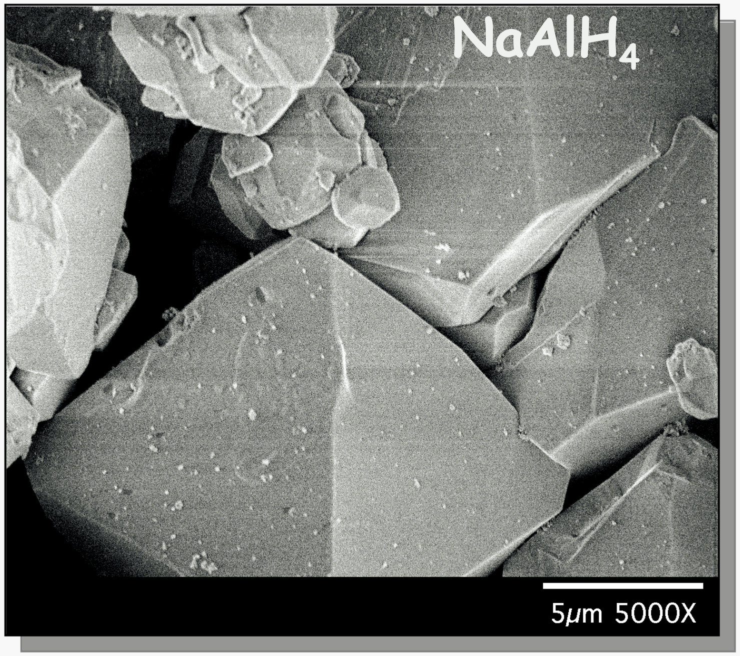
A. Zuttel

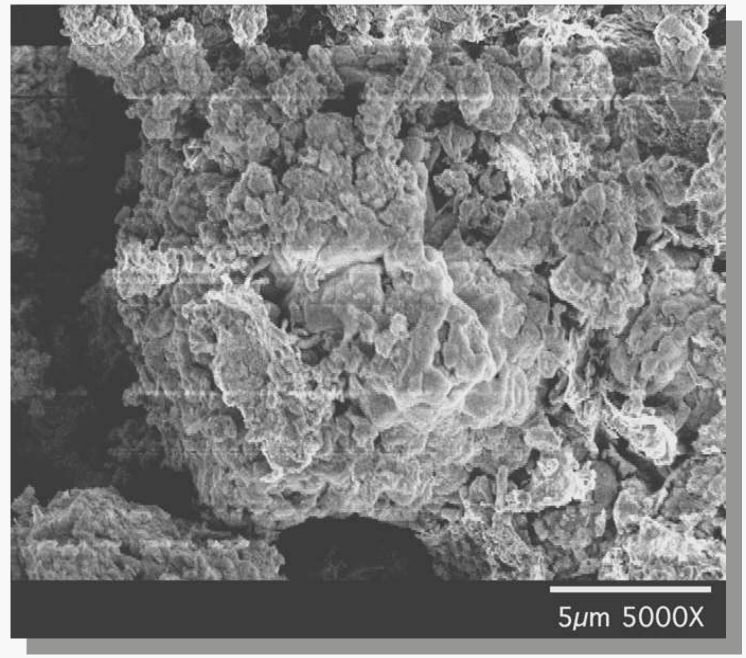
Energy Barrier



Thermodynamically Favorable Does Not Mean Kinetically Favorable

Reversible Metal Hydride System





Sodium alanate doped with Ti is a reversible material hydrogen storage approach.

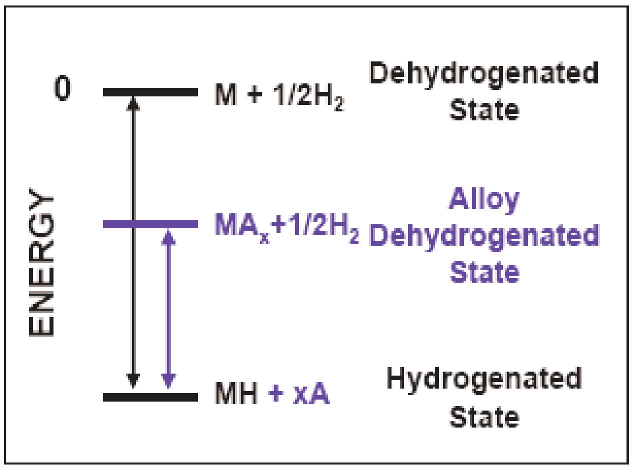
$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \rightarrow 3NaH + Al + 3/2H_2$$

3.7 wt% **1.8 wt%**

Low hydrogen capacity and slow kinetics are issues

System destabilization

Forming new alloys



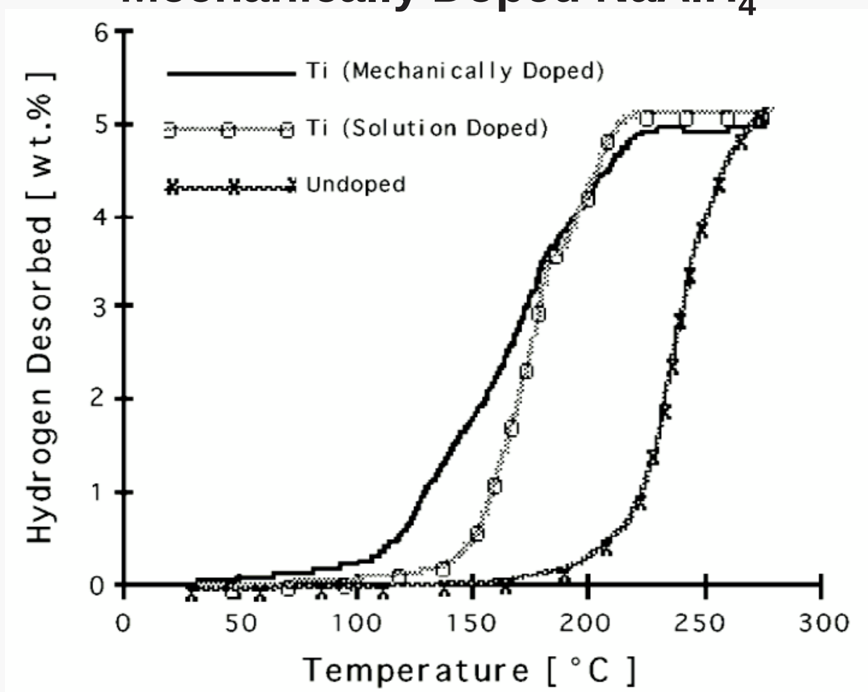
Gregory L. Olson *DOE 2005 Hydrogen Program Annual Review*

- Reduce energy (temperature) needed to liberate H_2 by forming dehydrogenated alloy
- System cycles between the hydrogen-containing state and the metal alloy instead of the pure metal
- Reduced energy demand means lower temperature for hydrogen release.

Doping with a catalyst

- Reduces the activation energy.
- Allows both exothermic and endothermic reactions to happen at lower temperature.

Mechanically Doped $NaAlH_4$

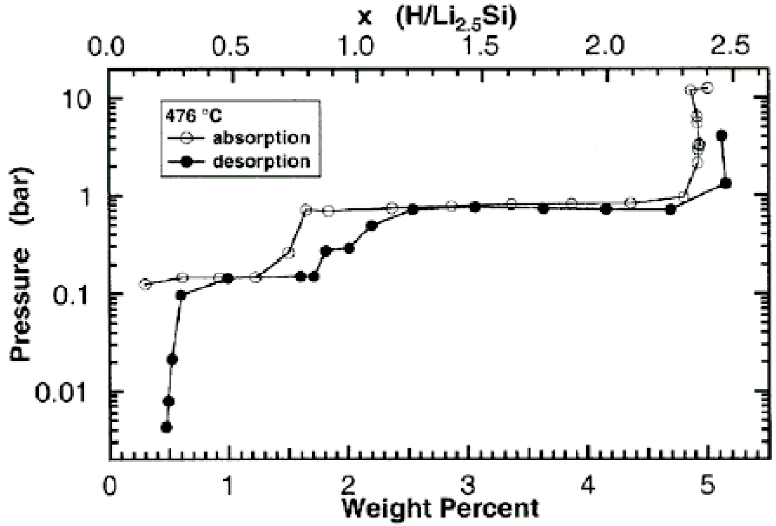


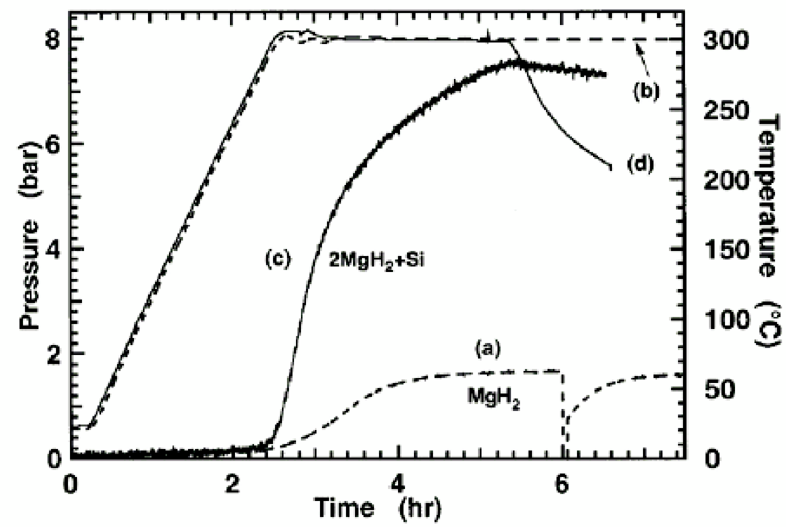
R.A. Zidan et al, J. Alloys and Compounds 285 (1999), pp. 119.

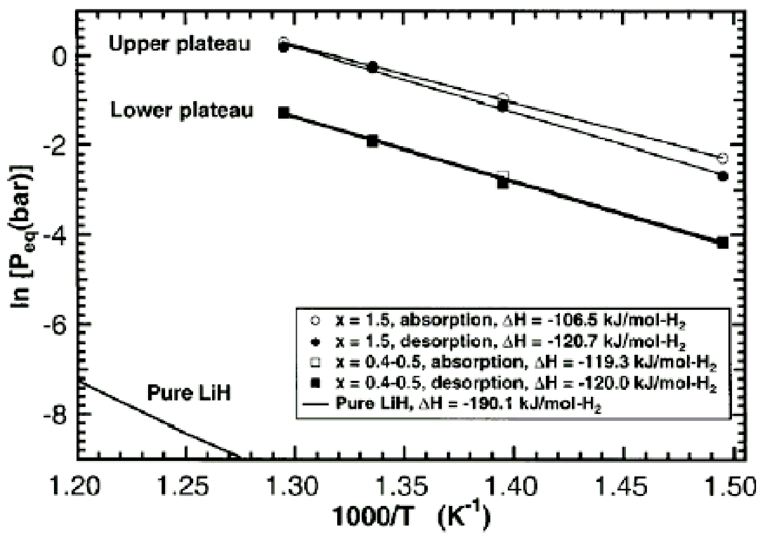
DESTABILISATION OF MgH_2

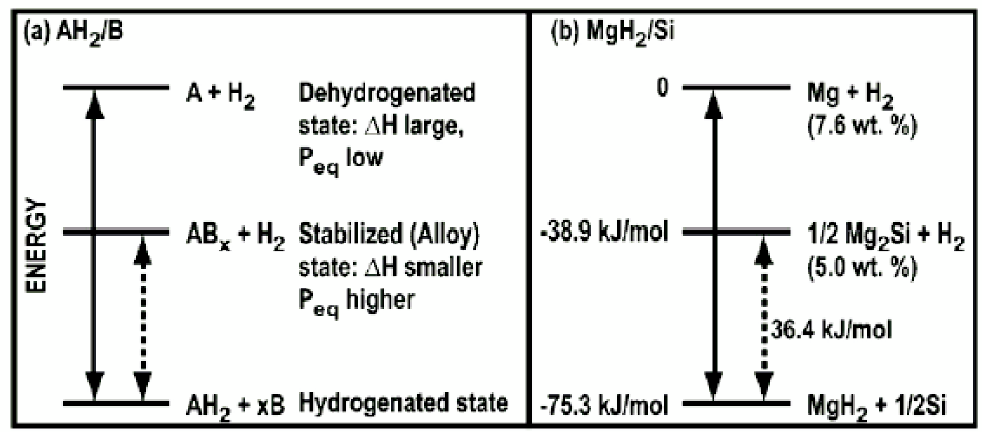
$2.5\ LiH + Si \longrightarrow Li_{2.5}Si + 1.25H_2$

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









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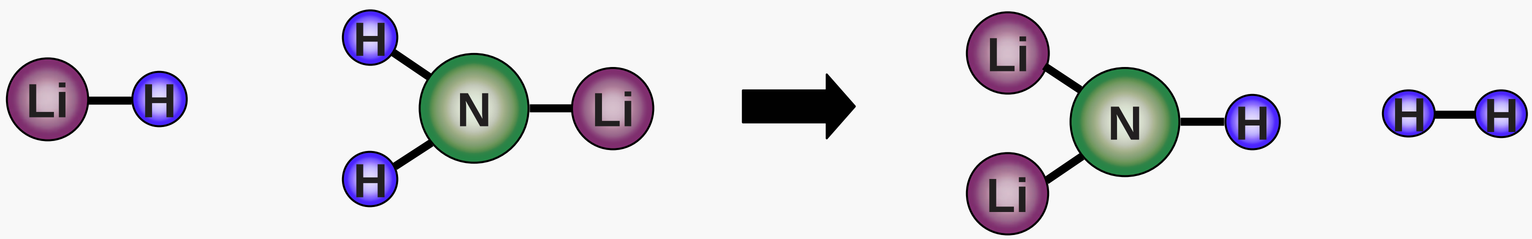
Ref.: J. J. Vajo, F. Mertens, C. C. Ahn, R. C. Bowman Jr, B. Fultz, J. Phys. Chem. B 108 (2004), 13977-13983

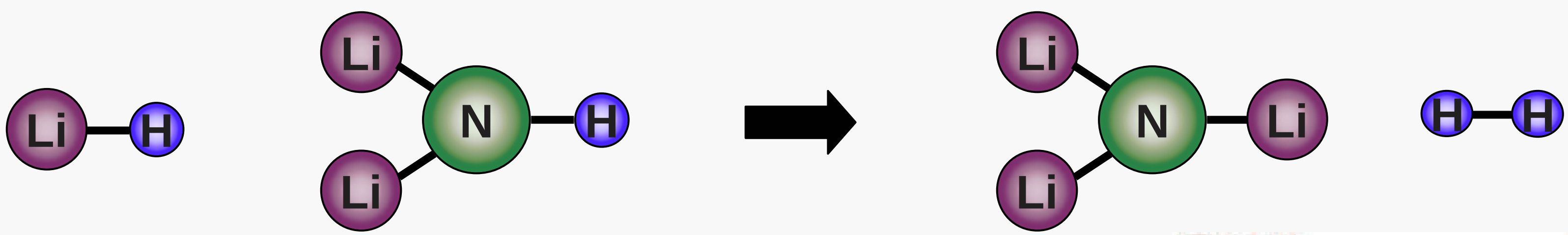
Imide (NH) and Amide (NH_2)

First step: $LiNH_2 + LiH \Leftrightarrow Li_2NH + H_2$ (6.55% @ 300C,1atm.)



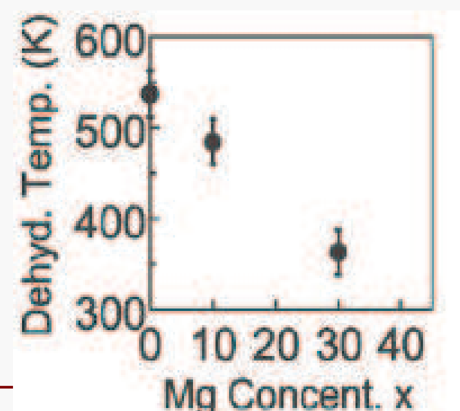
Second: $Li_2NH + LiH \Leftrightarrow Li_3N + H_2$ (5% @ 300c 0.05atm)

- Release temperature too high and low release pressure.



Partial Mg substitution reduces release temperature

$Li_{1-x}Mg_xNH_2$



S. Ohmo et al., Appl. Phys. A:Materials Science & Processing, Vol 79, No 7, p. 1765 - 1767.

Chemical Hydrides

Hydrolysis: $XH_n + n\ H_2O = n\ H_2 + X(OH)_n$ (e.g. $NaBH_4$, LiH)	Dehydrogenation: $H_nX\text{---}YH_n = n\ H_2 + XY$ (e.g. decalin -> naphthalene)
Dehydrocoupling: $XH_n + YH_n = n\ H_2 + XY$ (e.g. $NH_3 + BH_3$)	New compositions and pathways

Each reaction family has numerous opportunities

Irreversible Chemical Hydrides

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

- $NaBH_4$: 20 - 35% sol. Stabilized with 1-3% NaOH
- Catalyst
- $NaBO_2$: Borax in NaOH

$$2LiH + 2H_2O \rightarrow 2LiOH + 2H_2$$

- LiH: Light mineral oil slurry, proprietary stabilizers
- $LiOH$: Paste byproduct

- Hydrogen capacity is high at around 10 wt% hydrogen.
- Dehydrogenation kinetics are fast.
- Reactions are irreversible on-board vehicle.

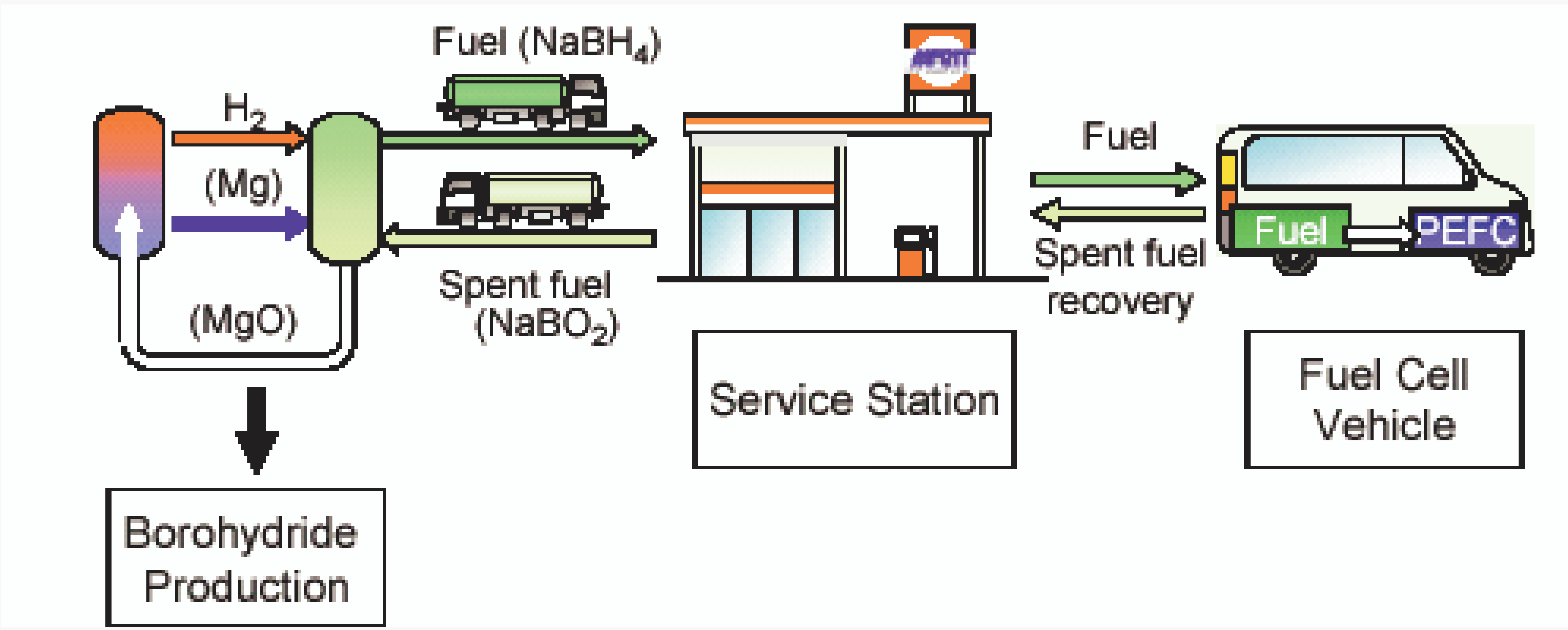
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

- Na: Polyethylene-coated pellets, mechanically cut to expose Na

Regeneration costs are a major issue

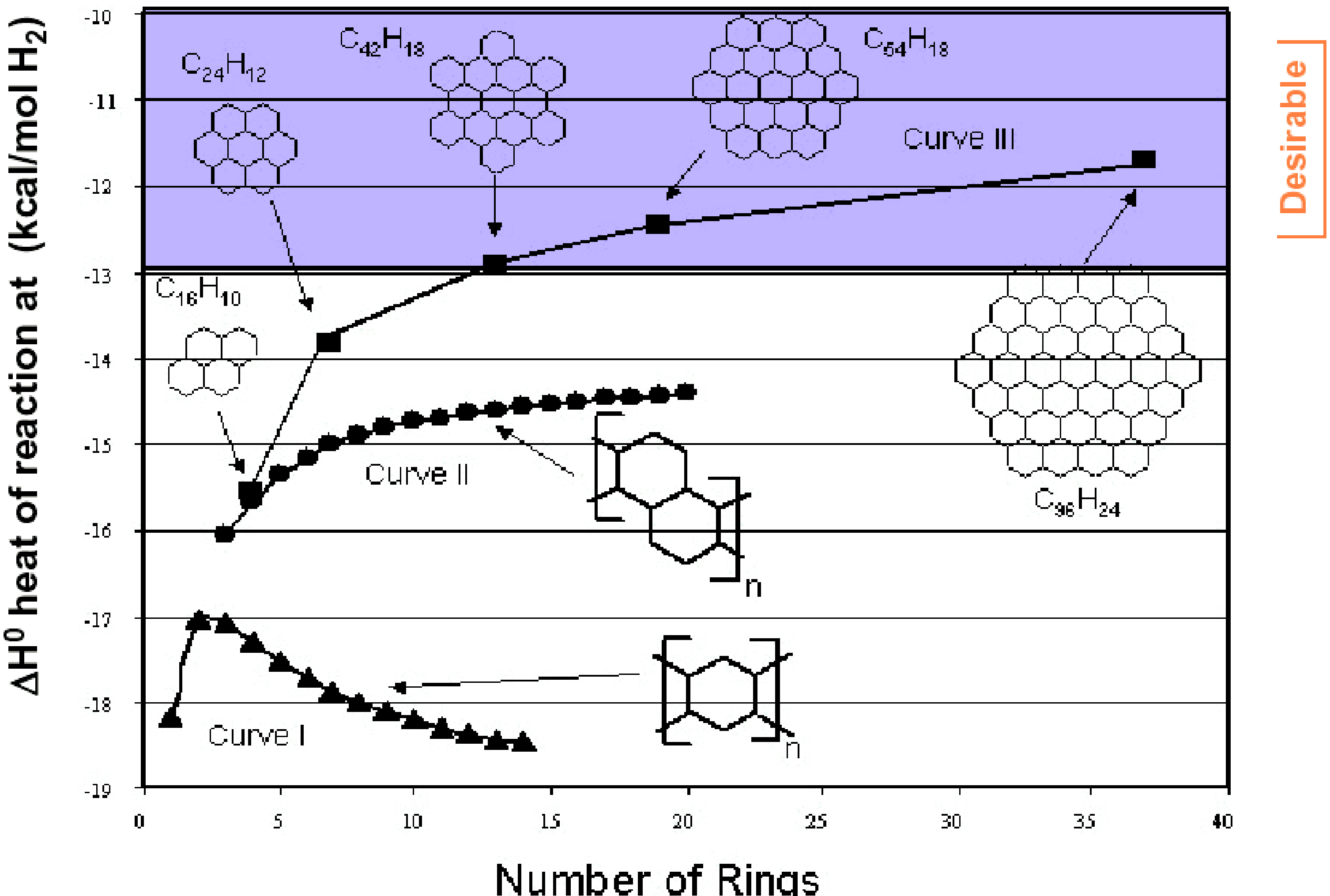
From Patrovic & Milliken (2003)

Fueling Cycle



From DOE BES Hydrogen Report

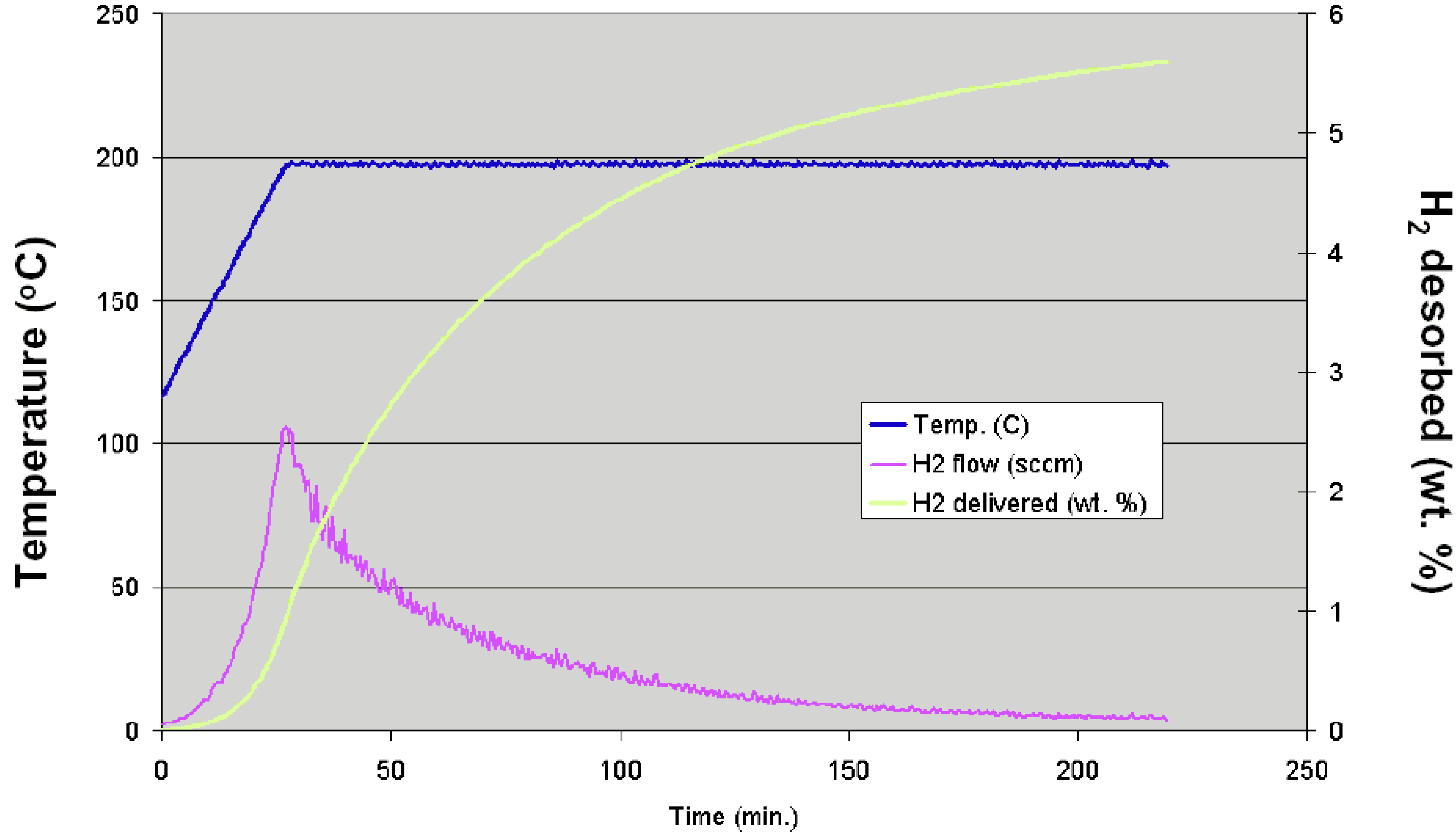
Calculated enthalpies of hydrogenation as a function of fused aromatic structure



Fused multi-ring aromatic systems desirably lower ΔH

Courtesy Air Products, Inc.

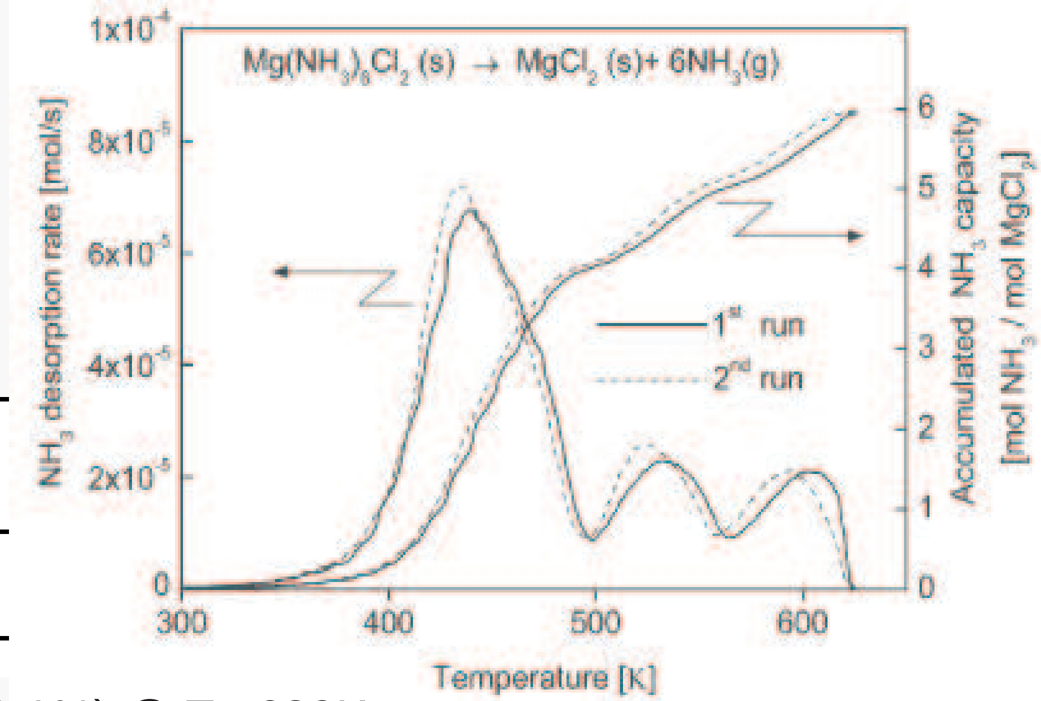
N-Ethylcarbazole (Air Products, Inc.)



GC/MS analysis after run termination showed loss of 5.7% wt H_2

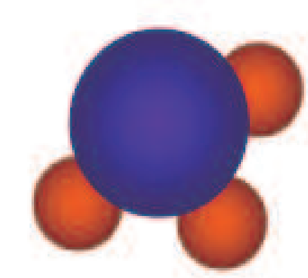
Metal ammine complexes

	Gravimetric H_2 density (% H_2)	Volumetric H_2 density/ (kg m^{-3})
$Mg(NH_3)_6Cl_2$	9.1	110
$Ca(NH_3)_8Cl_2$	9.7	120



- $Mg(NH_3)_6Cl_2 = MgCl_2 + 6NH_3$ (9.1%) @ T <620K
- Ammonia is toxic
- Can be used in high T solid oxide fuel cells.
- High temperature of hydrogen release

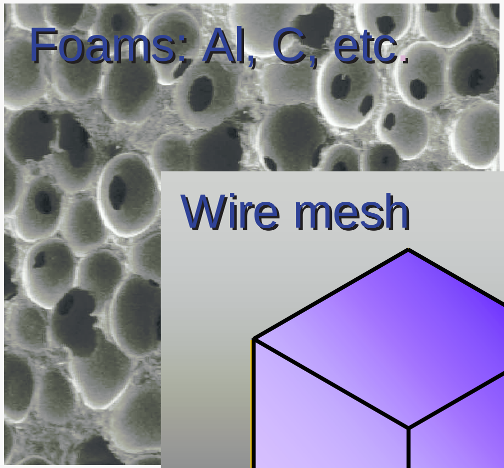
$$2NH_3 \rightarrow 3H_2 + N_2 \text{ @ } \sim 600K$$

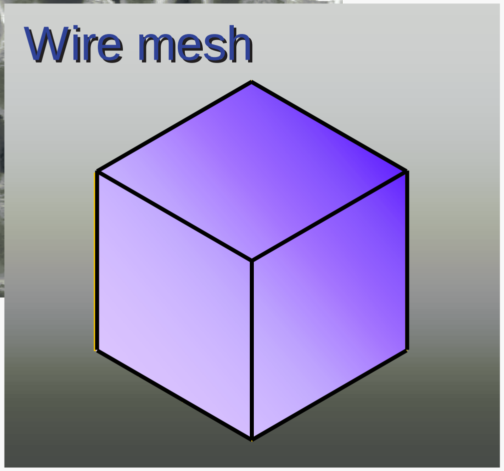


Christensen et al., J. Mater. Chem., 2005, 15, 4106–4108

Thermal Management

- Hyriding reaction: ~1 MW for 5 min.
- Nanostructured materials impair heat transfer
- Temperature rise suppresses hydriding reaction
- Typical hydride conductivity: k~0.1 W/m-K





Klein et. al., Int. J. Hydrogen Energy 29 (2003) 1503-1511

SOLUTIONS

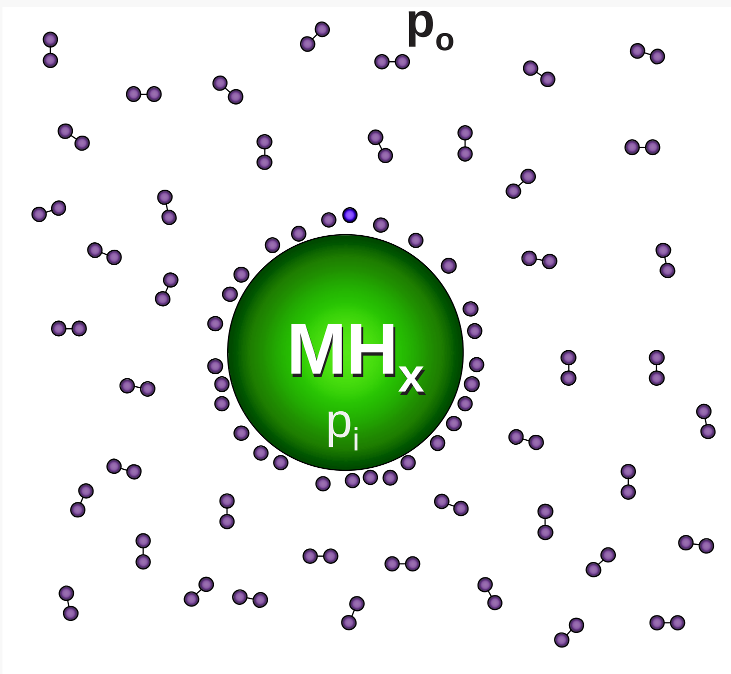
Conductive foams, fins and meshes

Expanded Graphite Compacts

See: Zhang et. al., J. Heat Transfer, **127** (2005) 1391-1399

Benefits of Nanostructures

- Increase kinetics: diffusion time ~ radius square/diffusivity
- Possibility of co-existence of chemi- and physi-sorption
- Possibility of changing thermodynamic properties



- **Yang's Equation:**

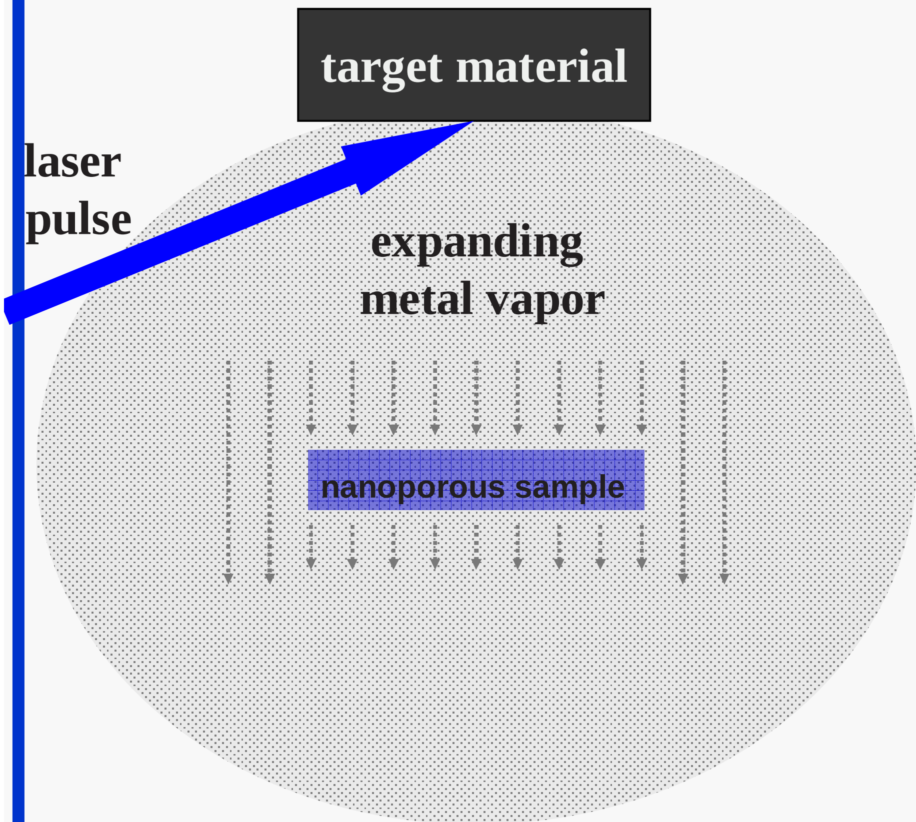
$$p_i - p_o = \frac{2\sigma}{r}$$

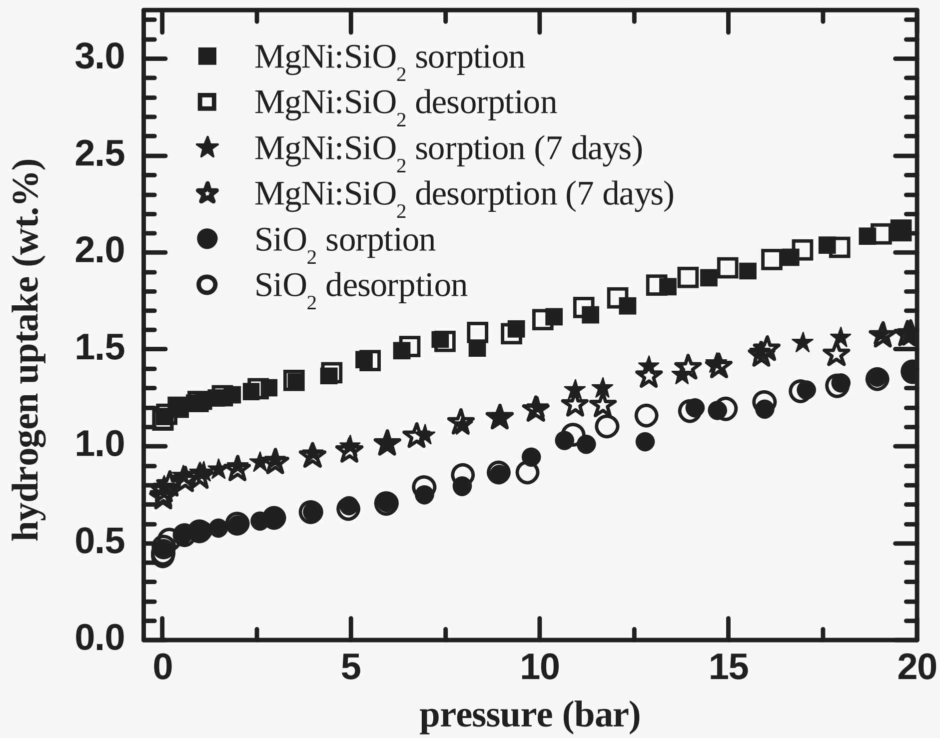
2σ ← Surface Tension

r ← Radius

- **Kelvin Theory:**
  - For multiphase system, transition temperature, equilibrium pressure and enthalpy of reaction change with radius.
  - For hydride, we can expect similar dependence in release temperature, equilibrium pressure and enthalpy of formation.

Simultaneous Physisorption and Chemisorption





S.Mao, LBNL

Size Effects on Thermodynamic Properties

Assuming the following reaction

$$M + H_2 \rightarrow MH_2$$

- At nanoscale, surface and size affect reaction enthalpy.
  - Increase the surface to volume ratio.
  - Increase adsorption sites due to low coordination surface atoms.
  - Lower binding energy in small metallic clusters.

Bulk molar free energy of formation

$$\Delta G = \Delta G_o + RT \ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right)$$

Van't Hoff relation

$$\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R}$$

Nanoparticle molar free energy of formation

$$\Delta G(r) = \Delta G_o(r) + RT \ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right) + \frac{3\overline{V_M}\Delta_{M \rightarrow MH}(\gamma, r)}{r}$$

$$\Delta_{M \rightarrow MH}(\gamma, r) = (\gamma_{MH}(r)\left(\frac{\overline{V_{MH}}}{\overline{V_M}}\right)^{2/3} - \gamma_M(r)) + E_{adsoption}$$

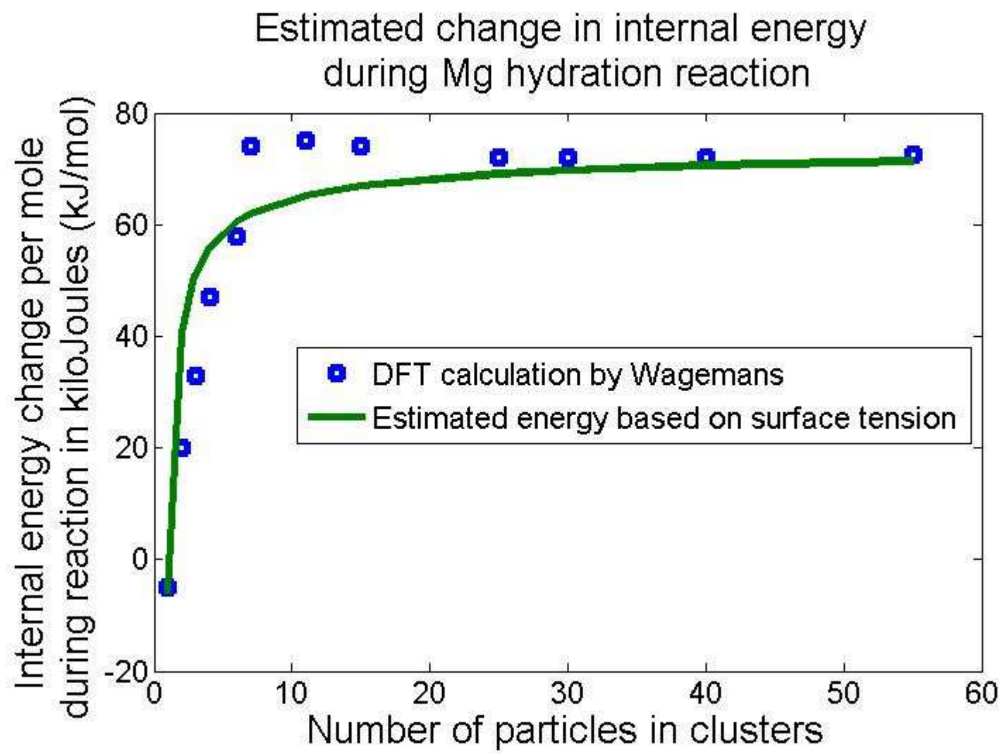
Modeling DFT Results

- If internal energy dependence on radius is all contained in the surface energy term

$$\Delta E(r) \approx \Delta E_{Bulk} + \frac{3\overline{V}_M \Delta_{M \rightarrow MH}(\gamma, r)}{r}$$

- Following Tolman's work, surface tension is allowed to vary with radius

$$\Delta = \frac{\Delta_o}{1 + \frac{a}{r}}$$

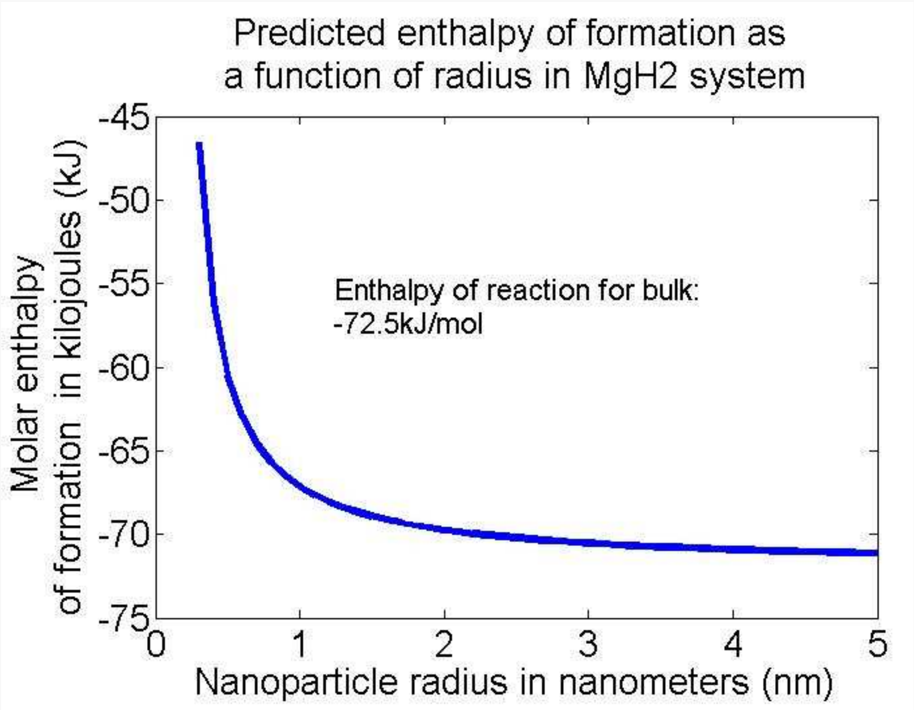


DFT values of internal energy calculated by Wagemans et al. J.Am. Chem. Soc. 2005, 127

Enthalpy of Reaction

$$\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} + \frac{3\overline{V}_M \Delta_{M \to MH}}{rRT} - \frac{\Delta S_o}{R}$$

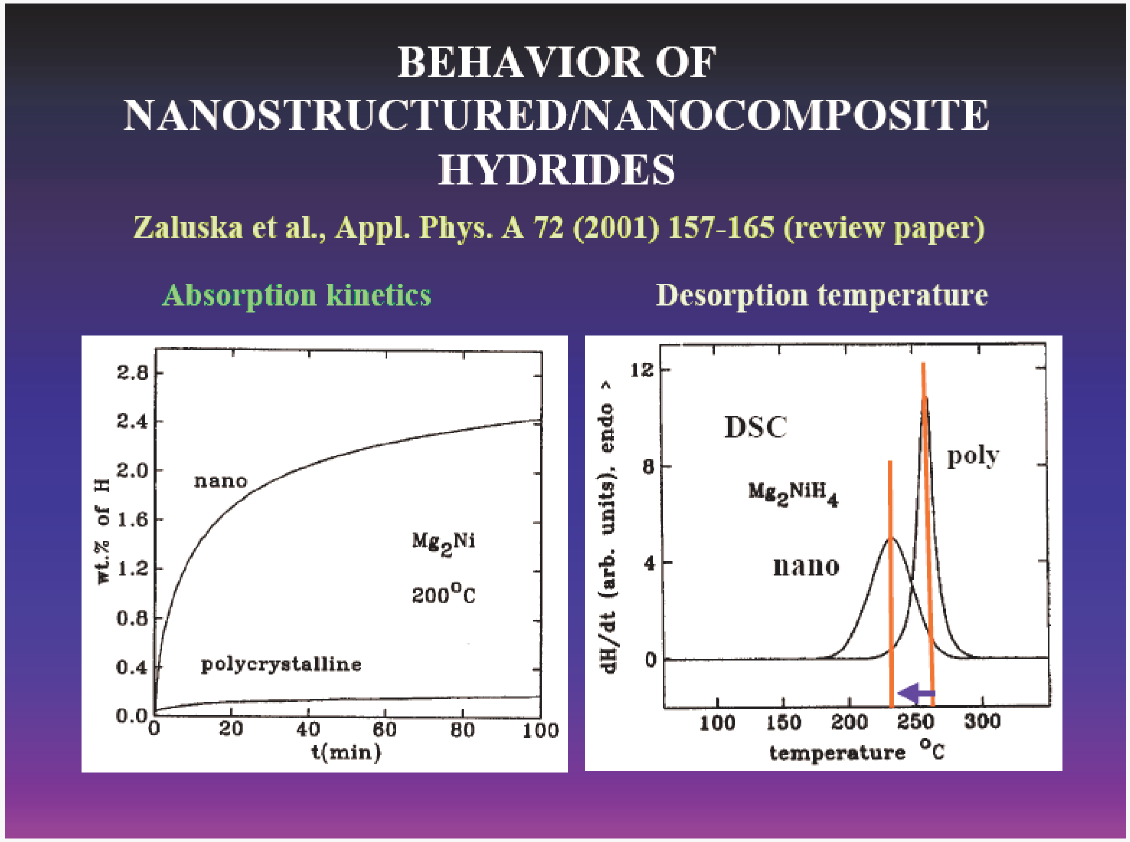
$$\Delta H_{eff} = \Delta H_o + \frac{3\overline{V}_M \Delta_{M \to MH}}{r}$$



- **Nanoparticles with positive Δ will have**

  Lower equilibrium temperature
  Less heat release during hydrogenation

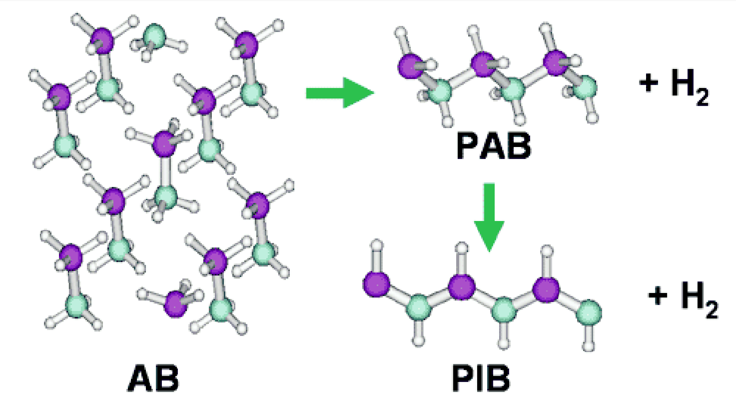
Improving sorptions properties with nanotechnology

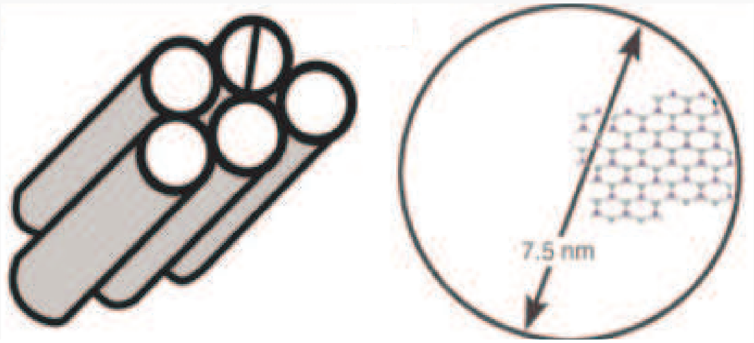


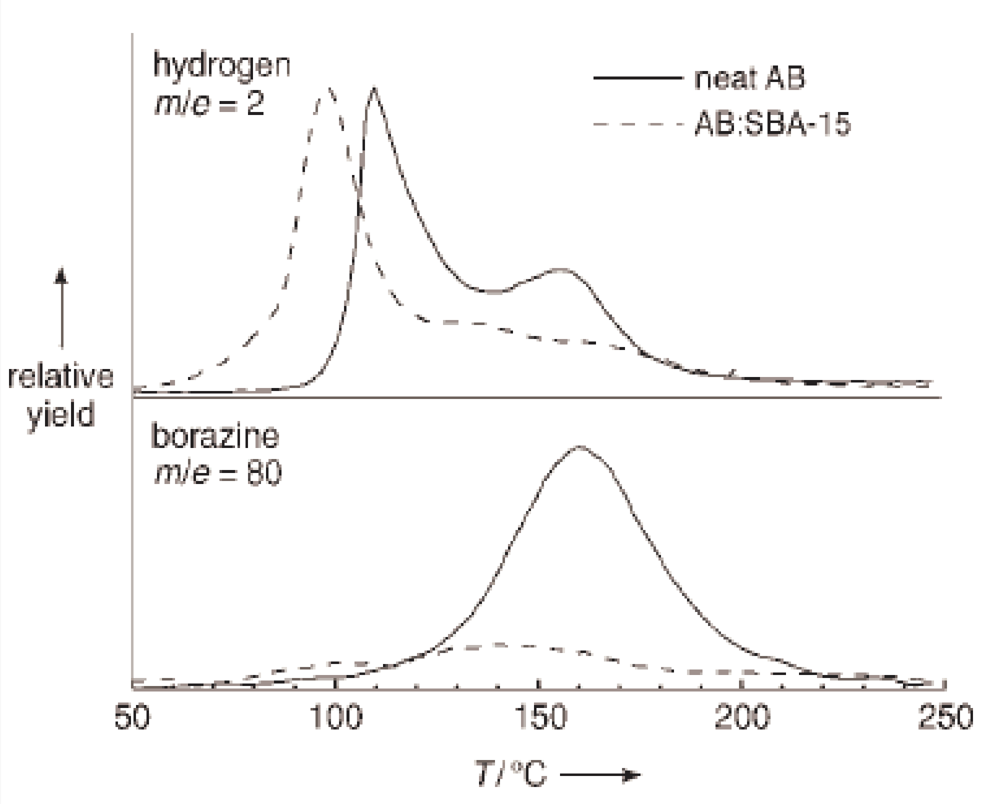
- The bulk hydride sorption rate is prohibitively small and release temperature is too high.
- Reducing grain and particle size increases kinetics and uptake.
- Surface energies and material properties at nanoscale offer ways to tune the energetics of absorption and desorption.

Nanoscafolding to improve kinetics and change thermodynamics: Borazane (NH_3BH_3)

- Nanoscaffolding improves kinetics and reduces enthalpy of formation (catalytic effect)
- Reduces emmisions of unwanted chemicals





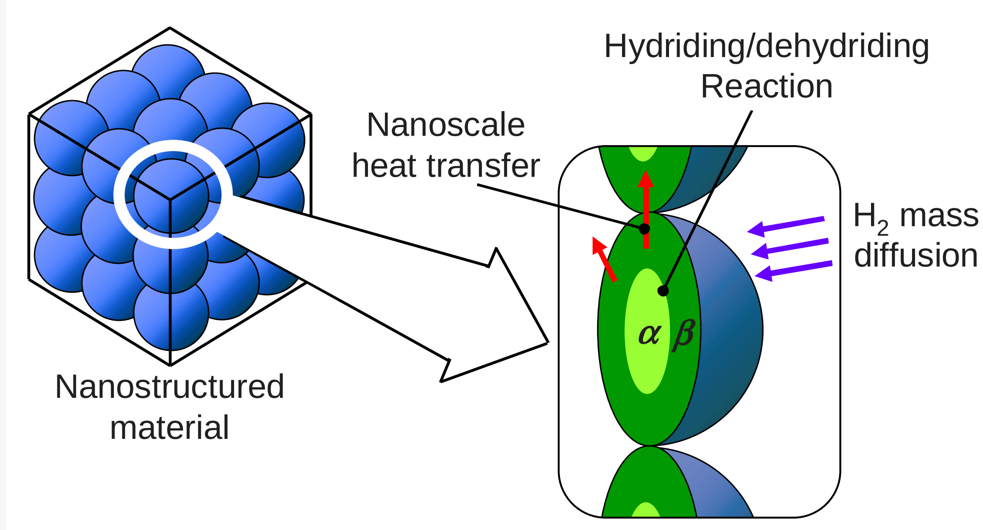


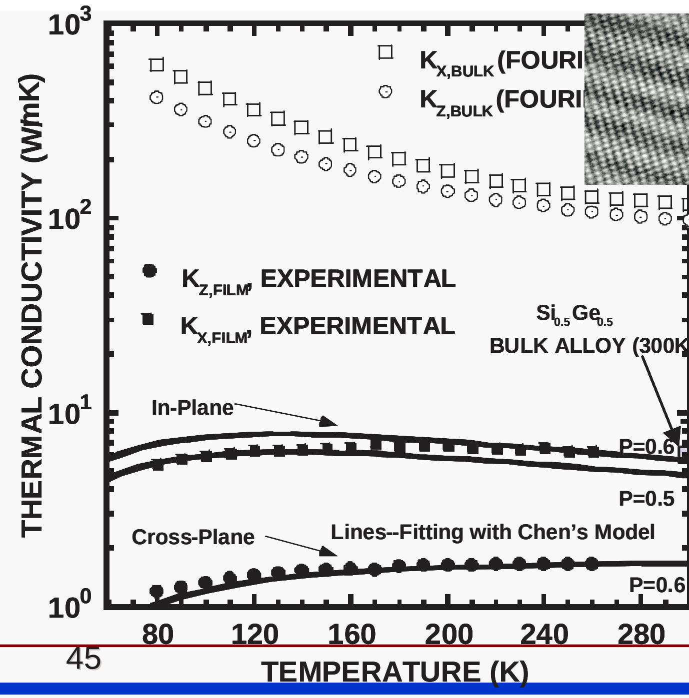
- Scaffolding decreases H wt-% by half.
- Reversibility is still an issue

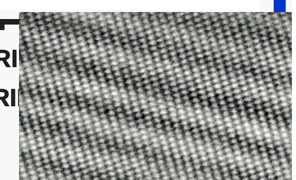
T. Autrey et al., Angew. Chem. Int. Ed. 2005, 44, 3578 –3582.

Mass and Heat Transfer

- Diffusion limited hydride reaction.
- Optimal pore and particle sizes: balance pore diffusion and diffusion in the solid particle to control kinetics.
- The strongly exothermic hydriding reaction increases the sample's temperature which reduces the reaction rate or even stops the reaction altogether.
- Rapid hydriding reaction thus requires effective heat removal solution.
- Nanostructures usually have poor heat transfer characteristics. Therefore, we need to balance mass diffusion kinetics with heat transfer.







Summary

- Key issues: volumetric and gravimetric density.
- Thermodynamics: sorption/desorption temperature.
- Kinetics, mass and heat transfer: pumping time
- Reversibility: cycling time
- Nanoscale effects on storage density, thermodynamics, kinetics, and heat transfer