Basic Research Needs for the Hydrogen Economy

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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

Population (millions)

- Oceania
- N. America
- S. America
- Europe
- Asia
- Africa

Population over time:
- 1750: 1.0 Billion
- 1800: 1.5 Billion
- 1850: 2.0 Billion
- 1900: 3.0 Billion
- 1950: 4.0 Billion
- 2000: 6.5 Billion
- 2050: 8.9 Billion

2005:
- Asia: 6.5 Billion
- Oceania
- N. America
- S. America
- Europe
- Africa

2050:
- Asia: 8.9 Billion
- Oceania
- N. America
- S. America
- Europe
- Africa
Growing world energy needs


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

40% of the world’s population is in the fast developing regions that have the fastest energy consumption increase.
The Energy Availability Challenge

New oil and gas reserves are not being discovered nearly as fast as they are being depleted.
The Energy Source Challenge

TODAY

14 Terawatts (world)

2003

Source: International Energy Agency

2050

30 – 60 Terawatts (world)

- 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

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
“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

Hydrogen: A National Initiative
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 $\text{H}_2$ to substrate and rapid $\text{H}_2$ 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

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 photoluminescence 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.


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))
... but electricity was not discovered via incremental improvements to the candle
Outline

• Overview of the global energy challenge
• Overview of nanostructured materials
• Overview of the hydrogen initiative/ the role that nanoscience and nanotechnology might play
The Hydrogen Economy – The Technology Gaps

Production
- 9M tons/yr
- 150M tons/yr (Light Cars and Trucks in 2040)

Storage
- 4.4 MJ/L (Gas, 10,000 psi)
- 8.4 MJ/L (LH2)

Use (in fuel cells)
- $200-3000/kW
- $30/kW (Internal Combustion Engine)

H₂O, solar, wind, hydro, nuclear/solar thermochemical cycles, fossil fuel reforming, Bio- and bioinspired, gas or hydride storage, H₂, automotive fuel cells, consumer electronics, stationary electricity/heat generation.
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

- Single Band-Gap “Ultimate” Conversion Efficiency of Solar Cells:
  Potential increase up to ~70%!

PbSe Nanocrystals

QE = 660%
Produced by Impact Ionization

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.

Gravimetric Energy Density
MJ/kg system

Volumetric Energy Density
MJ/L system

Energy Density of Fuels

gasoline

liquid H₂

compressed gas H₂

proposed DOE goal

chemical hydrides

complex hydrides

Gravimetric Energy Density
MJ/kg system
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

<table>
<thead>
<tr>
<th>Targeted Factor</th>
<th>2005</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific energy (MJ/kg)</td>
<td>5.4</td>
<td>7.2</td>
<td>10.8</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>4.5</td>
<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Energy density (MJ/L)</td>
<td>4.3</td>
<td>5.4</td>
<td>9.72</td>
</tr>
<tr>
<td>System cost ($/kg/system)</td>
<td>9</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Operating temperature (°C)</td>
<td>-20/50</td>
<td>-20/50</td>
<td>-20/50</td>
</tr>
<tr>
<td>Cycle life-time (absorption/desorption cycles)</td>
<td>500</td>
<td>1,000</td>
<td>1,500</td>
</tr>
<tr>
<td>Flow rate (g/s)</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Delivery pressure (bar)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Transient response (s)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Refueling rate (kg H₂/min)</td>
<td>0.5</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Source: Milliken (2003).*
The Hydrogen Bottlenecks

<table>
<thead>
<tr>
<th></th>
<th>DOE goal (2015)</th>
<th>Metal hydride</th>
<th>Chemical hydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage wt. %</td>
<td>9%</td>
<td>✔️</td>
<td>✔️</td>
</tr>
<tr>
<td>Storage vol. %</td>
<td>81 kg/m³</td>
<td>✔️</td>
<td>✔️</td>
</tr>
<tr>
<td>Reversibility (cycle)</td>
<td>1500 cycles</td>
<td>Limited</td>
<td>✗</td>
</tr>
<tr>
<td>System storage cost</td>
<td>$2/kWh</td>
<td>$50/kWh</td>
<td>$18/kWh</td>
</tr>
<tr>
<td>Fueling time (reaction kinetics)</td>
<td>30 s/kg-H₂</td>
<td>✗ (too slow)</td>
<td>✗</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>-40 - 60 °C</td>
<td>✗ (too high)</td>
<td>✔️</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>&lt;100 atm.</td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>

JoAnn Milliken (2002)
Hydrogen Storage in Condensed States

Physisorption
Adsorption on Surface

Chemisorption
Absorption into Matter
Potential energy for molecular and atomic hydrogen absorption

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

Chemisorption
High temperature
Atomic H

Physisorption
Low temperature
Molecular H₂

Hydrogen Storage Options

**Chemical hydrides:**
- Slow kinetics
- Heat management issues
- High release temperature

**Metal/complex 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$_3$BH$_3$
Metal ammine complexes

- Mg(NH$_3$)$_6$Cl$_2$ = 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
  \[ 2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2 \] @ ~600K
- Technology being developed for battery applications

<table>
<thead>
<tr>
<th>Complex</th>
<th>Gravimetric H$_2$ density (%)</th>
<th>Volumetric H$_2$ density/(kg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NH$_3$)$_6$Cl$_2$</td>
<td>9.1</td>
<td>110</td>
</tr>
<tr>
<td>Ca(NH$_3$)$_6$Cl$_2$</td>
<td>9.7</td>
<td>120</td>
</tr>
</tbody>
</table>

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

\[ (\text{NH}_2\text{BH}_2)_n + \text{H}_2 \rightarrow \text{NH}_3\text{BH}_3 \]

solid: di-hydrogen bonds

\[ \Delta E \approx +8.8 \text{ kcal/mole} \]
\[ \approx 120^\circ \text{C} \]

\[ (\text{NHBH})_n + \text{H}_2 \]

solid

\[ \Delta E \approx -3.2 \text{ kcal/mole} \]
\[ \approx 120^\circ \text{C} \]

>12% mass released as H₂

simulation: ~ thermo-neutral

nano-phase trapping

\[ \text{NH}_3\text{BH}_3 \text{ in mesoporous silica} \]

SBA-15

release rate increased 1-2 orders of magnitude

undesirable borazine eliminated

issues:

nanophase mechanism
reversibility

Imide (NH) and Amide (NH$_2$)

First step: $\text{LiNH}_2 + \text{LiH} \rightleftharpoons \text{Li}_2\text{NH} + \text{H}_2$ (6.55% @ 300C, 1atm.)

Second: $\text{Li}_2\text{NH} + \text{LiH} \rightleftharpoons \text{Li}_3\text{N} + \text{H}_2$ (5% @ 300C, 0.05atm)

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

Partial Mg substitution reduces release temperature

$\text{Li}_{1-x}\text{Mg}_x\text{NH}_2$

Potential energy for molecular and atomic hydrogen absorption

Activated reaction increases release temperature if no catalysts are used

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

Physisorption
Low temperature
Molecular H₂

Chemisorption
High temperature
Atomic H

Bond strength [kJ/mol]

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
  \[ dG = VdP \]

  \[ G^{H_2} = G^{H_2}_o + RT \ln\left(\frac{P^{H_2}}{P_o}\right) \]

- Where \( P_o = 1 \text{ atm} \) is the pressure at which the standard free energy \( G_o \) is measured.

- For a hydriding reaction we get

  \[ \Delta G^{\text{reaction}} = \Delta G^{\text{reaction}}_o - RT \ln P^{H_2} \]

- In equilibrium the change in free energy is 0

  \[ \Delta G^{\text{reaction}}_o = RT \ln(P^{H_2}_{eq}) \]

  \[ \frac{\Delta H^{\text{reaction}}_o}{RT} - \frac{\Delta S^{\text{reaction}}_o}{R} = \ln P^{H_2}_{eq} \]

- 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.

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

**Van’t Hoff Plot:**

- **In$P_{eq}$** vs **1/T**
- **Decreasing $r$**

**Bulk molar free energy of formation**

\[
\Delta G = \Delta G_o + RT \ln(\frac{a_{MH}}{a_M P_{H_2}})
\]

**Van’t Hoff relation**

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

**Nanoparticle molar free energy of formation**

\[
\Delta G(r) = \Delta G_o(r) + RT \ln(\frac{a_{MH}}{a_M P_{H_2}}) + \frac{3V_M \Delta(\gamma_{Mg}, \gamma_{MgH_2}, r)}{r}
\]

**Nanoscale Van’t Hoff relation**

\[
\ln P_{eq}^{H_2} = \frac{\Delta H_o}{RT} + \frac{3V_M \Delta}{rRT} - \frac{\Delta S_o}{R}
\]
Other Strategies to Lower Release Temperature

Forming new alloys

- Reduce energy (temperature) needed to liberate H₂ 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

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

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

Evolution of a Hydrogen Economy

Energy Payoff

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

- gas/liquid storage
- fossil fuel reforming
- combustion in heat engines

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

- fuel cell operation
- splitting water
- solid state storage

Evolution of a Hydrogen Economy
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