# Overview of the Hydrogen Initiative

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Collaborators H$_2$ report

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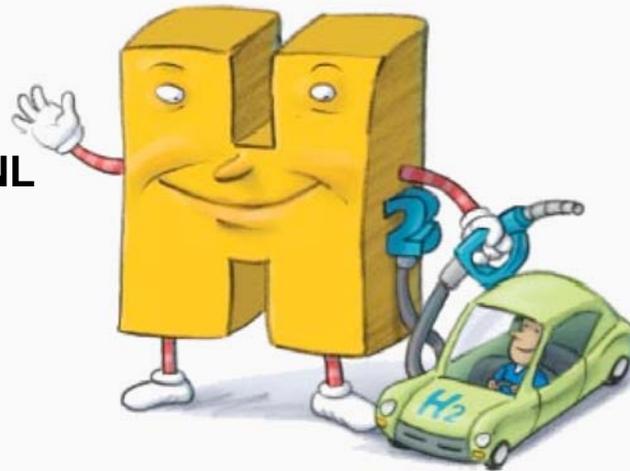
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Outline

- Overview of the energy challenge
- What is the hydrogen initiative?
- Hydrogen storage overview
- Some highlights of the DOE program

Demographic Expansion
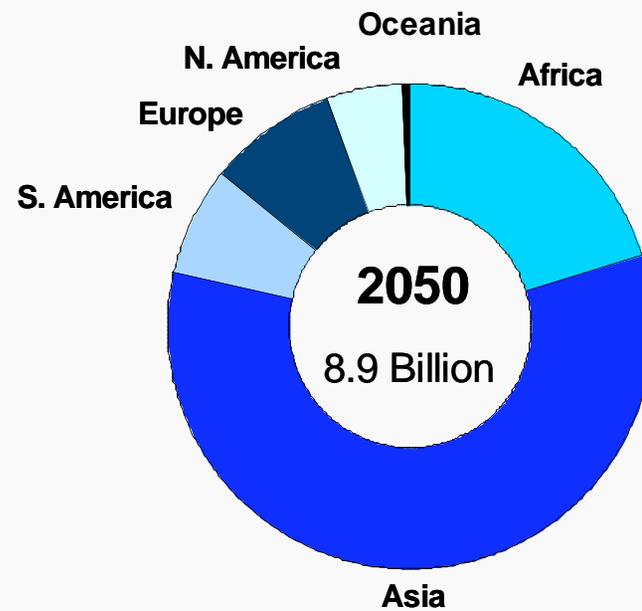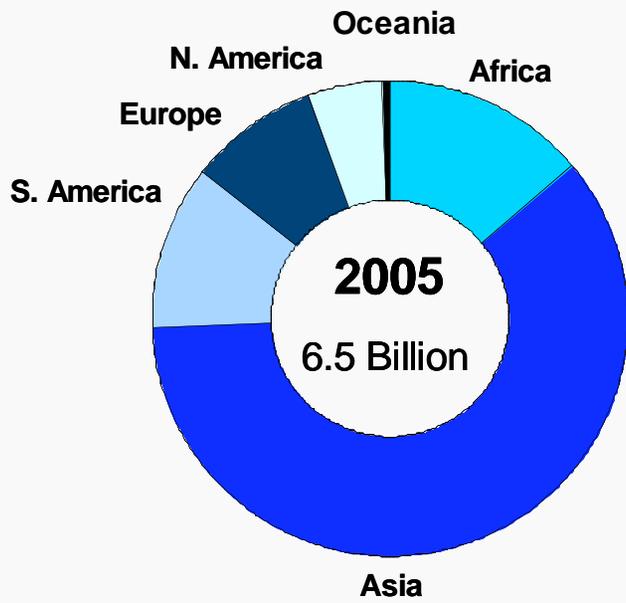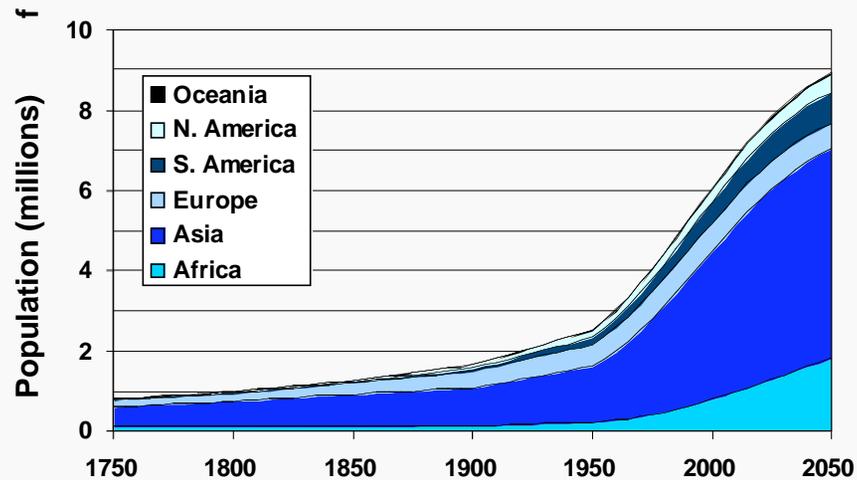
Growing world energy needs

Energy demand and GDP per capita (1980-2002)


World Energy Demand
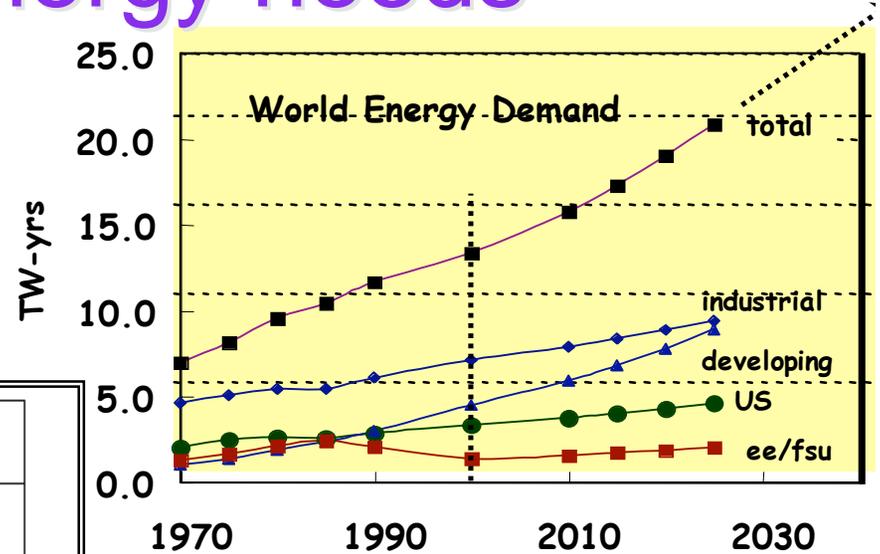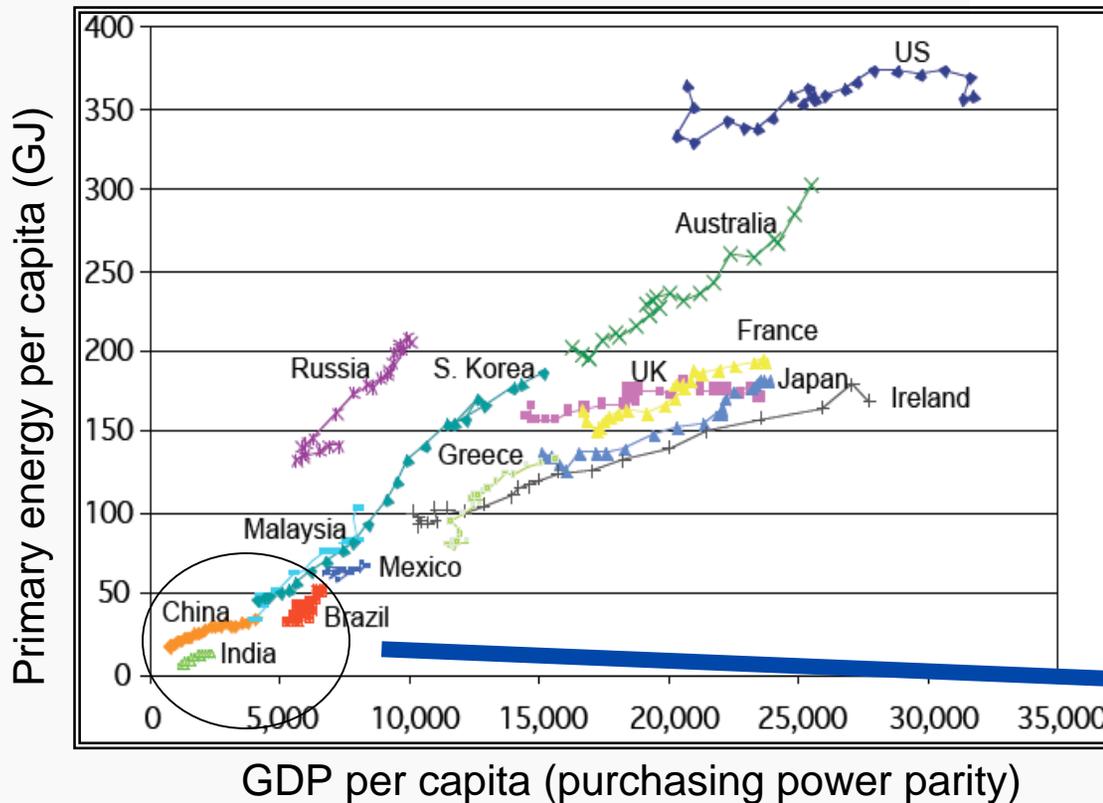
2000: 13 TW
2050: 30 TW
2100: 46 TW
(Hoffert et al Nature 395, 883,1998)

• 40% of the world's population is in the fast developing regions that have the fastest energy consumption increase.

The Energy Security/Access Challenge

World oil reserves/consumption 2001

OPEC: Venezuela, Iran, Iraq, Kuwait, Qatar, Saudi Arabia, United Arab Emirates, Algeria, Libya, Nigeria, and Indonesia
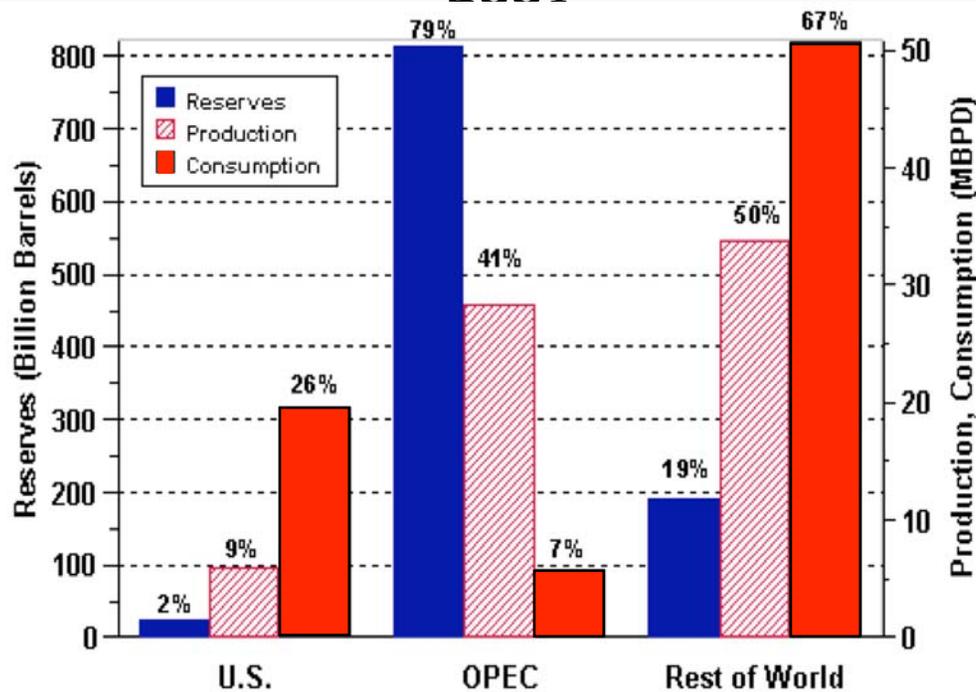
Estimated world reserves (R/P)

	Conventional reserves	Unconventional reserves	Yet to find
Oil	~ 22 years	~ 11 years	~ 7 years
Gas	~ 31 years	~ 12 years	~ 24 years
coal	~ 200 years	N/A	N/A

Source: BP estimate

Demand and supply are inversely correlated geographically

The Energy Source Challenge

2003

TODAY

14 Terawatts (world)

| (bar chart, vertical axis 0–50) |
| Oil: 35 |
| Coal: ~23.5 |
| Gas: ~21 |
| Fission: ~7 |
| Biomass: ~11 |
| Hydroelectric: ~2.5 |
| Solar, wind, geothermal: 0.5% |

Source: International Energy Agency

2050

2050

30 – 60 Terawatts (world)

| (bar chart, vertical axis 0–50) |
| Oil: ~7 |
| Coal: ~9 |
| Gas: ~10 |
| Fusion / Fission: ~15 |
| Biomass: ~6 |
| Hydroelectric: ~5 |
| Solar, wind, geothermal: ~48 |
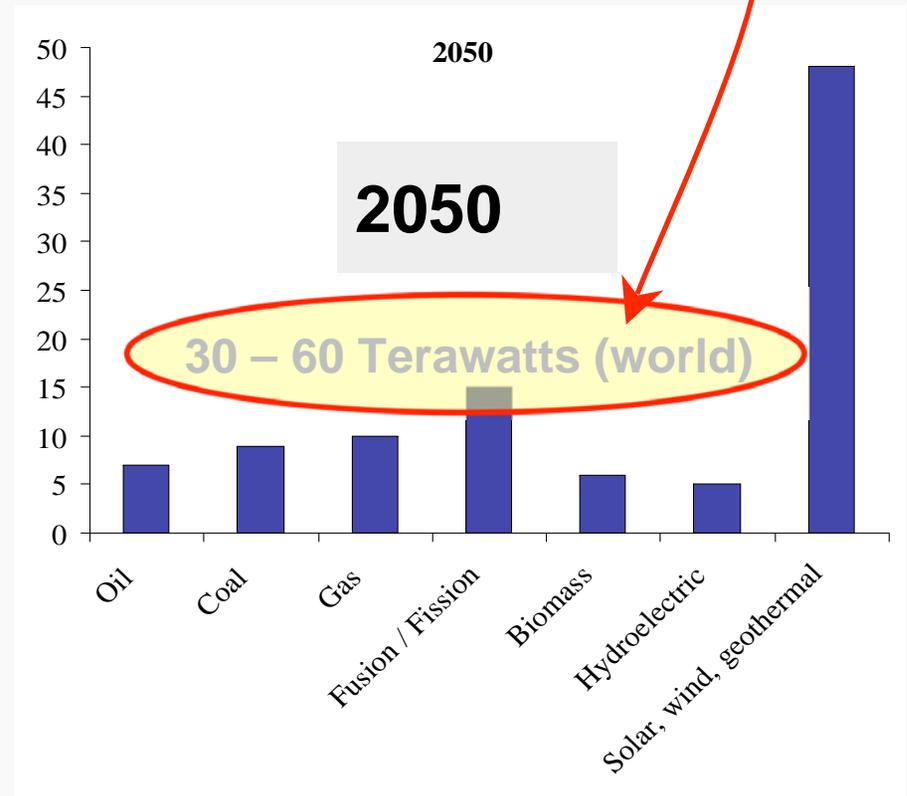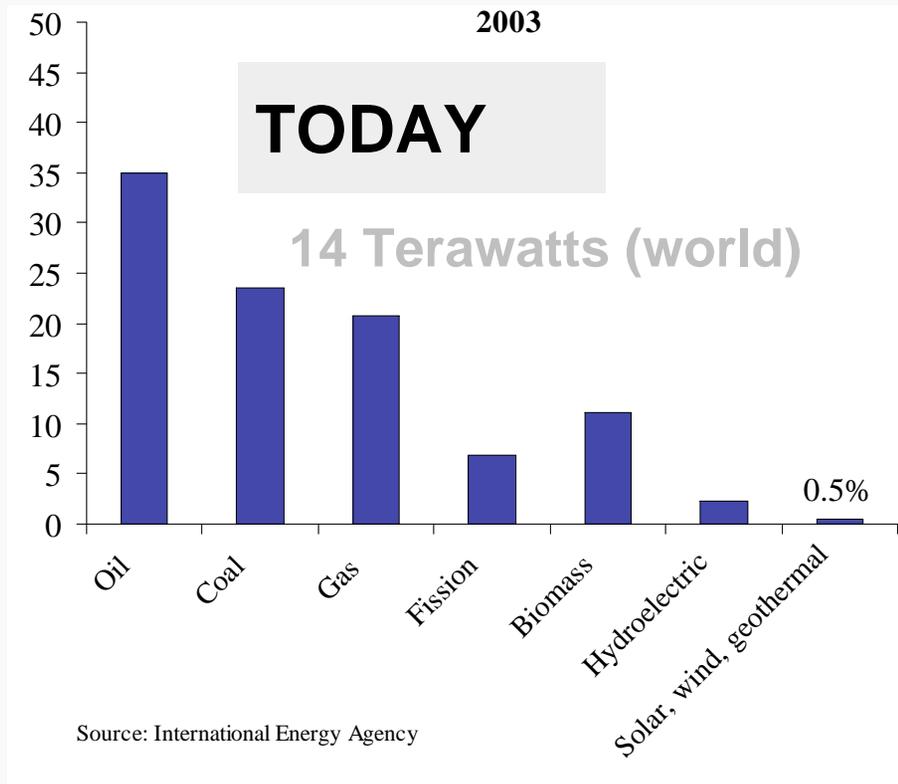
- The sun is the ultimate renewable energy source
- Achieve Energy sustainability through renewable energy.
- Find substitute for gasoline (portable high density energy)
- Achieve cost efficient technologies

# Energy Challenges: Climate Change
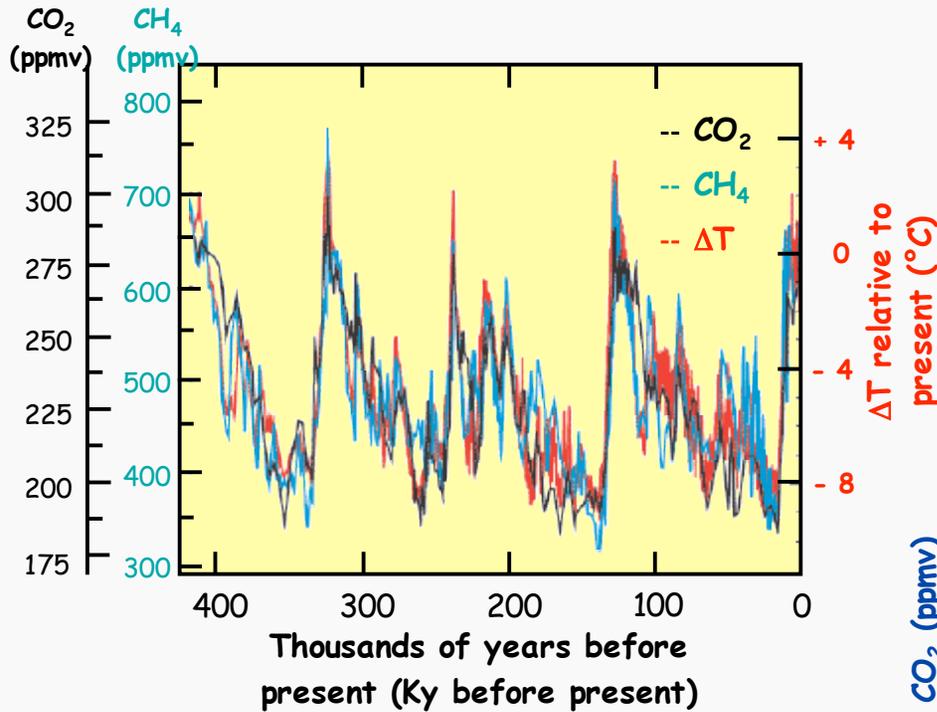
Relaxation times

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
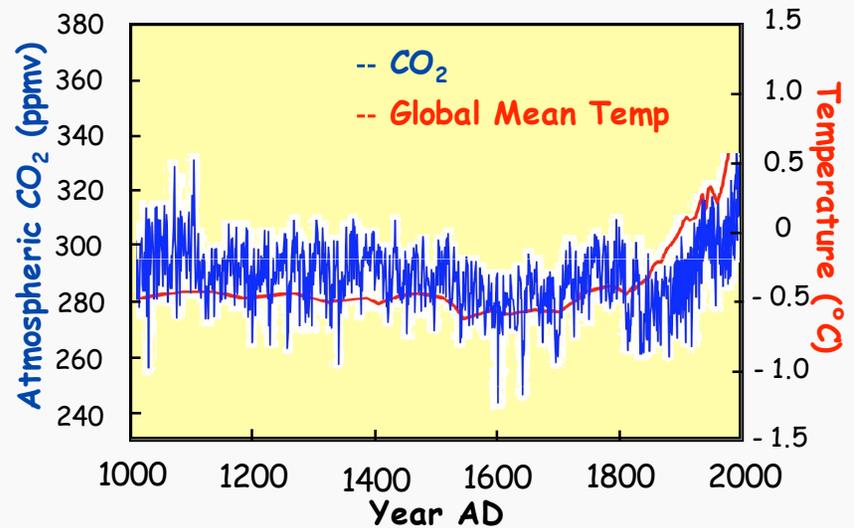
Challenge: Efficient Energy Conversion: Thermoelectricity (TE)

TE efficiency lags behind

$$ZT_{\text{TE}} \sim 1$$
$$ZT_{\text{Mech}} \sim 3$$

Heat

p n

I   I

Advantages of Thermoelectrics

- No moving parts

- Environmentally friendly

- No loss of efficiency with size reduction

- Can be integrated with electronic circuits (e.g. CPU)

- Rapid localized cooling with rapid response

Discovery of compounds with $ZT < 1$

Bi_2Te_3 and alloys with Sb, Se

(ZT)$_{300K}$ vs Year
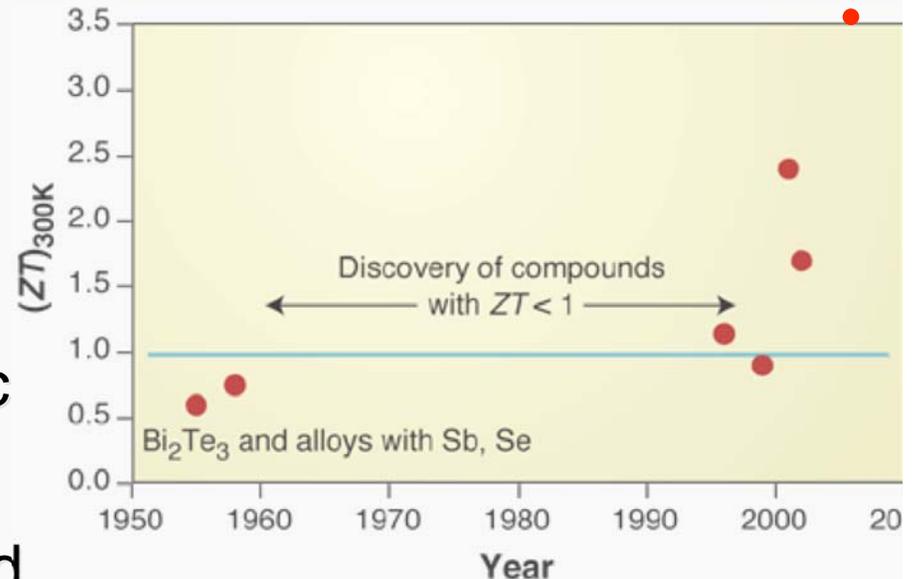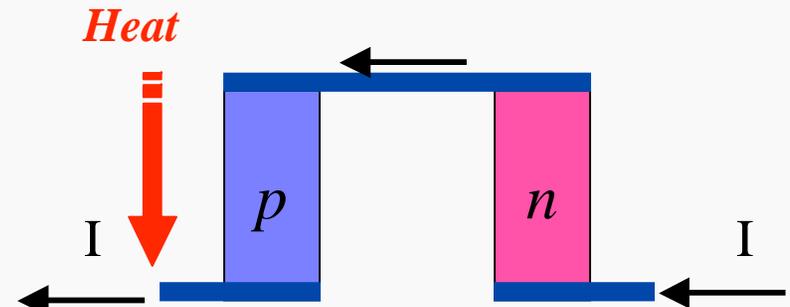
Nanostructures promise higher efficiencies

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Hydrogen: A US 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

Why Hydrogen? Abundant, clean, efficient

Production

Storage

Use

Biomass

Hydro
Wind
Solar

Nuclear

Oil

Coal

Natural
Gas

With Carbon Sequestration

Storage is Bottleneck

Transportation

Distributed Generation

HIGH EFFICIENCY & RELIABILITY

ZERO/NEAR ZERO EMISSIONS
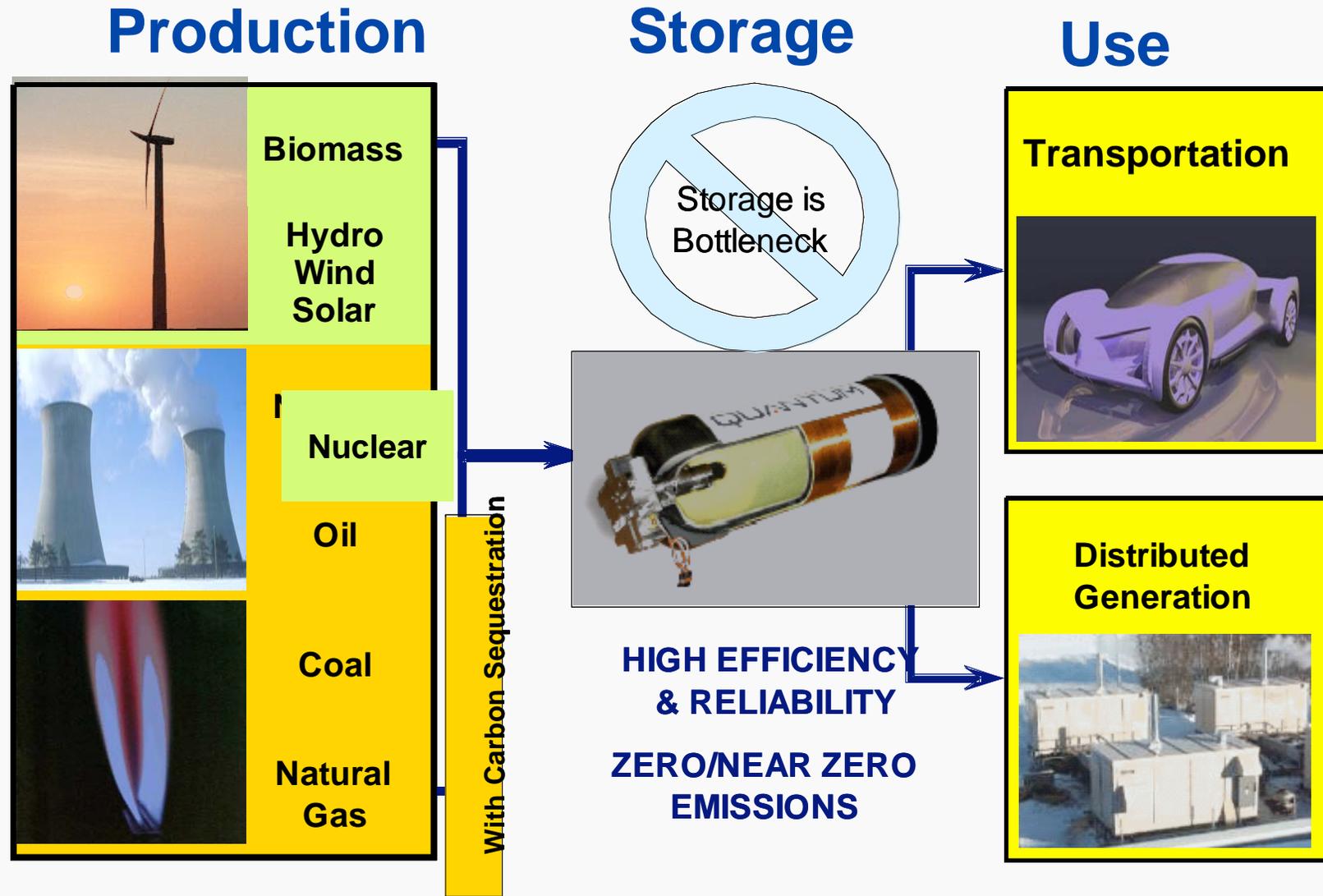
From Patrovic & Milliken (2003) and *James Wang Sandia National Laboratories*

The Hydrogen Economy – The Technology Gaps

H₂O

solar wind hydro

nuclear/solar thermochemical cycles

H_2

gas or hydride storage

H_2

automotive fuel cells

consumer electronics

stationary electricity/heat generation

Bio- and bioinspired

fossil fuel reforming
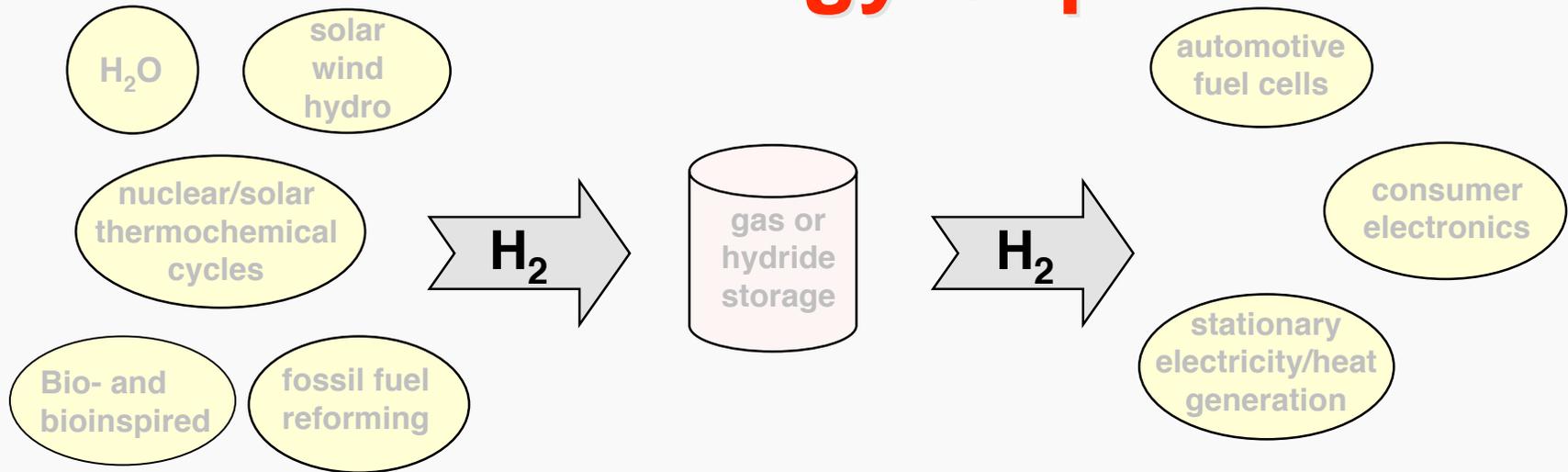
| *production*	*storage*	*use (in fuel cells)*
9M tons/yr	**4.4 MJ/L (Gas, 10,000 psi)** **8.4 MJ/L (LH2)**	**$200-3000/kW**
Gap	*Gap*	*Gap*
150M tons/yr **(Light Cars and Trucks in 2040)**	**9.7 MJ/L** **(2015 FreedomCAR Target)**	**$30/kW** **(Internal Combustion Engine)**

Hydrogen Storage

Current Technology for automotive applications

• **Tanks for gaseous or liquid hydrogen storage.**

• **Progress demonstrated in solid state storage materials.**

System Requirements

• **Compact, light-weight, affordable storage.**

• **System requirements set for FreedomCAR: 4.5 wt% hydrogen for 2005, 9 wt% hydrogen for 2015.**

• **No current storage system or material meets all targets.**
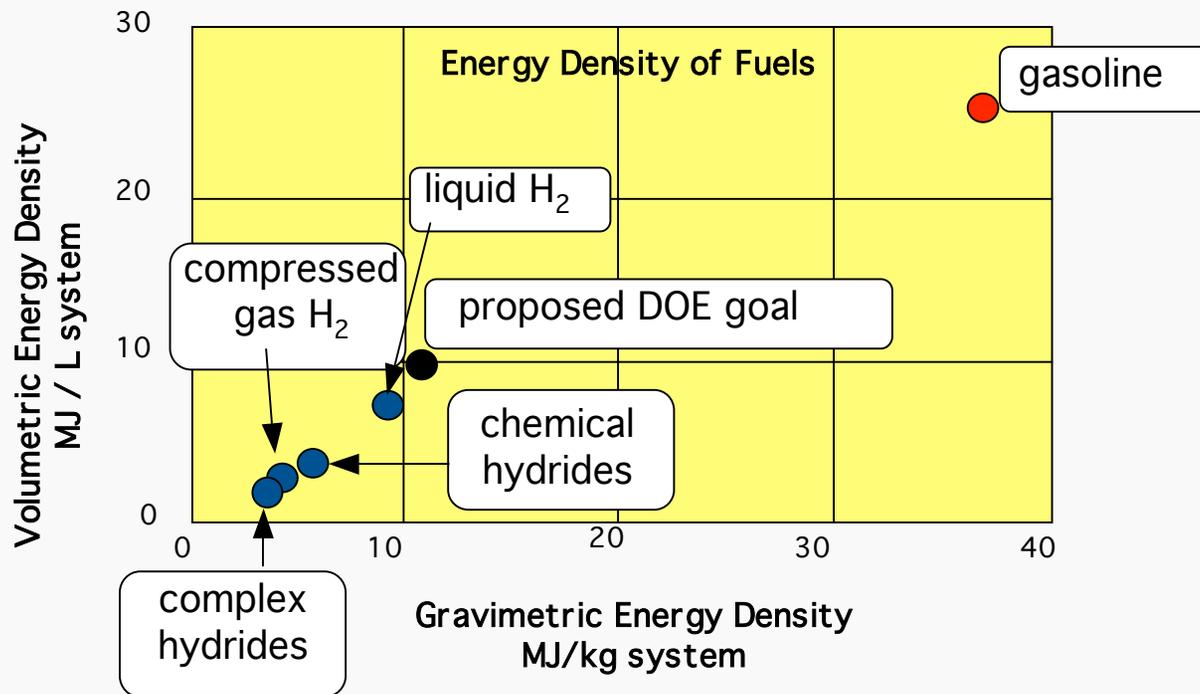
Summary: Research for Short-term Showstoppers and Long-term Challenges

Energy Payoff

fuel cell operation

splitting water

solid state storage

Short-term: Incremental advances via basic research and technology development

Longer-term: Breakthrough technologies via new materials and catalysts, bio-mimetics, nanoscale architectures, and more.

combustion in heat engines

gas/liquid storage

fossil fuel reforming

Evolution of a Hydrogen Economy

Hydrogen storage is largest bottleneck

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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/kW-h	$50/kW-h	$18/kW-h
Fueling time (reaction kinetics)	30 s/kg-H$_2$	✖ (too slow)	✖
Operating temperature	-40 to 60 °C	✖ (too high)	✔
Operating pressure	<100 atm.	✔	✔

JoAnn Milliken (2002)

Storage Options

Metal/complex hydrides:

- Slow kinetics
- Heat management issues
- High release temperature

Chemical hydrides:

- ▲ Not reversible (on-board)
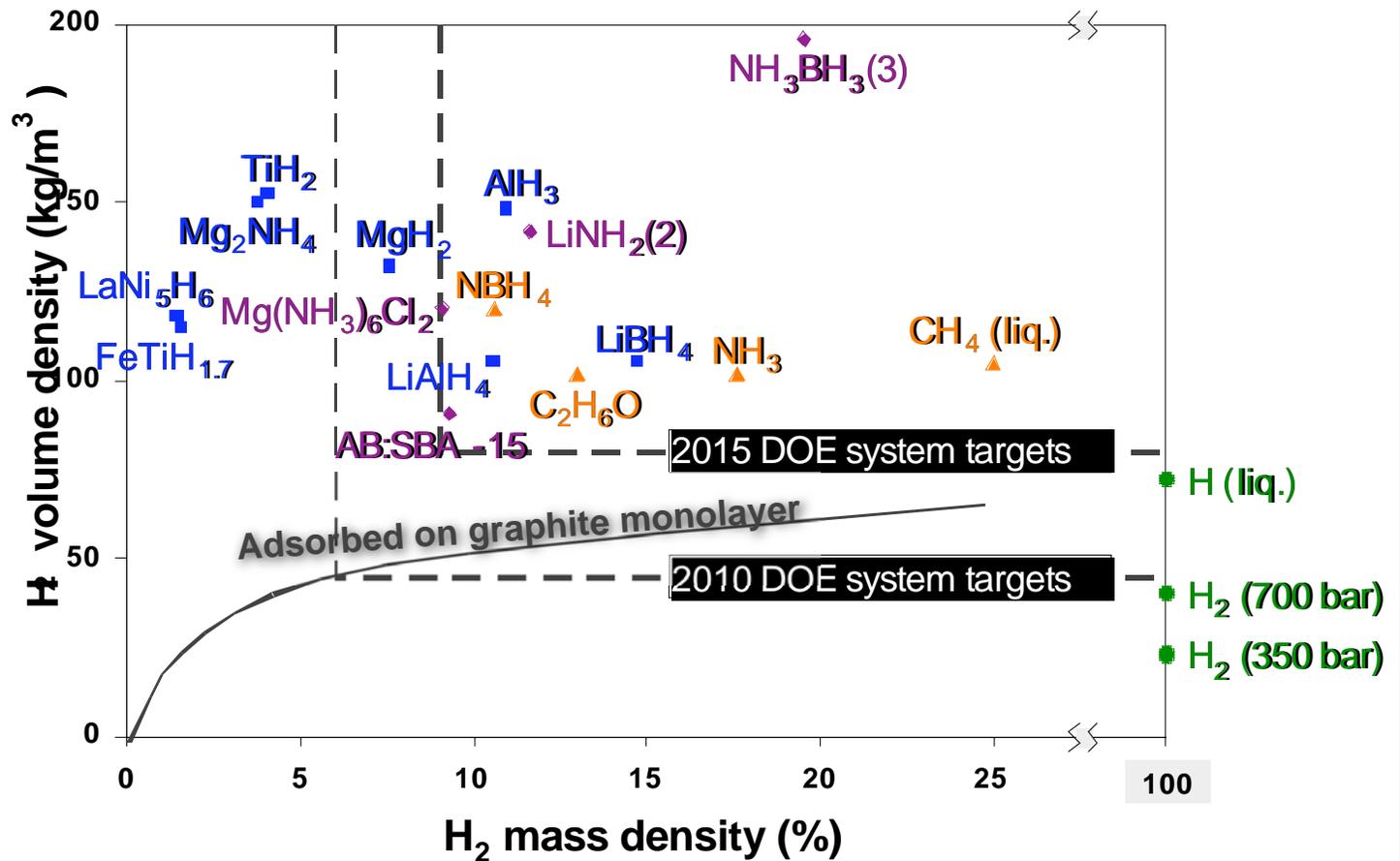
Carbon structures:

- Low temperature
- Low wt. %

**Hydrogen:**

- Low volumetric density
- High compression cost

Chart axes: H_2 volume density (kg/m^3) vs. H_2 mass density (%)

Data points: NH_3BH_3(3), TiH_2, AlH_3, Mg_2NH_4, $LiNH_2$(2), MgH_2, $LaNi_5H_6$, $Mg(NH_3)_6Cl_2$, NBH_4, $FeTiH_{1.7}$, CH_4 (liq.), $LiBH_4$, NH_3, $LiAlH_4$, C_2H_6O, AB:SBA –15, H (liq.), H_2 (700 bar), H_2 (350 bar)

2015 DOE system targets, 2010 DOE system targets, Adsorbed on graphite monolayer

Metal ammine complexes

	Gravimetric H$_2$ density (% H$_2$)	Volumetric H$_2$ density/ (kg m^{-3})
Mg(NH$_3$)$_6$Cl$_2$	9.1	110
Ca(NH$_3$)$_8$Cl$_2$	9.7	120

Mg(NH$_3$)$_6$Cl$_2$ (s) → MgCl$_2$ (s)+ 6NH$_3$(g)
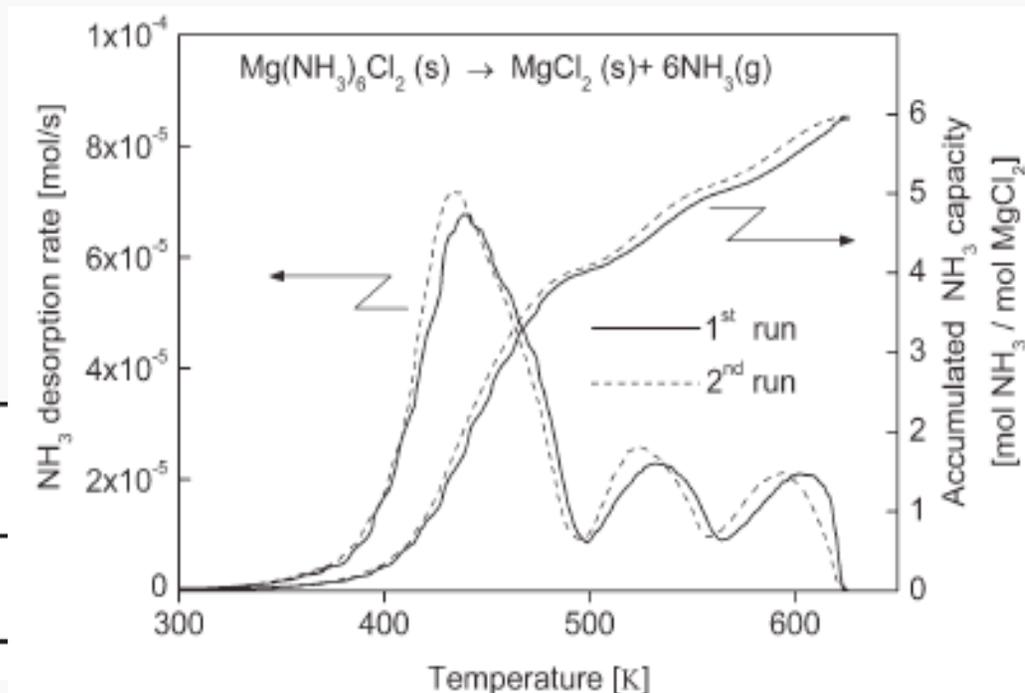
- Mg(NH$_3$)$_6$Cl$_2$ = MgCl$_2$ + 6NH$_3$ (9.1%) @ T <620K
- Ammonia is toxic
- NH$_3$ can be used in high T solid oxide fuel cells.
- High temperature of hydrogen release

$$2NH_3 \rightarrow 3H_2 + N_2 @ \sim600K$$

Christensen et al., J. Mater. Chem., 2005, 15, 4106–4108
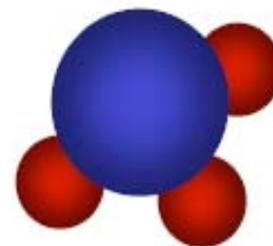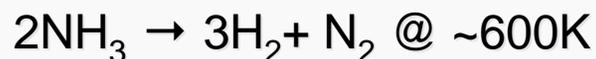
Imide (NH) and Amide (NH_2)

First step: $LiNH_2 + LiH \Longleftrightarrow Li_2NH + H_2$ (6.55% @ 300C,1atm.)
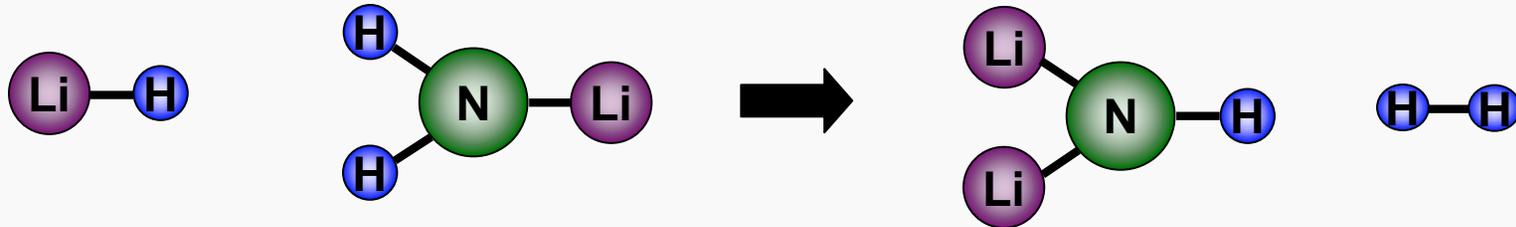
Second: $Li_2NH + LiH \Longleftrightarrow Li_3N + H_2$ (5% @ 300C 0.05atm)

•Release temperature too high (573K) and low release pressure.
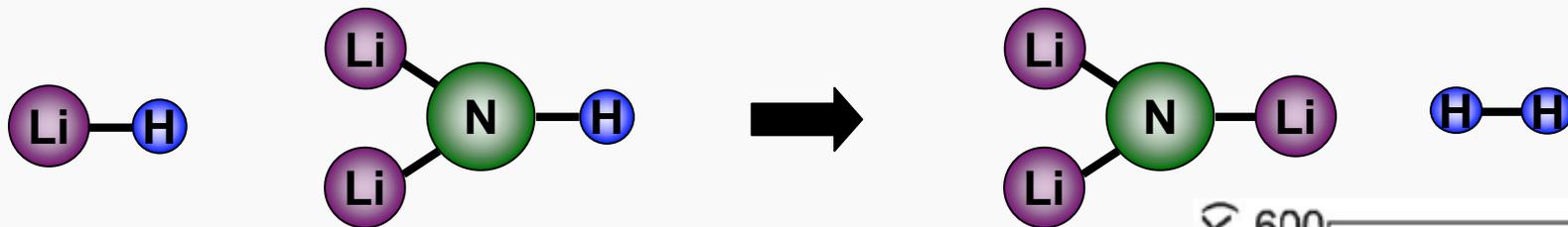
Partial Mg substitution reduces release temperature
$Li_{1-x}Mg_xNH_2$

S. Orimo et al., Appl. Phys. A:Materials Science & Processing, Vol 79, No 7, p. 1765 - 1767. (200??)
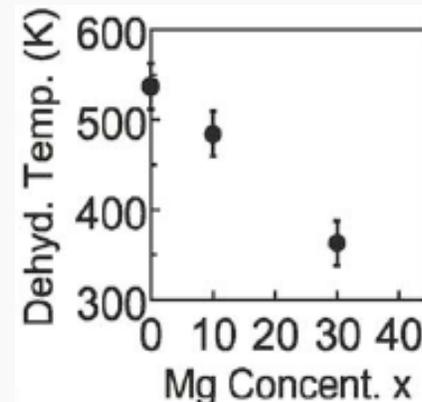
Desired binding energy range

J. E.Lennard-Jones, Trans. FaradaySoc. 28 (1932),pp. 333.
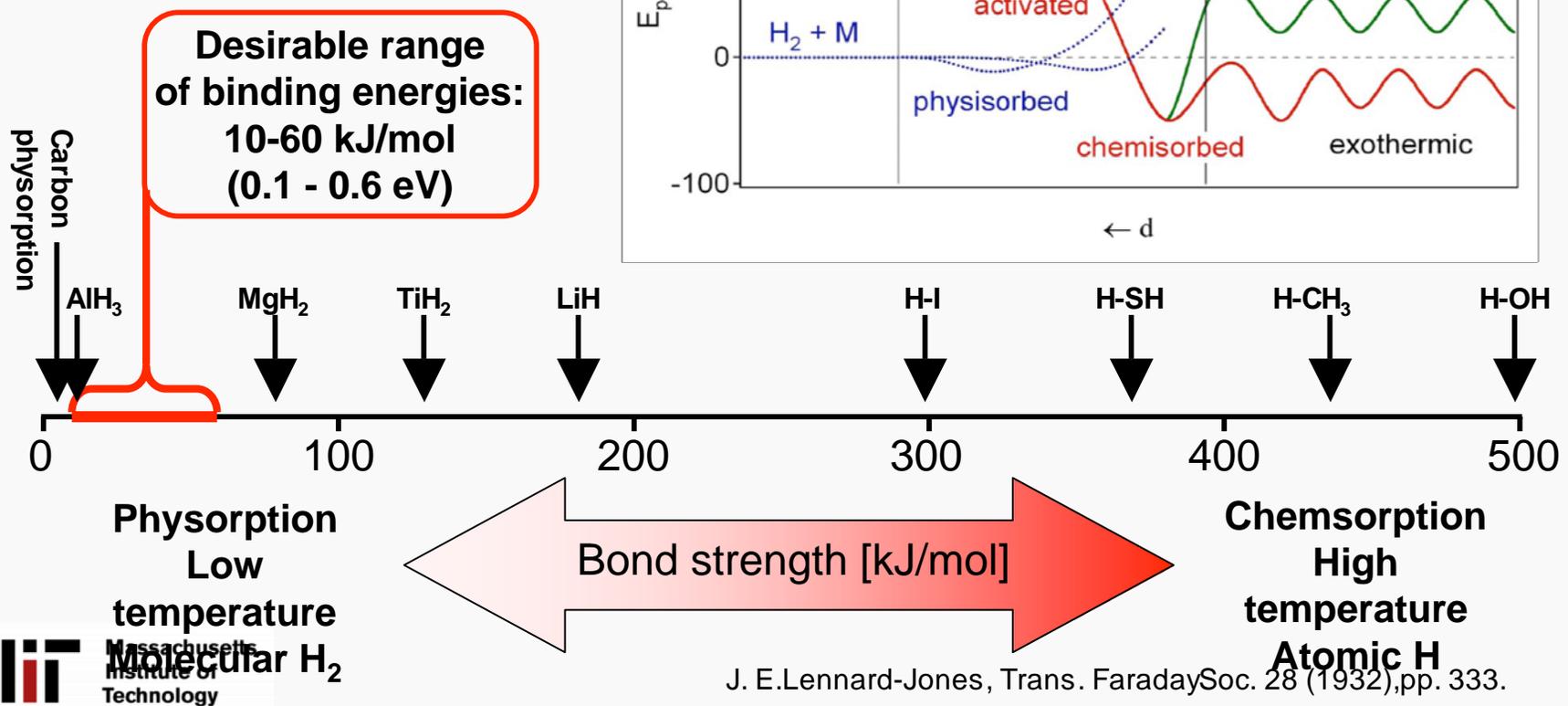
Improving sorption properties with nanotechnology

- The bulk hydride sorption rate is prohibitively small and release temperature is too high.
- Poor heat transfer leads to process interruption.
- Reducing grain and particle size increases kinetics and uptake.
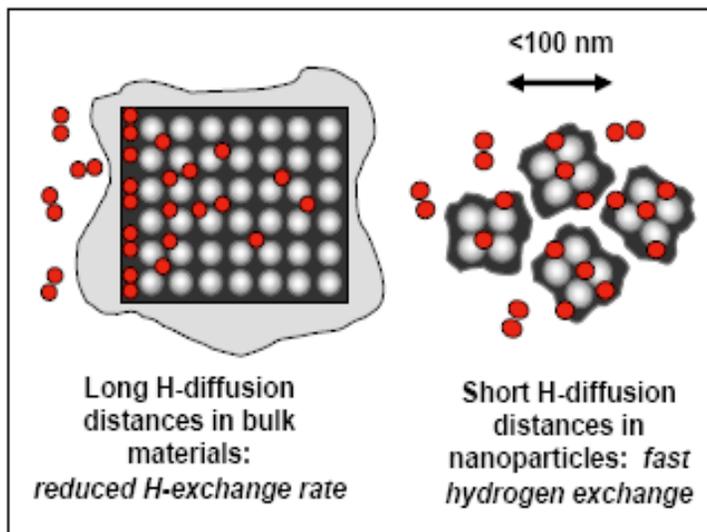

BEHAVIOR OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

Zaluska et al., Appl. Phys. A 72 (2001) 157-165 (review paper)

Absorption kinetics
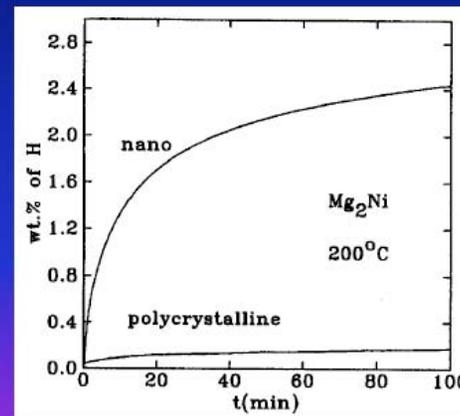
Desorption temperature


Long H-diffusion distances in bulk materials: *reduced H-exchange rate*

Short H-diffusion distances in nanoparticles: *fast hydrogen exchange*
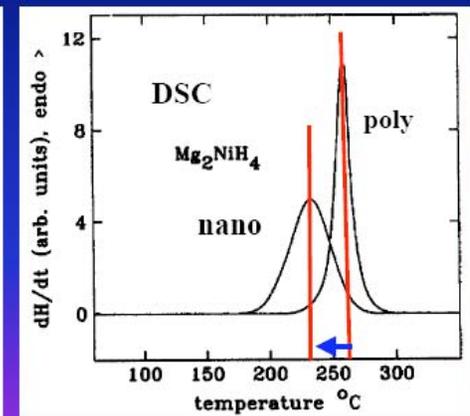
- Increased porosity and smaller size increase diffusion limited rates.
- Surface energies and material properties at the nanoscale offer ways to tune the energetics of absorption and desorption to reduce the release temperature and speed up release process

Nanoscale thermodynamics of absorption

Assuming the following reaction

$$M + H_2 \rightarrow MH_2$$
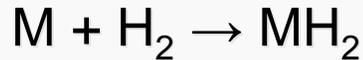
- At nanoscale, surface and size effects affect reaction enthalpy.
  - Increase surface to volume ratio.
  - Increase adsorption sites due to low coordination surface atoms.
  - Weaker binding energy in small metallic clusters.
  - Stability of a small metal cluster becomes dependent on number of atoms (electronic and geometric shell).

Bulk molar free energy of formation

$$\Delta G = \Delta G_o + RT \ln(\frac{a_{MH_2}}{a_M P_{H_2}})$$

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

$$\Delta G(r) = \Delta G_o(r) + RT \ln(\frac{a_{MH_2}}{a_M P_{H_2}})$$

$$+ \frac{3\Delta_{M \rightarrow MH_2}(\gamma A) + E_{adsorption}}{4\pi r^3}$$

$$\Delta_{M \rightarrow MH_2}(\gamma A) = 4\pi r_o^2(\gamma_{MH_2}(r)\left(\frac{\overline{V_{MH_2}}}{\overline{V_M}}\right)^{2/3} - \gamma_M(r))$$

$$E_{ads} = 4\pi r^2 \gamma_{MH_2 - H}(r)\left(\frac{\overline{V_{MH_2}}}{\overline{V_M}}\right)^{2/3}$$

# Nanoscale thermodynamics of absorption

Van't Hoff relation for nanosystem

$$\ln P_{H_2}^{eq} = \frac{\Delta H_o(r)}{RT} + \frac{3\overline{V_M}\overline{\gamma}}{rRT} - \frac{\Delta S_o(r)}{R}$$

$$\Delta H_{eff}(r) = \frac{\Delta H_o(r)}{R} + \frac{3\overline{V_M}\overline{\gamma}}{rR}$$

$$\overline{\gamma} = \left(\gamma_{MH}(r) + \gamma_{MH-H}(r)\right)\left(\frac{\overline{V_{MH}}}{\overline{V_M}}\right)^{2/3} - \gamma_M(r)$$

Assume one hydrided nanoparticle is in equilibrium with its non-hydrided counterpart, then any system for which the extra surface energy term   is positive will have a smaller enthalpy of formation and will release hydrogen at a lower temperature.

Van't Hoff plot for a model MH_2 hydride

VAN'T HOFF PLOT:

ln P_{eq}

Decreasing r

$$\ln P_{eq} = \frac{\Delta H_0}{RT} + \frac{3\overline{V_M}\overline{\gamma}}{rRT} + \frac{\Delta S_0}{R}$$

$$\overline{\gamma} = \gamma_{MH_x}\left(\overline{V_{MH_x}}/\overline{V_M}\right)^{2/3} - \gamma_M$$

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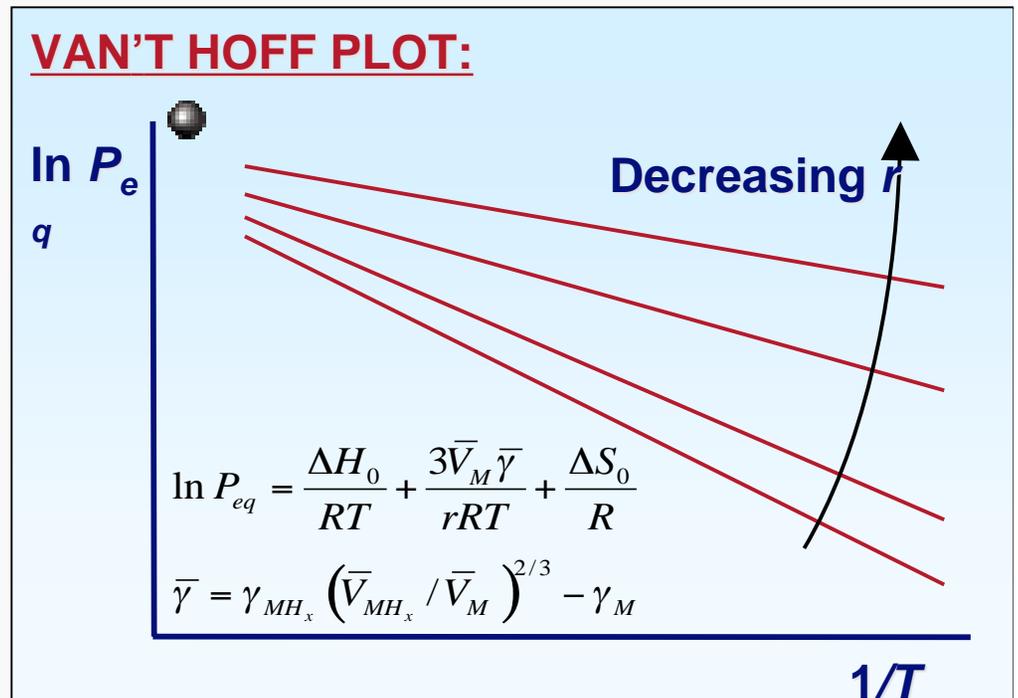
Nanoscafolding to improve kinetics and change thermodynamics: Borazane (NH_3BH_3)

- Nanoscaffolding improves kinetics and reduces enthalpy of formation (catalytic effect)
- Reduces emissions of unwanted chemicals (borazine)
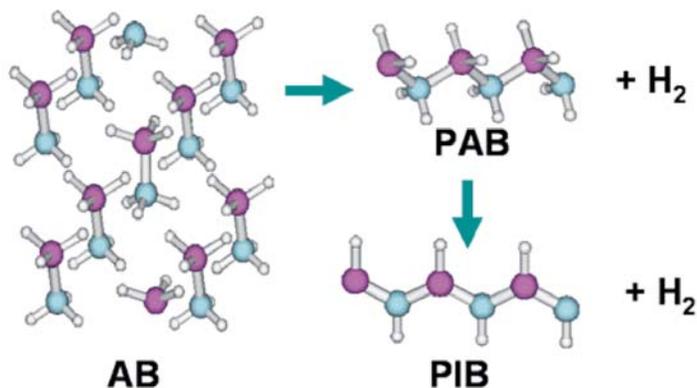
Remaining challenges

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

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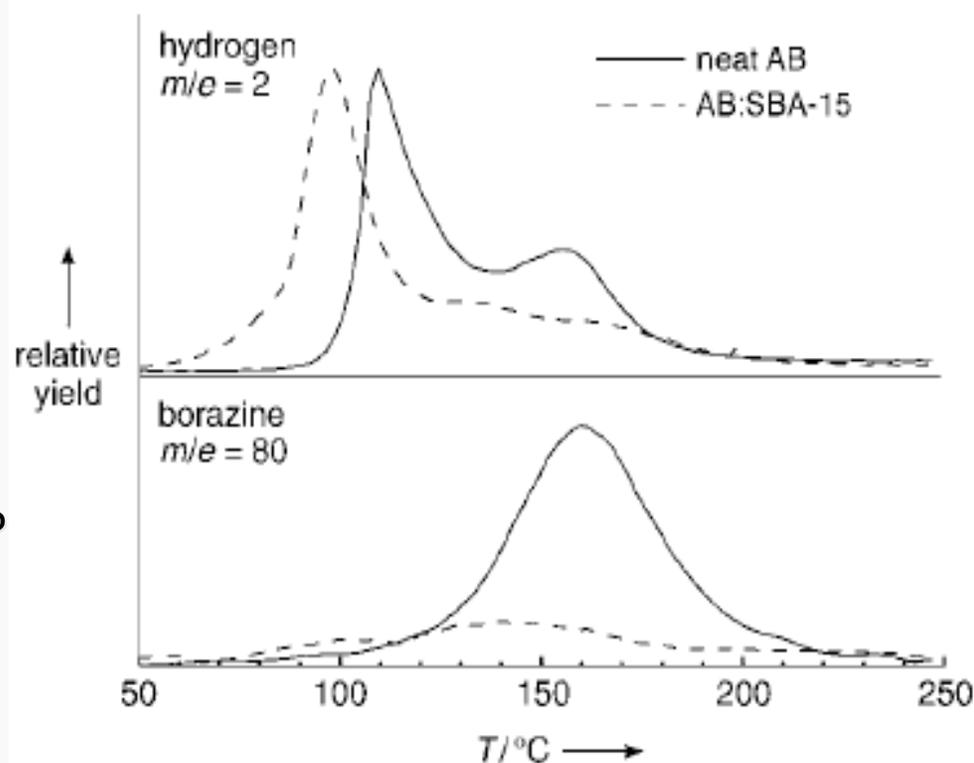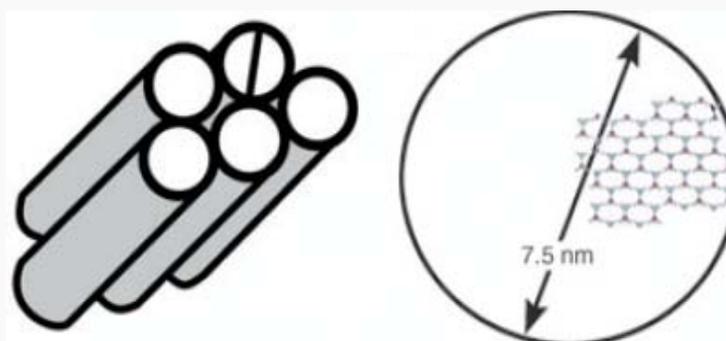
Thermal Management

- Hyriding reaction: ~1 MW for 5 min (5Kg H_2).

- Nanostructured materials impair heat transfer

- Temperature rise suppresses reaction that evolves hydrogen

- Typical hydride conductivity: k~0.1 W/m-K

SOLUTIONS

Foams: Al, C, etc

Wire mesh

Klein et. al., Int. J. Hydrogen Energy 29 (2003) 1503-1511
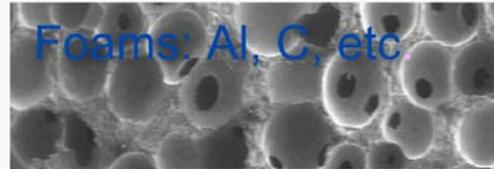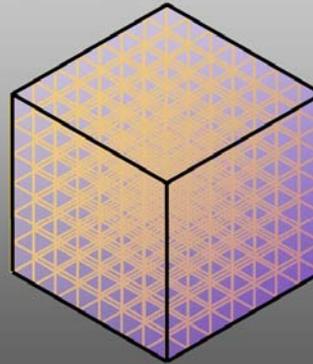
Conductive foams, fins and meshes

Expanded Graphite Compacts

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

Strategies to lower release temperature
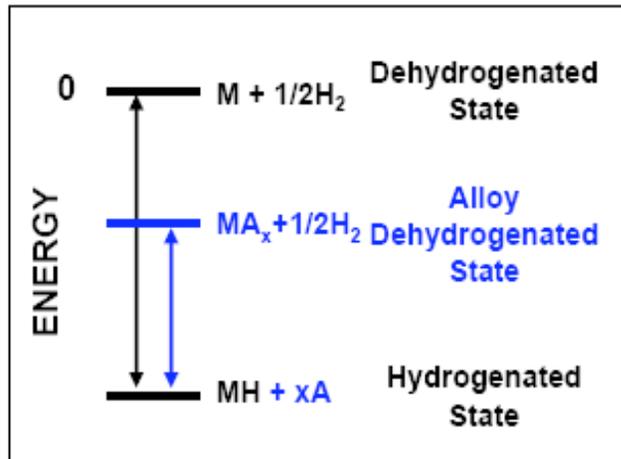
**Gregory L. Olson** *DOE 2005 Hydrogen Program Annual Review*

Forming new alloys

•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$_4$
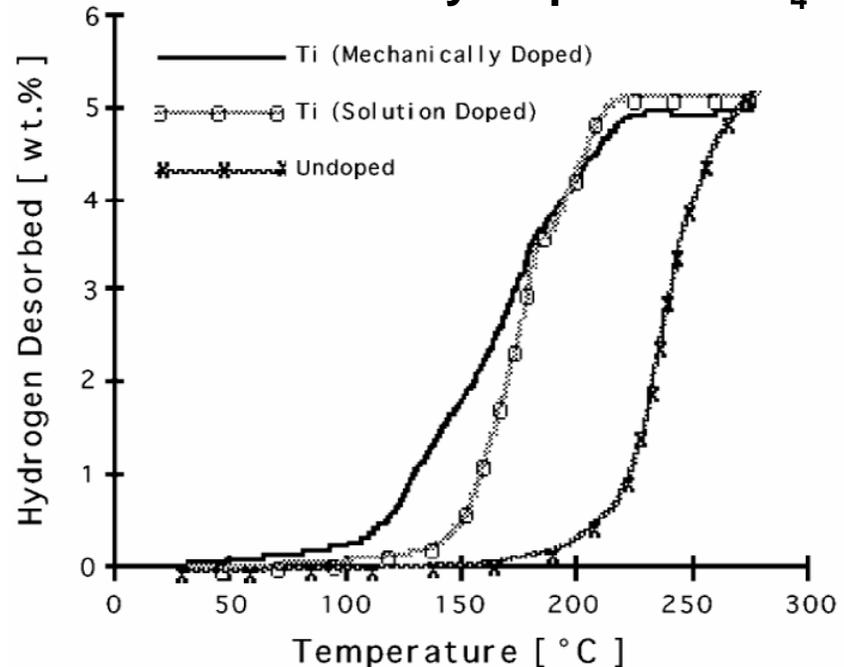
R.A. Zidan et al, J. Alloys and Compounds 285 (1999), pp. 119.

# High Throughput Screening of Nanostructured Hydrogen Storage Materials

Combinatorial nanoparticle synthesis system

Nanoporous synthesis system

Intematix

Elemental ratio of binary alloy (A/B)	Laser Pyrolysis Condition	
	1	2
1:1		
1:1.5		
1:2		
1:3		

Berkeley
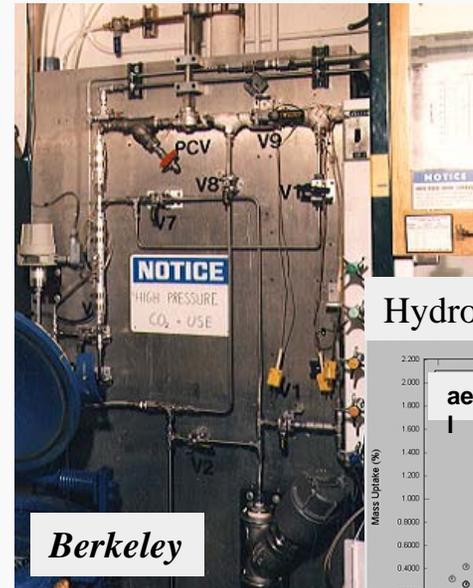
Hydrogen sorption results

aerogel

Mg-Ni nanoparticle library

NC State
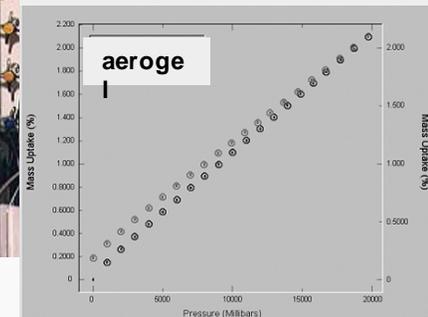
Left Vial - pure aerogel (no additives)
Middle Vial - aerogel with MgH_2 (~50 wt%)
Right Vial - aerogel with MgH_2 (~50 wt%) and a catalyst with a size of 100nm (~2 wt%)

Chen, Dresselhaus, Grigoropoulos, Mao, Xiang, and Zeng

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Discovery of Near-Surface Alloys for Hydrogen-Bearing Catalysts from First Principles

The study of catalysts that would activate hydrogen-containing molecules to produce hydrogen at ultra-low temperature led to the theoretical discovery of near-surface alloys. In near-surface alloys, a solute metal is present near the surface of a host metal in concentrations different from the bulk. Such nanostructures possess unique electronic properties that in turn affect their surface catalytic properties. Using density functional theory calculations, M. Mavrikakis showed that some alloys, e.g., Ni/Pt(111) and V/Pd(111), bind atomic hydrogen (H) as weakly as the noble metals (Cu, Au) while, at the same time, dissociate H_2 much more easily. This unique behavior will permit those alloys –as some preliminary experiments have suggested-- to catalyze reactions in hydrogen fuel cells and in hydrogen storage materials at very low-temperature.
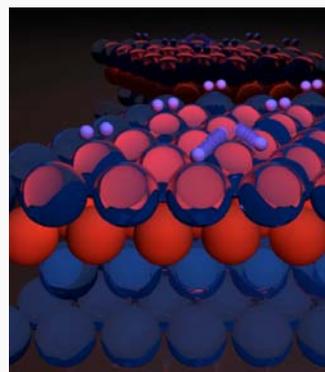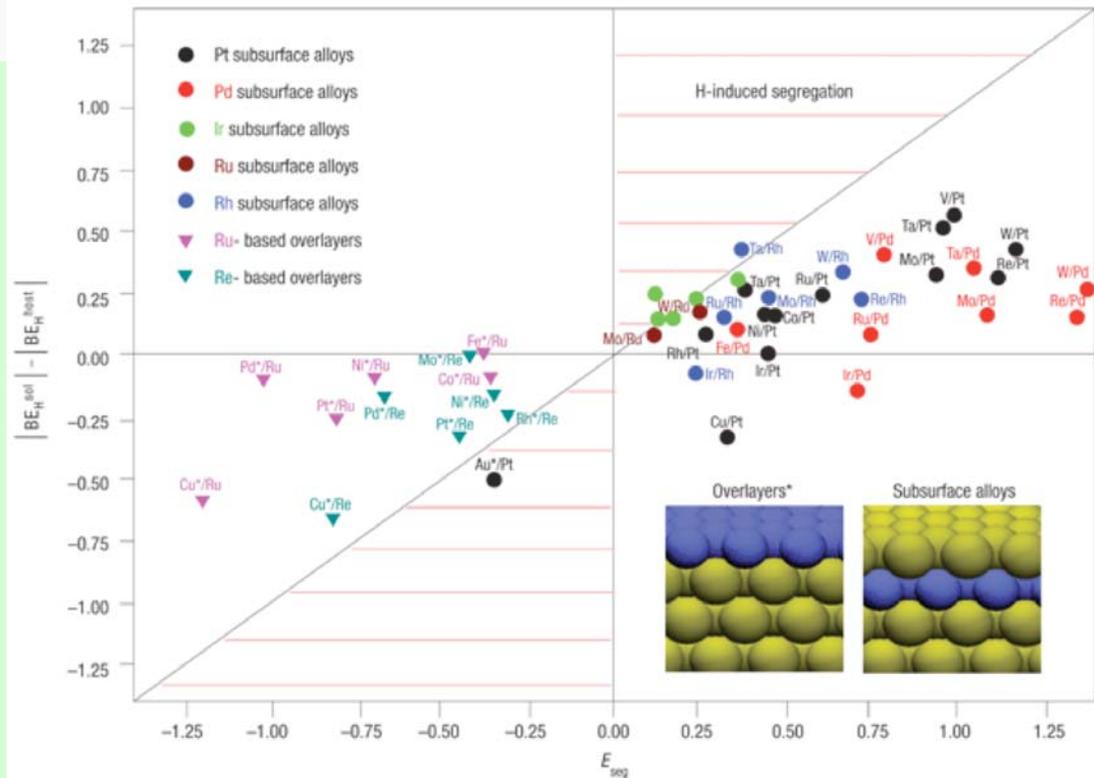

Energetics of hydrogen binding on metal alloys. The diagram shows also which subsurface alloys are stable—do not segregate– under hydrogen at above 0-K temperature, an important issue for practical catalysis.

H_2 dissociation on near-surface alloys

M. Mavrikakis et al., *Nature Materials* (2004) (**3:** 810–815)

Metal Reactivity – Size and Shape Dependence for Hydrogen Evolution

Professor T. **Madey**'s group at Rutgers University has developed the ability to chemically restructure metal surfaces, attain a controllable and reproducible fraction of high-index planes, and uniquely identify the chemical reactions that occur on specific crystal planes of specific dimensions. Recently they described the modification of the Ir(211) surface into pillar-like features controllable in size from 5 to 11 nm that are stable to high temperature and chemical environments. Techniques of surface science, reaction kinetics, synchrotron-based spectroscopy and scanning tunneling microscopy have led to a detailed description of the structural and chemical behavior of the preferential facets. Thus, they have inferred that the size of facets significantly influences the per-atom activity and selectivity for reactions such as ammonia decomposition, hydrogen formation, and nitrogen formation. This knowledge provides the foundation for the rational design of nanostructured noble metal catalysts with preferential selectivity for hydrogen atom recombination.
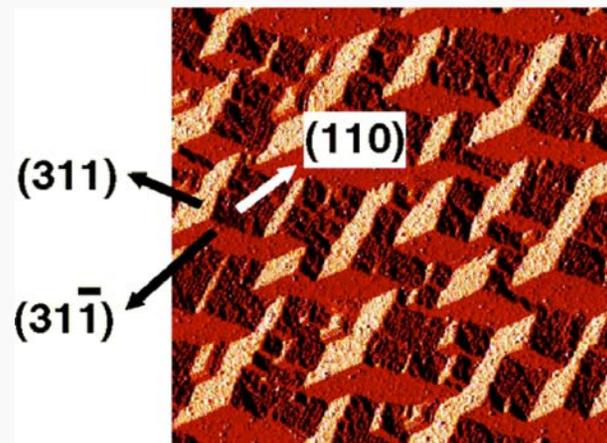
STM (100 nm × 100 nm) of an oxygen-covered faceted Ir(210) prepared by flashing Ir(210) in O2 (5 × 10-8 Torr) to $T > 1700$ K and subsequent cooling in O2 to 300 K.
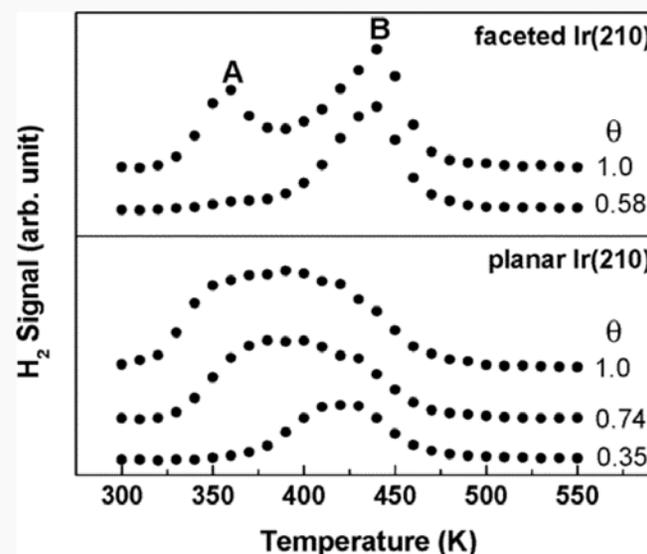

TPD spectra of H2 from faceted Ir(210) (<l> = 14 nm) following adsorption at 300 K. Coverages fraction at 300 K.

Novel Platinum and Gold-Porphyrin Nanotubes Active for Hydrogen Evolution

Self-assembled porphyrin nanotubes have been synthesized that are able to photochemically reduce metal salts to produce metallic nanoparticles of Pt and Au of uniform dimension. Those particles will form and self-support selectively in the interior or exterior walls of the nanotubes, as determined by the ratio of cationic and anionic porphyrins, that is, by the charge of the metal complex shown below. The macroscopic porphyrins with metal on them are shown on the micrographs at right.

70 nm

70 nm
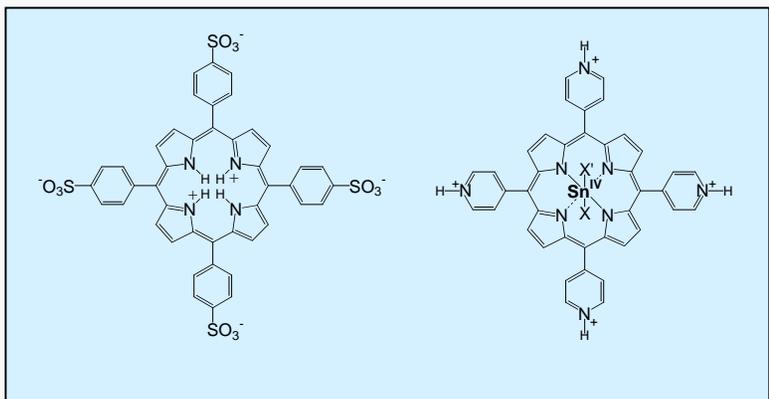
The quantum-dot sized platinum nanoparticles and the porphyrin nanotubes may be used as catalysts for proton reduction. In the presence of an electron donor such as ascorbic acid and some excitation source such as light or mild temperature, hydrogen is produced by the reaction:

$$2SnP^{-\bullet} + 2H^+ \xrightarrow{\;\;Pt\;\;} 2SnP + H_2$$
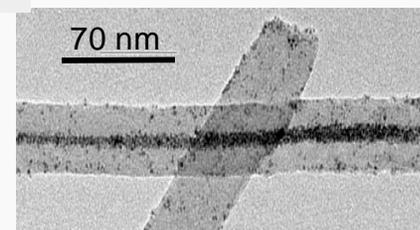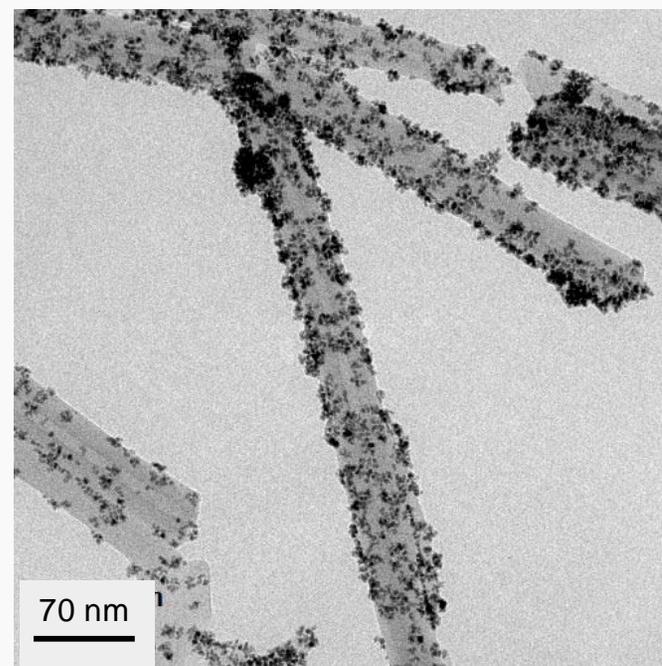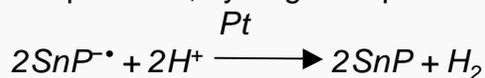
Shelnutt J A., et al., **J. Am. Chem. Soc. 2004**, *126*, 635-645.

Hydrogen for use in fuel cells must be ultra-pure to preserve the longevity of electrodes. Thus, the highly efficient removal of CO has become a critical scientific challenge.

GOLD, unrecognized as a catalytically active material before 1989, has proven to be the magic bullet for very efficient CO removal by oxidation at low temperature. Such activity arises when gold is in the form of atom clusters of under 8 nm size supported on titanium or other reducible metal oxide.

The origin of such reactivity has recently been clarified. Numerous parameters are important and usually cross-correlated: particle dimension and shape, metal oxidation state, oxide support reducibility, and interaction of the gold with the support material. To simplify this analysis, Goodman et al. synthesized ultra-thin films with precise arrangements of gold atoms (depicted in the cartoon at top right) as (A) bilayers or (B) monolayers of Au on Mo over Ti oxide, preventing the intimate interaction of Au with the Ti oxide support. Then they showed that the bilayer Au(1x3) structure is 10 times more active for CO oxidation than the monolayer Au(1x1) structure, and 50 times more active than the best Au/TiO$_2$ catalyst prepared by conventional methods. Gold slabs over two layers thick are also poorly active. Supported by CO HREELS and electronic structure calculations, they concluded that the Au(1x1) atoms are slightly electron-rich and activate O$_2$, while the Au(1x3) atoms chemisorb CO, and that both combined lead to a low activation barrier for the oxidation of CO.

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

This work was carried out by **D.W. Goodman** et al. (TAMU)
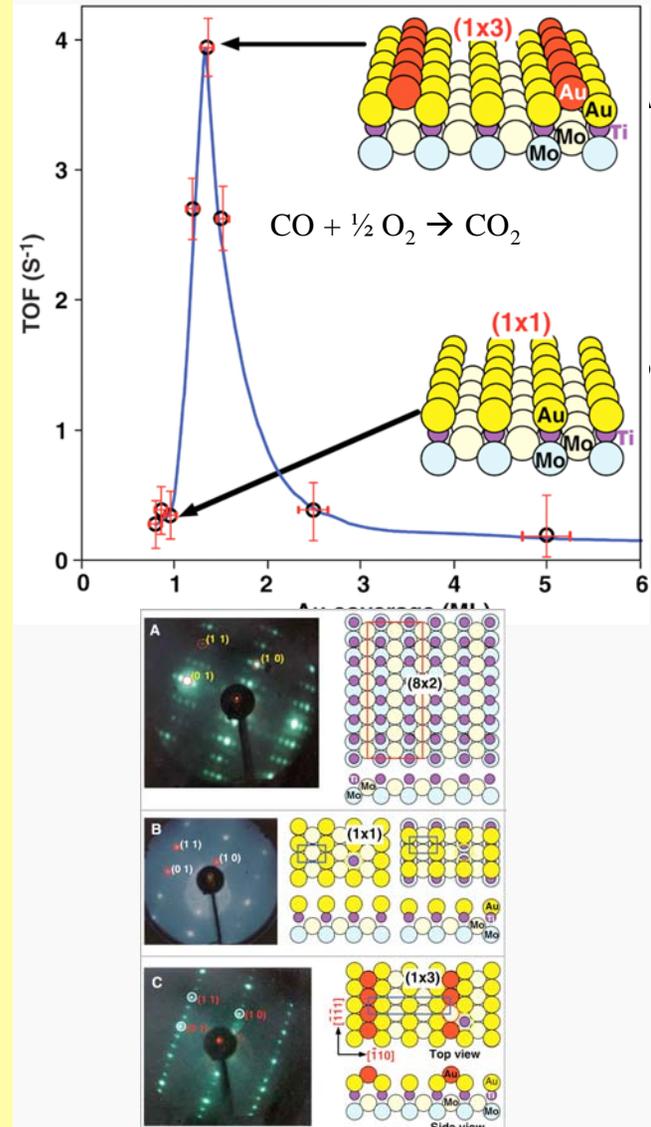
D.W. Goodman et al. (**Science** 2004 **306**: 252-255).

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Conclusions

- Solid hydrides can in principle reach DOE goals for volumetric and gravimetric densities.
- High release temperature as well as slow hydrogen absorption and desorption remain important issues to address.
- Chemical hydrides provide good kinetics and storage capacity but must be made reversible and cheap for car applications.
- Destabilization of storage material may be achieved by doping, scaffolding, adding catalysts or changing particle size.
- Increasing the reaction rate and lowering release temperature of hydrogen by doping, scaffolding or alloying is usually done at the expense of the storage capacity.
- Nanotechnology may provide new ways to tune the thermodynamic and thermal properties of materials.
- Heat management during hydriding phase must be addressed to reach DOE's fueling time goals.
- Nanotechnology also offers ways to engineer specific catalysts for hydrogen production, storage and utilization.