DOE Hydrogen Program Annual Review
May 19, 2006

Addressing Grand Challenges Through Advanced Materials

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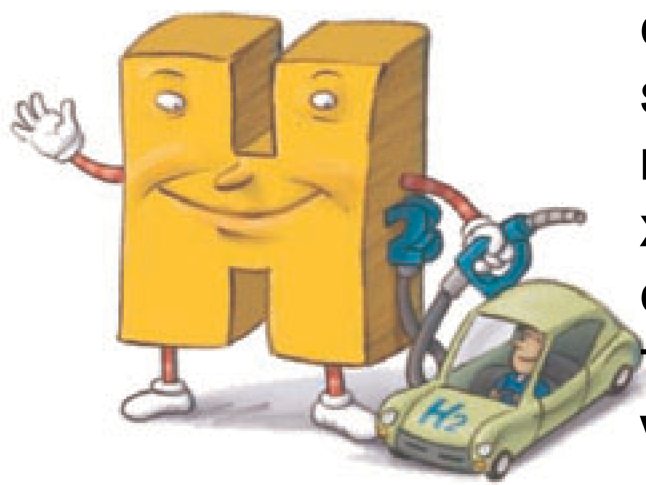
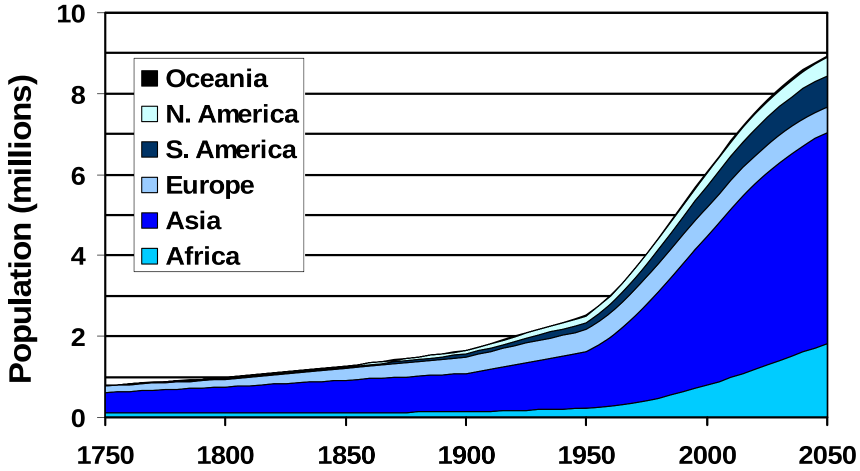
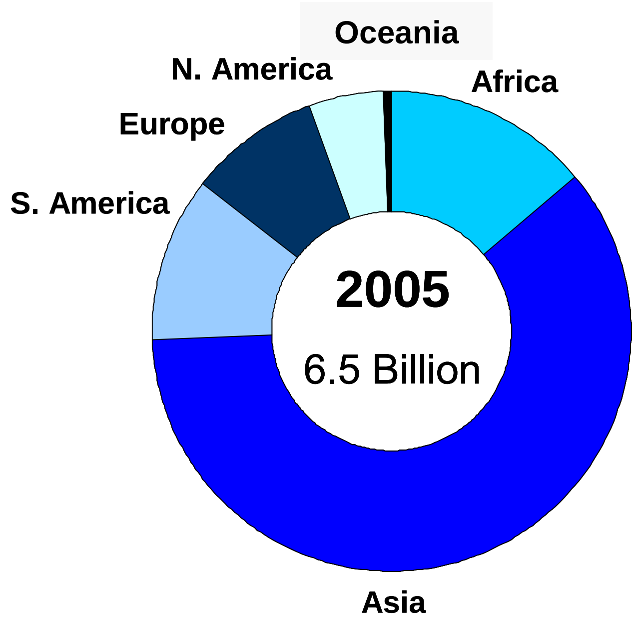


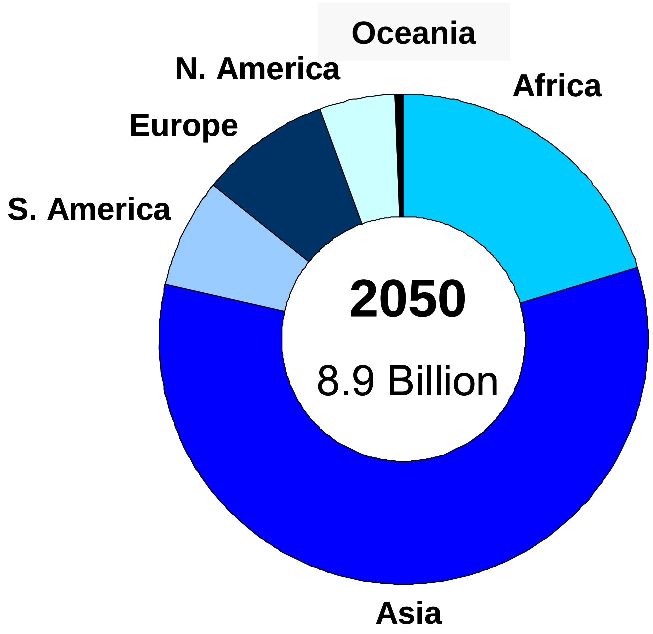
Outline

- Overview of the global energy challenge
- Overview of nanostructural materials
- Overview of the hydrogen initiative and of the role that nanoscience and nanotechnology might play

Demographic Expansion

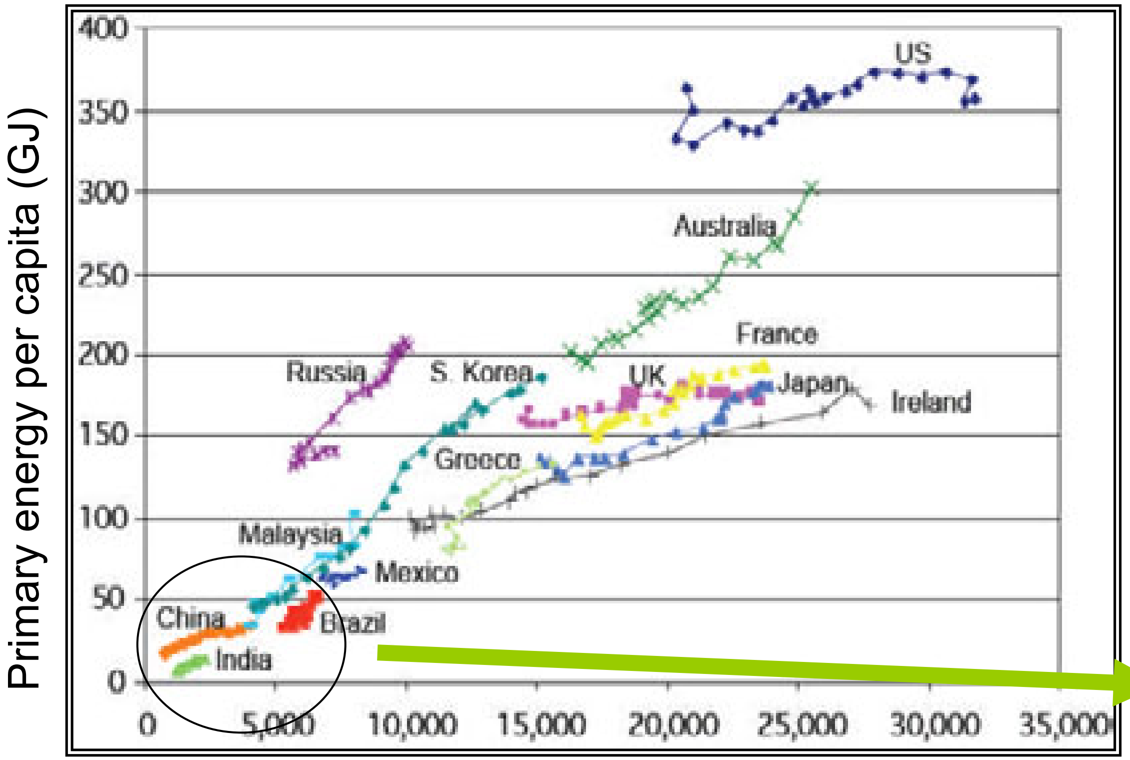


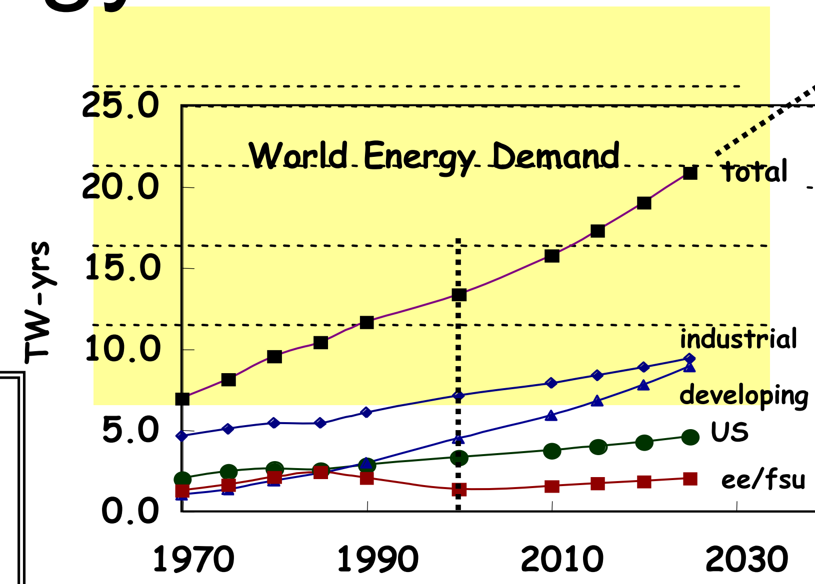




Growing world energy needs

Energy demand and GDP per capita (1980-2002)





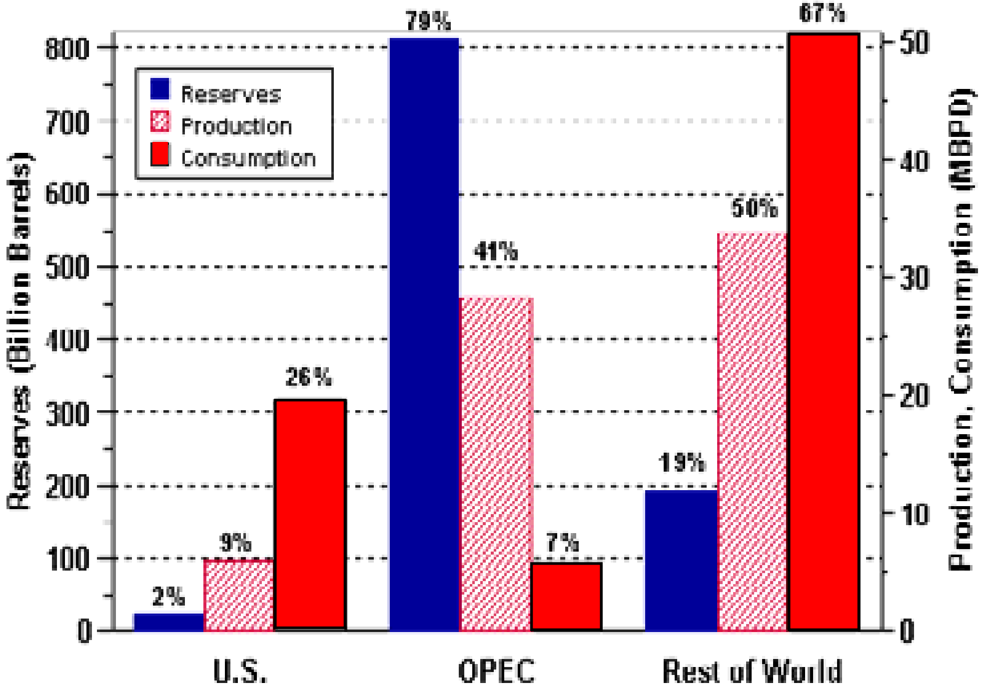
2000: 13 TW
2050: 30 TW
2100: 46 TW

(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 Availability Challenge

World oil reserves/consumption 2001



OPEC: Venezuela, Iran, Iraq, Kuwait, Qatar, Saudi Arabia, United Arab Emirates, Algeria, Libya, Nigeria, and Indonesia

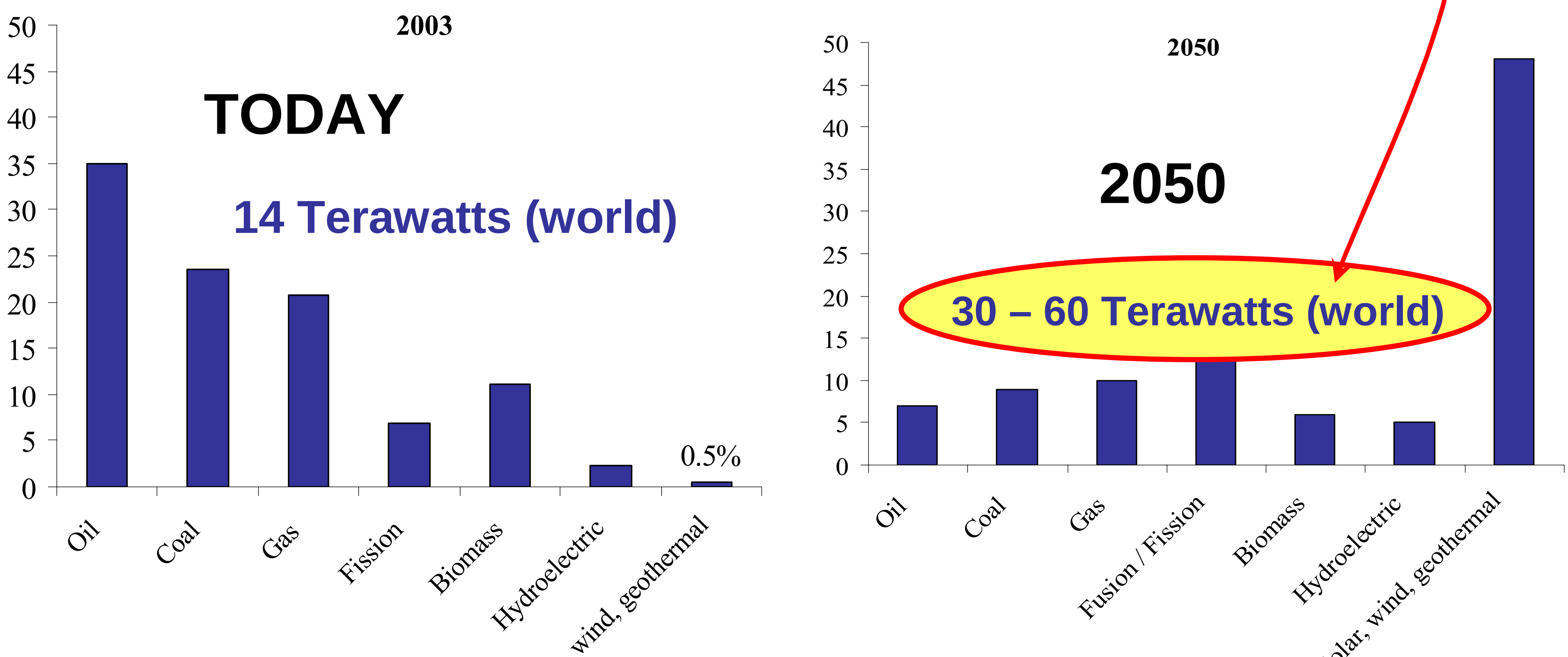
Estimated world reserves (R/P)

	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

New oil and gas reserves are not being discovered nearly as fast as they are being depleted

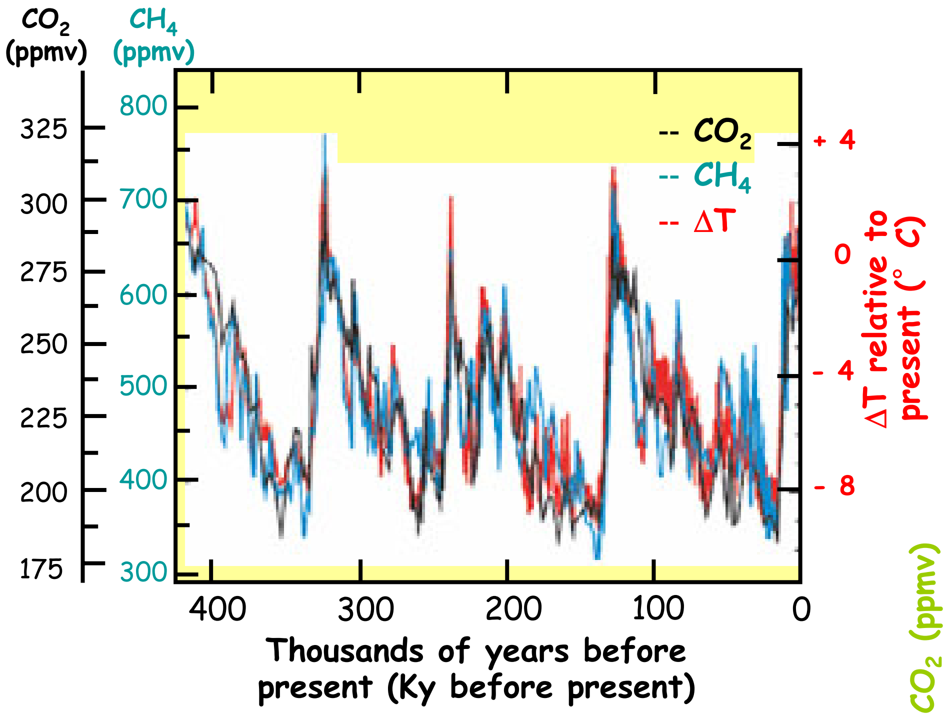
The Energy Source Challenge



Source: International Energy Agency

- Achieve Energy sustainability through renewable energy.
- Find substitute for gasoline (portable high energy density) in a renewable fuel
- Achieve cost efficient renewable technologies
- The sun is essentially the only renewable energy source with a sufficient capacity

The Climate Change Challenge

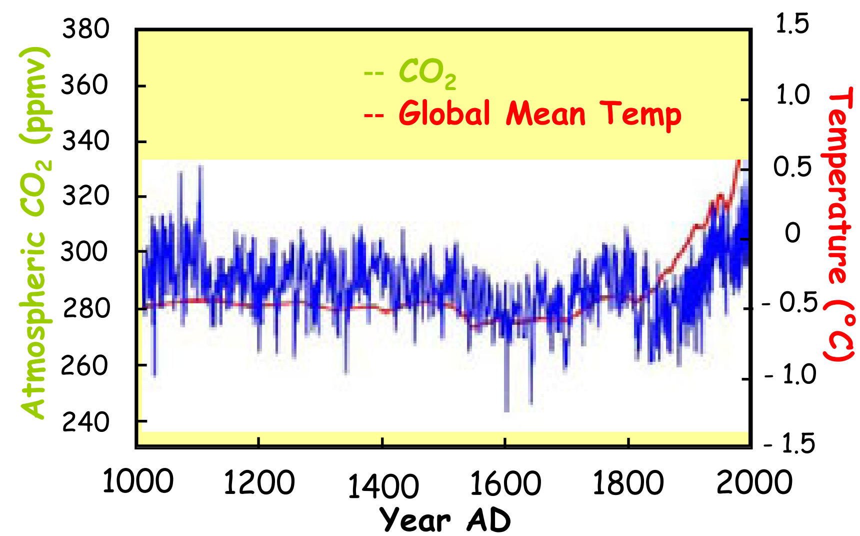


Intergovernmental Panel on Climate Change, 2001
http://www.ipcc.ch

Relaxation times

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

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



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

Outline

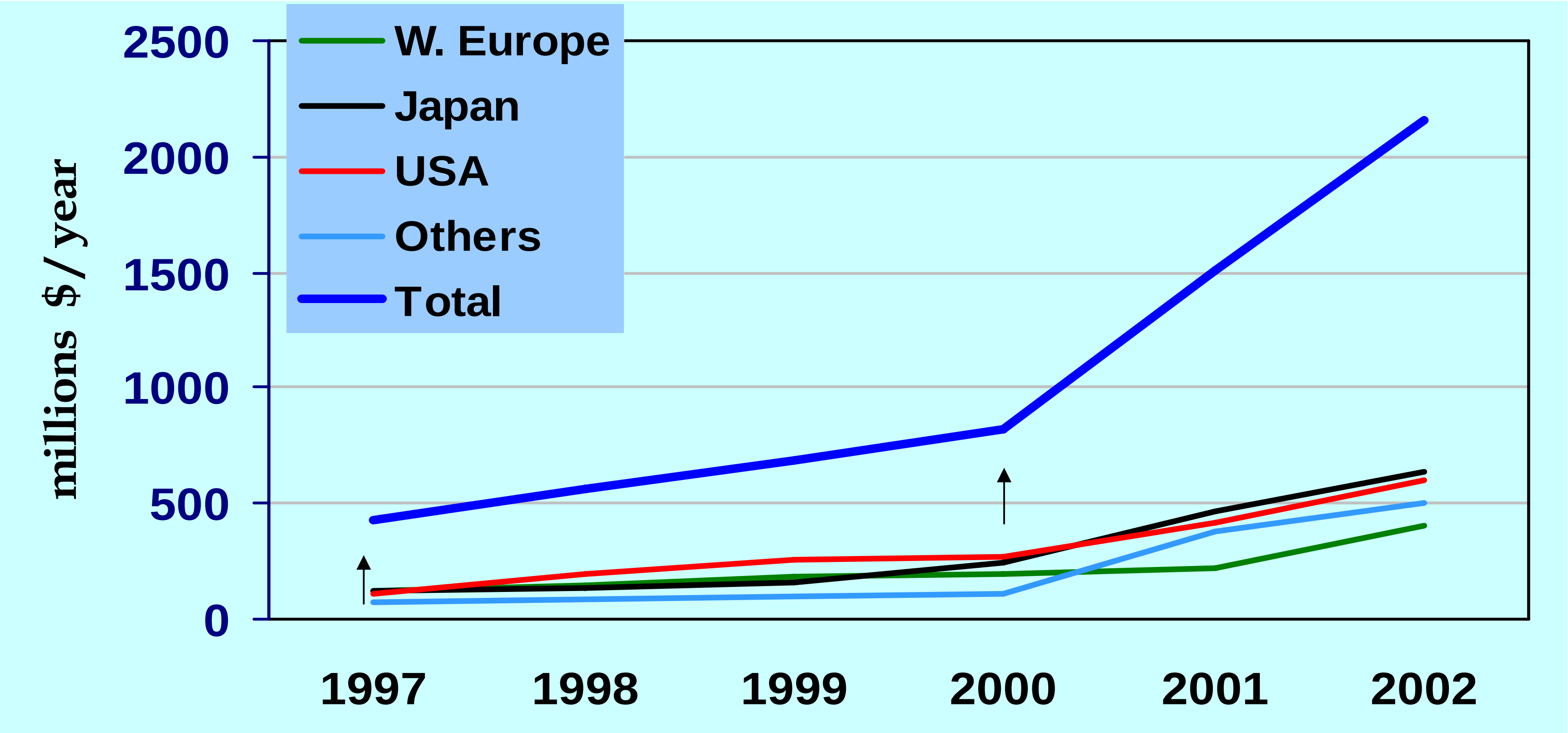
- Overview of the global energy challenge
- Overview of nanostructural materials
- Overview of the hydrogen initiative and of the role that nanoscience and nanotechnology might play

Why Nanostructural materials are important for energy-based applications

- New desirable properties are available at the nanoscale but not found in conventional 3D materials-e.g., higher diffusion coefficient to promote hydrogen release
- Higher surface area – promotes catalytic interactions
- Independent control of materials parameters which are interdependent for 3D – e.g., simultaneous increase in power factor and decrease in thermal conductivity in thermoelectric materials.

Context – Nanotechnology in the World

Government investments 1997-2002

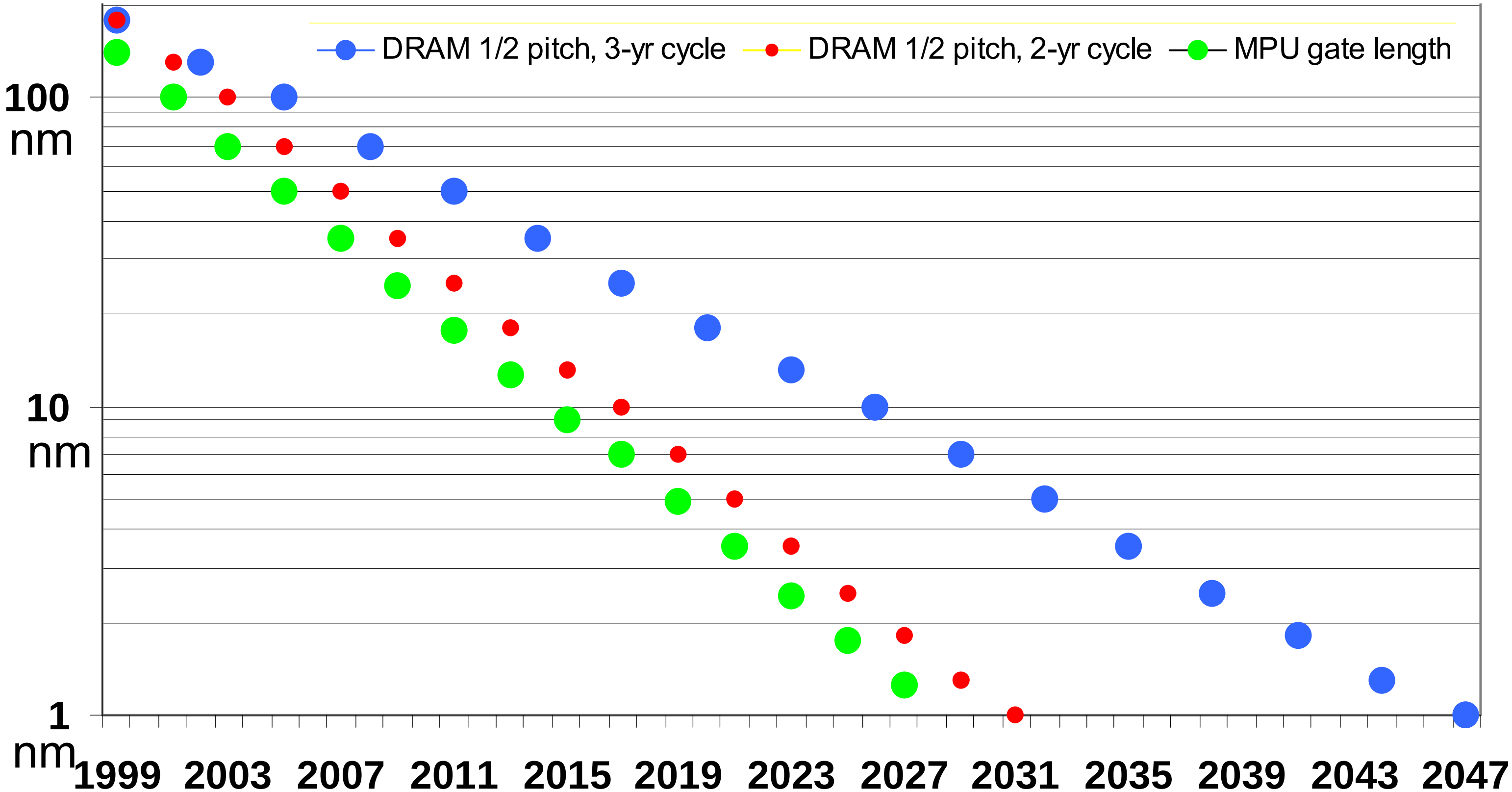


Note:
- U.S. begins FY in October, six month before EU & Japan in March/April
- U.S. does not have a commanding lead as it was for other S&T megatrends (such as BIO, IT, space exploration, nuclear)

Senate Briefing, May 24, 2001 (M.C. Roco), updated on February 5, 2002

Moore's Law for semiconductor electronics

soon, all microchips will be nanoscale devices



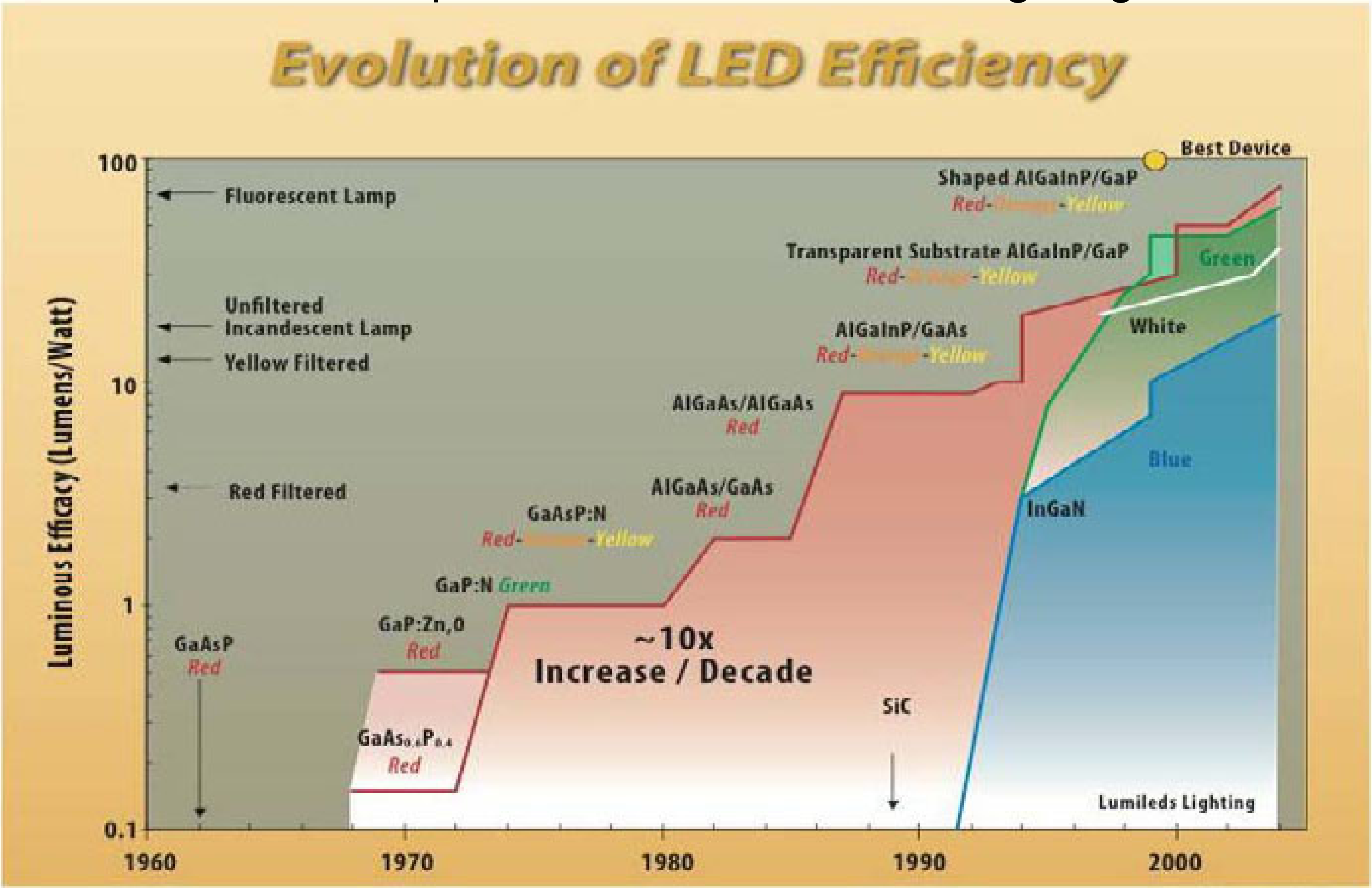
CONCLUSION: *The semiconductor industry already has a large effort underway for producing devices whose minimum design features are 100nm. It is only a matter of time before nearly all chips are nanotech devices. Hence, there is substantial value in synchronizing the large research effort already funded by industry & driven by the International Technology Roadmap for Semiconductors (ITRS), with the large research effort expected to be funded worldwide.*

Semiconductor Research Corporation

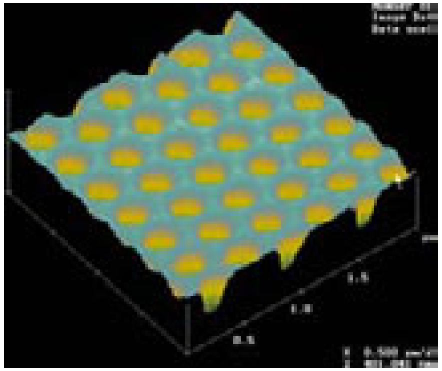
Extension of Moore's Law to the Energy Industry

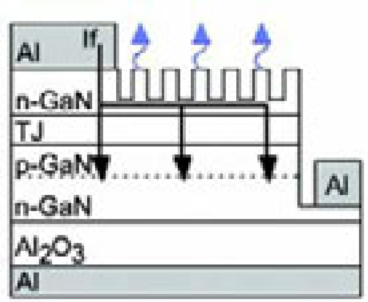
- Moore's law has for many years been working to set goals for electronics, opto-electronics, and magnetics industries.
- We now need to apply Moore's law to set goals for the energy industry.

Solid-State Lighting at Half the Energy Consumption as for Conventional Lighting

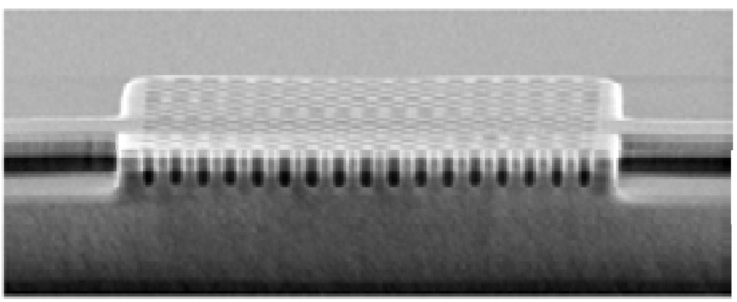


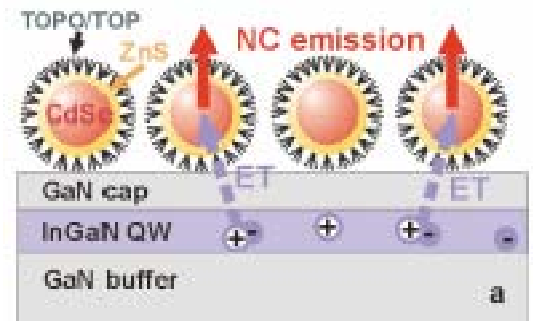
Emerging Nanotechnologies will further increase Solid State Lighting energy efficiency

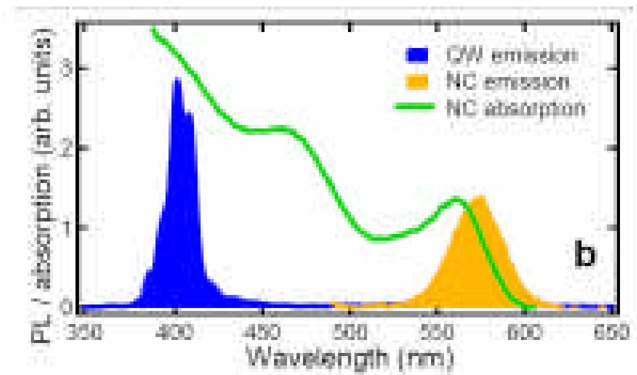




AFM Image courtesy of Lumileds & Sandia







Photonic Crystal LEDs

Patterning of LEDs with 2D photonic lattices could suppress the in-plane photonic density of states, forcing all emission to be normal to the surface to eliminate trapping of light due to total internal reflection, which wastes 50% or more of the light emitted in conventional LED device structures.

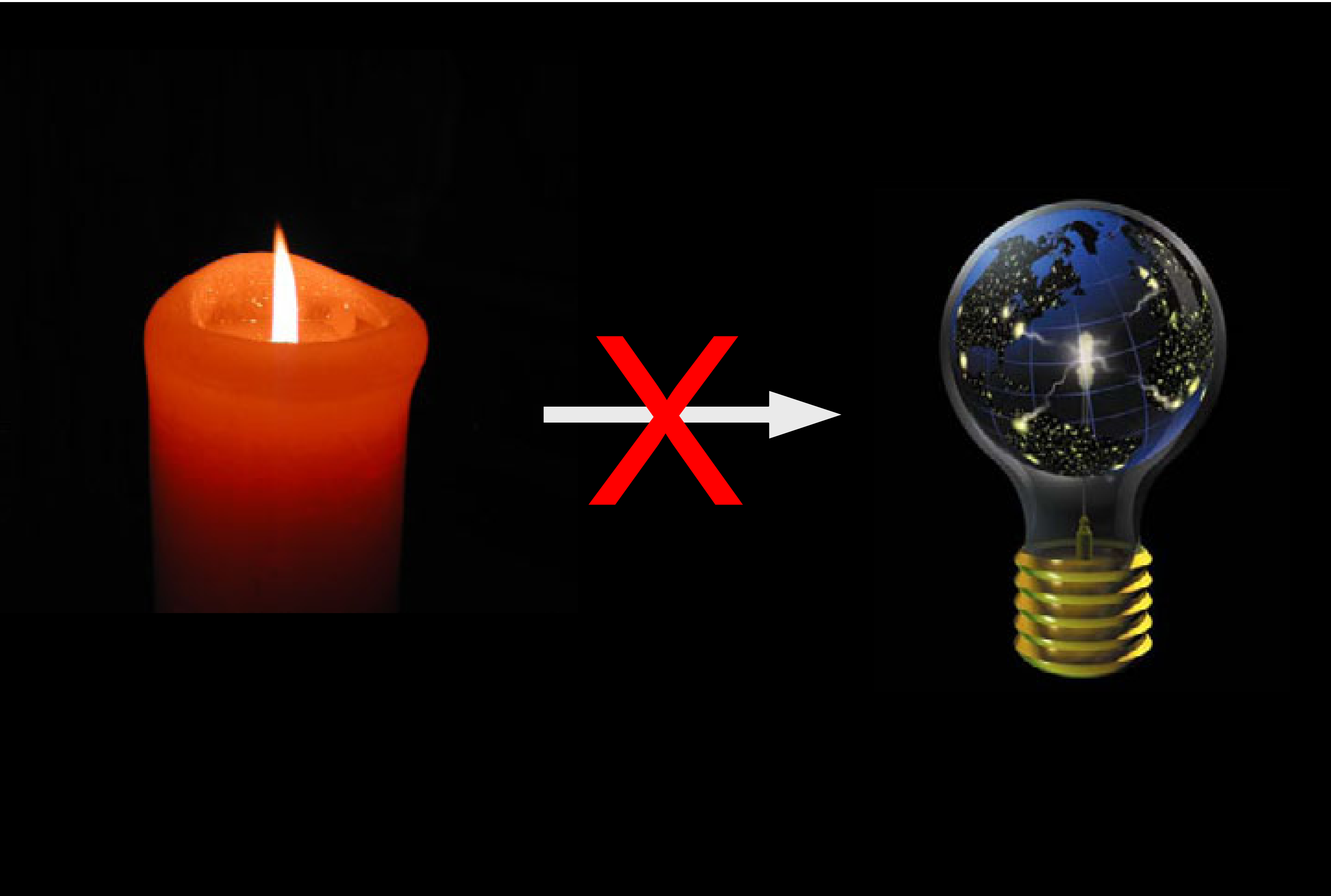
(J. Weirer et al., APL 84, 3885, (2004))

Nanocrystalline Quantum Dots as Phosphor Alternatives

Schematic illustration of a hybrid quantum dot - quantum well structure in which the InGaN/GaN quantum well is coupled to the CdSe quantum dots via dipole-dipole energy transfer. The lower panel shows the photoluminesence spectra of the quantum well (blue) and the dots (orange) compared to the absorption spectra of the quantum dots (green line). Nanoscale dimensions of the quantum dots allows for an efficiency of more than 50% and tunable output wavelength.

(M. Achermann et al., Nature 429, 642, (2004))

… but electricity was not discovered via incremental improvements to the candle



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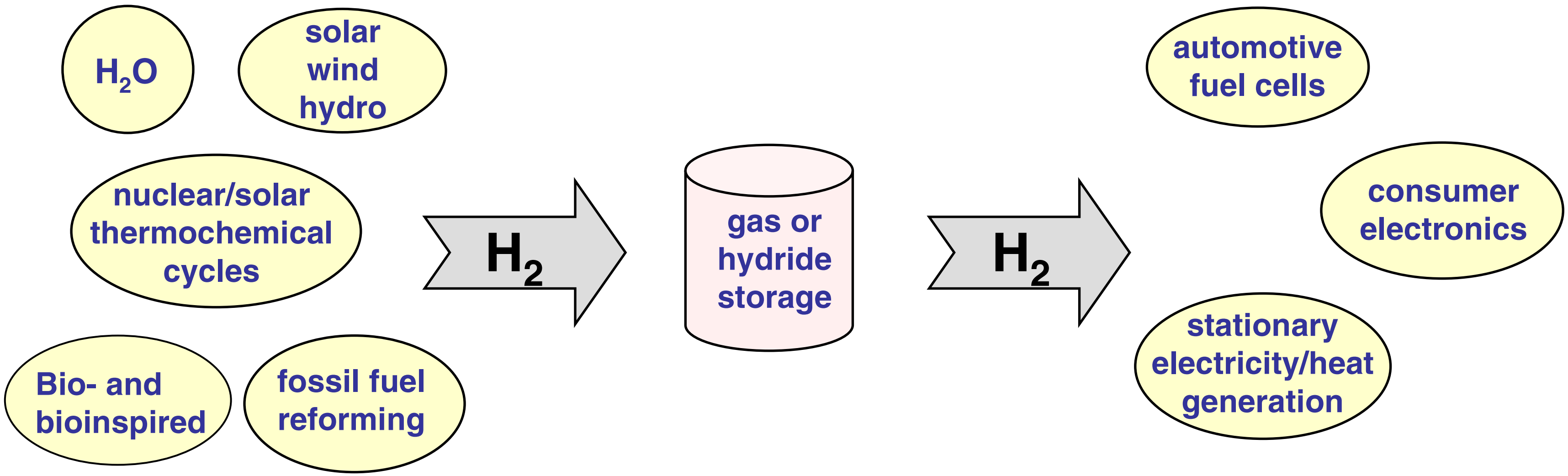
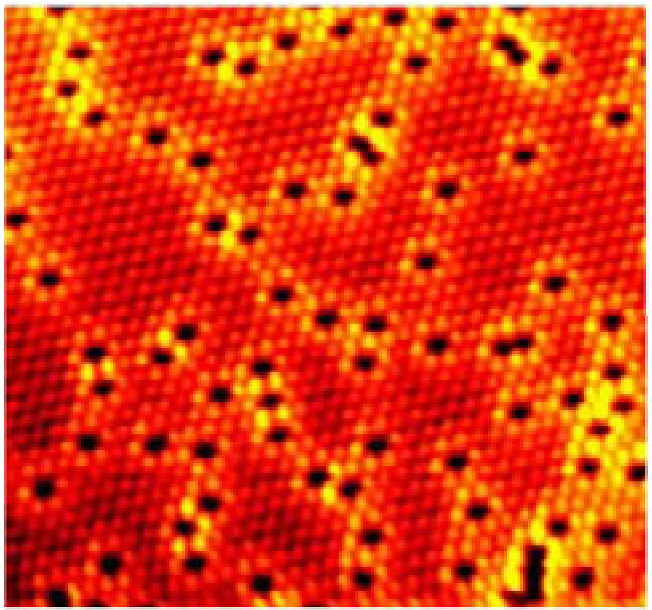
The Hydrogen Economy – The Technology Gaps

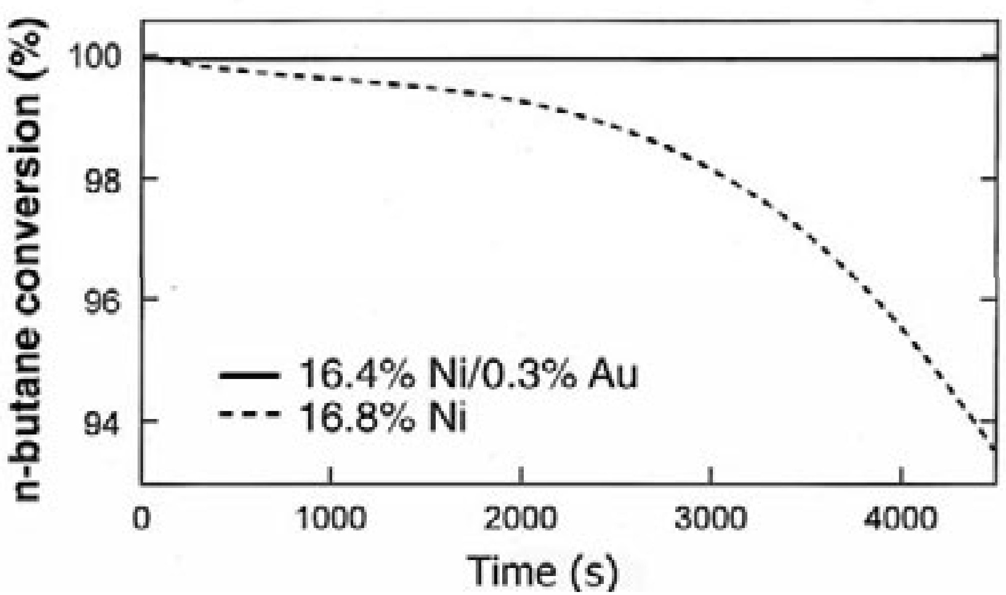


production	storage	use (in fuel cells)
9M tons/yr	4.4 MJ/L (Gas, 10,000 psi) 8.4 MJ/L (LH2)	$200-3000/kW
↓ *Gap*	↓ *Gap*	↓ *Gap*
150M tons/yr (Light Cars and Trucks in 2040)	**9.7 MJ/L** (2015 FreedomCAR Target)	**$30/kW** (Internal Combustion Engine)

Fossil Fuel Reforming in Hydrogen Production

- For the next decade or more, hydrogen will mainly be produced using fossil fuel feedstocks.
- Development of efficient inexpensive catalysts will be key.
- Modeling and simulation will play a significant role.

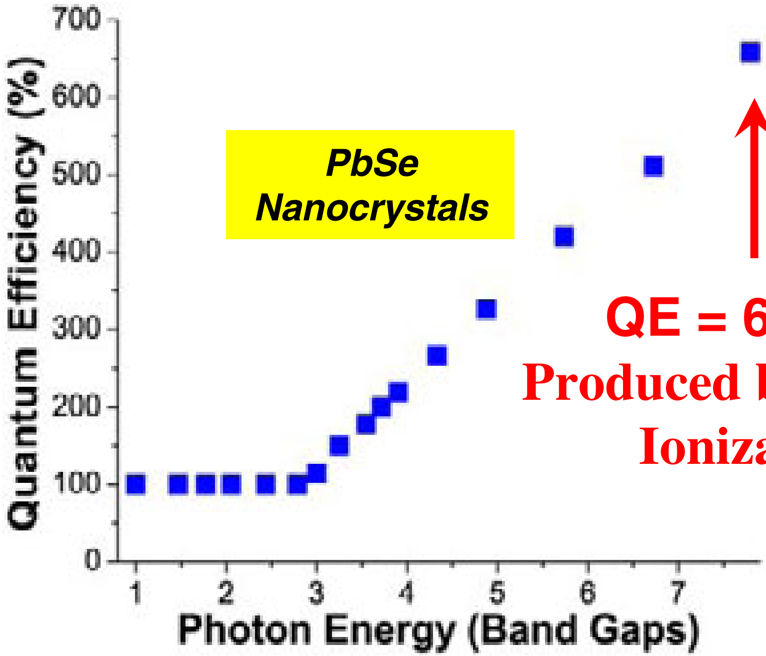




Inspired by quantum chemical calculations, Ni surface-alloyed with Au (black) on the left is used to reduce carbon poisoning of catalyst, as verified experimentally on the right.

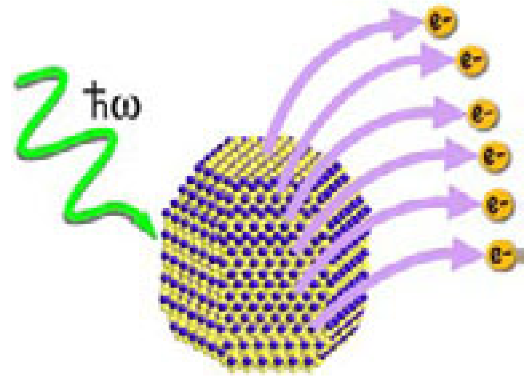
Discovery of Ultra-Efficient Carrier Multiplication in Semiconductor Nanocrystals

➢ **Observation of more than 6 e-h pairs produced by 1 photon**



QE = 660%

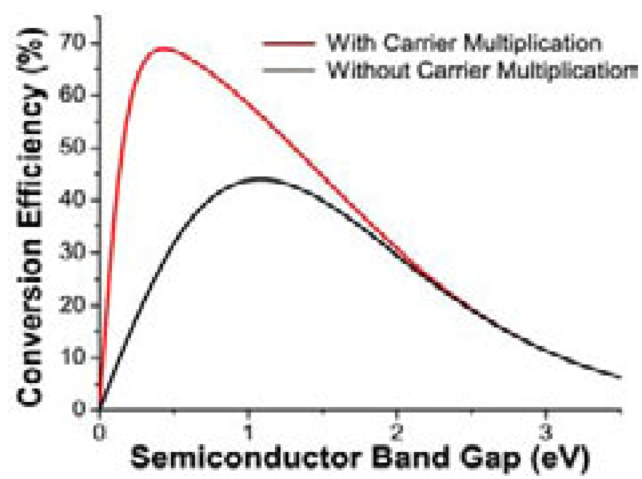
Produced by Impact Ionization



R. D. Schaller & V. I. Klimov, *Phys. Rev. Lett.* 92, 186601 (2004)

➢ **Single Band-Gap "Ultimate" Conversion Efficiency of Solar Cells:**

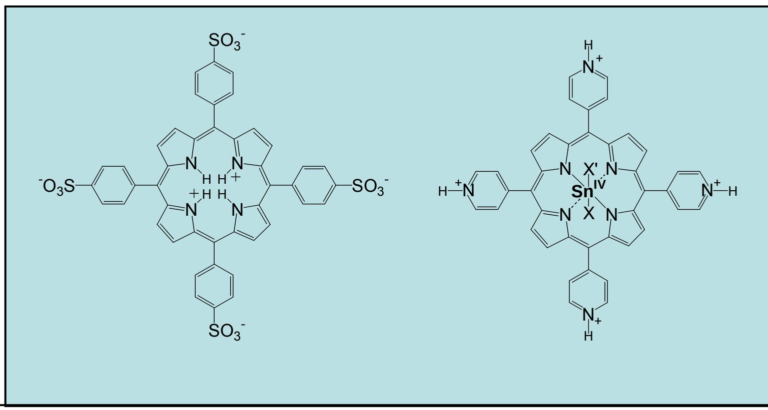
Potential increase up to ~70% !

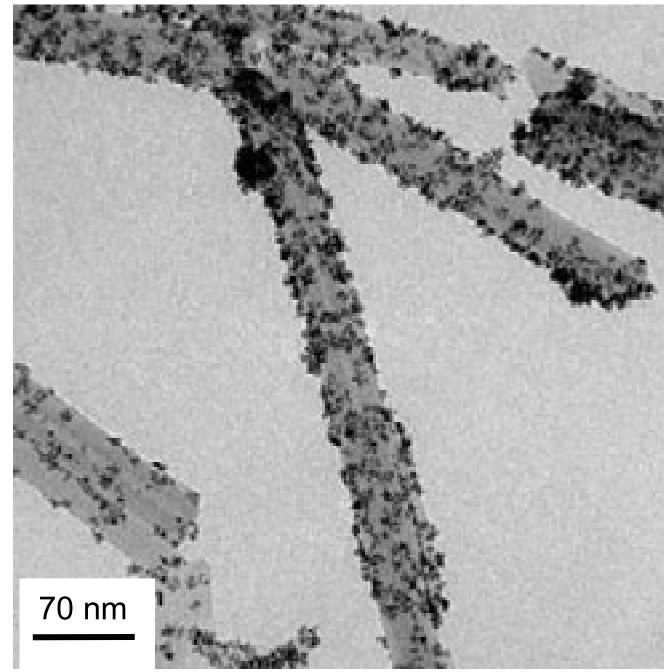


Los Alamos

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.





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.

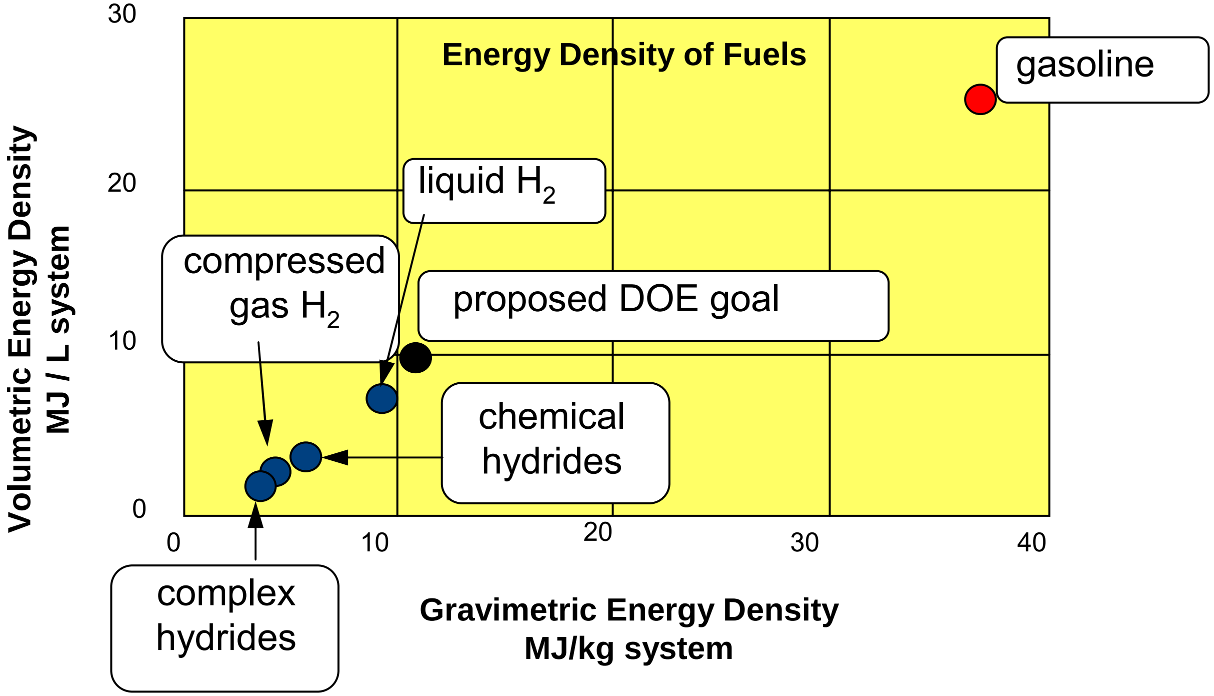
Hydrogen Storage

Current Technology for automotive applications

- Tanks for gaseous or liquid hydrogen storage.
- Progress demonstrated in solid state storage materials.

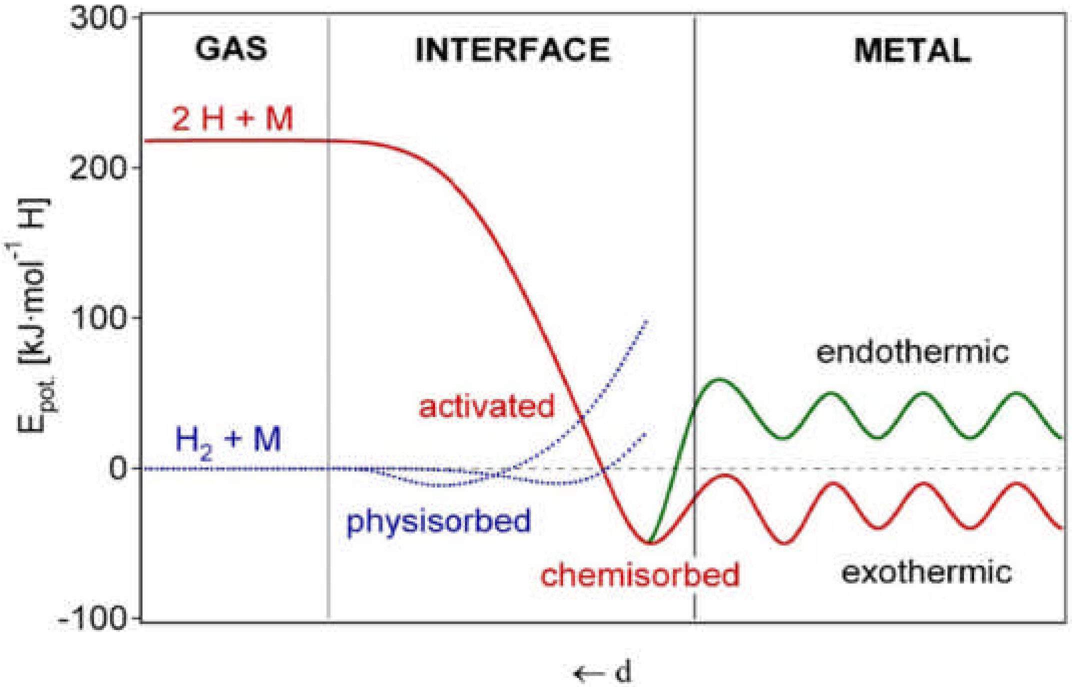
System Requirements

- 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.

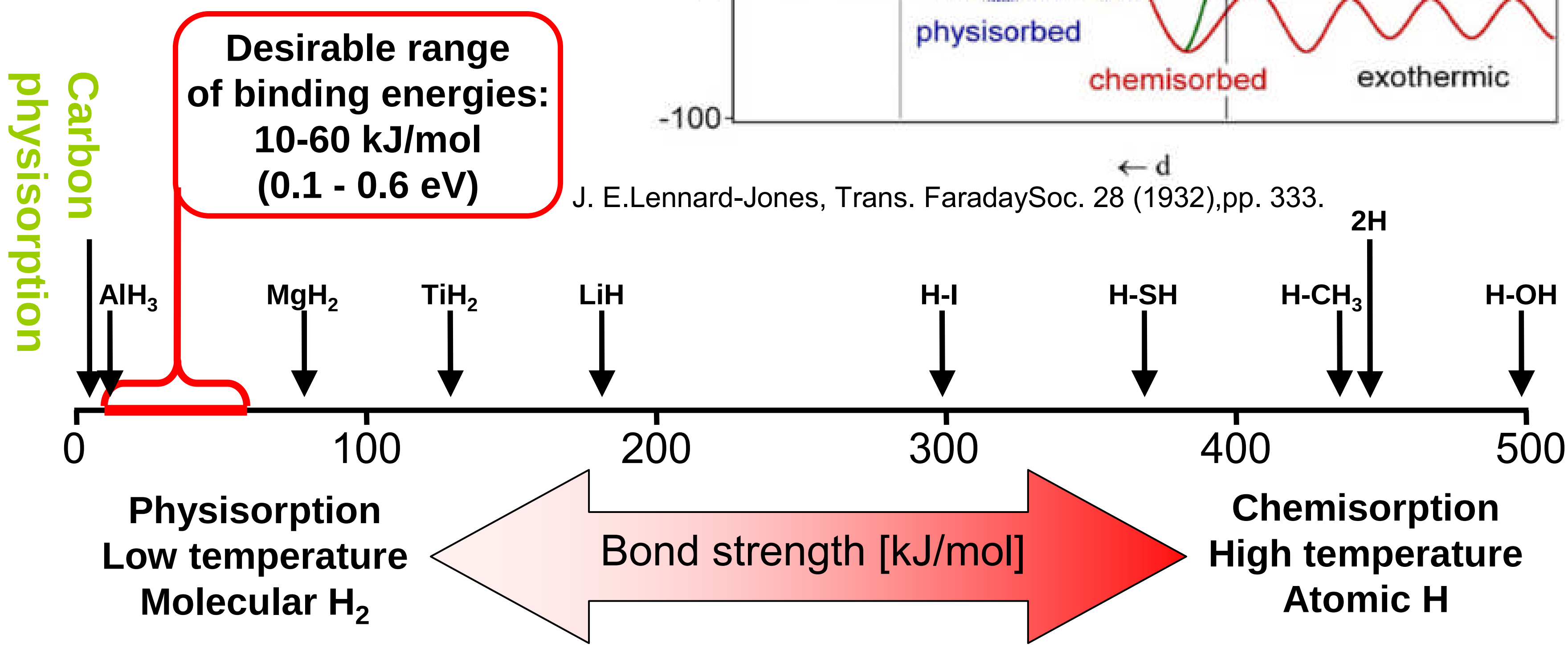


Desired binding energy range

Potential energy for molecular and atomic hydrogen absorption



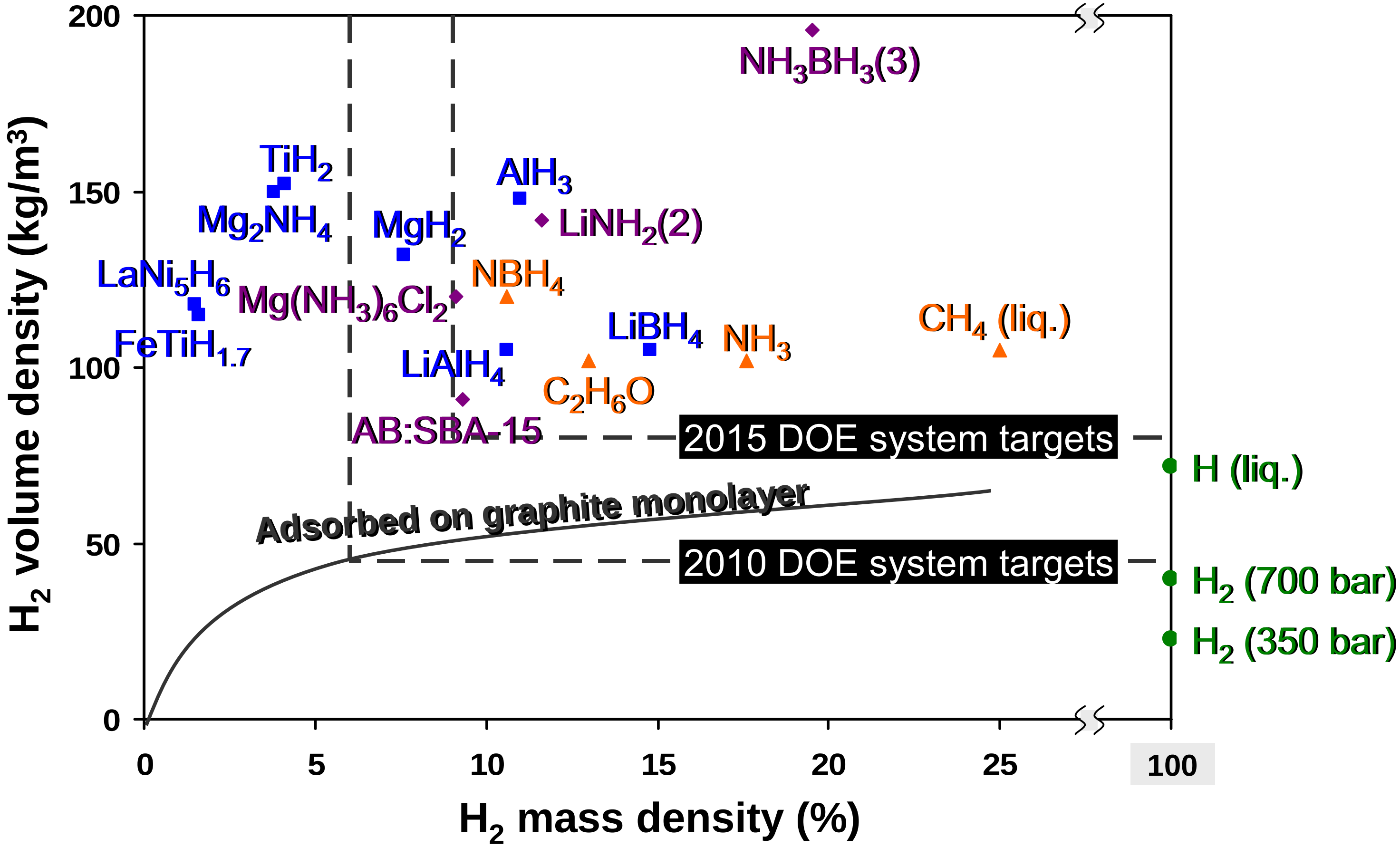
J. E.Lennard-Jones, Trans. FaradaySoc. 28 (1932),pp. 333.



Hydrogen Storage Options

Metal/complex hydrides:
- Slow kinetics
- Heat management issues
- High release temperature

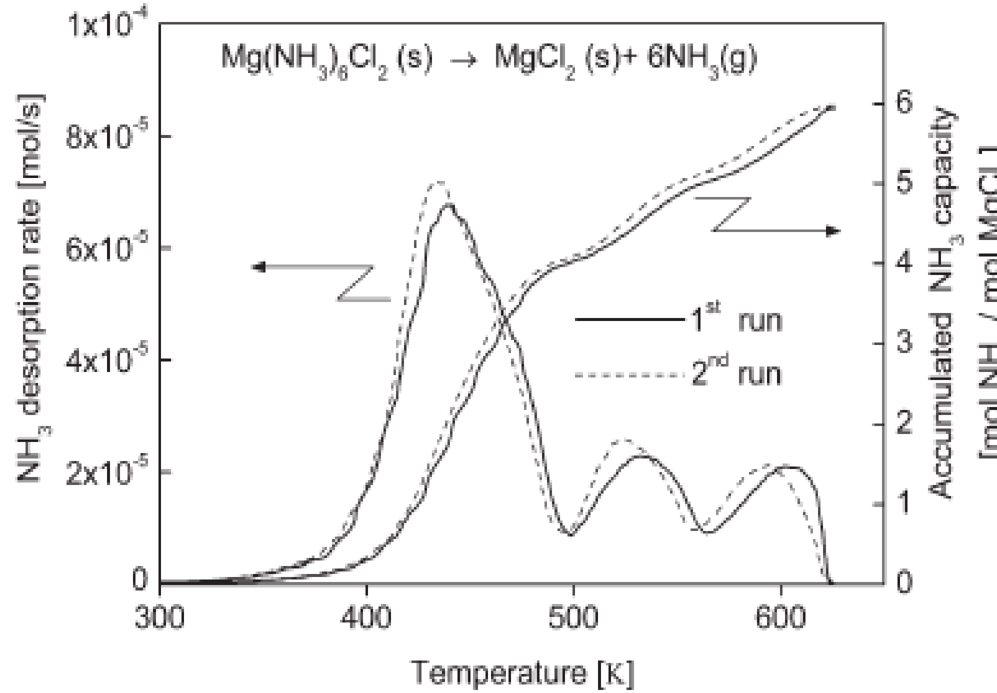
Chemical hydrides:
- Not reversible (on-board)



Carbon structures:
- Low temperature
- Too low wt. % for 2015
- Low energy barrier for hydrogen release

Metal ammine complexes

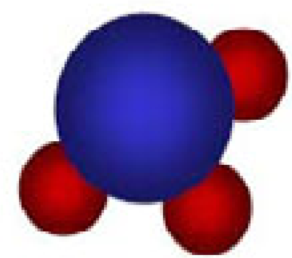
	Gravimetric H_2 density (% H_2)	Volumetric H_2 density/ (kg m^{-3})
$Mg(NH_3)_6Cl_2$	9.1	110
$Ca(NH_3)_8Cl_2$	9.7	120



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

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

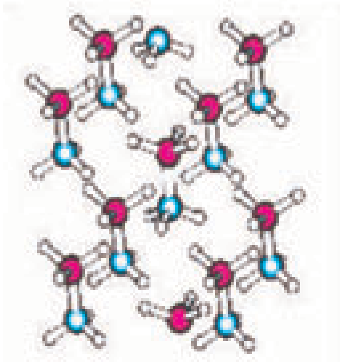
- Technology being developed for battery applications



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

Hydrogen Storage: Chemistry and Nanoscience

NH_3BH_3

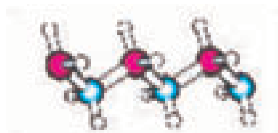


Ammonia Borane

solid: di-hydrogen bonds

ΔE ~ + 8.8 kcal/mole ~ 120°C

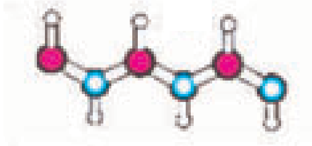
$(NH_2BH_2)_n + H_2$



solid

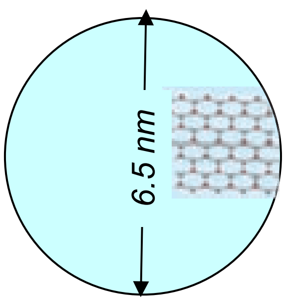
ΔE ~ - 3.2 kcal/mole ~ 120°C

$(NHBH)_n + H_2$



solid

> 12% mass released as H_2
simulation: ~ thermo-neutral



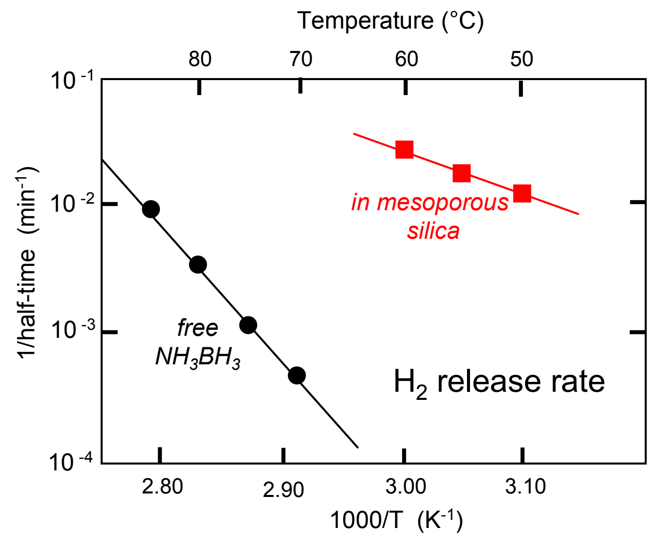
nano-phase trapping

NH_3BH_3 in mesoporous silica

SBA-15

release rate increased
1-2 orders of magnitude

undesirable borazine
eliminated

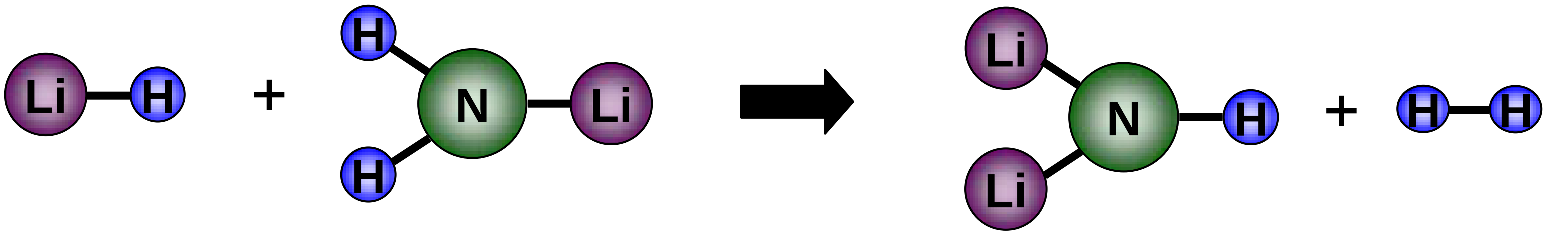


issues:
nanophase mechanism
reversibility

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

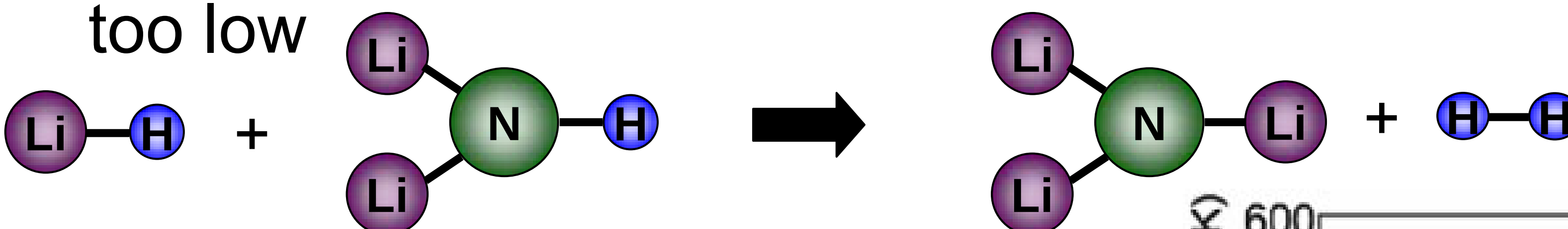
Imide (NH) and Amide (NH_2)

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



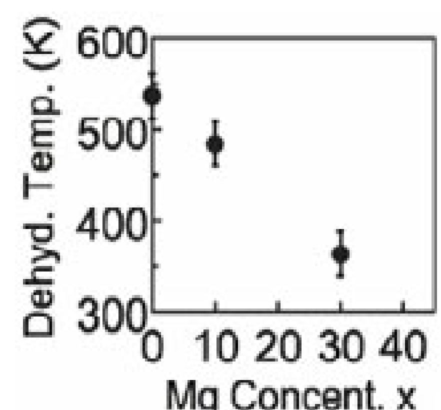
Second: Li_2NH + LiH ⬌ Li_3N + H_2 (5% @ 300c, 0.05atm)

- Release temperature is too high and release pressure is too low



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.

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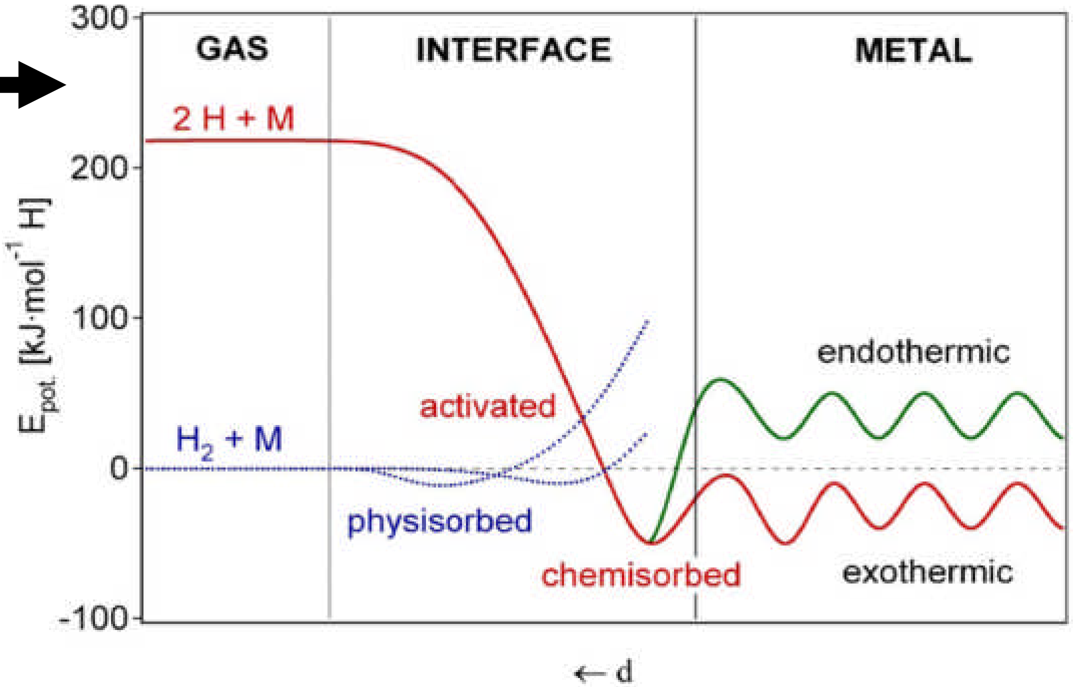
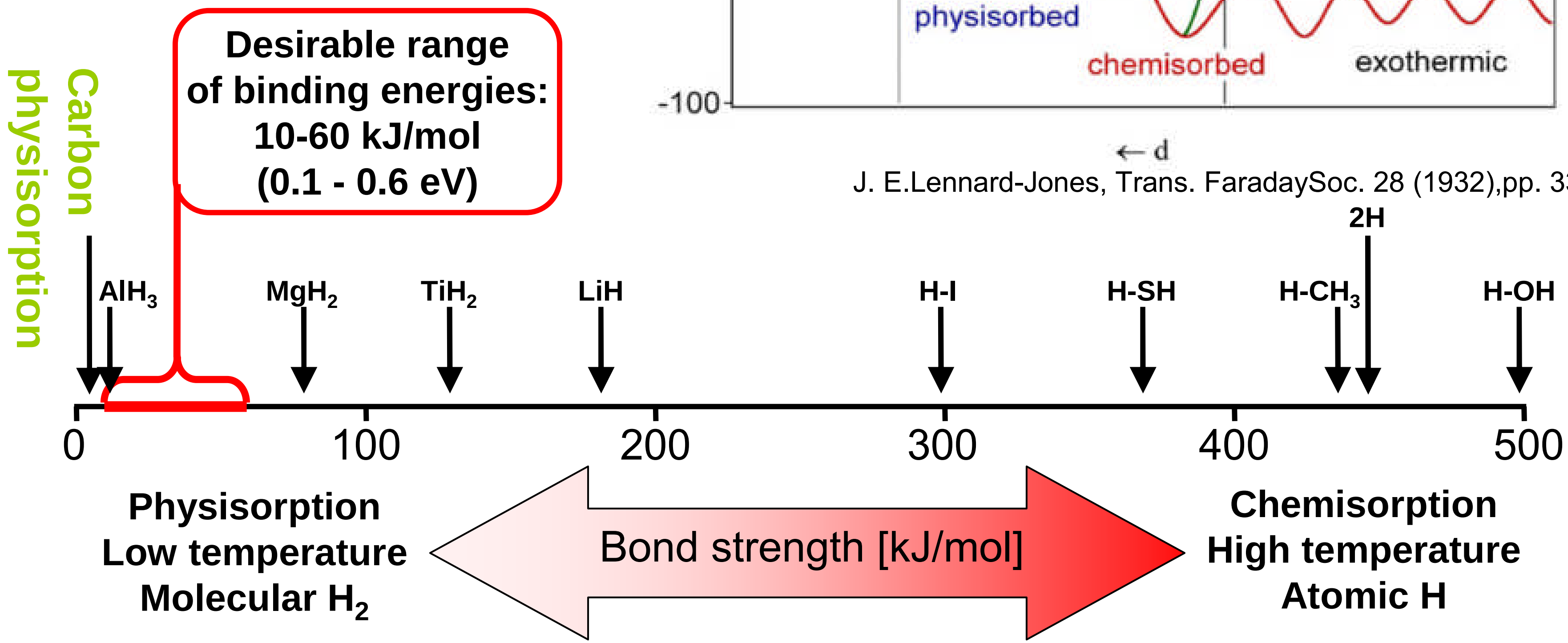


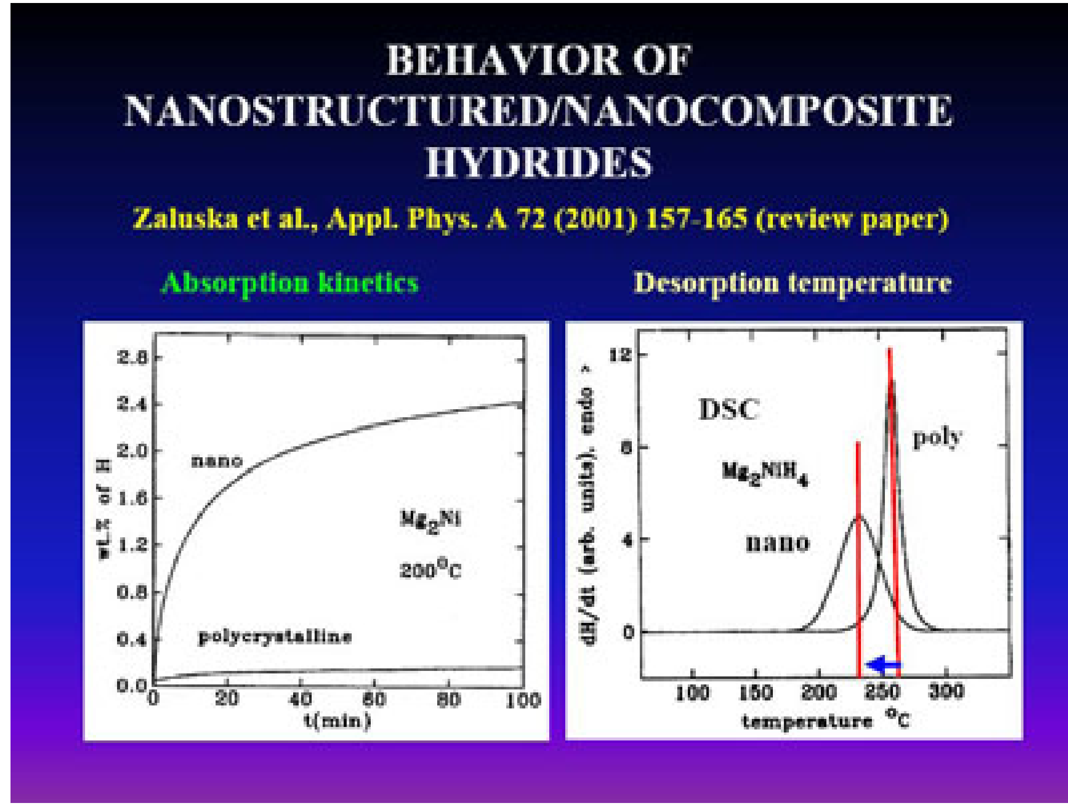
J. E.Lennard-Jones, Trans. FaradaySoc. 28 (1932),pp. 333.

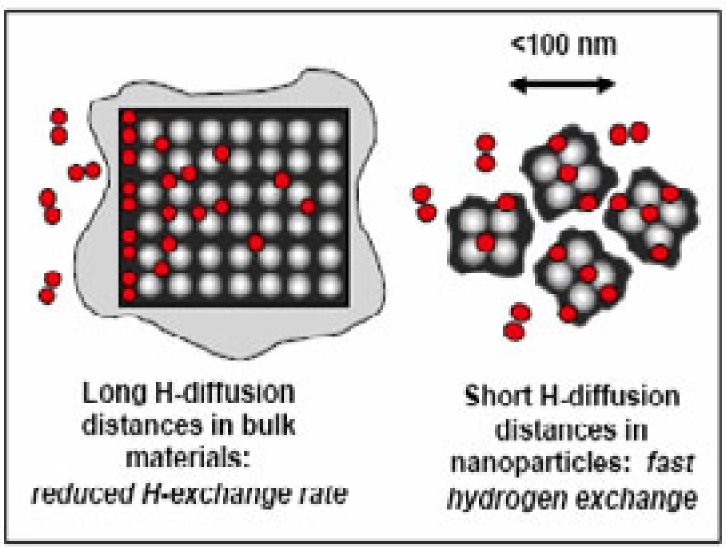
Activated reaction increases release temperature if no catalysts are used



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 hydrogen uptake.





•Increased porosity and smaller size increase diffusion rate.

•Surface energies and material properties at nanoscale offer ways to tune the energetics of absorption and desorption to reduce release temperature and to speed up release process.

Van't Hoff plots

- At constant temperature, a change in free energy obeys

$$dG = VdP$$

$$G^{H_2} = G_o^{H_2} + RT\ln\left(\frac{P^{H_2}}{P_o}\right)$$

- Where P_o=1atm is the pressure at which the standard free energy G_o is measured.
- For a hydriding reaction we get

$$\Delta G^{reaction} = \Delta G_o^{reaction} - RT\ln P^{H_2}$$

- In equilibrium the change in free energy is 0

$$\Delta G_o^{reaction} = RT\ln(P_{eq}^{H_2})$$

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

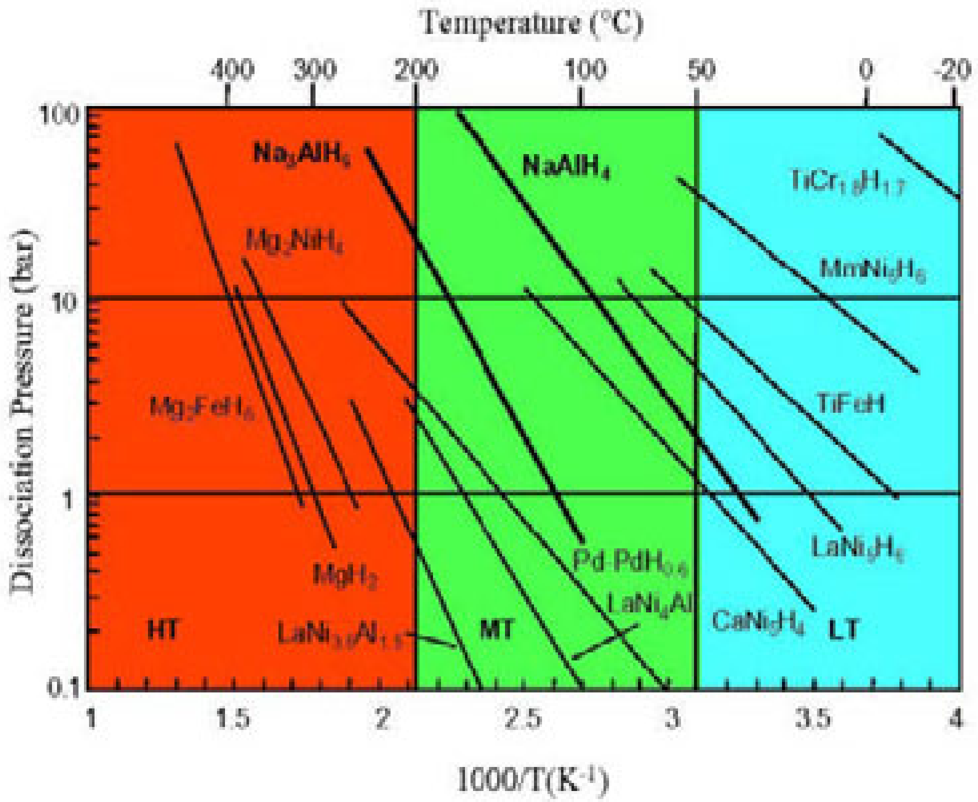


Figure 6 van't Hoff Diagram Showing Dissociation Pressures and Temperatures of Various Hydrides (Source: Bogdanovic and Sandrick 2002)

- The slope of a plot of $\ln(P_{eq})$ as a function of 1/RT gives the enthalpy of the reaction and the entropy change is given by the intersection with the ordinate axis.

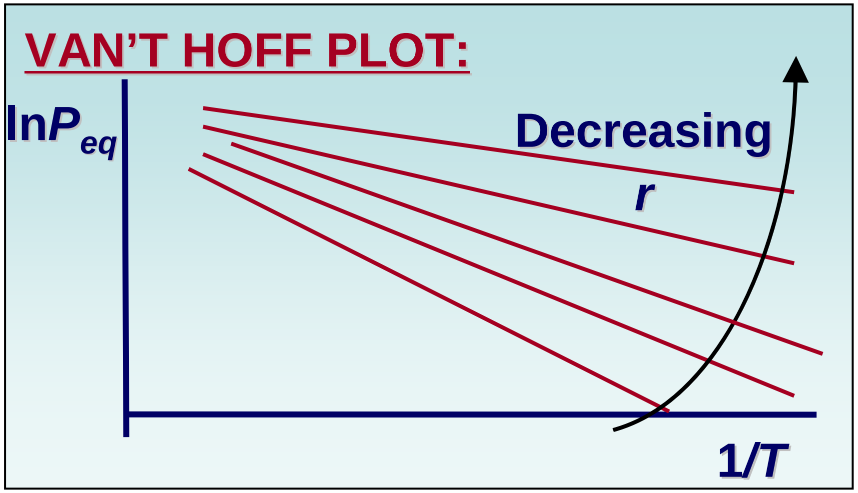
Size Effects on Thermodynamic Properties

Assuming the following reaction

$$M + H_2 \rightarrow MH_2$$

- At the nanoscale, the surface energy becomes important and it modifies the free energy.
- If the surface energy term Δ is positive, enthalpy of formation will be reduced for smaller particles.

Van't Hoff plot for a model MH_2 hydride



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

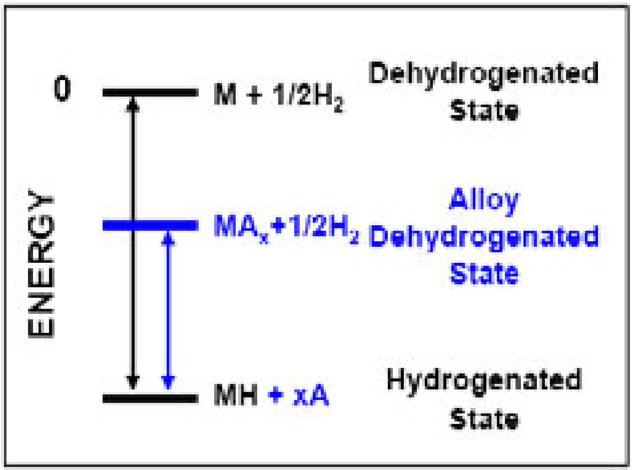
$$\Delta G(r) = \Delta G_o(r) + RT\ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right) + \frac{3\overline{V}_M \Delta(\gamma_{Mg}, \gamma_{MgH_2}, r)}{r}$$

Nanoscale Van't Hoff relation

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

Other Strategies to Lower Release Temperature

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.

Summary of strategies to reduce release temperature:

- Ball milling of hydride or other methods to create nanoparticles
- Doping with transition metals
- Use of catalysts
- Forming ternary, quaternary and higher order alloys
- Use of templates

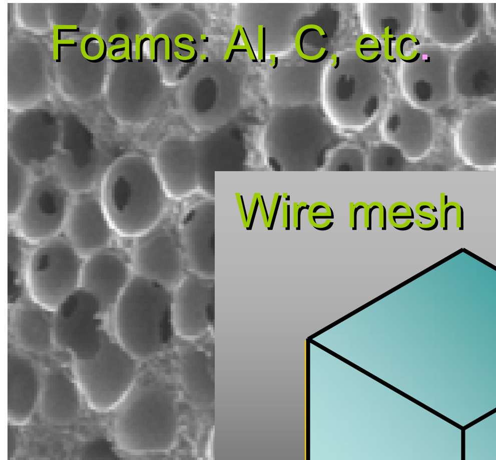
Thermal Management

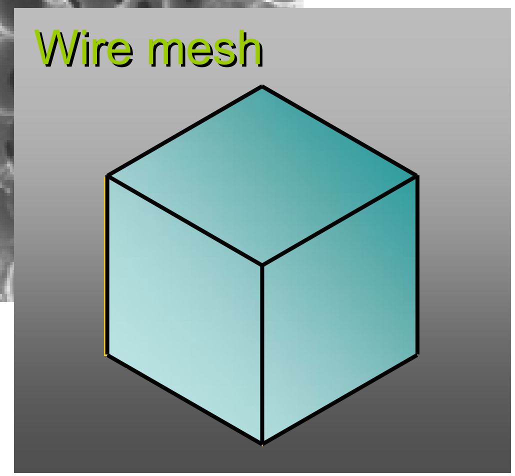
- Forming hydride is exothermic:

~1 MW for 5 min.

- Temperature rise suppresses hydriding reaction
- For typical hydrides the thermal conductivity is: k~0.1 W/m-K
- Nanostructured materials impair heat transfer

SOLUTIONS





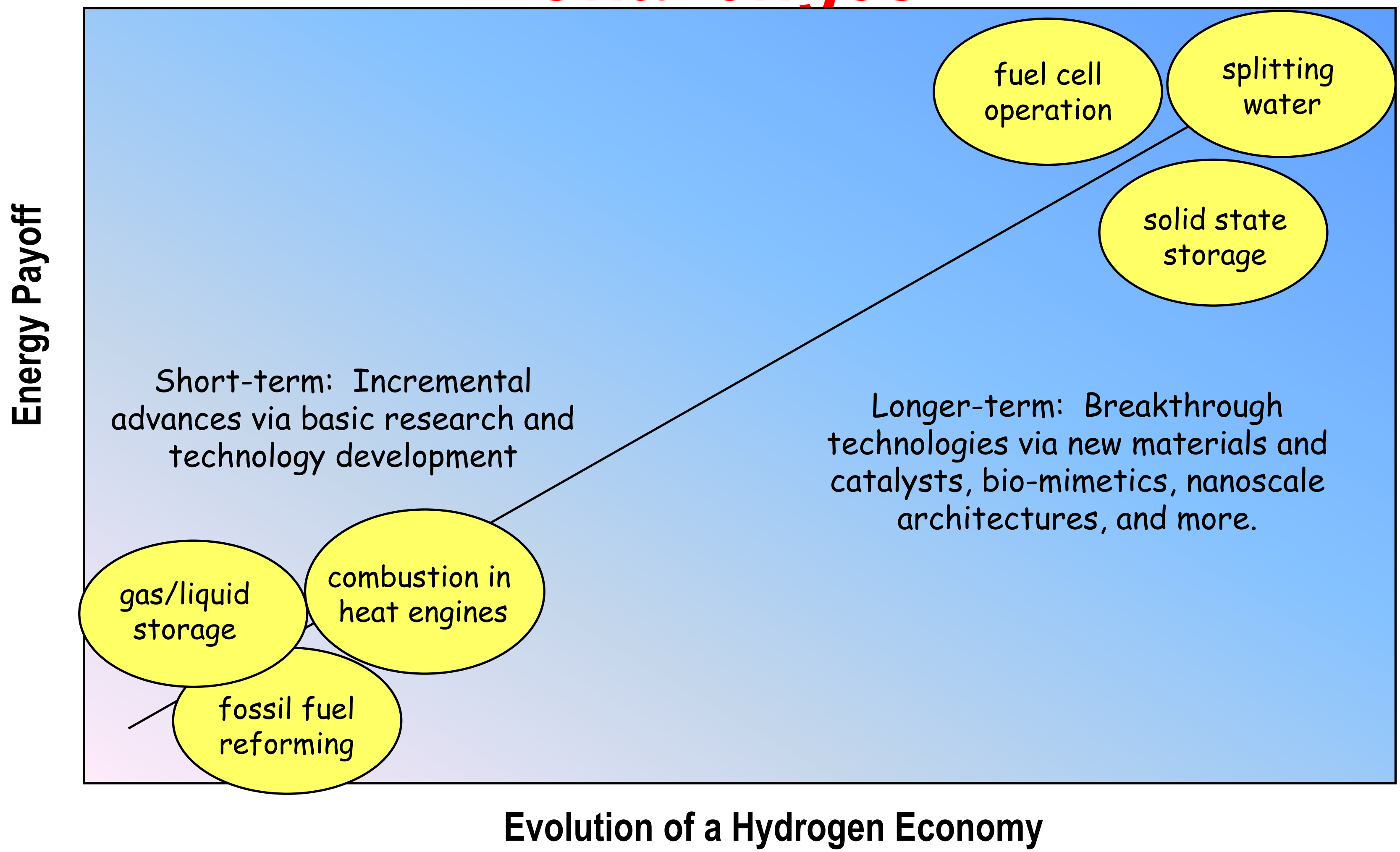
Make composites by adding carbon foams, fins and meshes and carbon nanotubes to hydrides

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

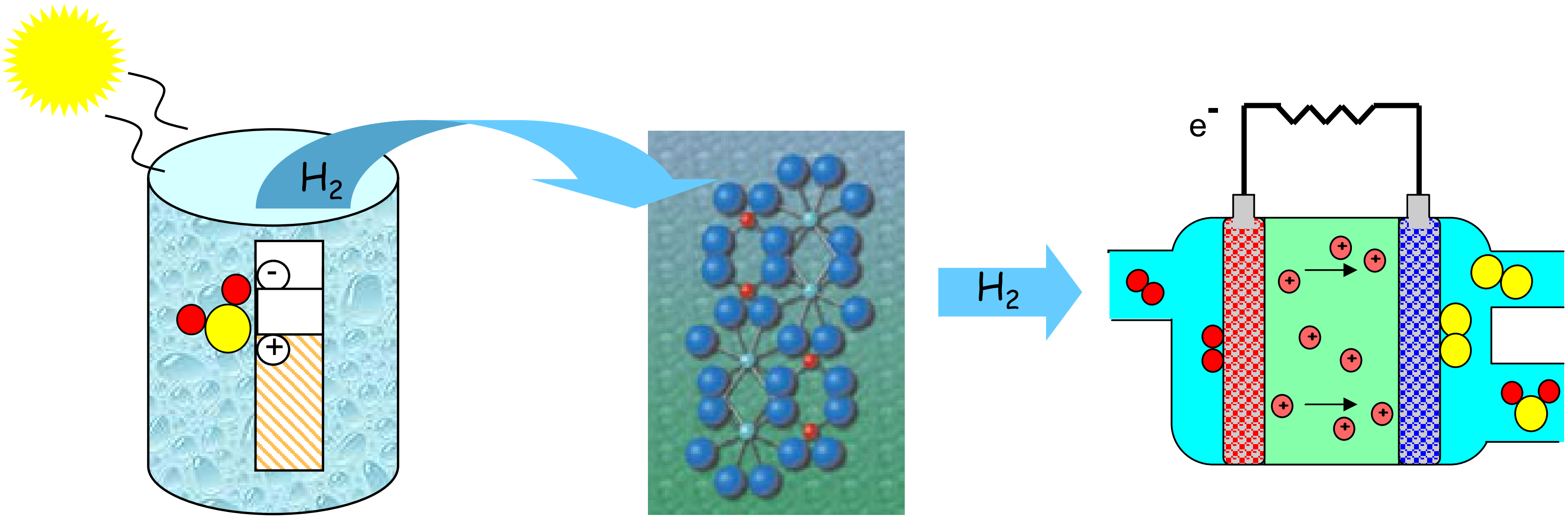
Expanded Graphite Compacts

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

Summary: Research for Short-term Showstoppers and Long-term Grand Challenges



Outlook: the Mature Hydrogen Economy



production:
split water renewably

storage:
solid state materials

use:
fuel cells

high impact on energy challenges
supply, security, pollution, climate

science within reach
breakthrough research discoveries
catalysis, membranes,
nanoscale architectures, bio-mimetics

Messages

- Enormous gap between present state-of-the-art capabilities and requirements that will allow hydrogen to be competitive with today's energy technologies
  - production: 9M tons $\Rightarrow$ 150M tons (vehicles)
  - storage: 4.4 MJ/L (10K psi gas) $\Rightarrow$ 9.7 MJ/L
  - fuel cells: $200-3000/kW $\Rightarrow$ $30/kW (gasoline engine)
- Enormous R&D efforts will be required
  - Simple improvements of today's technologies will not meet requirements
  - Technical barriers can be overcome only with high risk/high payoff basic research
- Research is highly interdisciplinary, requiring chemistry, materials science, physics, biology, engineering, nanoscience, computational science
- Basic and applied research should couple seamlessly

http://www.sc.doe.gov/bes/hydrogen.pdf

Conclusions

Hydrogen storage requirements

- Sufficiently high volumetric, gravimetric hydrogen capacity (DOE 2015)
  - Candidate materials have been identified

- Sufficiently fast hydrogen kinetics
  - Hydriding reaction in 5 minutes for car applications
  - Good control over release rate
  - Release temperature ~ 350K
  - Strategies have been identified and progress has been made

- Thermal management considerations
  - Minimize heat release during hydriding
  - Minimize temperature rise during hydriding
  - Increase thermal conductivity of hydrogen storage material
  - Some strategies have been identified

- Energy efficiency and safety considerations