# The Hydrogen Economy

**If the fuel cell is to become the modern steam engine, basic research must provide breakthroughs in understanding, materials, and design to make a hydrogen-based energy system a vibrant and competitive force.**

**George W. Crabtree, Mildred S. Dresselhaus,**
**and Michelle V. Buchanan**

**December 2004 Physics Today**

# Introduction (1/3)

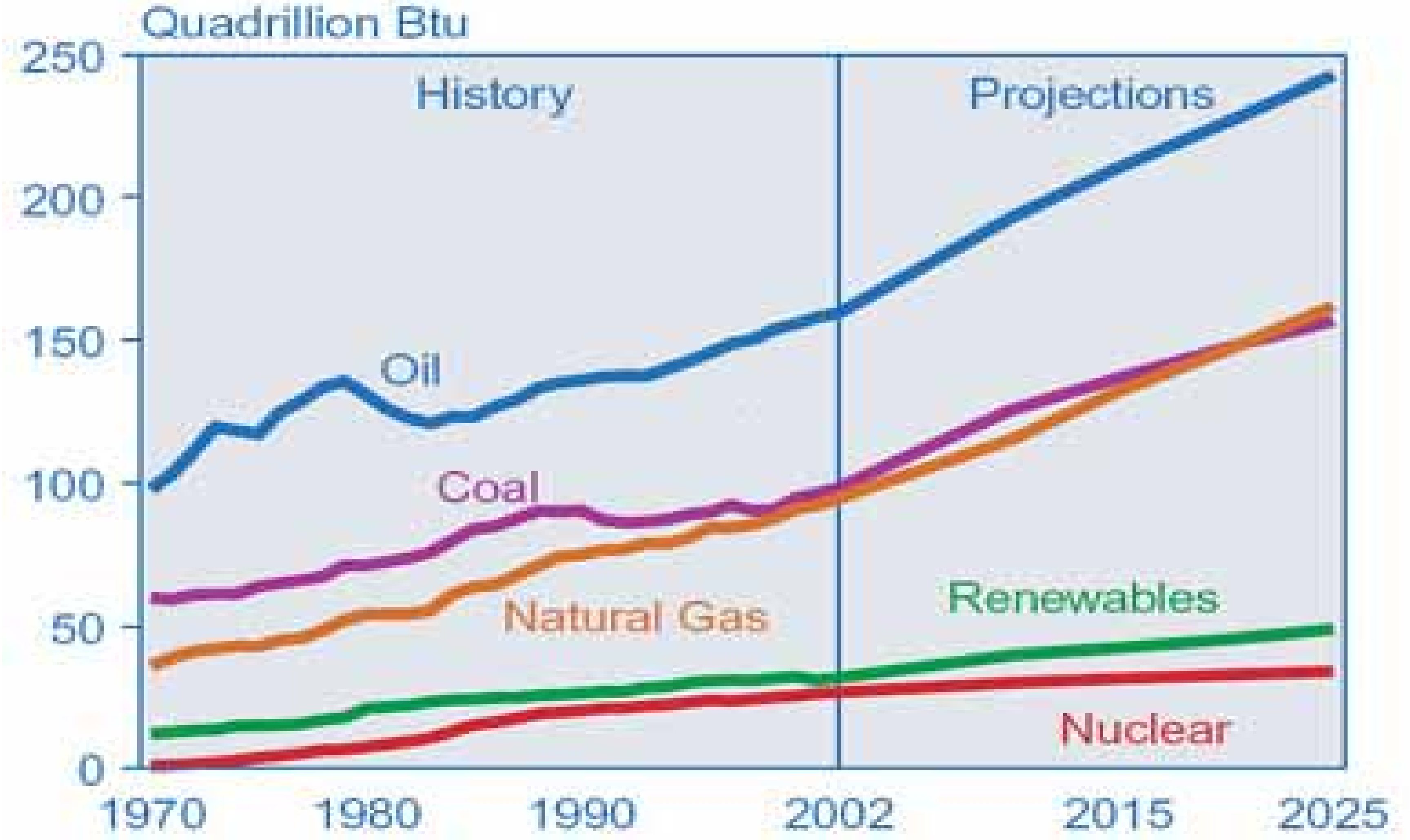
## World Marketed Energy Consumption By Region, 1970-2025

**In contrast to the emerging economies, increases in energy consumption for the mature market economies and transitional economies are projected to be more modest.**

Source: International Energy Outlook 2005, p. 1
http://www.eia.doe.gov/oiaf/ieo/

# Introduction (2/3)

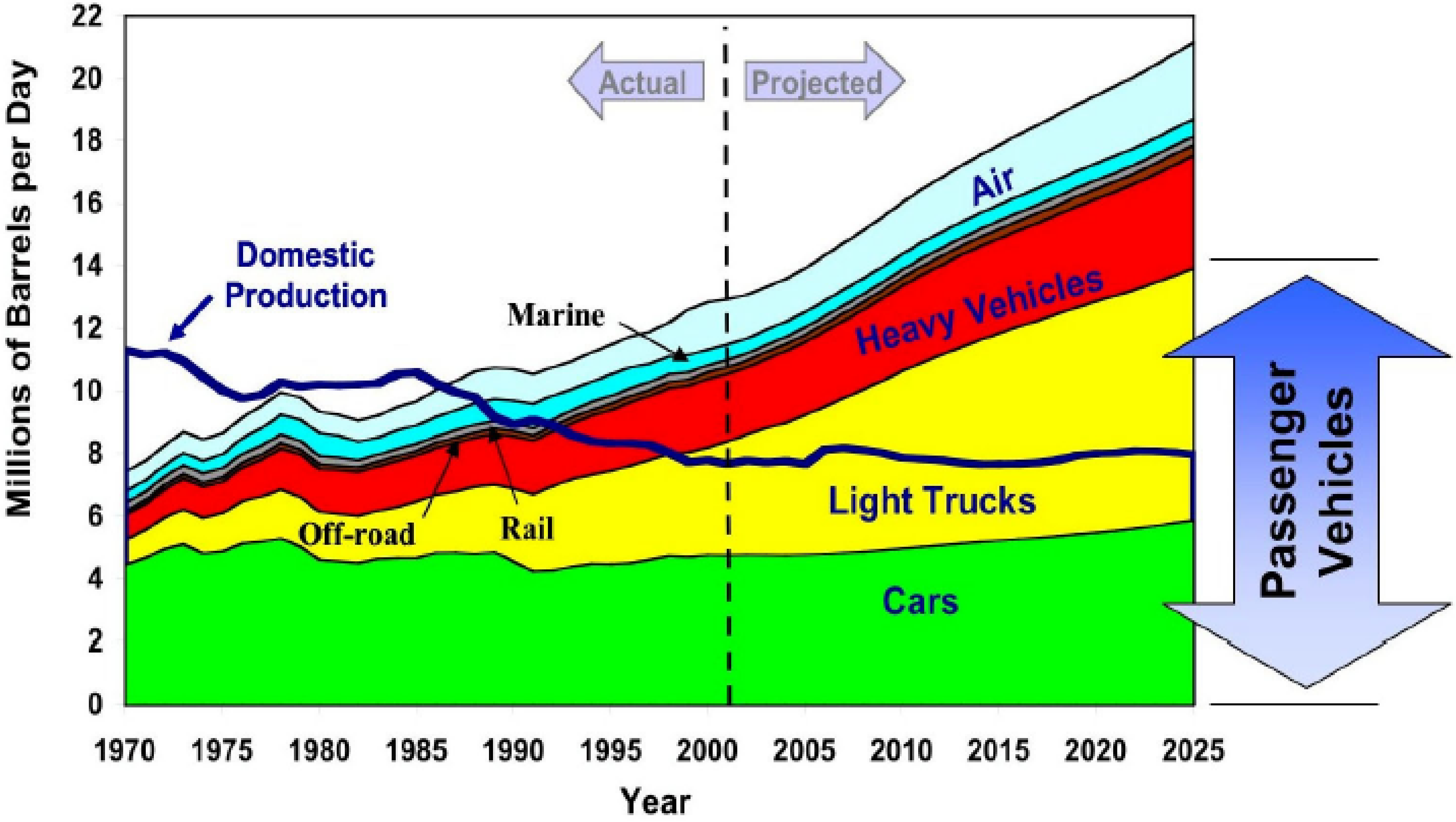
## World Market Energy Use by Energy Type, 1970-2025



Source: International Energy Outlook 2005, p. 3
http://www.eia.doe.gov/oiaf/ieo/

# Introduction (3/3)

**Transportation Petroleum Use by Mode, 1970-2025**

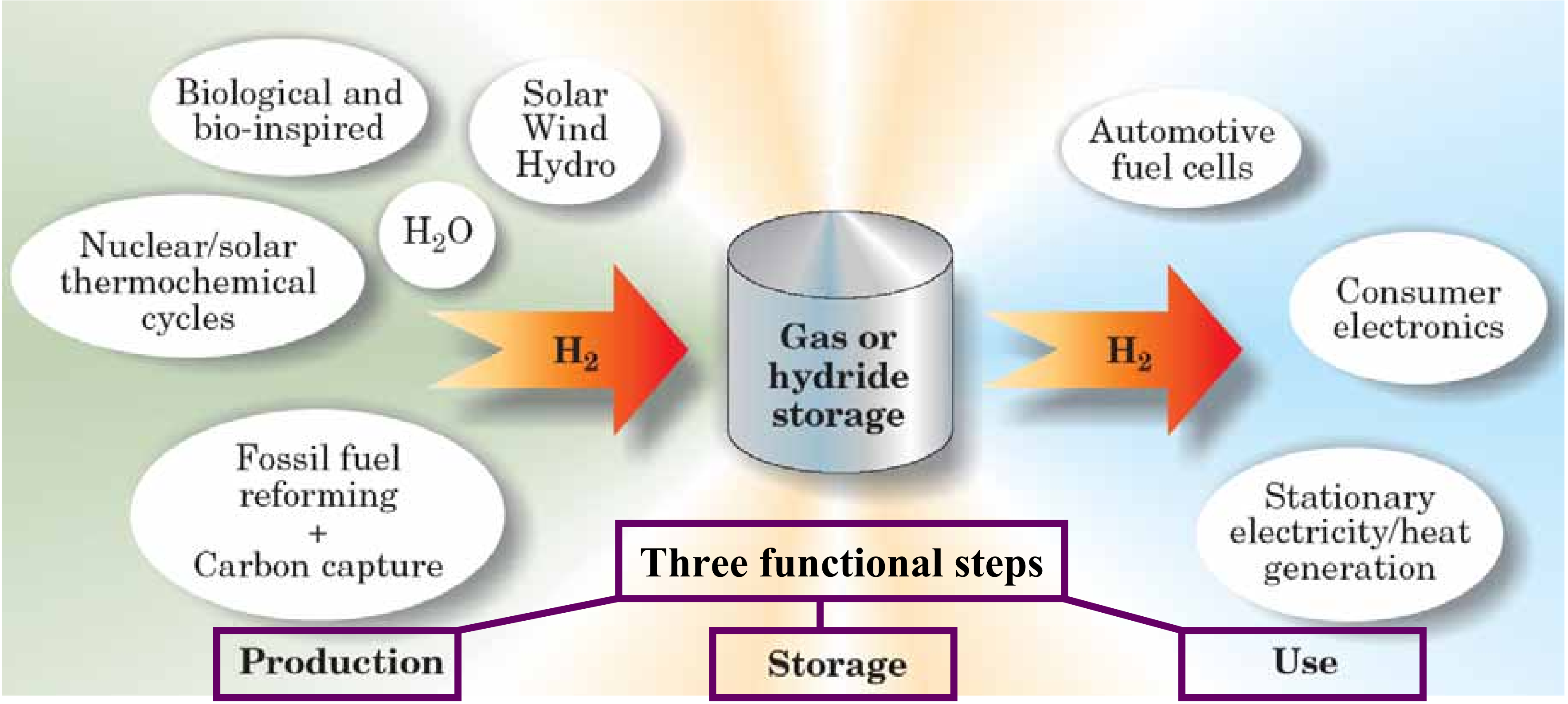


Source: Basic Research Needs for the Hydrogen Economy, p. 10
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Hydrogen as energy carrier

## Why “Hydrogen”?

**Hydrogen is abundant, clean, efficient and generously distributed throughout the world without regard for national boundaries.**

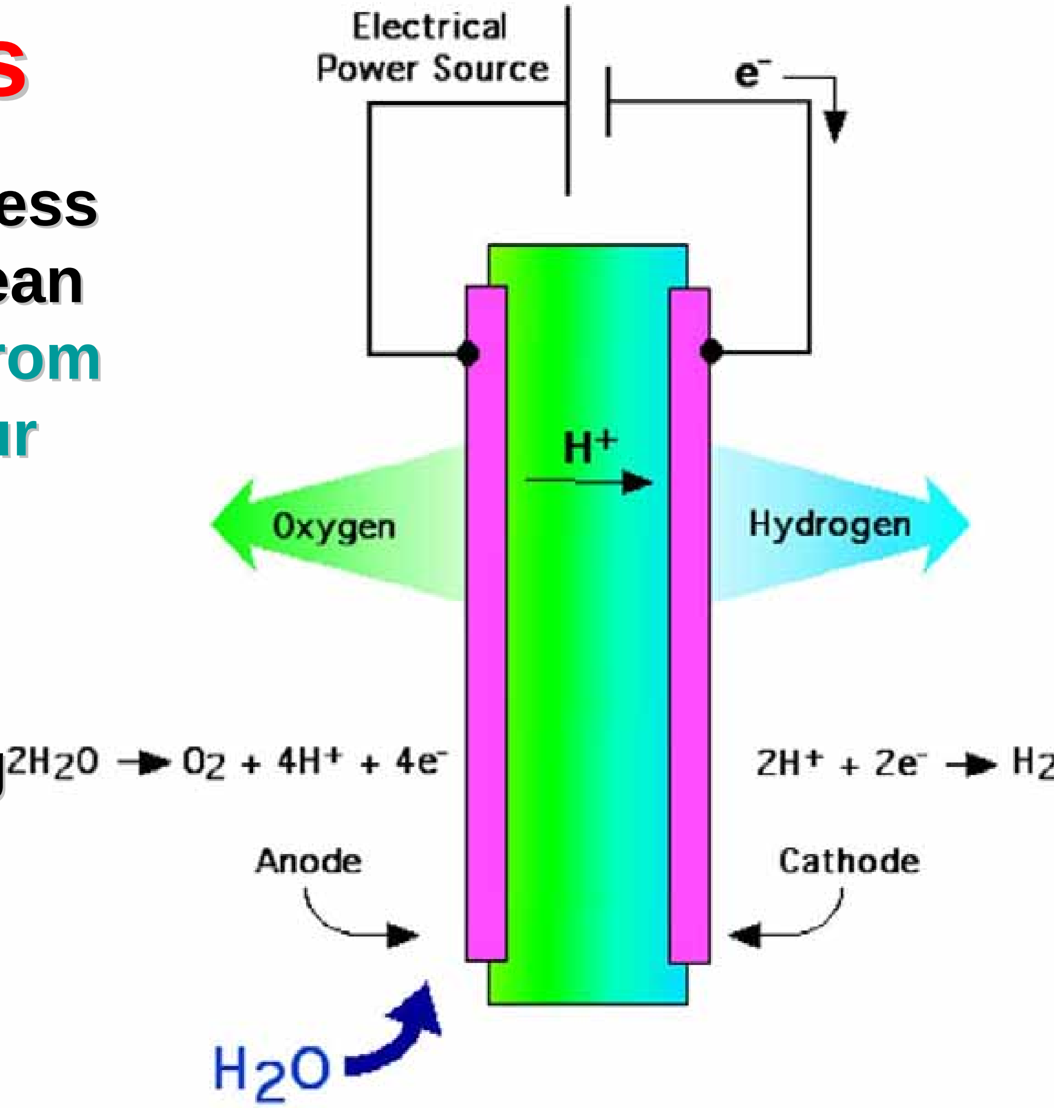


# Beyond reforming (1/4)

## Water electrolysis

**The advantage of this process is that it supplies a very clean hydrogen fuel that is free from carbon（non–fossil）and sulfur impurities.**

**The disadvantage is that the process is expensive, relative to steam reforming of natural gas, because of the cost of the electrical energy needed to drive the process.**



Source: Basic Research Needs for the Hydrogen Economy, p. 12
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Beyond reforming (2/4)

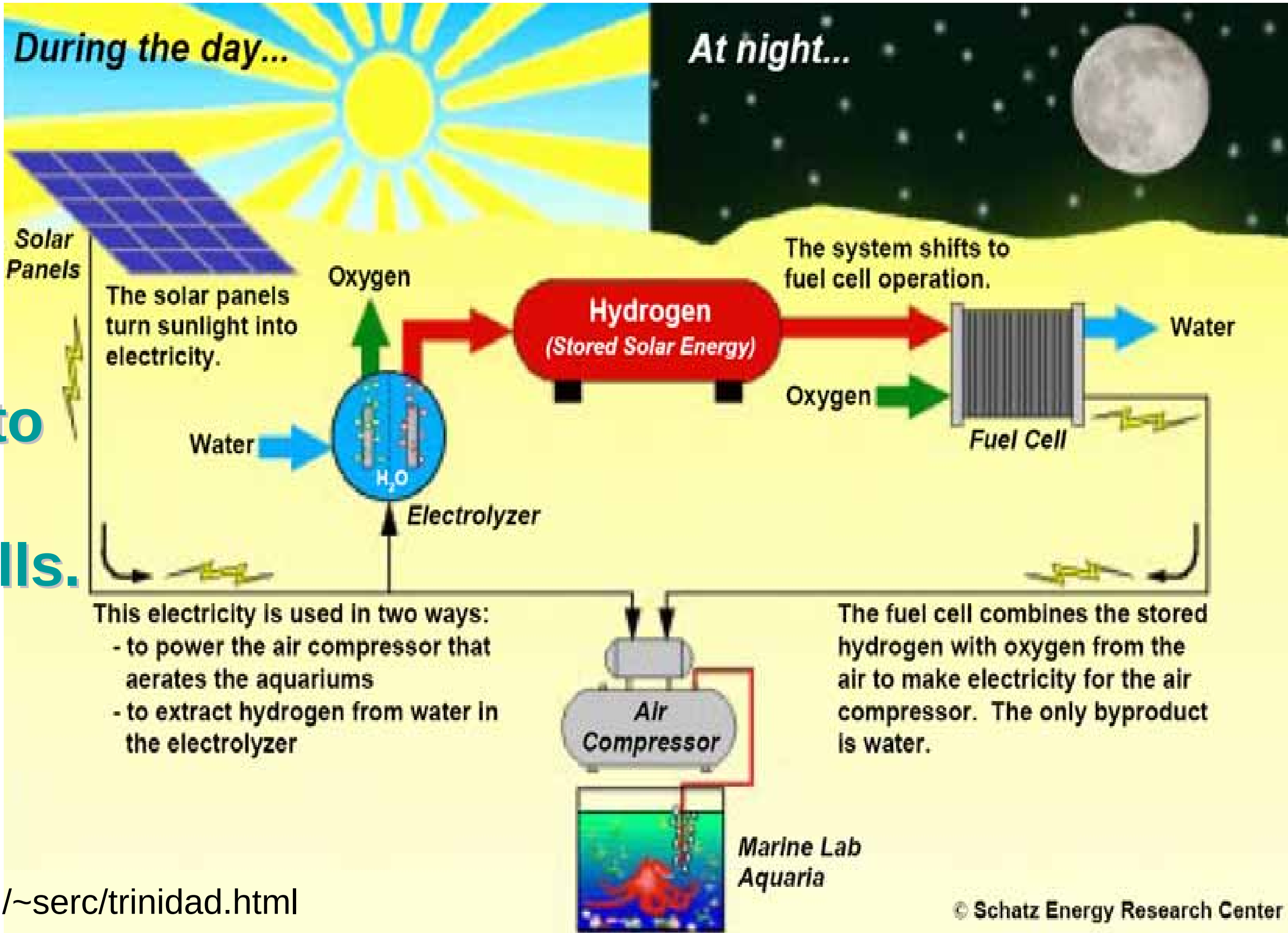
## Solar Hydrogen

**Water and sunlight, both natural and abundant, are used in a cycle to produce power. Hydrogen stores solar energy, so the power is available whenever it is needed.**

**Established technology splits water in 2 steps:**

**I. Conversion of solar radiation to electricity in photovoltaic cells.**

**II. Electrolysis of water in a separate cell.**



The solar panels turn sunlight into electricity.

The system shifts to fuel cell operation.

This electricity is used in two ways:
- to power the air compressor that aerates the aquariums
- to extract hydrogen from water in the electrolyzer

The fuel cell combines the stored hydrogen with oxygen from the air to make electricity for the air compressor. The only byproduct is water.

Source: http://www.humboldt.edu/~serc/trinidad.html

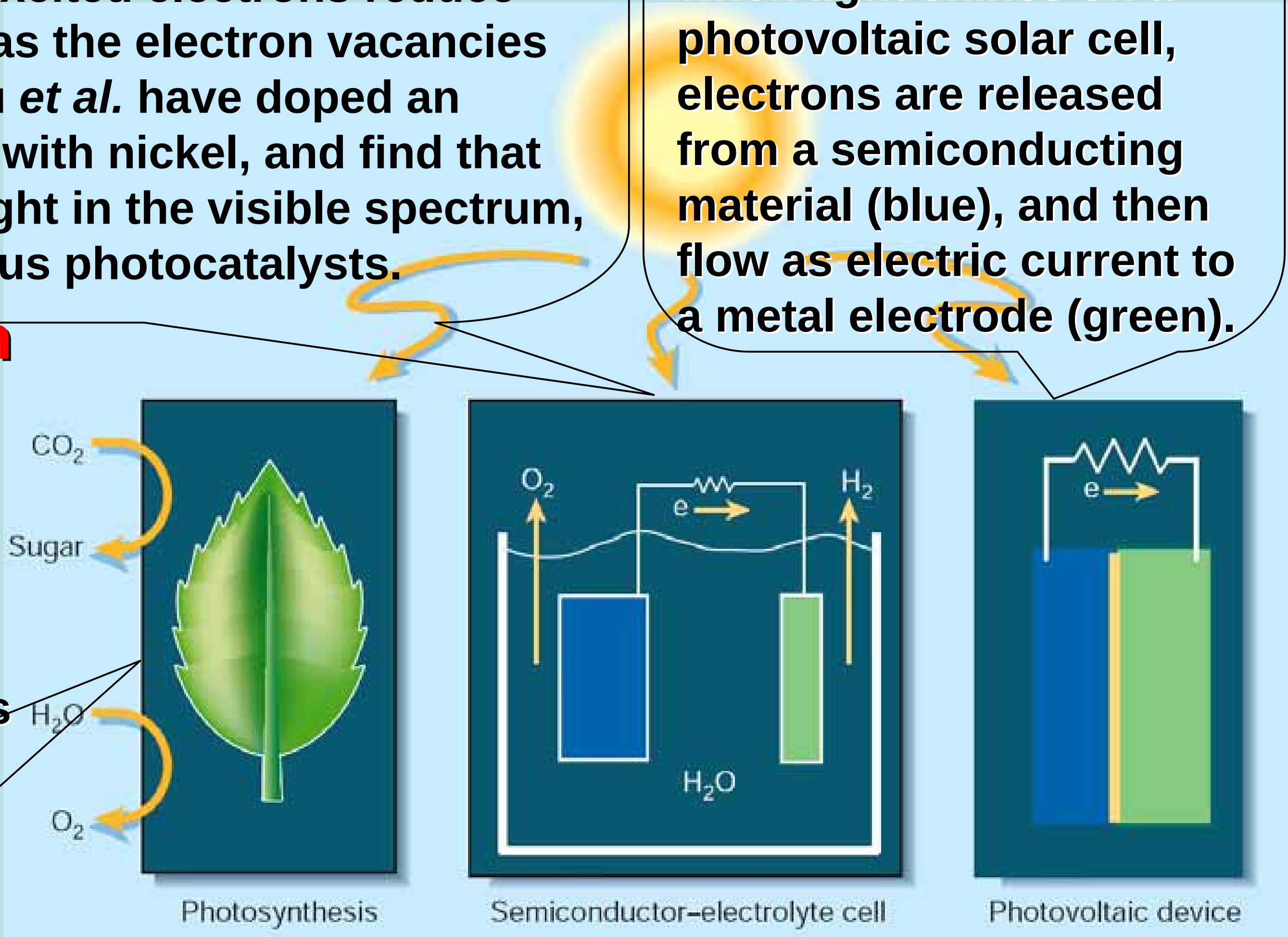
# Beyond reforming (3/4)

**The system used by Zou *et al., which* produces $H_2$ as the potential fuel. The semiconducting material and metal electrode are immersed in water. Under light irradiation, photoexcited electrons reduce water to give $H_2$, whereas the electron vacancies oxidize water to $O_2$. Zou *et al.* have doped an indium–tantalum-oxide with nickel, and find that this material absorbs light in the visible spectrum, an advance over previous photocatalysts.**

**Photovoltaic devices can convert solar energy directly into electricity: when light shines on a photovoltaic solar cell, electrons are released from a semiconducting material (blue), and then flow as electric current to a metal electrode (green).**

**Energy-conversion strategies for creating fuel or electricity from sunlight.**

**In photosynthesis, plants use solar radiation, in conjunction with $CO_2$ and water, to produce sugars (the fuel) and $O_2$.**

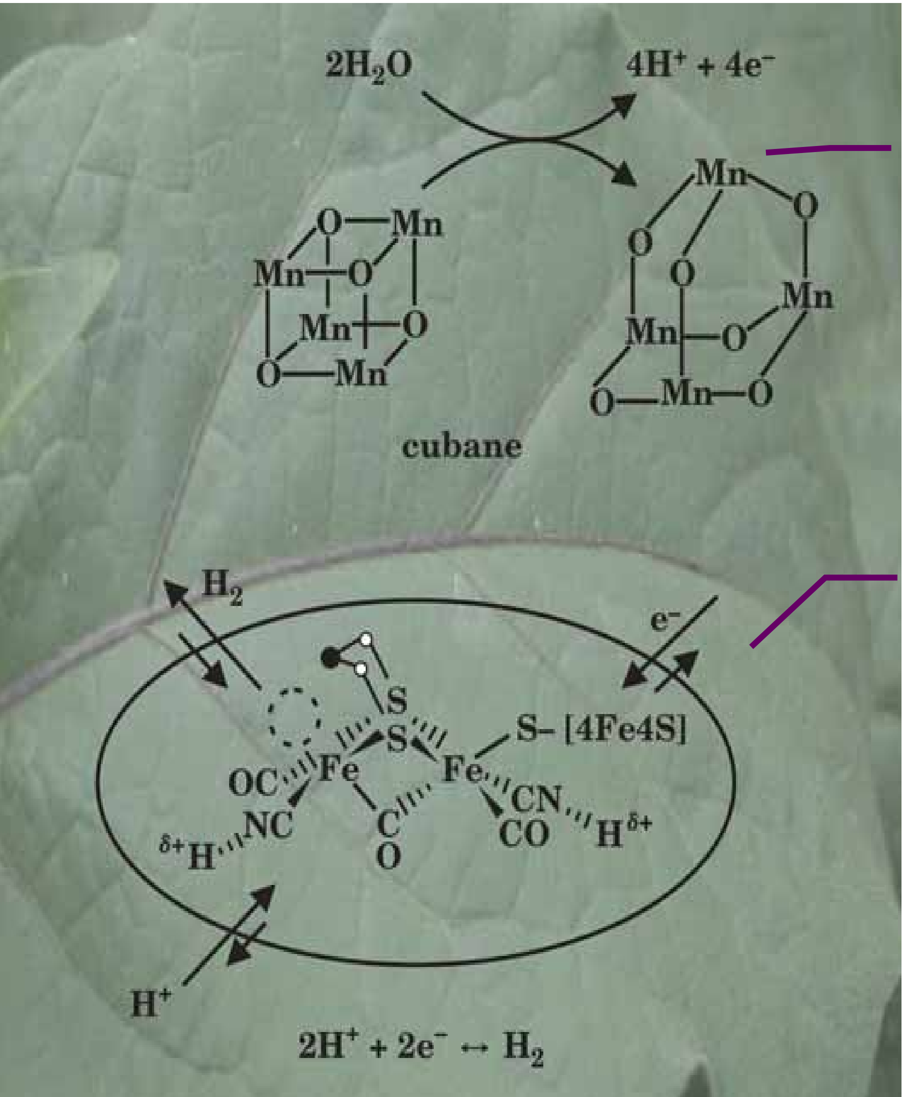


Source: Nature vol. 414,p. 589 (2001)

# Beyond reforming (4/4)

**Nature has developed remarkably simple and efficient methods to split water and transform $H_2$ into its component protons and electrons.**

## Bio-inspired processes

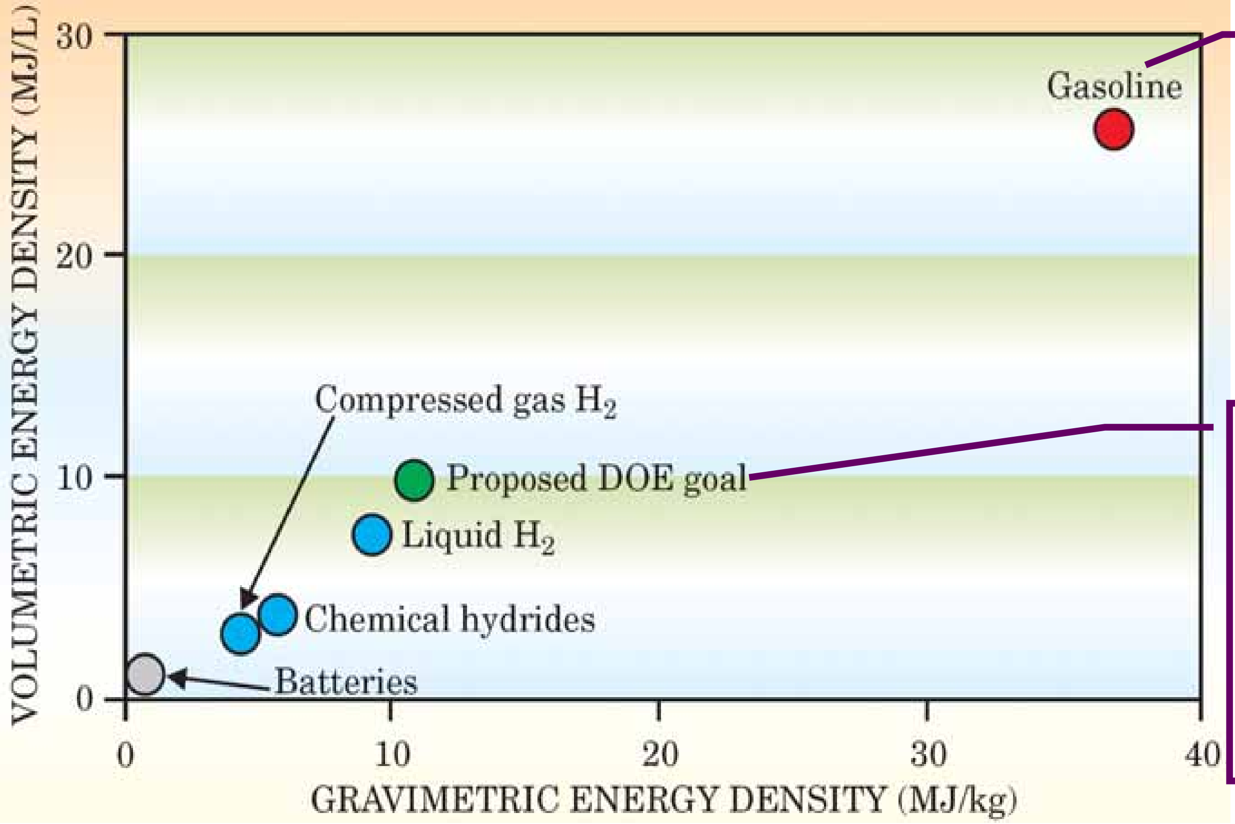


**The basic constituent of the catalyst that splits water during photosynthesis is cubane — clusters of manganese and oxygen. Researchers are only beginning to understand cubane's oxidation states using crystallography and spectroscopy.**

**Bacteria use the iron-based cluster to catalyze the transformation of two protons and two electrons into $H_2$. The roles of this enzyme's complicated structural and electronic forms in the catalytic process can be imitated in the laboratory. The hope is to create synthetic versions of these natural catalysts.**

# Storing hydrogen (1/6)

**The challenge by showing the gravimetric and volumetric energy densities of fuels, including the container and apparatus needed for fuel handling.**

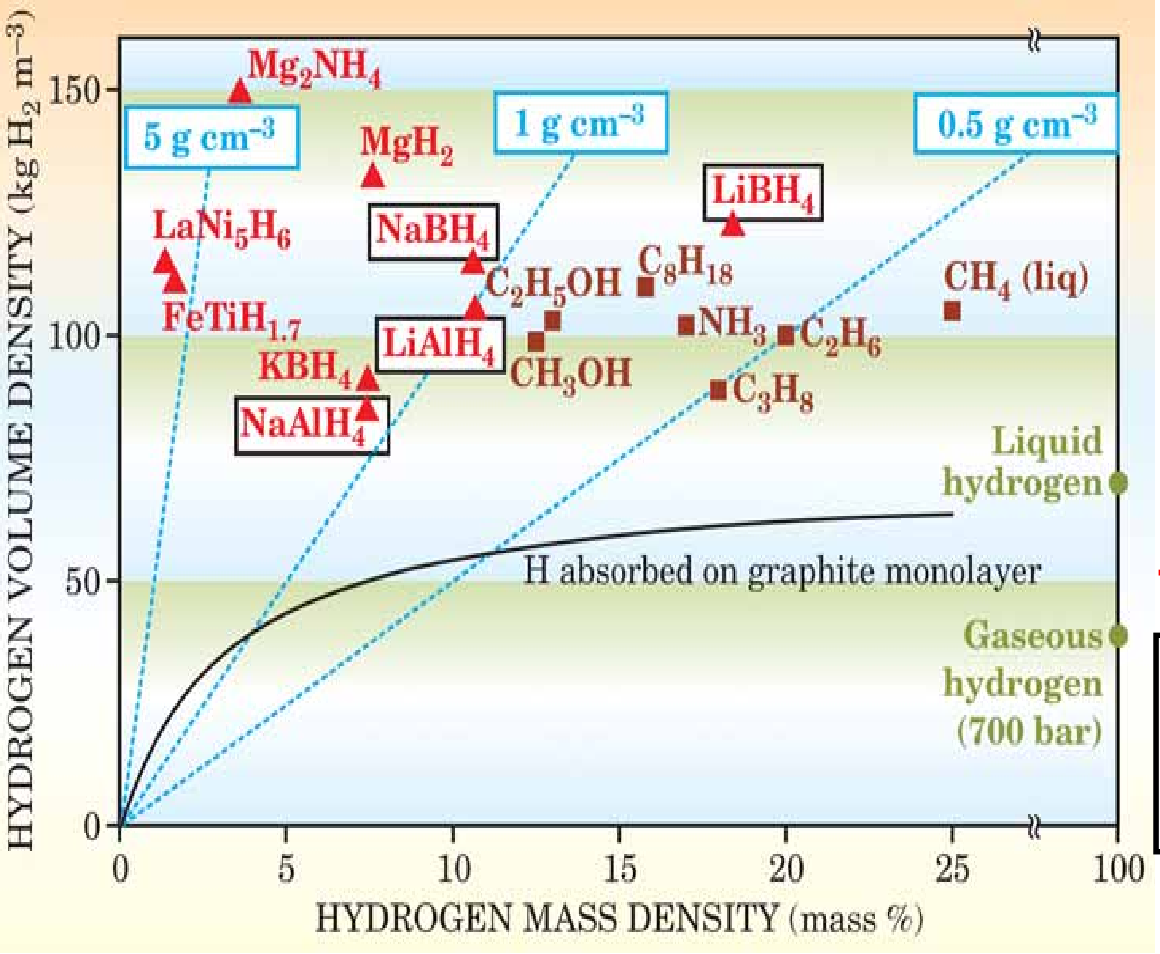


**Gasoline significantly outperforms lithium-ion batteries and hydrogen in gaseous, liquid, or compound forms.**

**The proposed DOE goal refers to the energy density that the US Department of Energy envisions as needed for viable hydrogen-powered transportation in 2015.**

**For on-vehicle use, hydrogen need store only about half of the energy that gasoline provides because the efficiency of fuel cells can be greater by a factor of two or more than that of internal combustion engines.**

# Storing hydrogen (2/6)



**Green data:** liquid and gaseous $H_2$ densities.

**Straight lines:** the total density of the storage medium, including hydrogen and host atoms.

**Rectangles:** organic materials

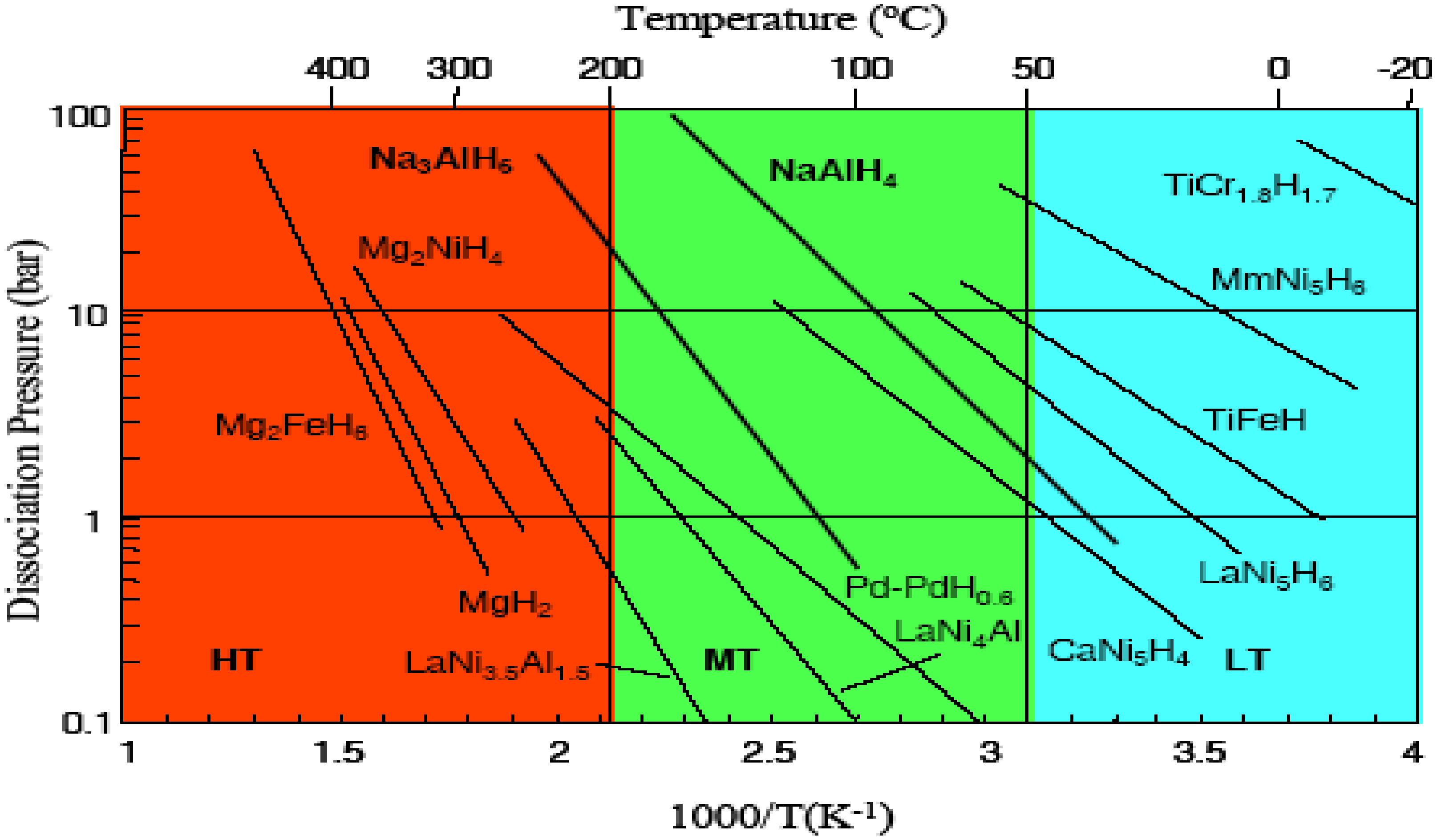
**Triangles:** inorganic materials

**The most promising hydrogen-storage fuel-cell materials.**

- The most effective storage media are in the **upper-right quadrant of the figure**. （**Highest mass fraction and volume density of hydrogen.**）

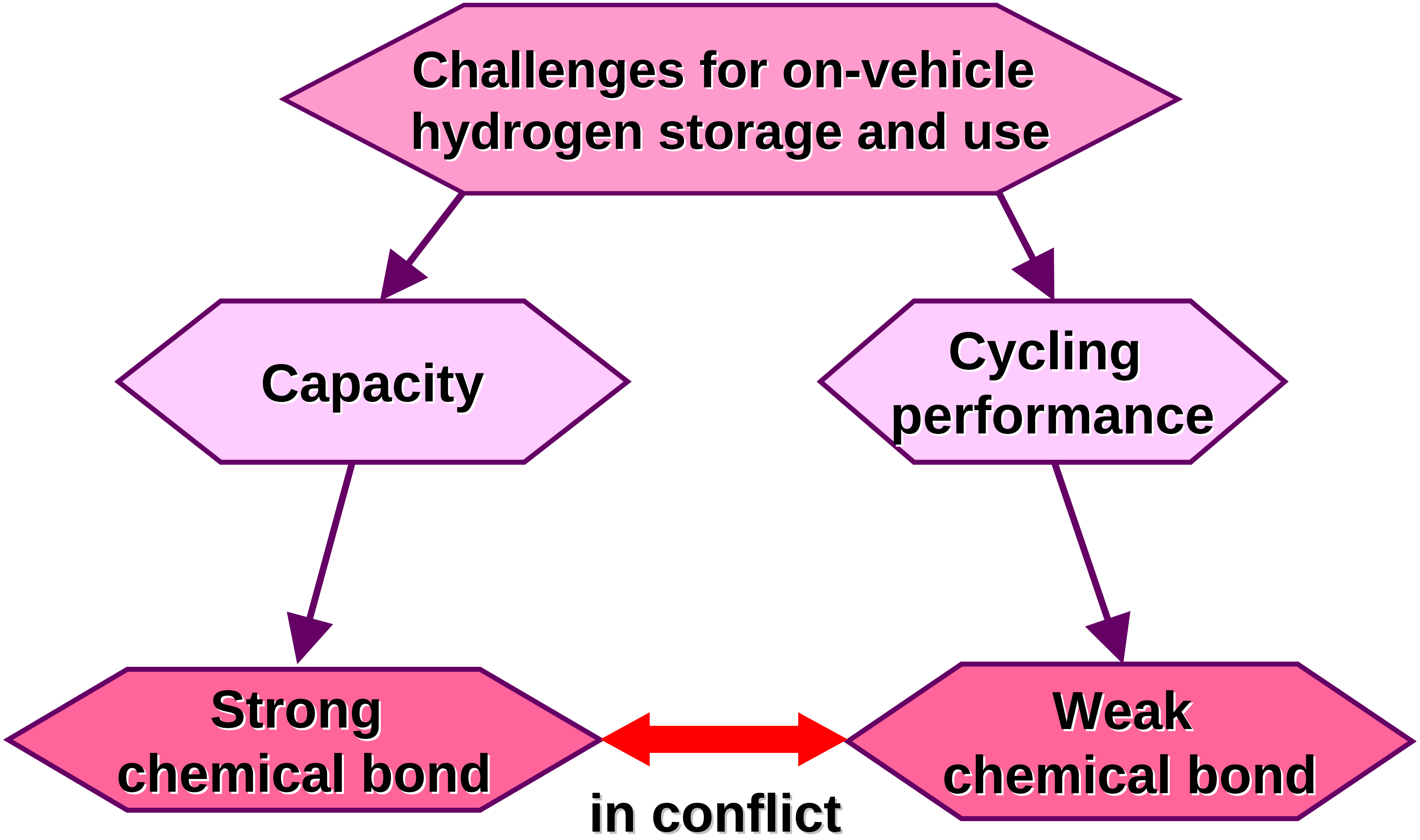
# Storing hydrogen (3/6)

**van’t Hoff Diagram Showing Dissociation Pressures and Temperatures of Various Hydrides**



Source: Basic Research Needs for the Hydrogen Economy, p. 39
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Storing hydrogen (4/6)



Challenges for on-vehicle hydrogen storage and use

Capacity

Cycling performance

Strong chemical bond

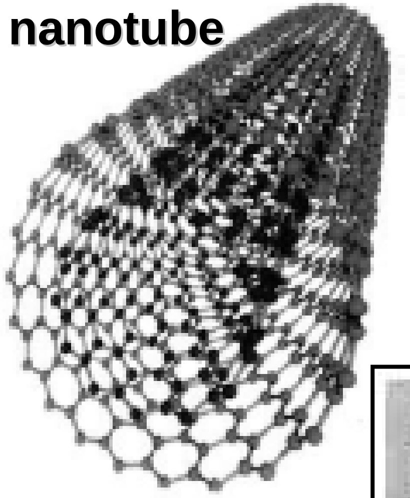
Weak chemical bond

in conflict

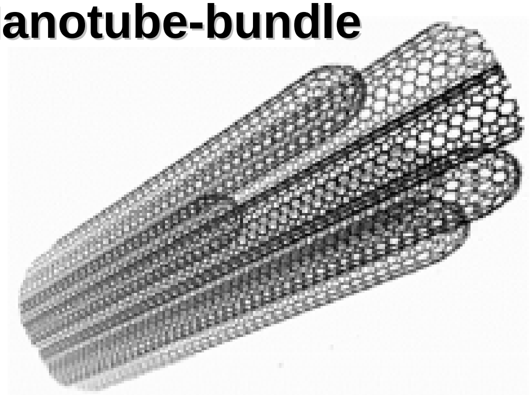
# Storing hydrogen (5/6)

- Currently, there is considerable excitement about a new class of materials with unique properties that stem from their reduced length scale (1<d<100nm).

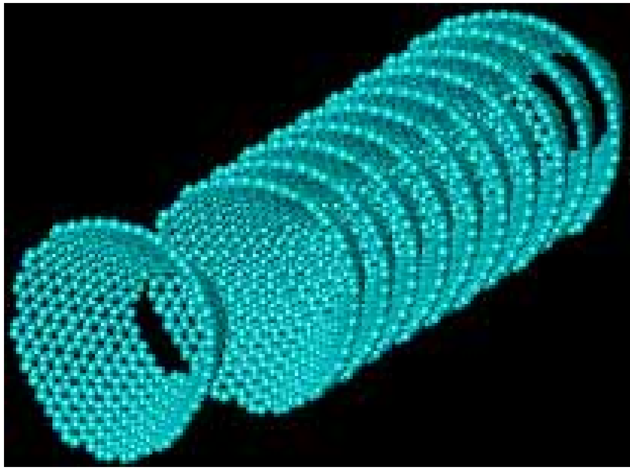
**Double-wall nanotube**



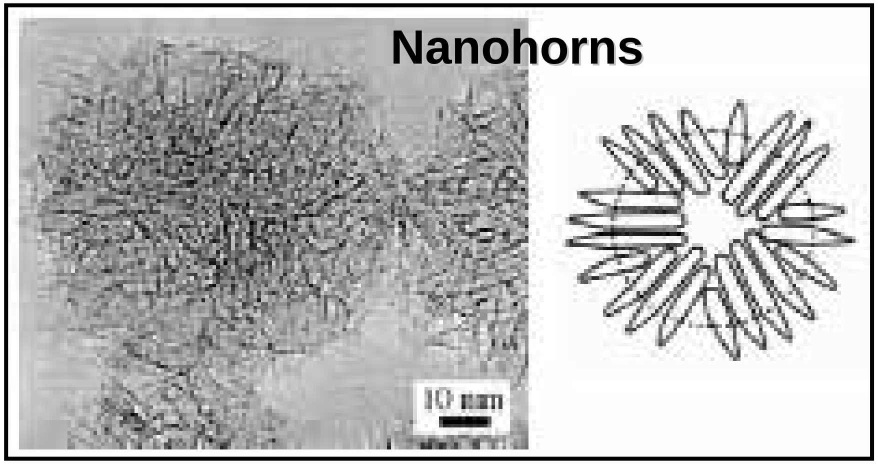
**Nanotube-bundle**



**Cup-stacked Carbon Nanofiber**



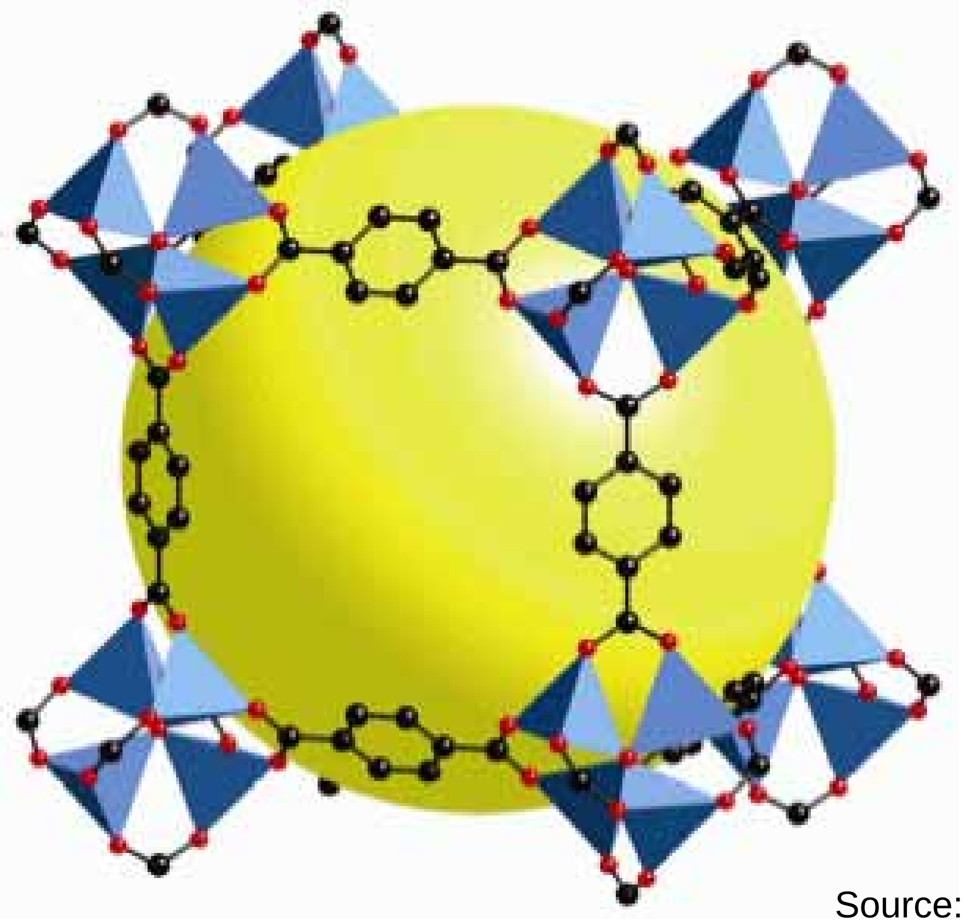
**Nanohorns**



Source: Basic Research Needs for the Hydrogen Economy, p.43
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Storing hydrogen (6/6)

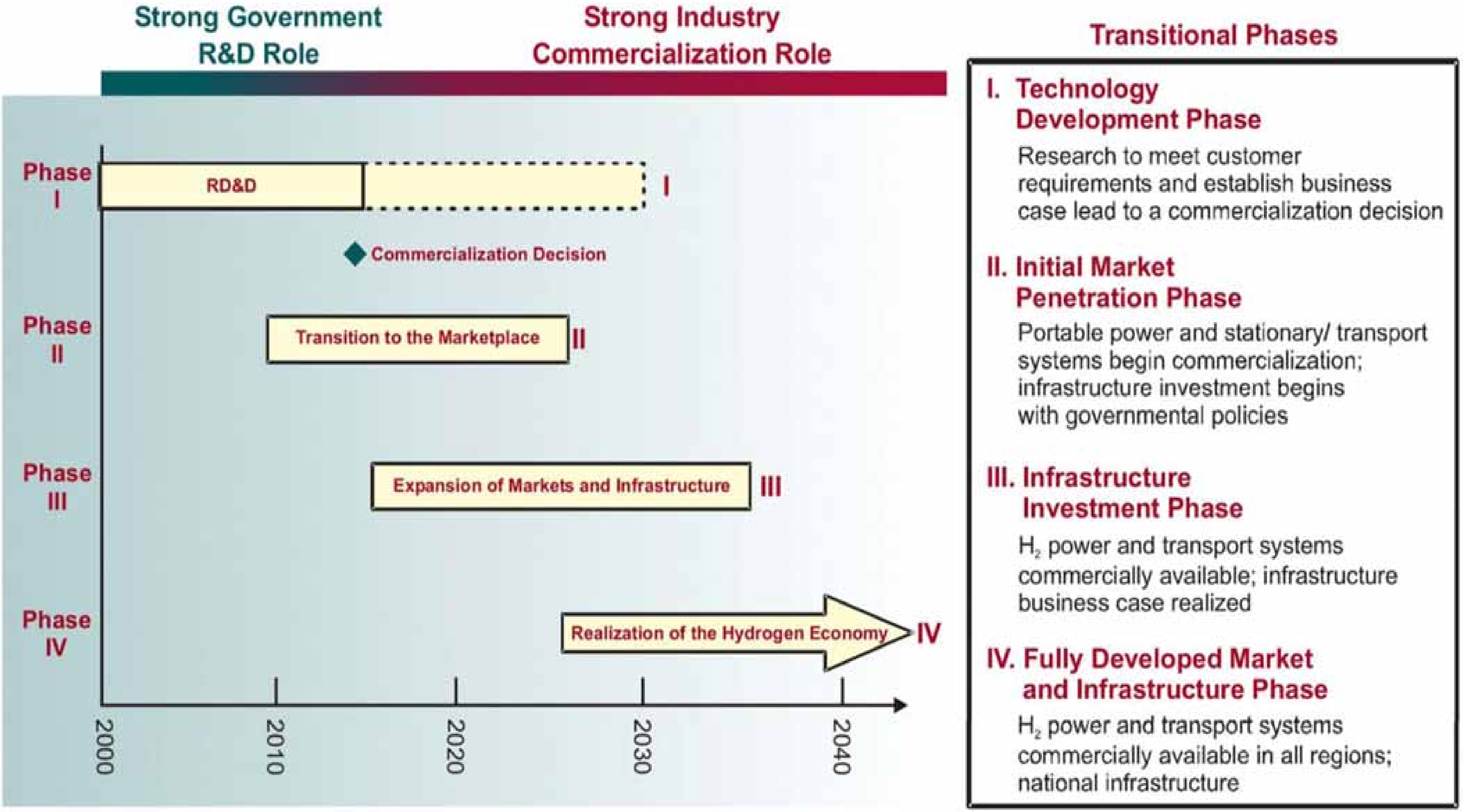
**Another approach is to use 3-D solids with open structures, such as metal–organic frameworks in which hydrogen molecules or atoms can be adsorbed on internal surfaces.**



Schematic of a Single Crystal X-ray Structure for the Metal-organic Framework of Composition $Zn_4O$(1,4-benzene dicarboxylate)$_{3.}$ Showing a Single Cube Fragment of a Cubic 3-D Extended Porous Structure (This metal-organic compound adsorbed up to 4.5 wt% hydrogen at 78 K and 1 wt% at ambient temperature and 20 bar. Variants of this structure show promise for even better performances regarding hydrogen storage.)

Source: Basic Research Needs for the Hydrogen Economy, p.45
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Realizing the promise (1/6)



**Transitional Phases**

**I. Technology Development Phase**

Research to meet customer requirements and establish business case lead to a commercialization decision

**II. Initial Market Penetration Phase**

Portable power and stationary/ transport systems begin commercialization; infrastructure investment begins with governmental policies

**III. Infrastructure Investment Phase**

$H_2$ power and transport systems commercially available; infrastructure business case realized

**IV. Fully Developed Market and Infrastructure Phase**

$H_2$ power and transport systems commercially available in all regions; national infrastructure

**Economy Positive commercialization decision in 2015 leads to beginning of mass-produced hydrogen fuel cell cars by 2020.**

Source: http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/mfg_wkshp_plenary.pdf

# Realizing the promise (2/6)

**Hydrogen Powered Cars & Trucks**

**Hydrogen Powered Airplanes**

**Hydrogen Powered Rockets**

# Realizing the promise (3/6)

- Electronics applications may be the first to widely reach the consumer market, establish public visibility, and advance the learning curve for hydrogen technology.

**Casio**

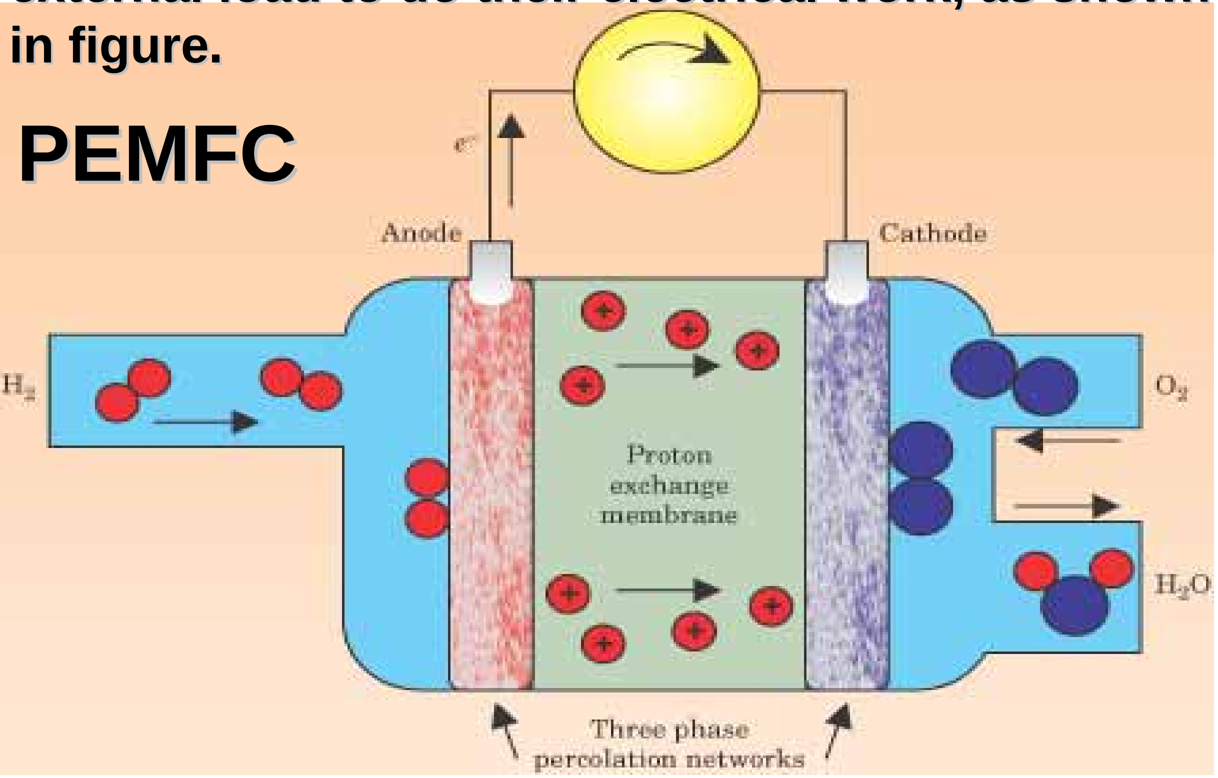
**NTT Prototypes**
**$H_2$-fuelled**
**Compact PEFC**

**Jadoo Power Systems**

# Realizing the promise (4/6)

**The heart of the fuel cell is the ionic conducting membrane that transmits protons or oxygen ions between electrodes while electrons go through an external load to do their electrical work, as shown in figure.**

**PEMFC**



$$2H_2 + O_2 \rightarrow 2H_2O + \text{electrical power} + \text{heat}$$

**Each of the half reactions at work in that circuit requires catalysts interacting with electrons, ions, and gases traveling in different media.**

**Designing nanoscale architectures for these triple percolation networks that effectively coordinate the Interaction of reactants with nanostructured catalysts is a major opportunity for improving fuel-cell performance.**

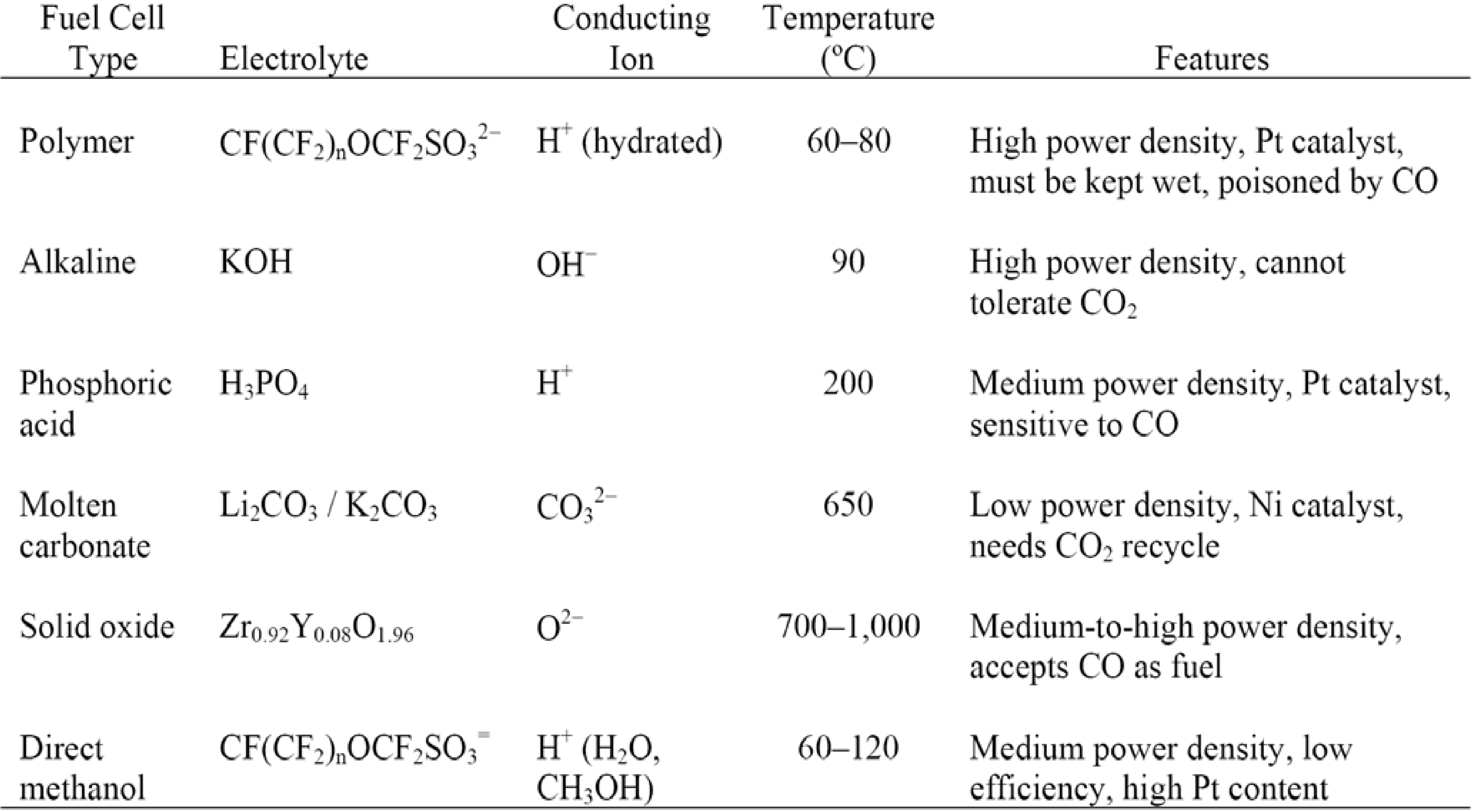
**1.5 mm thick**

**Caltech solid-acid fuel cell**

http://www.physicstoday.org/pt/vol-54/iss-7/p22.html

# Realizing the promise (5/6)

## Fuel Cell Types and Their Operating Features



| Fuel Cell Type | Electrolyte | Conducting Ion | Temperature (°C) | Features |
|---|---|---|---|---|
| Polymer | $CF(CF_2)_nOCF_2SO_3^{2-}$ | $H^+$ (hydrated) | 60–80 | High power density, Pt catalyst, must be kept wet, poisoned by CO |
| Alkaline | KOH | $OH^-$ | 90 | High power density, cannot tolerate $CO_2$ |
| Phosphoric acid | $H_3PO_4$ | $H^+$ | 200 | Medium power density, Pt catalyst, sensitive to CO |
| Molten carbonate | $Li_2CO_3$ / $K_2CO_3$ | $CO_3^{2-}$ | 650 | Low power density, Ni catalyst, needs $CO_2$ recycle |
| Solid oxide | $Zr_{0.92}Y_{0.08}O_{1.96}$ | $O^{2-}$ | 700–1,000 | Medium-to-high power density, accepts CO as fuel |
| Direct methanol | $CF(CF_2)_nOCF_2SO_3^-$ | $H^+$ ($H_2O$, $CH_3OH$) | 60–120 | Medium power density, low efficiency, high Pt content |

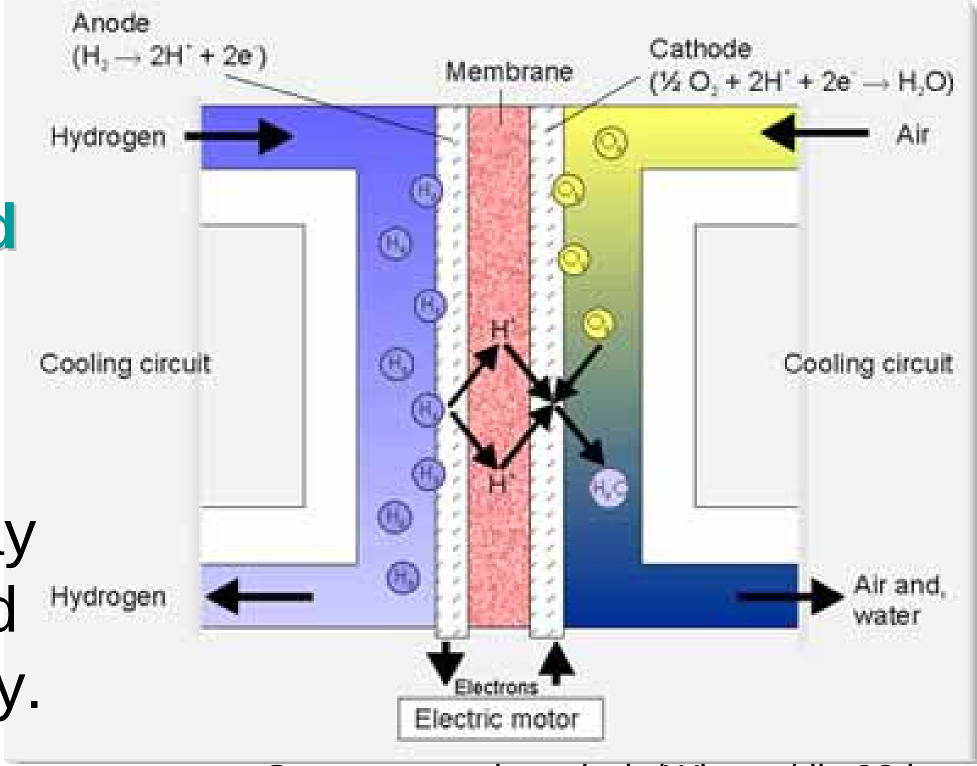
Source: Basic Research Needs for the Hydrogen Economy, p.54
http://www.sc.doe.gov/bes/reports/abstracts.html#NHE

# Realizing the promise (6/6)

Primary limits for PEMFC performance: **the slow kinetics of the oxygen reduction reaction at the cathode.**

The causes of the slow kinetics, and solutions for speeding up the reaction, are hidden in the complex reaction pathways and intermediate steps of the oxygen reduction reaction.

It is now becoming possible to understand this reaction at the atomic level using **sophisticated surface-structure and spectroscopy tools** such as vibrational spectroscopies, scanning probe microscopy, x-ray diffraction and spectroscopy, and transmission electron microscopy.



Source: www.hyweb.de/Wissen/dkv98.htm

# Outlook (1/5)

## Hydrogen Infrastructure

Widespread commercialization of hydrogen fuel cell vehicles will require development of an accompanying hydrogen infrastructure. The infrastructure will require changes that address all transport and safety concerns.

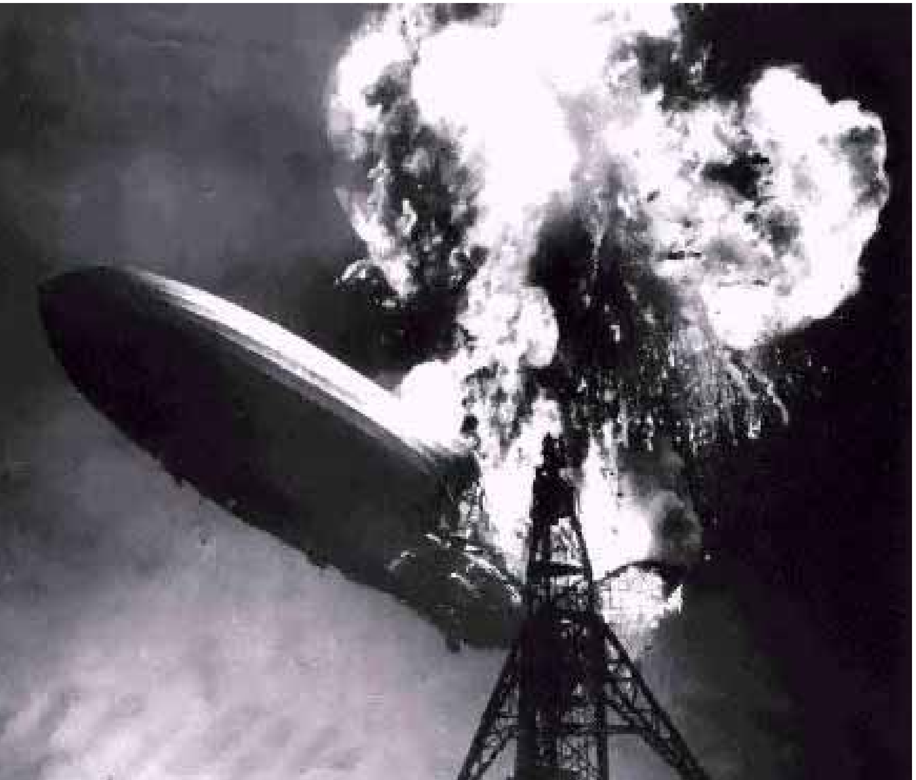
Several steps, ranging from R&D through creating design and performance standards, are necessary to achieve insurable commercial systems. R&D is the most important element of the safety pyramid because it provides the critical data needed to create performance standards.

Source: www.climatetechnology.gov

# Outlook (2/5)

## **Hydrogen Disaster-** **Lakehurst . May 6, 1937.**

The bags of hydrogen that provided the lifting force for the Hindenburg were NOT the main contributor to the fire. The surface of the ship was coated with a combination of dark iron oxide and reflective aluminum paint. These components are extremely flammable and burn at a tremendously energetic rate once ignited. The skin of the airship was ignited by electrical discharge from the clouds while docking during an electrical storm.

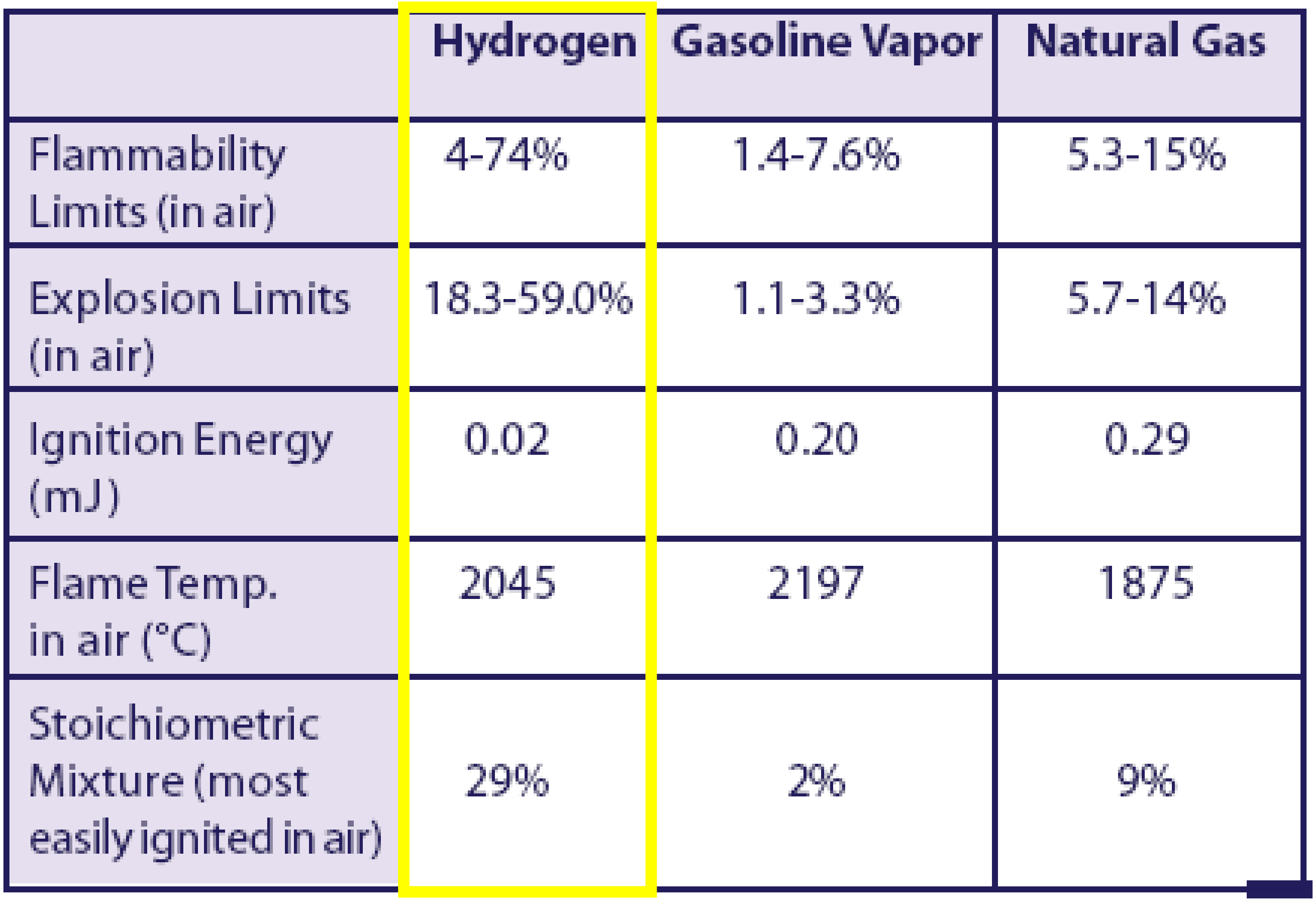


The Hindenburg would have burned if it had been filled with inert helium gas. Even if the Hindenburg had not been lifted by hydrogen, the ignition of the covering would still have happened, and would then have set ablaze the diesel stores, resulting in the same disaster.

Source: www.hydrogennow.org

# Outlook (3/5)

## Fuel Comparisons



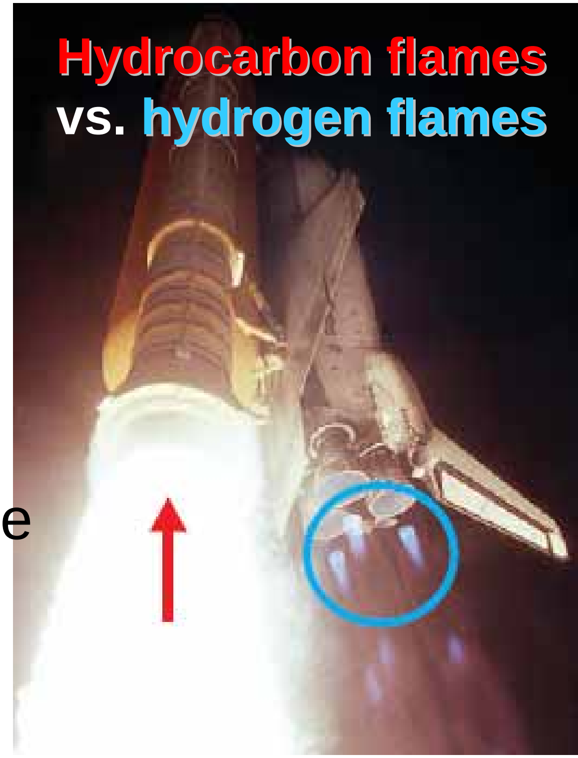
| | Hydrogen | Gasoline Vapor | Natural Gas |
|---|---|---|---|
| Flammability Limits (in air) | 4-74% | 1.4-7.6% | 5.3-15% |
| Explosion Limits (in air) | 18.3-59.0% | 1.1-3.3% | 5.7-14% |
| Ignition Energy (mJ) | 0.02 | 0.20 | 0.29 |
| Flame Temp. in air (°C) | 2045 | 2197 | 1875 |
| Stoichiometric Mixture (most easily ignited in air) | 29% | 2% | 9% |

Source: http://www.hydrogenus.com

# Outlook (4/5)

**Some of the most notable differences between gaseous hydrogen and other common fuels:**

- Hydrogen is lighter than air and diffuses rapidly.
- Hydrogen is odorless, colorless and tasteless.
- Hydrogen flames have low radiant heat. (Right)



## Combustion

Like any flammable fuel, hydrogen can combust. But hydrogen's buoyancy, diffusivity and small molecular size make it difficult to contain and create a combustible situation.

**At the time of this photo (60s after ignition), the hydrogen flame has begun to subside, while the gasoline fire is intensifying.**

Source: http://www.hydrogenus.com

# Outlook (5/5)

To significantly increase the energy supply and security, and to decrease carbon emission and air pollutants, however, the hydrogen economy must go well beyond incremental advances. Hydrogen must replace fossil fuels through efficient production using solar radiation, thermochemical cycles, or bio-inspired catalysts to split water.

The emphasis of the hydrogen research agenda varies with country; communication and cooperation to share research plans and results are essential.

Bringing hydrogen and fuel cells to that level of impact is a fascinating challenge and opportunity for basic science, spanning chemistry, physics, biology, and materials.