ICMR Symposium on Materials Issues in Hydrogen Generation and Storage

August 21, 2006

# Basic Research Needs for the Hydrogen Economy

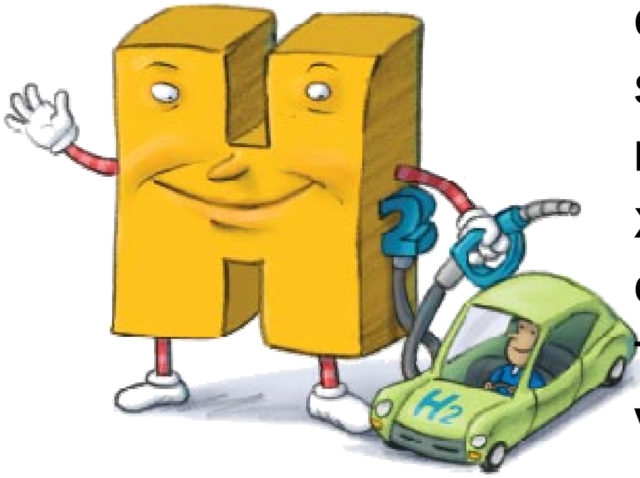
**Mildred Dresselhaus**

**Massachusetts Institute of Technology**
**Cambridge, MA**

**Collaborators $H_2$ report**

**George Crabtree, ANL**

**Michelle Buchanan, ORNL**



**Collaborators $H_2$ Research :**

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**Costas Grigoropoulos, UCB**

**Samuel Mao, UC Berkeley**

**Heng Pan, UC Berkeley**

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**Qizhen Xue, Intematix**

**Taofang Zeng, NCSU**

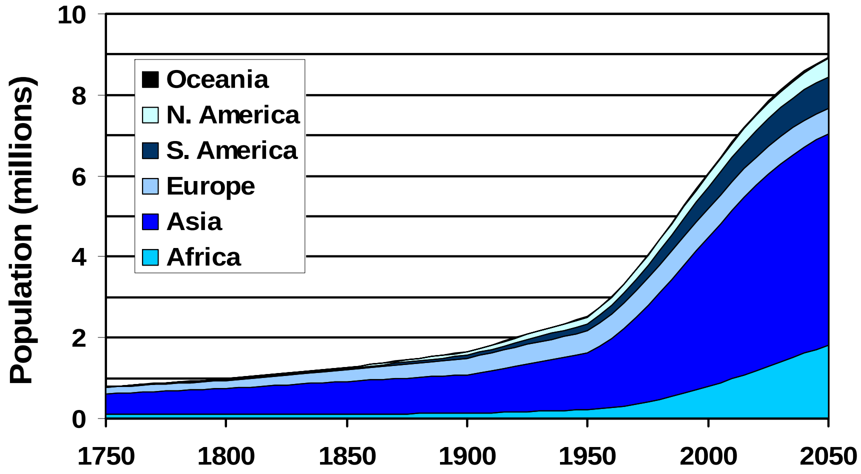
**Vincent Berube, MIT**

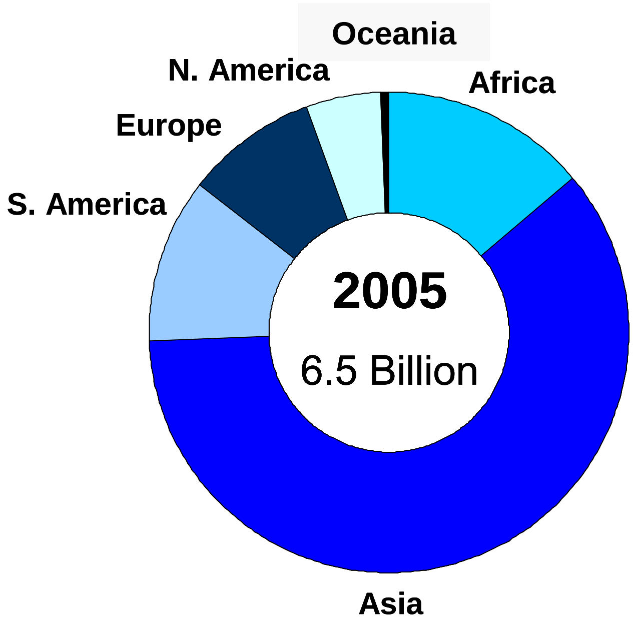
**Gregg Radtke, MIT**

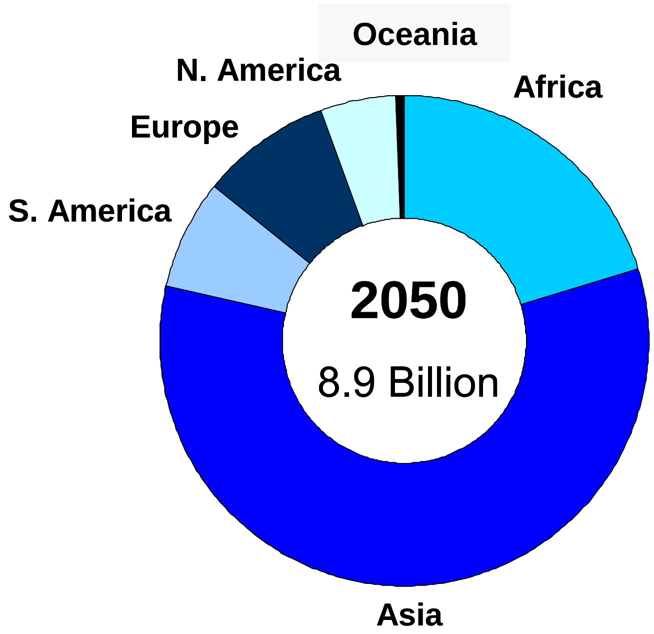
# Outline

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

# Demographic Expansion

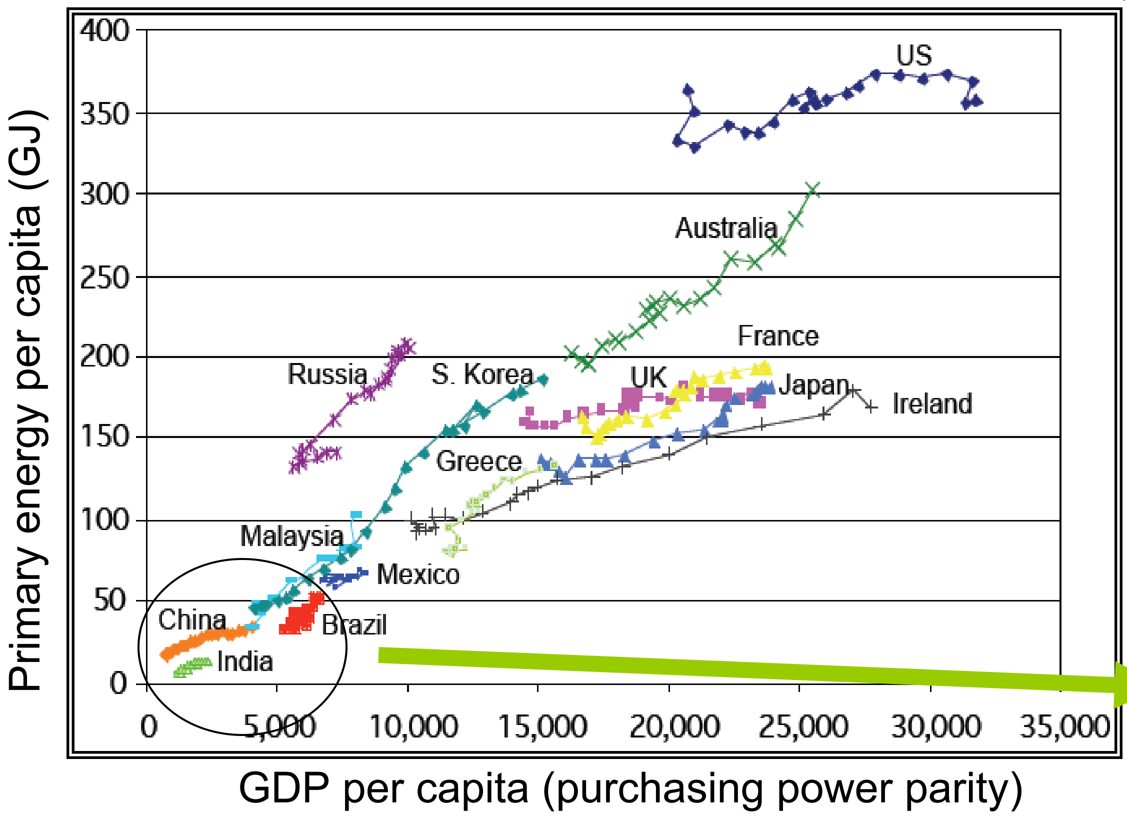


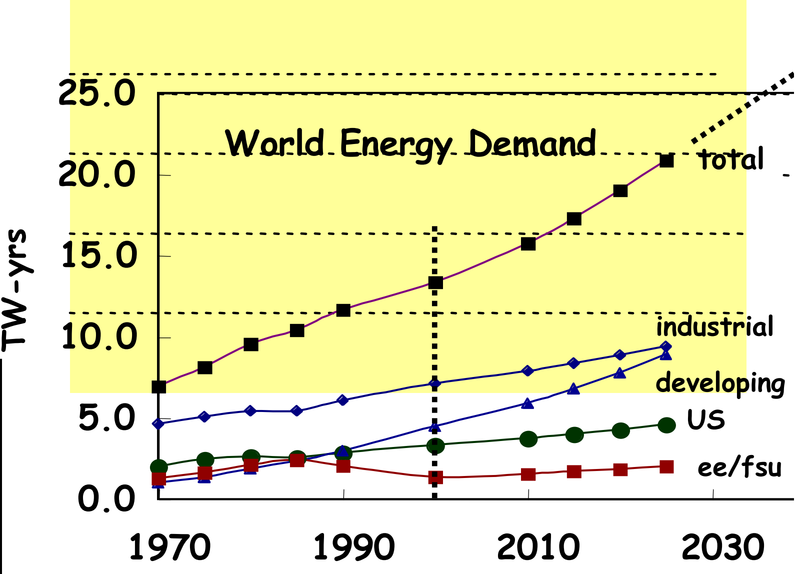




# Growing world energy needs

Energy demand and GDP per capita (1980-2002)





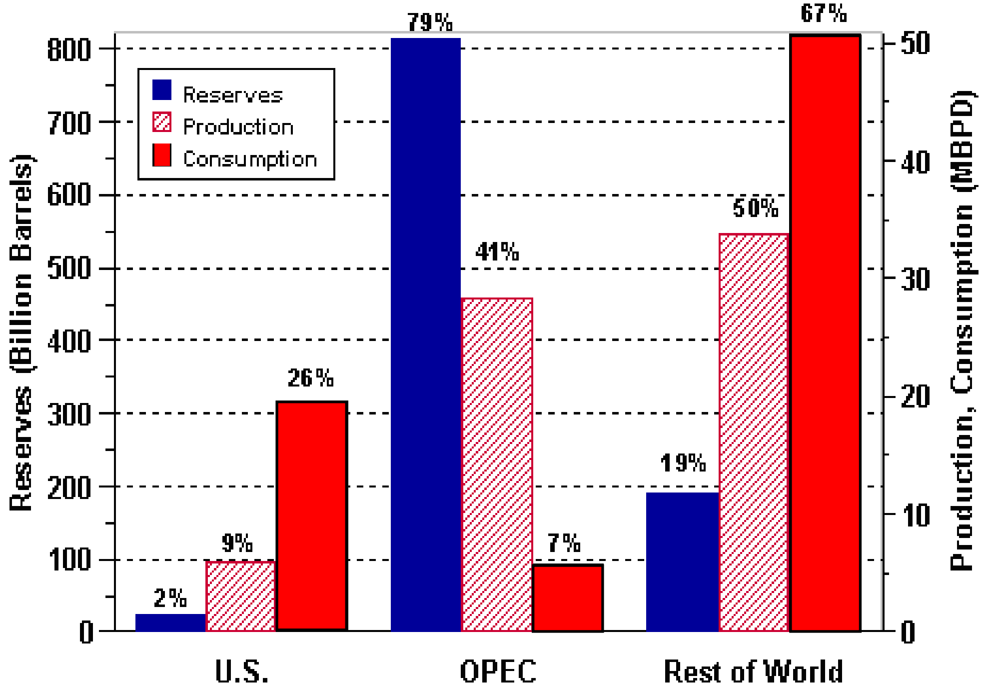
**2000: 13 TW**
**2050: 30 TW**
**2100: 46 TW**

(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**

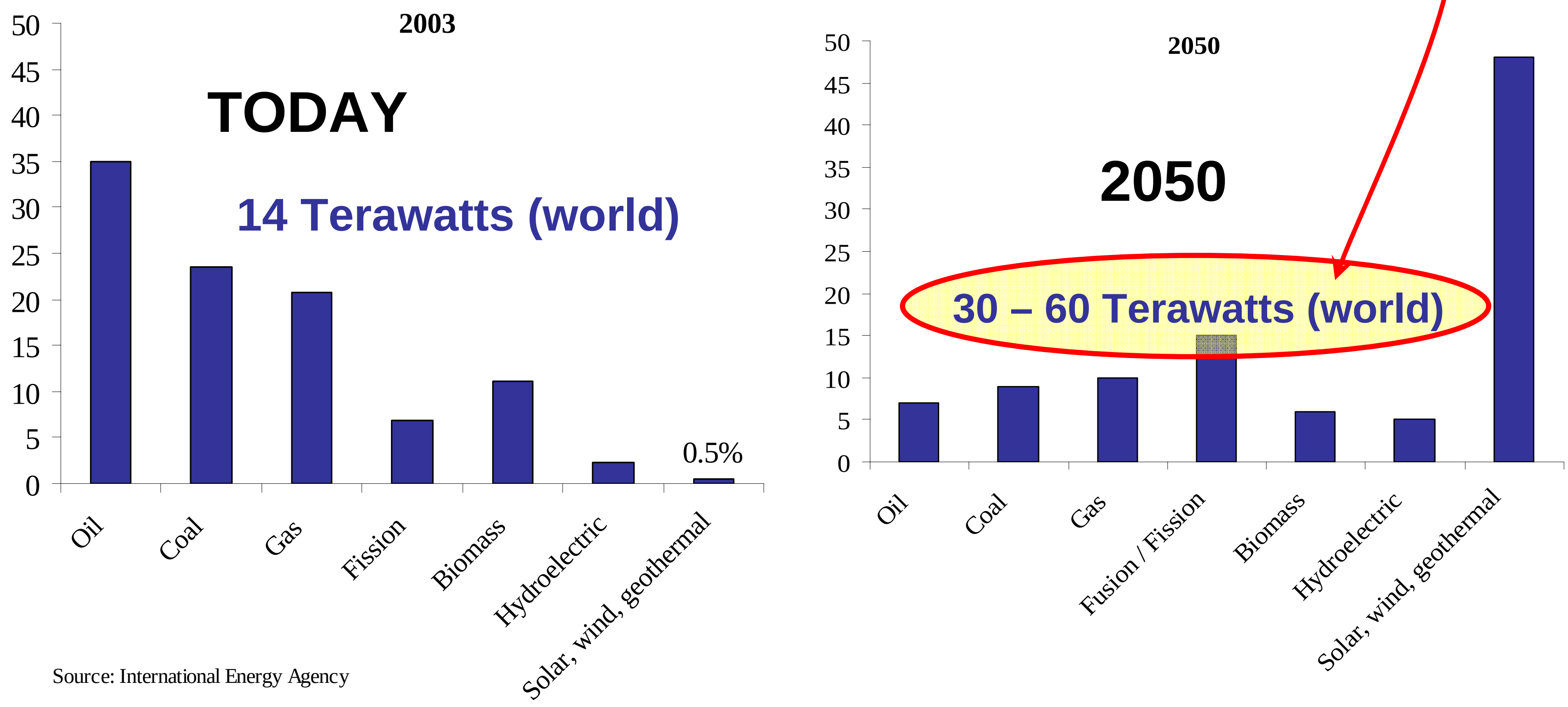
## Estimated world reserves (R/P)

| | 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**

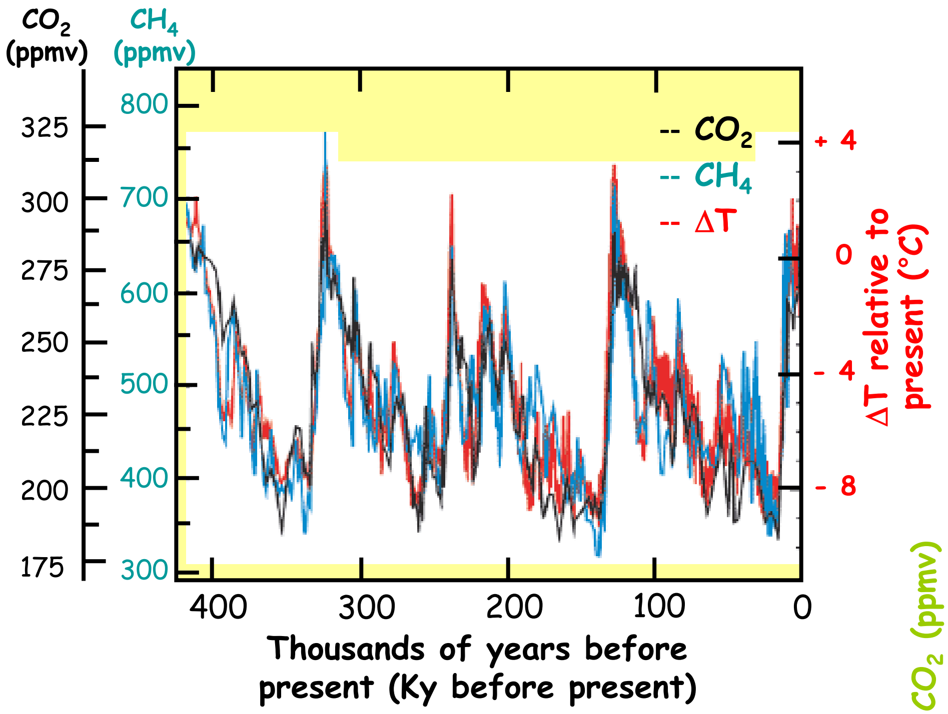
# The Energy Source Challenge



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

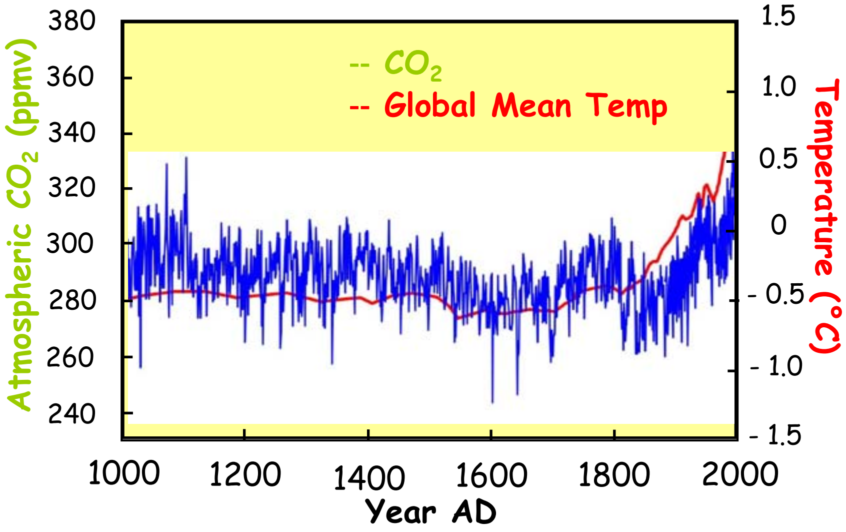


*Intergovernmental Panel on Climate Change, 2001*
http://www.ipcc.ch

***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 nanostructured materials
- Overview of the hydrogen initiative/ the role that nanoscience and nanotechnology might play

# Why Nanostructural materials are important for energy-based applications

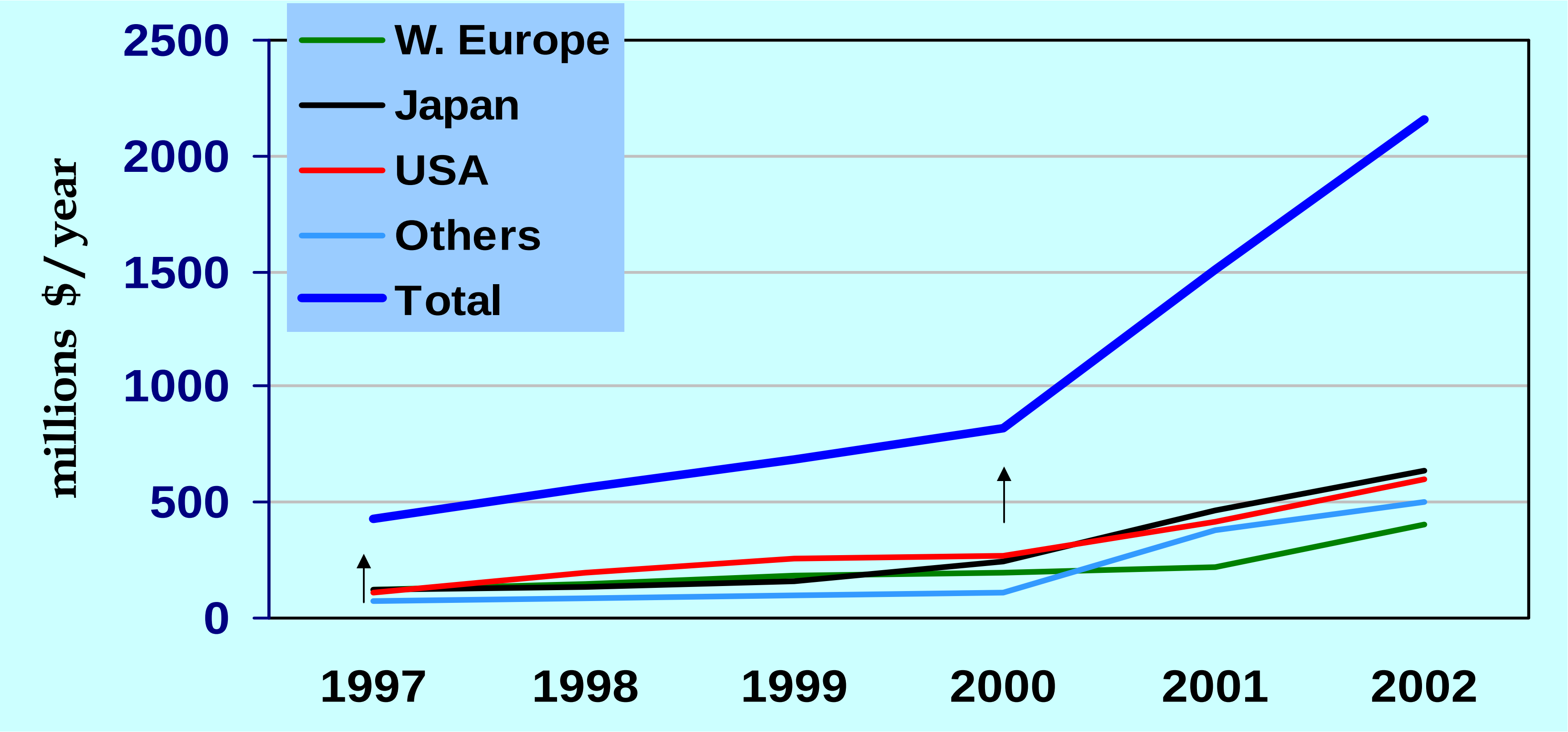
- New desirable properties are available at the nanoscale but not found in conventional 3D materials-e.g., higher diffusion coefficient to promote hydrogen release

- Higher surface area – promotes catalytic interactions

- Independent control of materials parameters which are interdependent for 3D – e.g., strong binding of $H_2$ to substrate and rapid $H_2$ release

# Context – Nanotechnology in the World

## Government investments 1997-2002



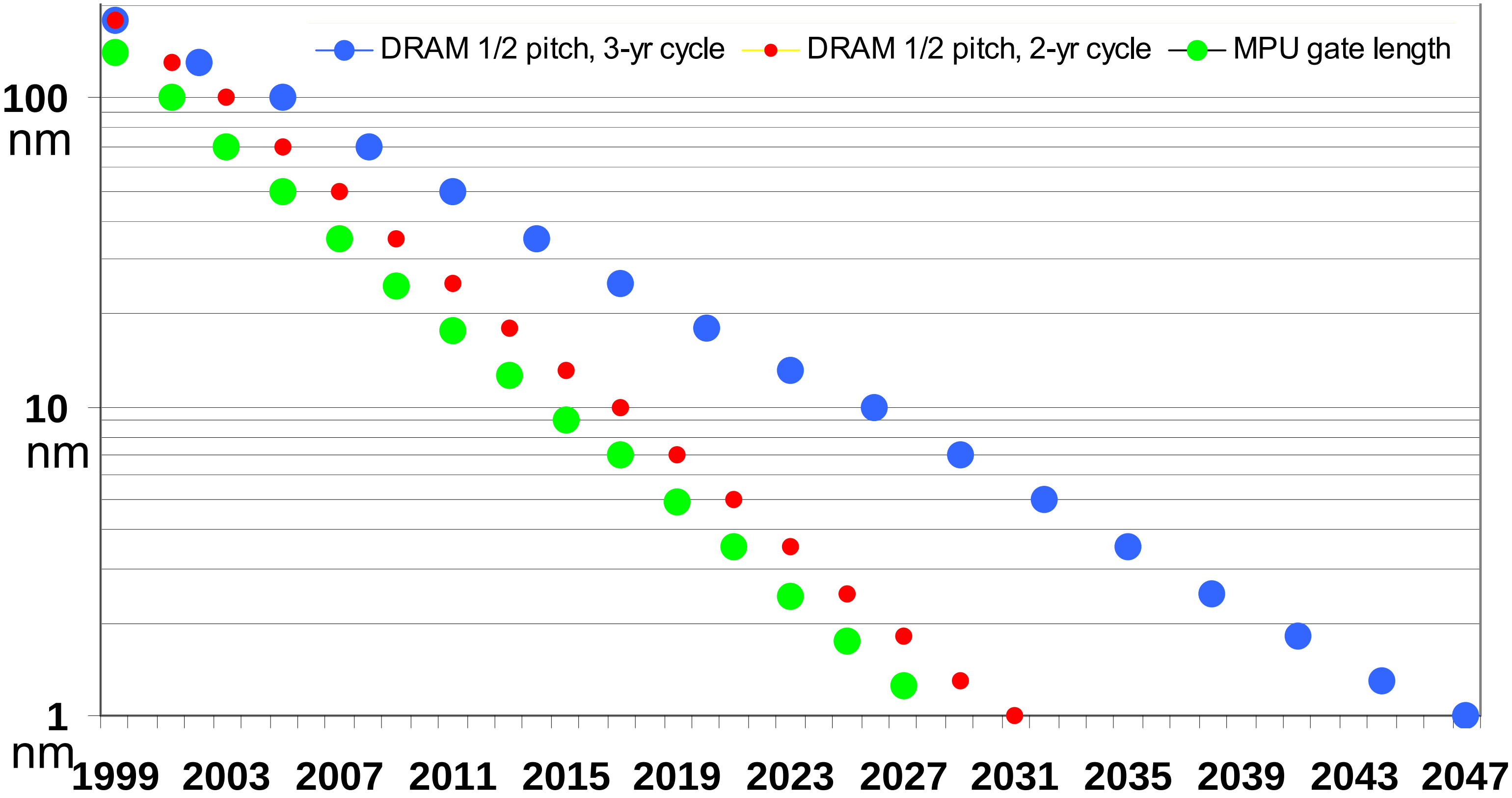
**Note:**

- 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



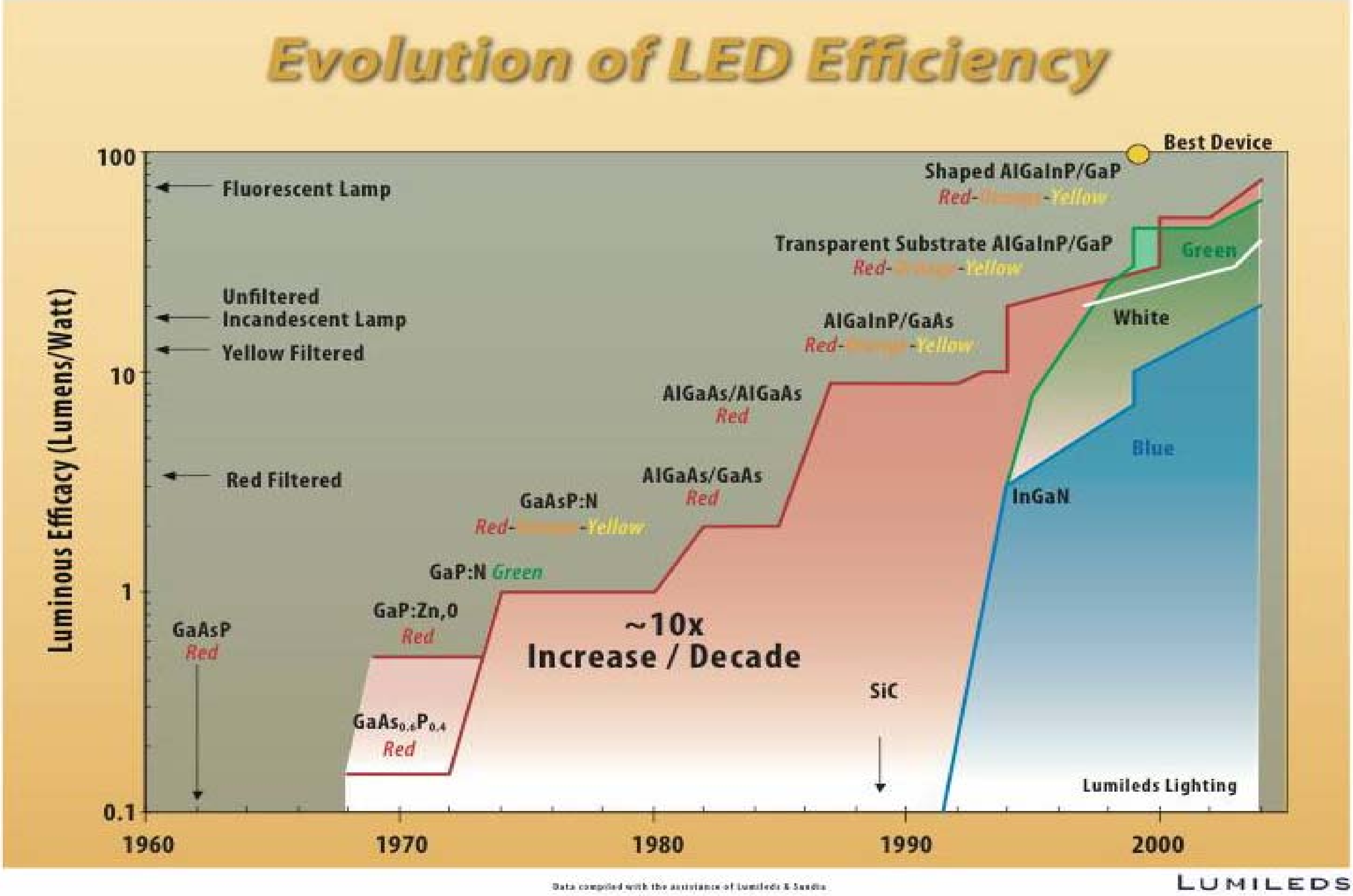
***CONCLUSION:*** *The semiconductor industry already has a large effort underway for producing devices whose minimum design features are 100nm. It is only a matter of time before nearly all chips are nanotech devices. Hence, there is substantial value in synchronizing the large research effort already 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**

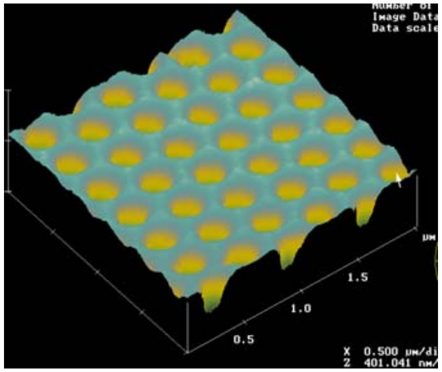
# Extension of Moore's Law to the Energy Industry

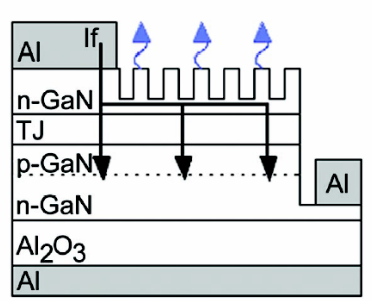
- Moore's law has for many years been working to set goals for electronics, opto-electronics, and magnetics industries.
- We now need to apply Moore's law to set goals for the energy industry.

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

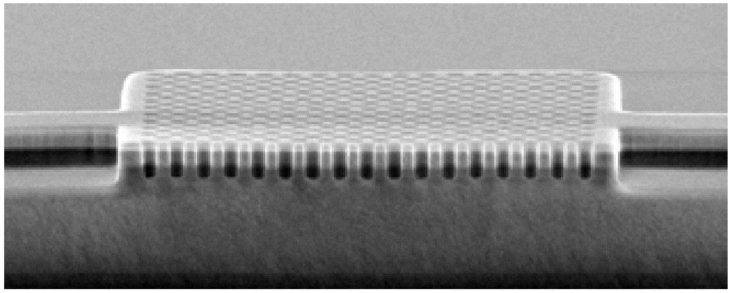


# Emerging Nanotechnologies will further increase Solid State Lighting energy efficiency





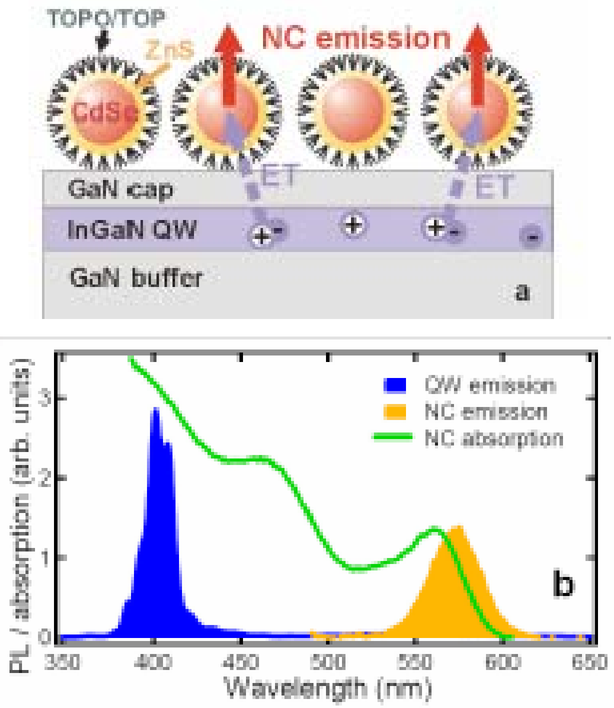
*AFM Image courtesy of Lumileds & Sandia*



**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))

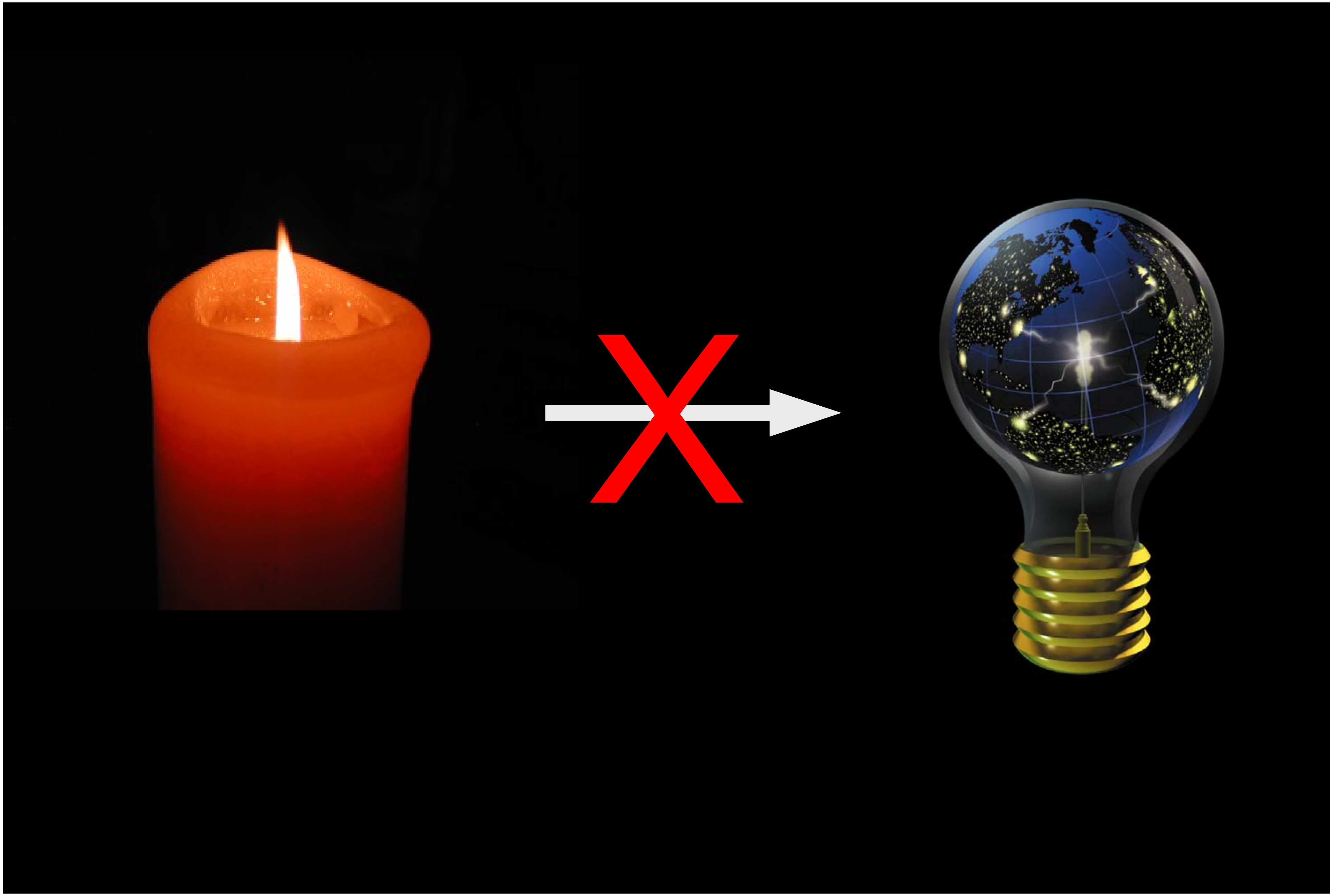


**Nanocrystalline Quantum Dots as Phosphor Alternatives**

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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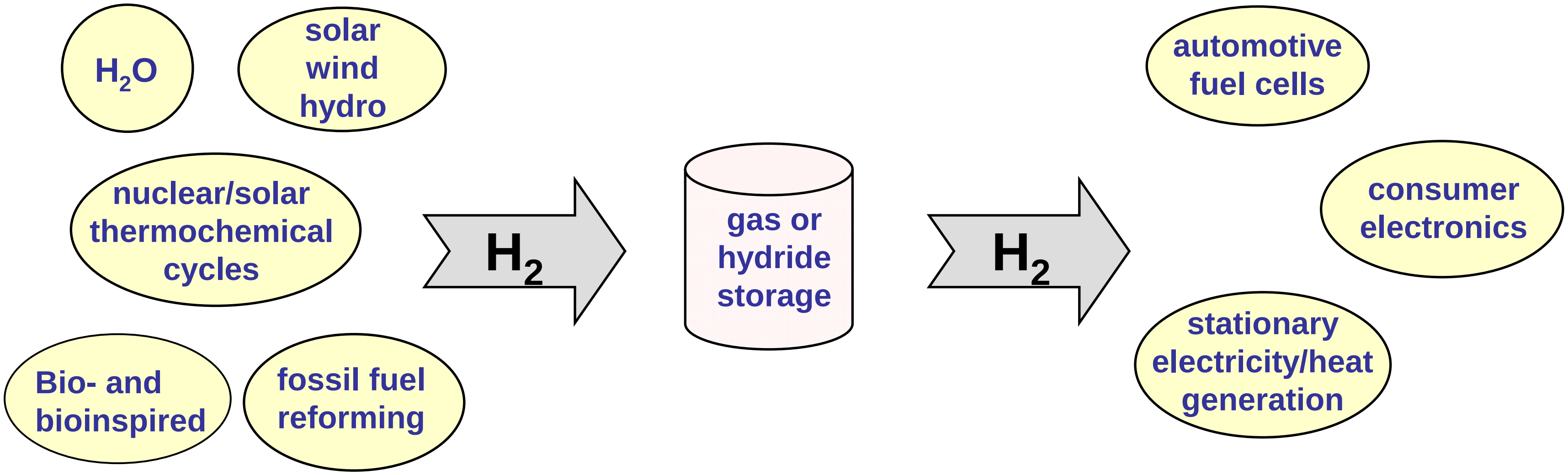
# The Hydrogen Economy – The Technology Gaps



$H_2O$

solar
wind
hydro

nuclear/solar
thermochemical
cycles

Bio- and
bioinspired

fossil fuel
reforming

$H_2$

gas or
hydride
storage

$H_2$

automotive
fuel cells

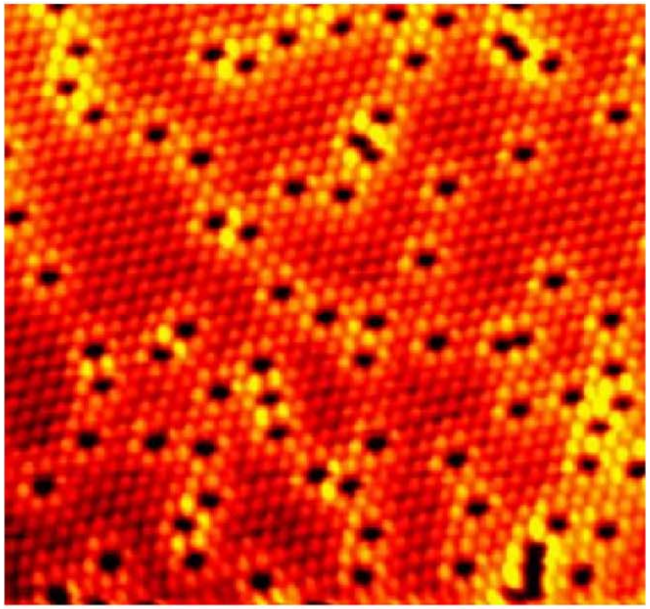
consumer
electronics

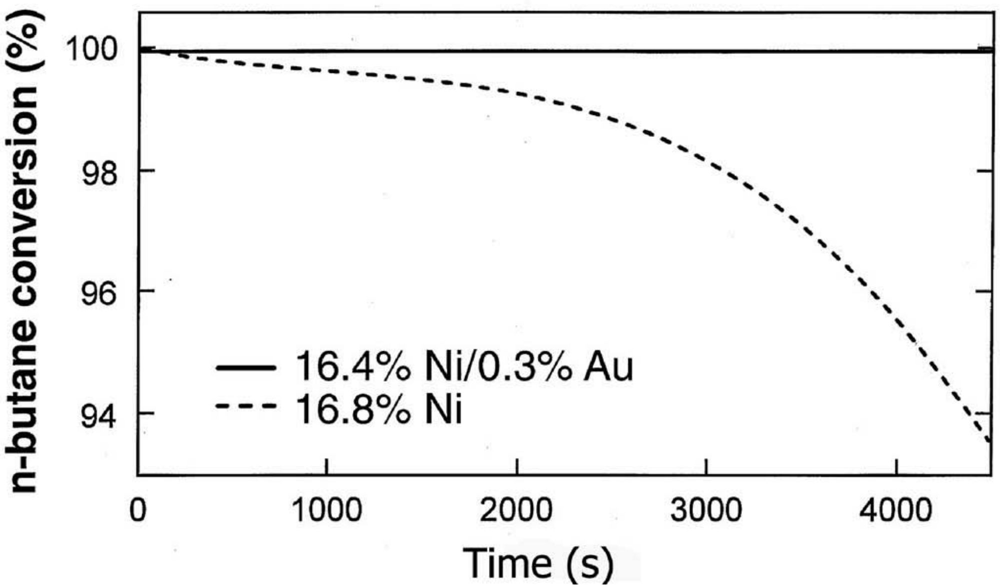
stationary
electricity/heat
generation

| *production* | *storage* | *use (in fuel cells)* |
|---|---|---|
| **9M tons/yr** | **4.4 MJ/L (Gas, 10,000 psi)**<br>**8.4 MJ/L (LH2)** | **$200-3000/kW** |
| ⬇ *Gap* | ⬇ *Gap* | ⬇ *Gap* |
| **150M tons/yr**<br>**(Light Cars and Trucks in 2040)** | **9.7 MJ/L**<br>**(2015 FreedomCAR Target)** | **$30/kW**<br>**(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 <u>catalysts</u> will be key.**
- **<u>Modeling and simulation</u> will play a significant role.**

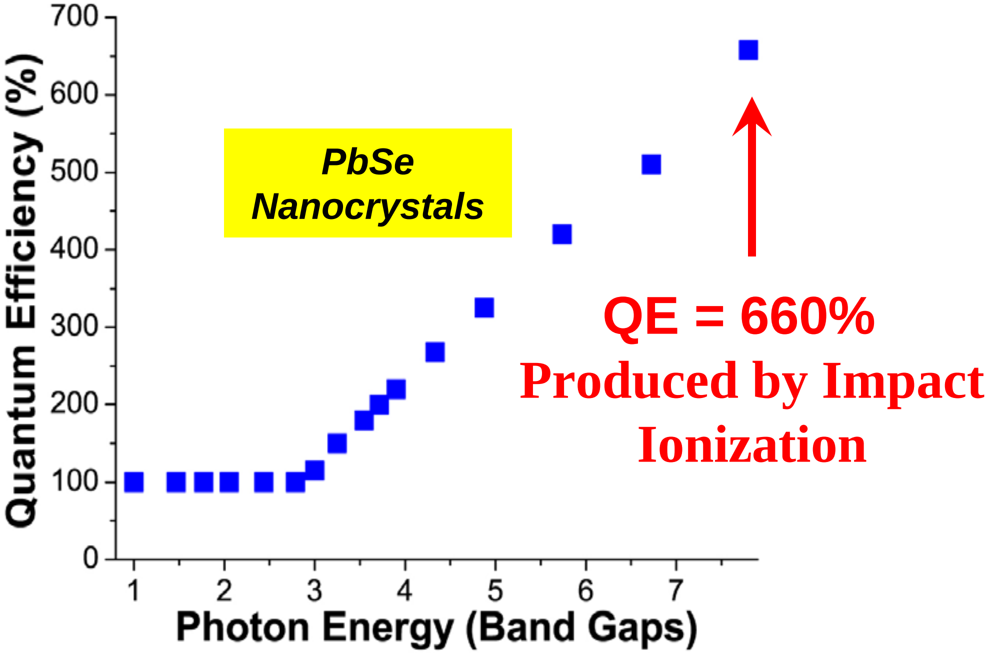


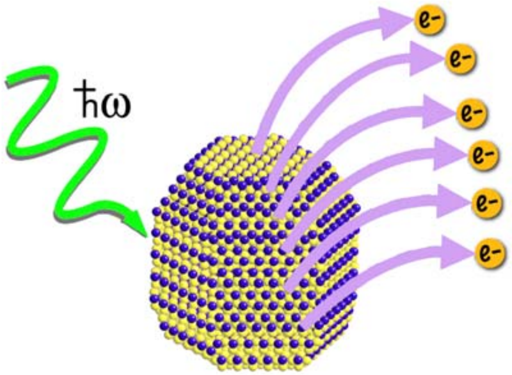


**Inspired by quantum chemical calculations, Ni surface-alloyed with Au (black) on the left is used to reduce carbon poisoning of catalyst, as verified experimentally on the right.**

# Discovery of Ultra-Efficient Carrier Multiplication in Semiconductor Nanocrystals

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

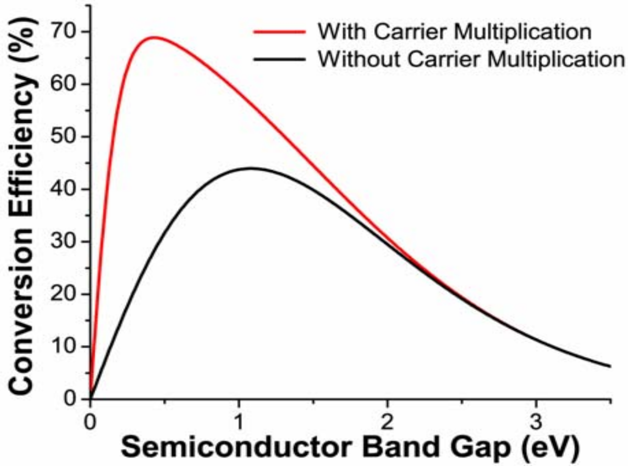




**R. D. Schaller & V. I. Klimov, *Phys. Rev. Lett.* 92, 186601 (2004)**

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

***Potential increase up to ~70% !***



Los Alamos

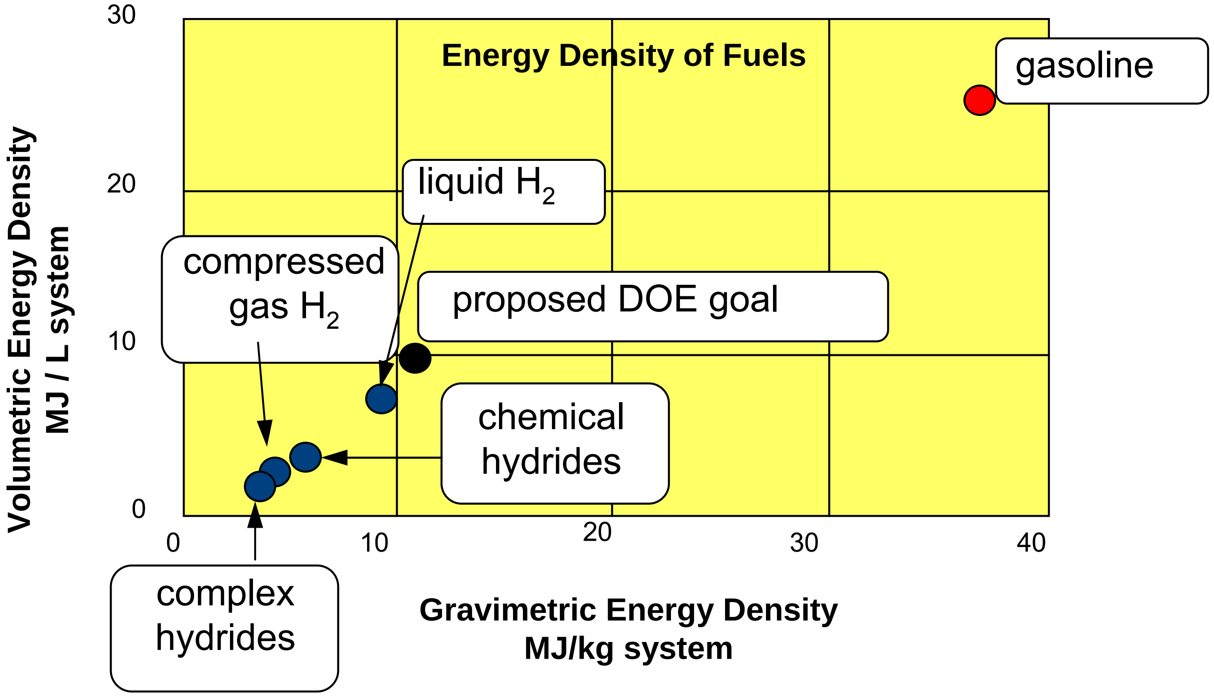
# Hydrogen Storage

**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.**



# Ways to Store Hydrogen

- Compressed gas
- Liquid hydrogen
- Condensed state

Issues

- Volumetric density
- Gravimetric density
- Kinetics
- Heat transfer
- Energy Efficiency
- Reversibility

# DOE Targets

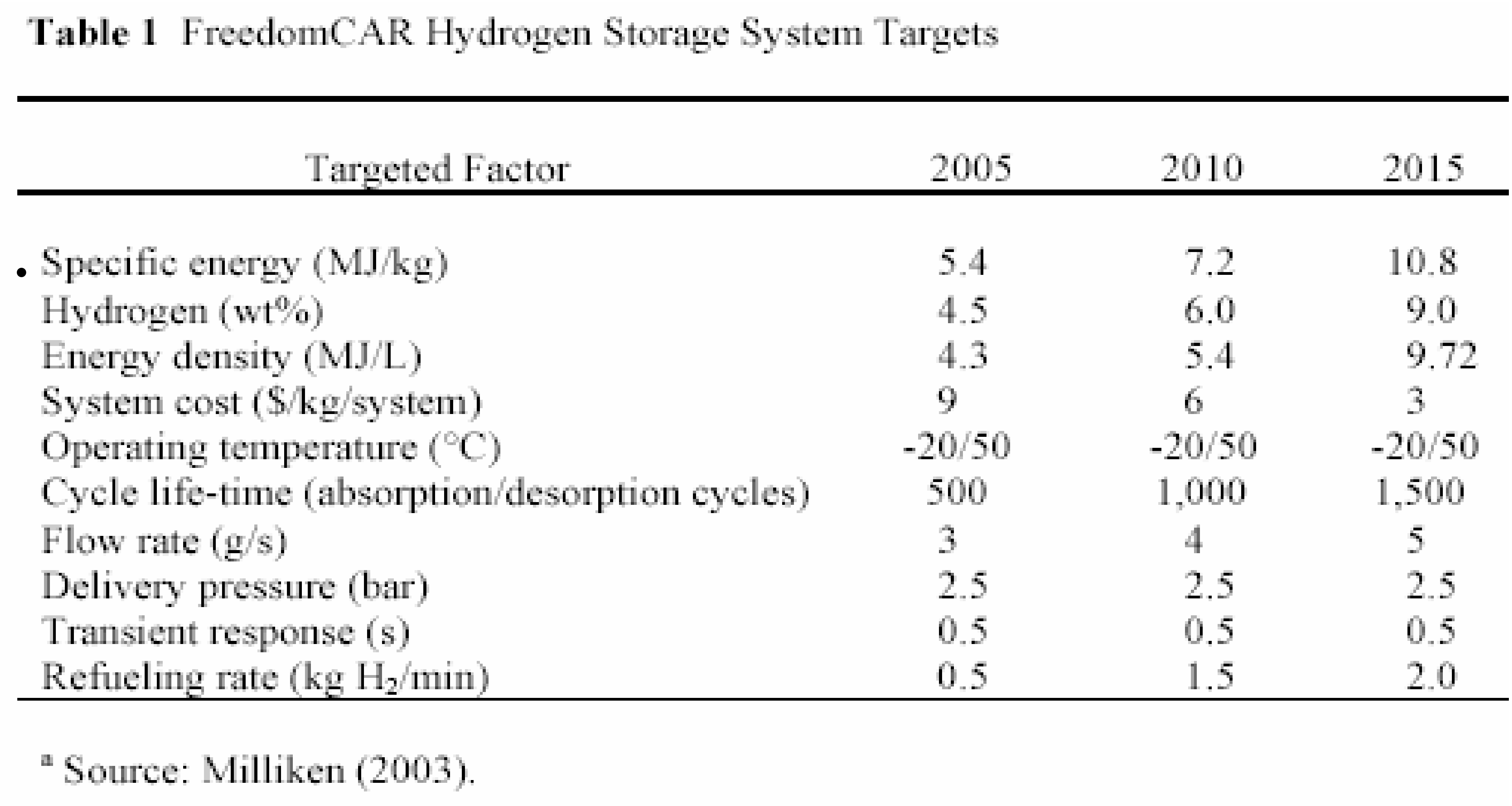


**Table 1** FreedomCAR Hydrogen Storage System Targets

| 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).

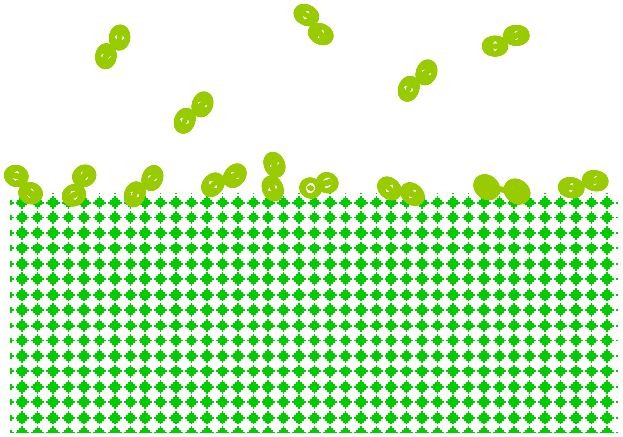
# The Hydrogen Bottlenecks

| | 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$** | ✗<br>**(too slow)** | ✗ |
| **Operating temperature** | **-40 - 60 °C** | ✗<br>**(too high)** | ✓ |
| **Operating pressure** | **<100 atm.** | ✓ | ✓ |

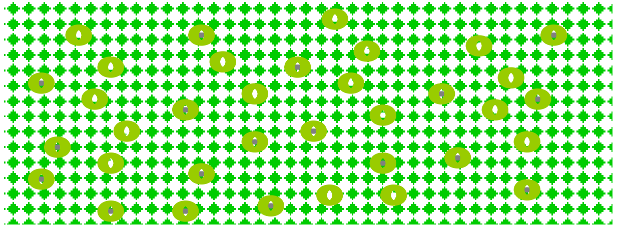
2)

JoAnn Milliken (2002)

# Hydrogen Storage in Condensed States



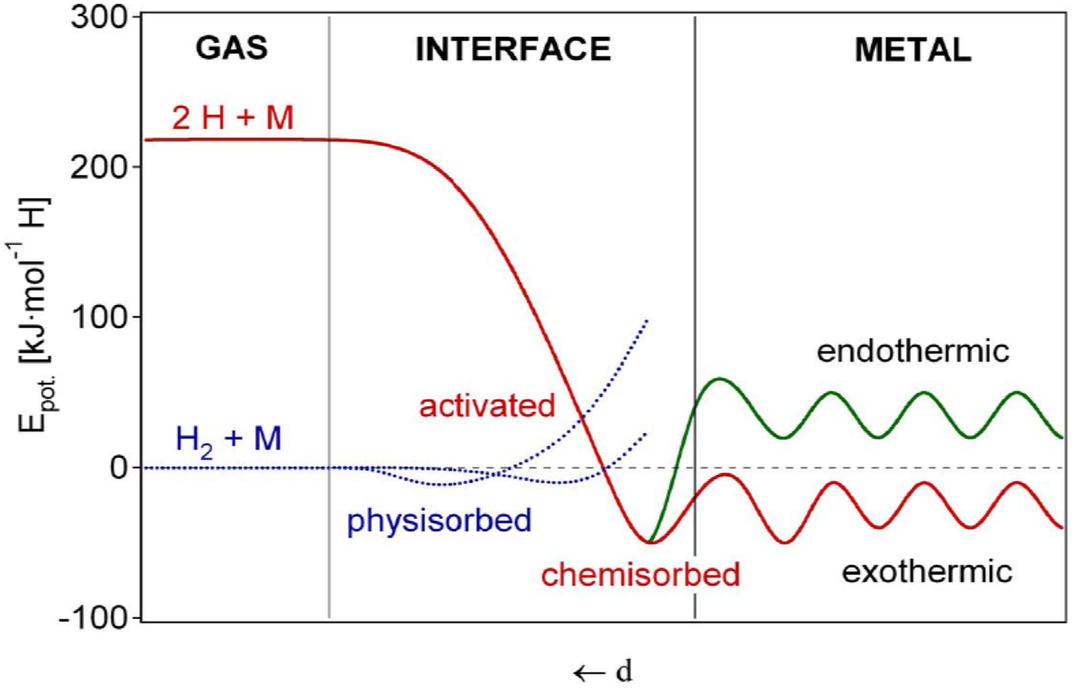
Physisorption
Adsorption on Surface



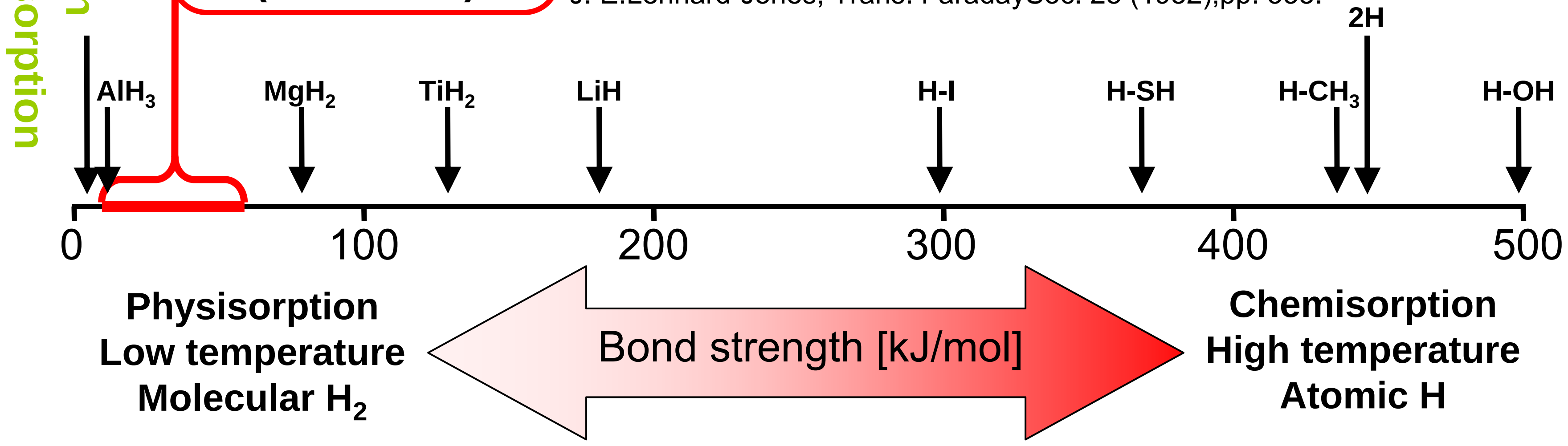
Chemisorption
Absorption into Matter

# Desired binding energy range

Potential energy for molecular and atomic hydrogen absorption



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



**Desirable range of binding energies: 10-60 kJ/mol (0.1 - 0.6 eV)**

**Physisorption**
**Low temperature**
**Molecular $H_2$**

**Chemisorption**
**High temperature**
**Atomic H**

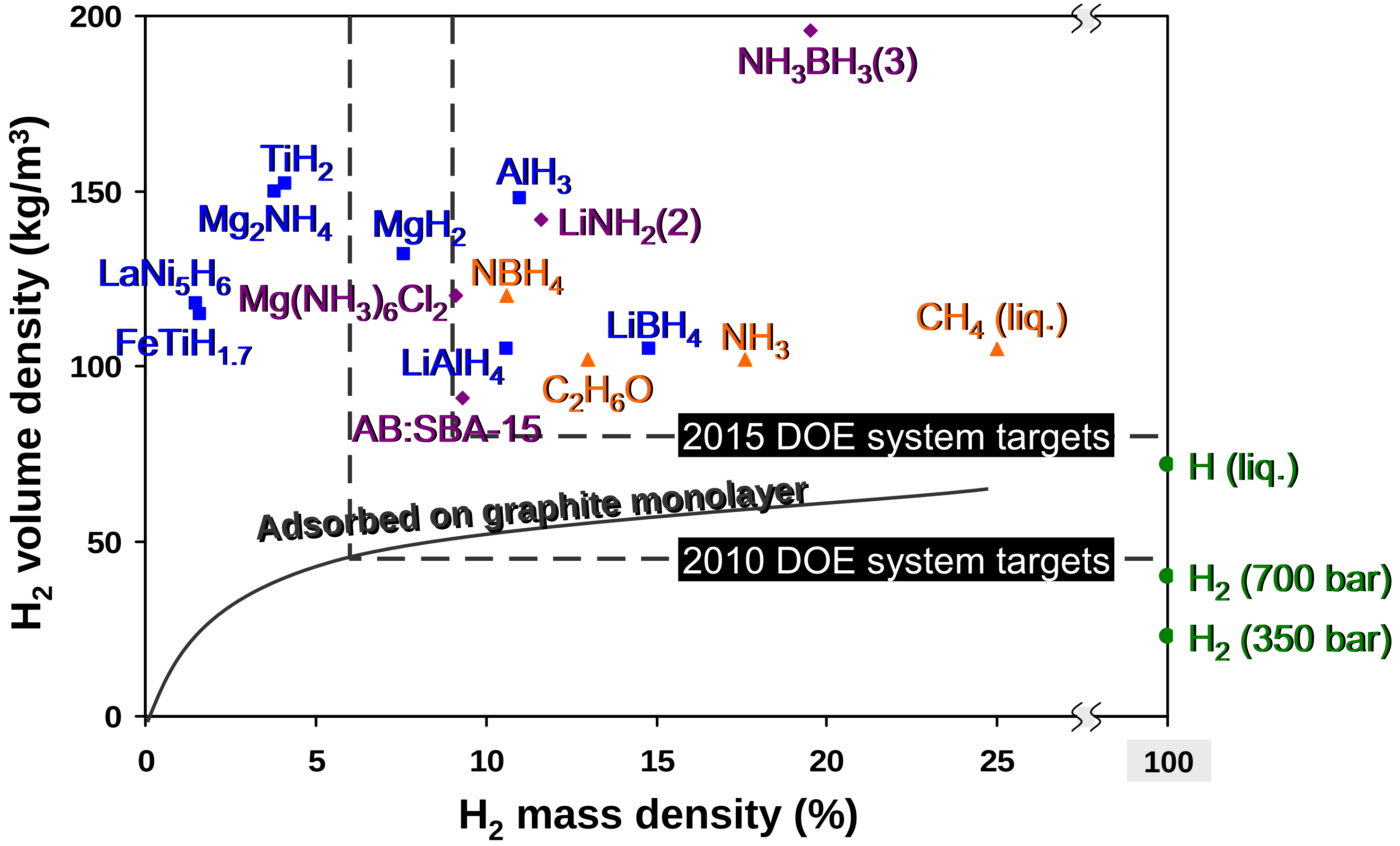
# Hydrogen Storage Options

**Metal/complex hydrides:**

- ■ Slow kinetics
- ■ Heat management issues
- ■ High release temperature

**Chemical hydrides:**

- ▲ Not reversible (on-board)

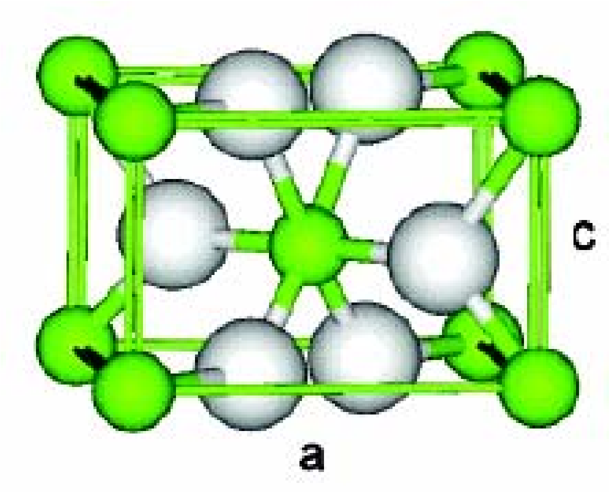


**Carbon structures:**

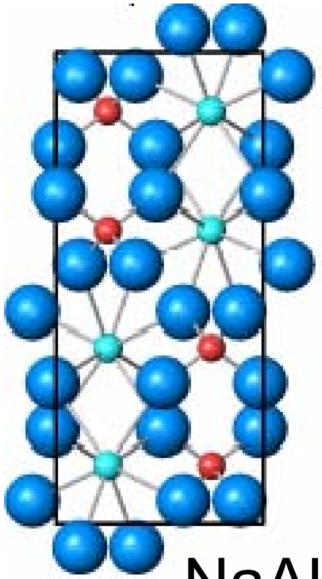
- Low temperature
- Too low wt. % for 2015
- Low energy barrier for hydrogen release

# Classification

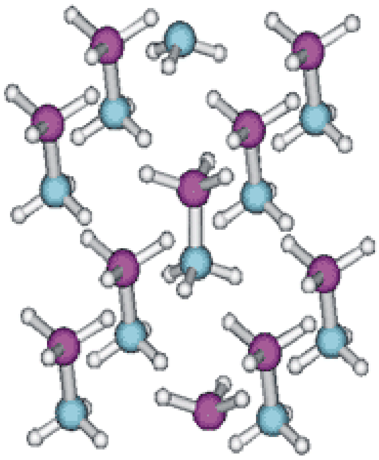
- Metal hydrides: $MgH_2$
- Complex hydrides: $NaAlH_4$
- Chemical hydrides: $LiBH_4$, $NH_3BH_3$



$MgH_2$

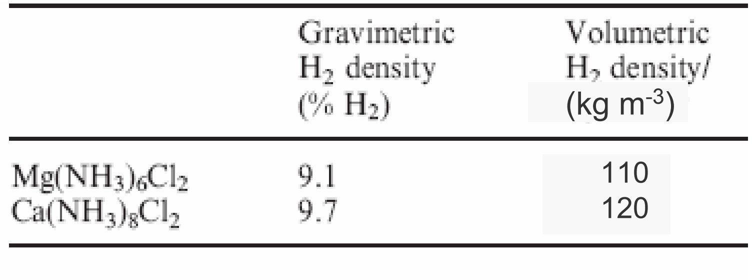


$NaAlH_4$

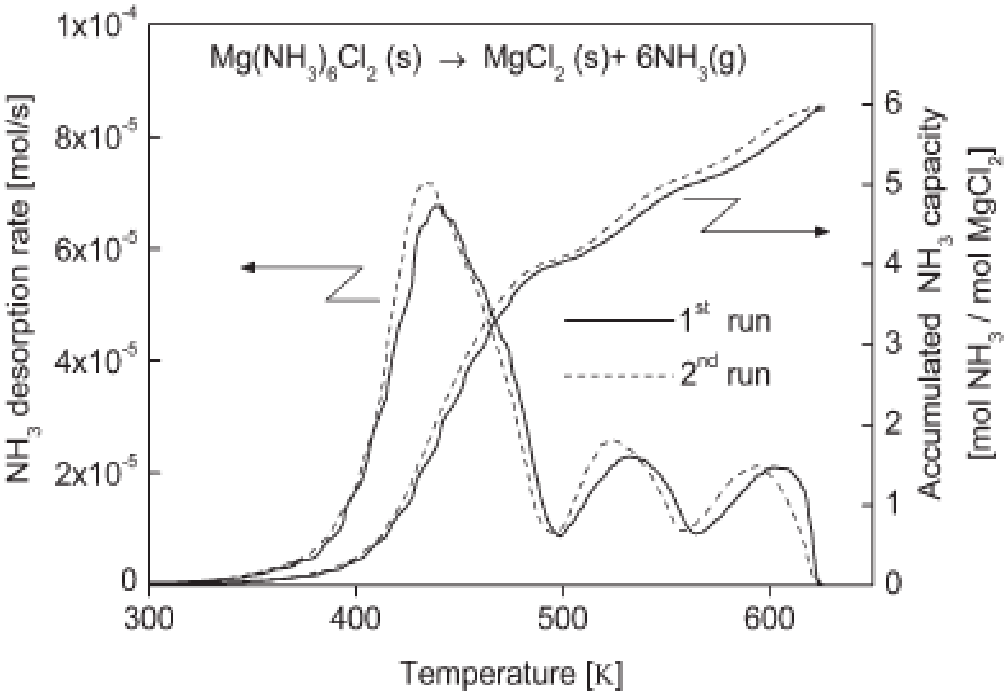


$NH_3BH_3$

# Metal ammine complexes

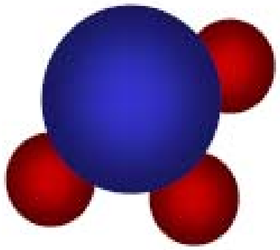


| | Gravimetric $H_2$ density (% $H_2$) | Volumetric $H_2$ density/ (kg $m^{-3}$) |
|---|---|---|
| $Mg(NH_3)_6Cl_2$ | 9.1 | 110 |
| $Ca(NH_3)_8Cl_2$ | 9.7 | 120 |



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

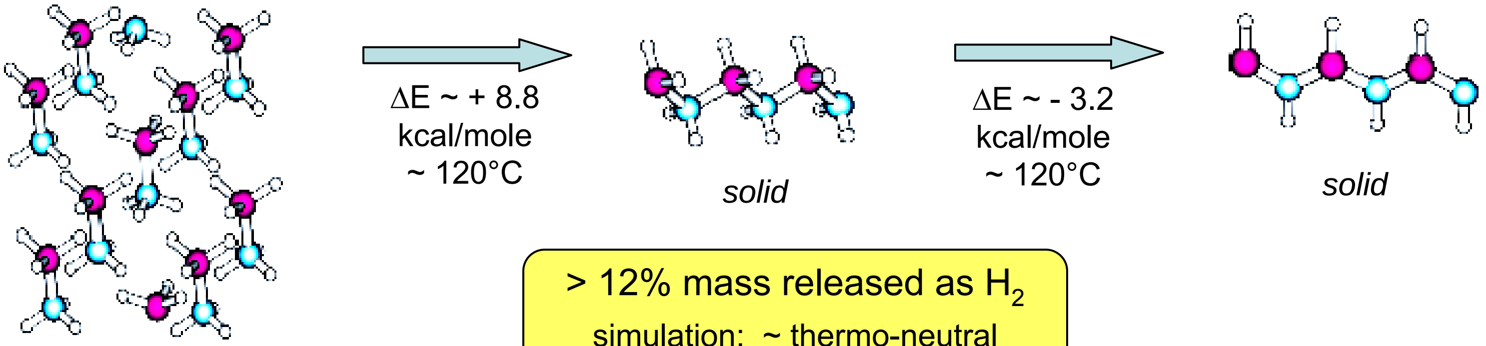
  $2NH_3 \rightarrow 3H_2 + N_2$ @ ~600K
- Technology being developed for battery applications



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

# Hydrogen Storage: Chemistry and Nanoscience

$NH_3BH_3$ → $(NH_2BH_2)_n + H_2$ → $(NHBH)_n + H_2$



ΔE ~ + 8.8
kcal/mole
~ 120°C

*solid*

ΔE ~ - 3.2
kcal/mole
~ 120°C

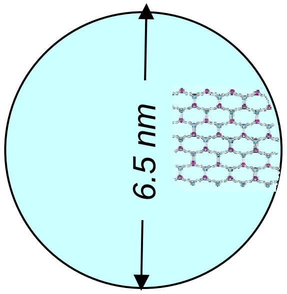
*solid*

Ammonia Borane

*solid: di-hydrogen bonds*

> 12% mass released as $H_2$

simulation: ~ thermo-neutral



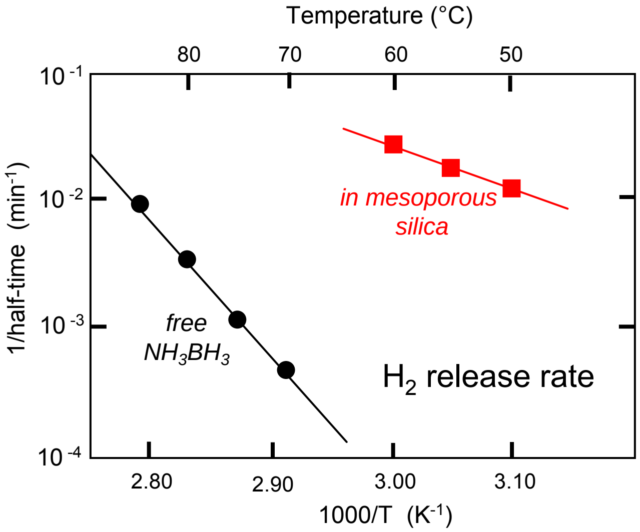
*nano-phase trapping*

$NH_3BH_3$ in mesoporous silica

SBA-15

release rate increased
1-2 orders of magnitude

undesirable borazine
eliminated

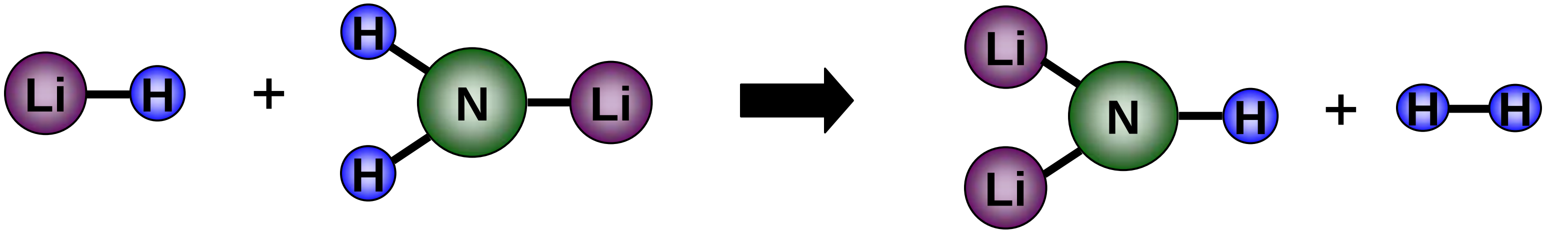


*issues:*
nanophase mechanism
reversibility

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

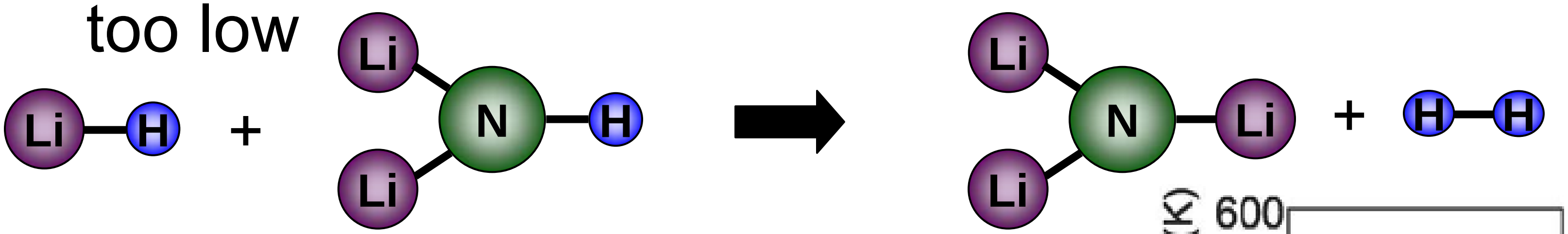
# Imide (NH) and Amide ($NH_2$)

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



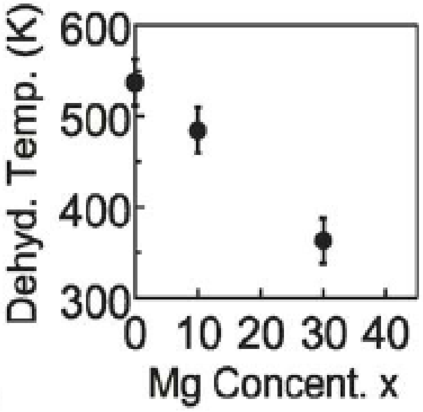
Second: $Li_2NH$ + LiH $\Leftrightarrow$ $Li_3N$ + $H_2$ (5% @ 300C, 0.05atm)

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



Partial Mg substitution reduces release temperature

**$Li_{1-x}Mg_xNH_2$**

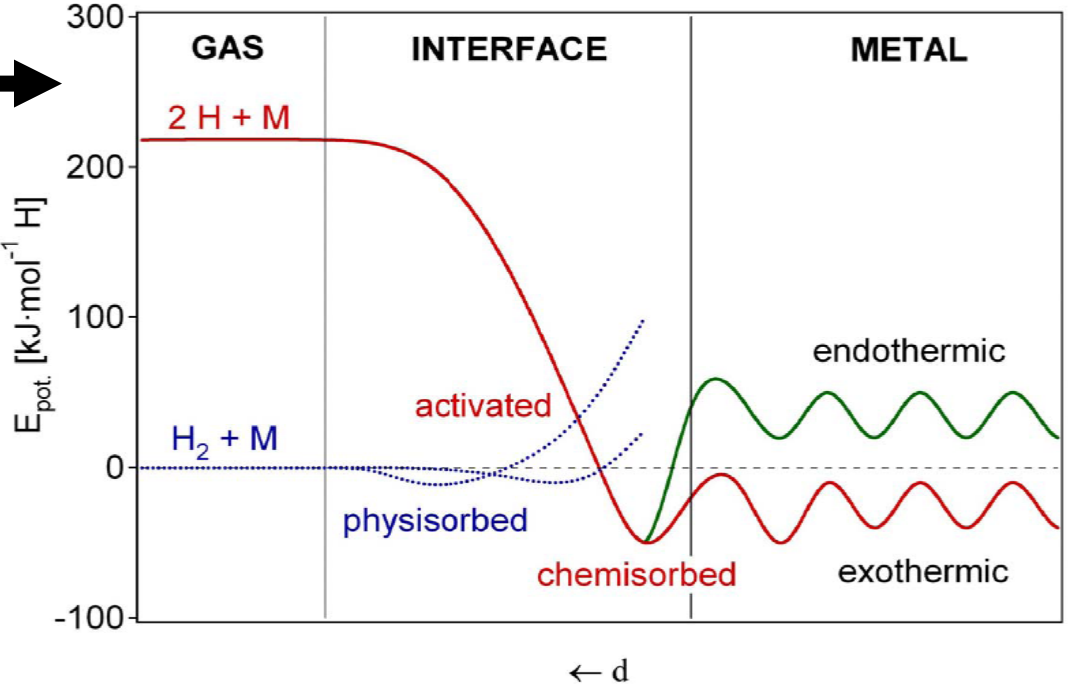


S. Orimo et al., Appl. Phys. A:Materials Science & Processing, Vol 79, No 7, p. 1765 - 1767.

# Desired binding energy range

Potential energy for molecular and atomic hydrogen absorption →

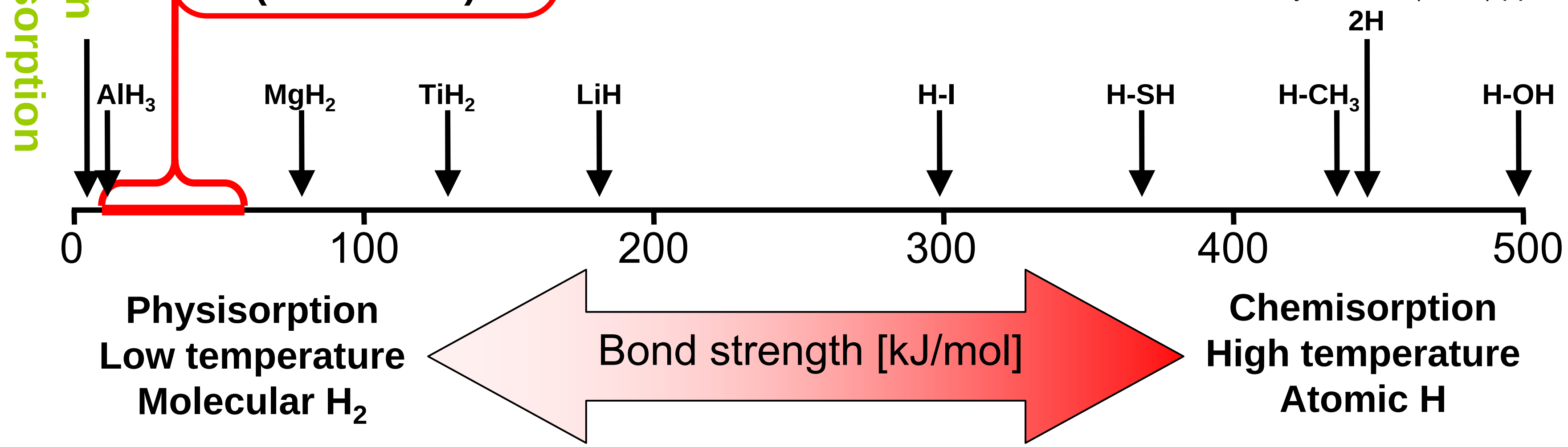
Activated reaction increases release temperature if no catalysts are used



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

**Desirable range of binding energies: 10-60 kJ/mol (0.1 - 0.6 eV)**

Carbon physisorption



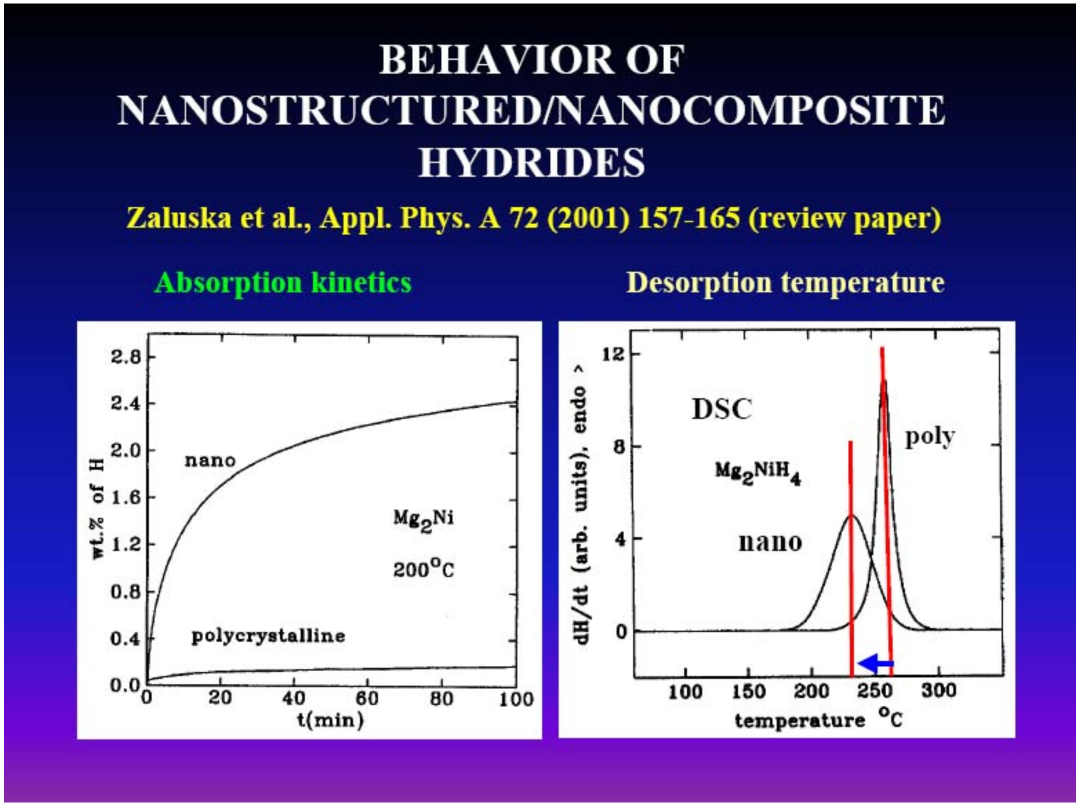
**Physisorption**
**Low temperature**
**Molecular $H_2$**

Bond strength [kJ/mol]

**Chemisorption**
**High temperature**
**Atomic H**

# 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.

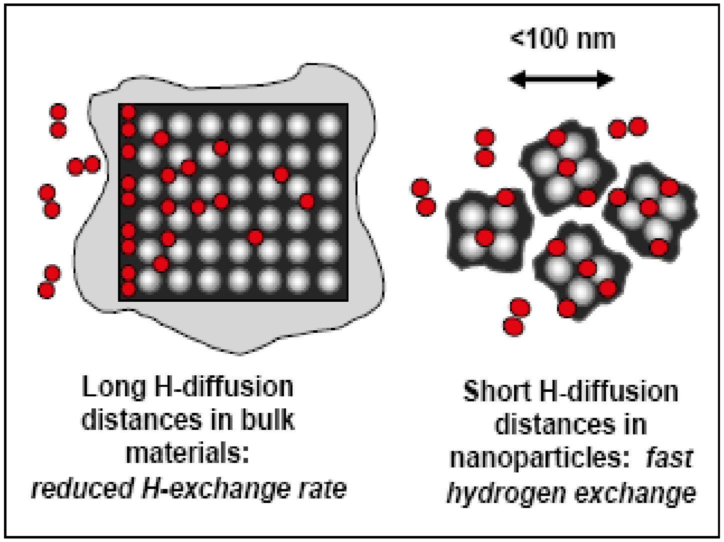


**BEHAVIOR OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES**

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 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

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

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

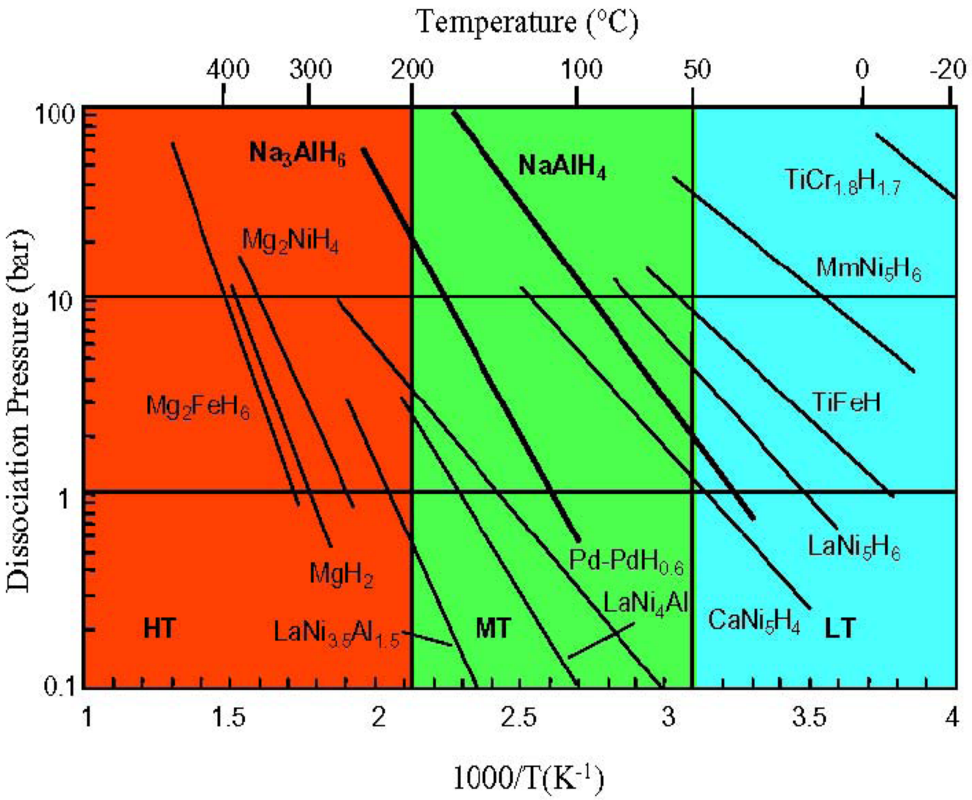


**Figure 6** van’t Hoff Diagram Showing Dissociation Pressures and Temperatures of Various Hydrides (Source: Bogdanovic and Sandrick 2002)

- 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.

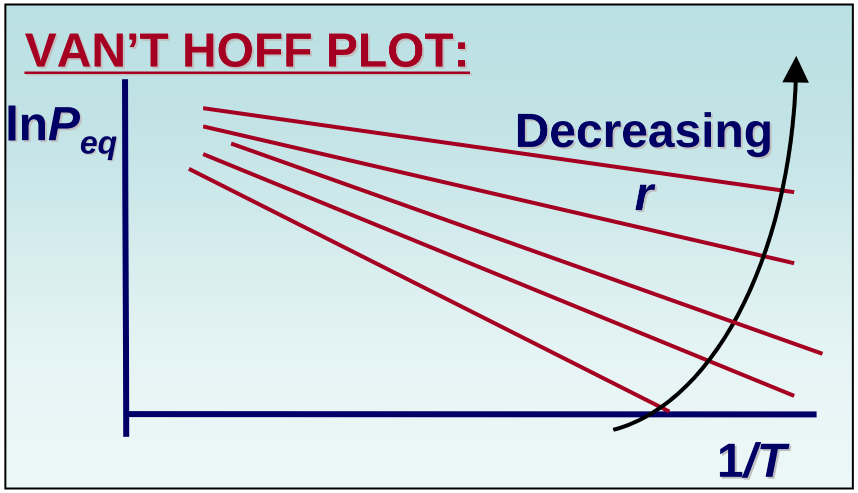
# Size Effects on Thermodynamic Properties

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 is positive, the 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

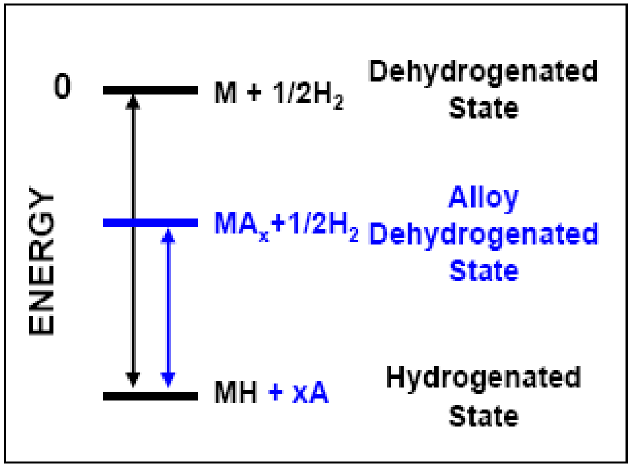
$$\Delta G(r) = \Delta G_o(r) + RT\ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right) + \frac{3\overline{V}_M \Delta(\gamma_{Mg}, \gamma_{MgH_2}, r)}{r}$$

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

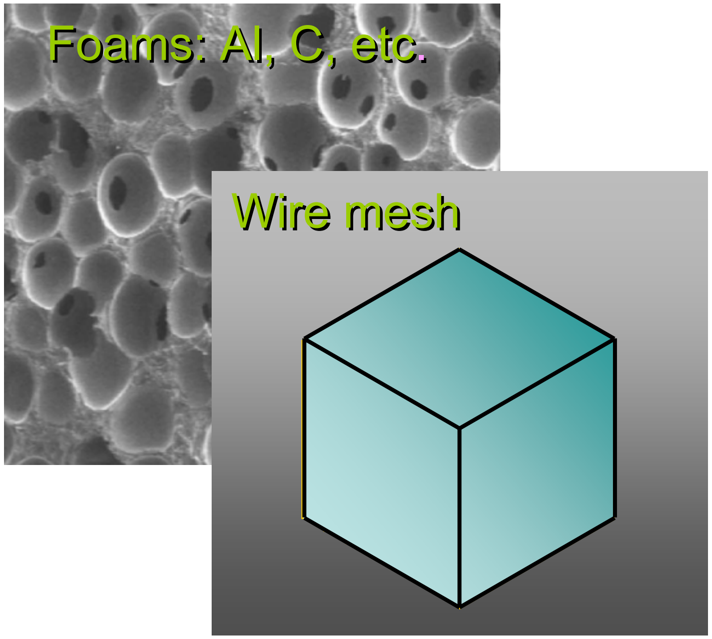
# Thermal Management

- Forming hydride is exothermic:

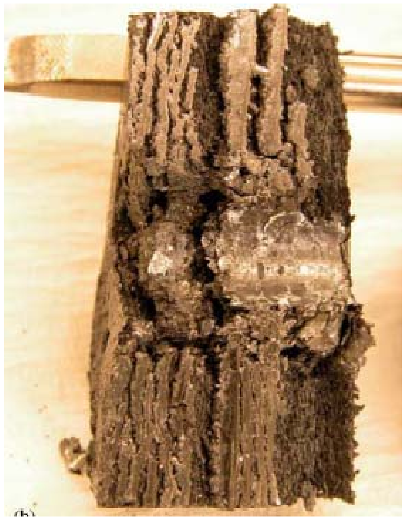
~1 MW for 5 min.

- 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

# Conclusions on Hydrogen Storage

## Nanostructures are key to improved performance – but it isn't easy

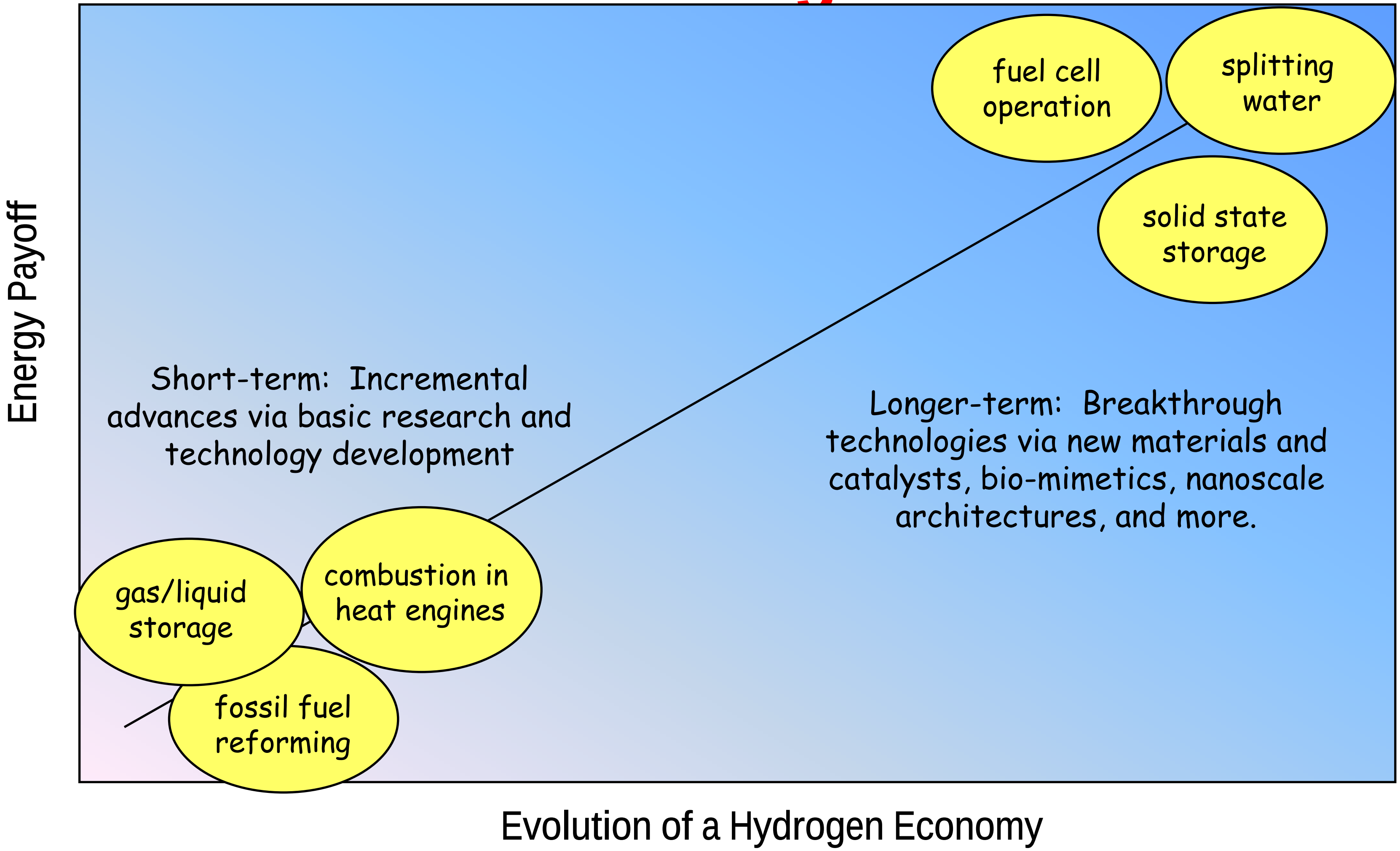
- Key Issue: Sufficiently high volumetric, gravimetric hydrogen capacity (DOE 2015)
  - Candidate materials have been identified

- Thermodynamics:
  - Controlled sorption/desorption temperature and reversibility are needed
  - Release temperature ~350K is desired
- Kinetics
  - Fast kinetics: Hydriding reaction in 5 minutes for car
  - Good control over release rate
  - Strategies have been identified and progress has been made

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

- Energy efficiency and safety considerations
  - These must be high priority concerns

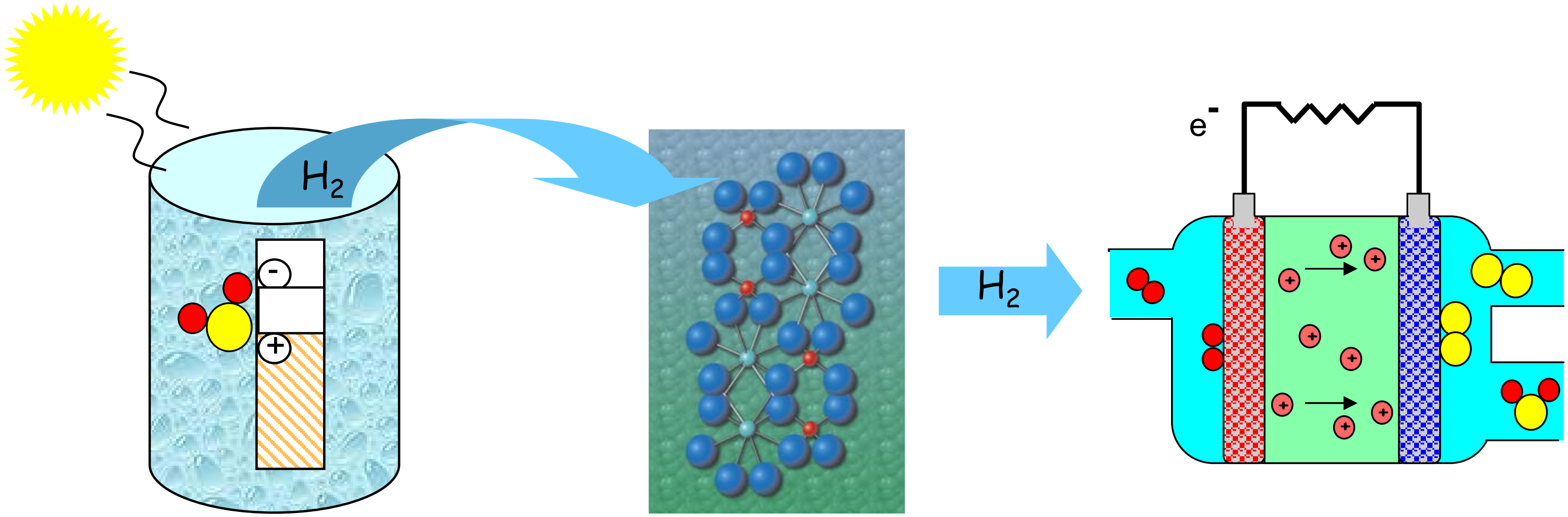
# Summary: Research for Short-term Showstoppers and Long-term Grand Challenges



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.

# Outlook: the Mature Hydrogen Economy



production:
split water renewably

storage:
solid state materials

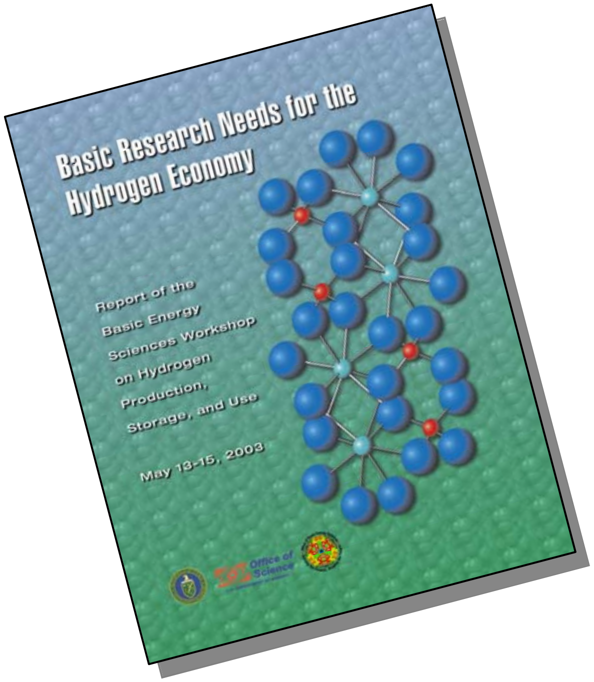
use:
fuel cells

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 ⇒ 150M tons (vehicles)
  - storage: 4.4 MJ/L (10K psi gas) ⇒ 9.7 MJ/L
  - fuel cells: \$200-3000/kW ⇒ \$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



Basic Research Needs for the Hydrogen Economy

Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use

May 13-15, 2003

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