School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Hydrogen as Energy Carrier

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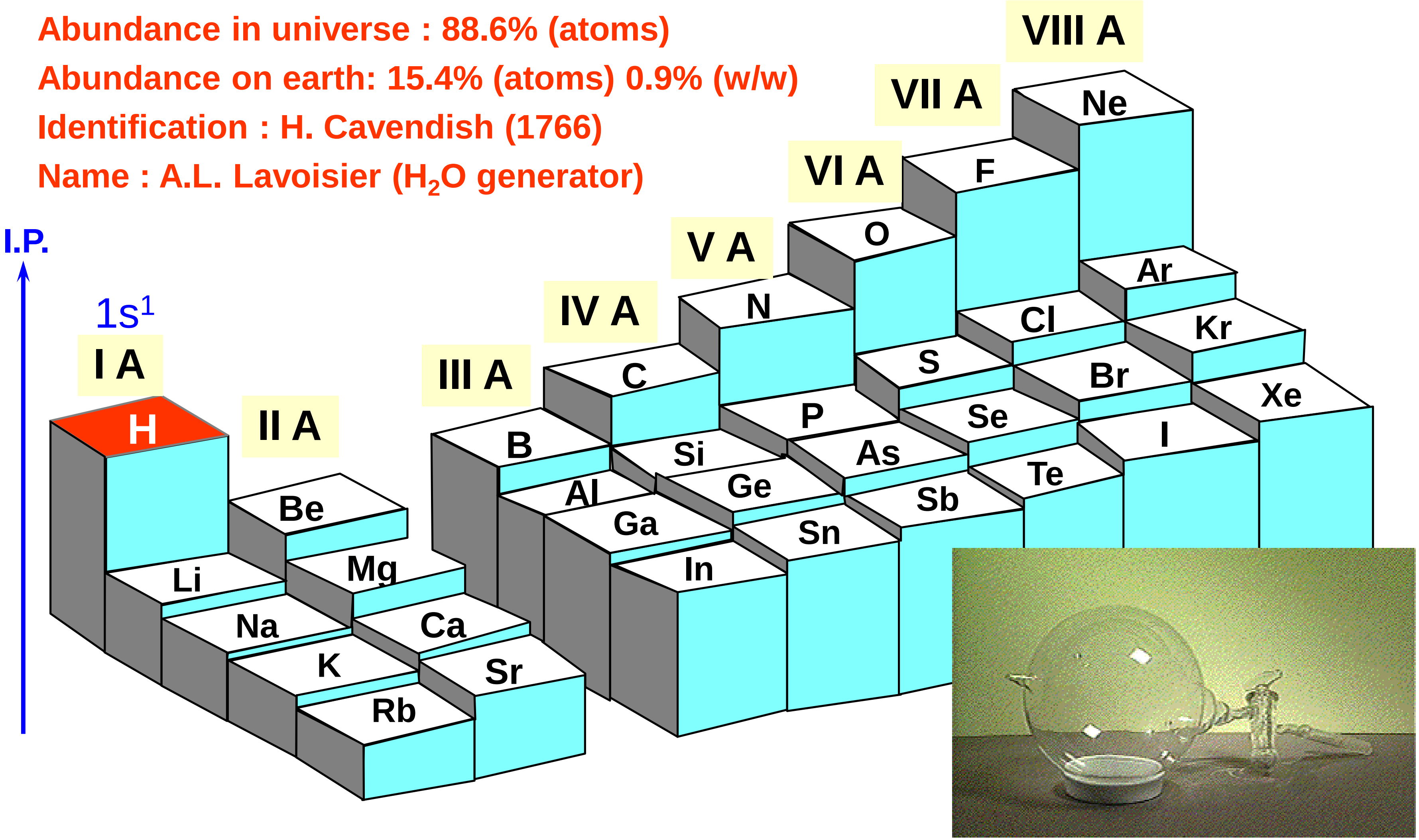
The Hydrogen Element.

Abundance in universe : 88.6% (atoms)

Abundance on earth: 15.4% (atoms) 0.9% (w/w)

Identification : H. Cavendish (1766)

Name : A.L. Lavoisier (H_2O generator)

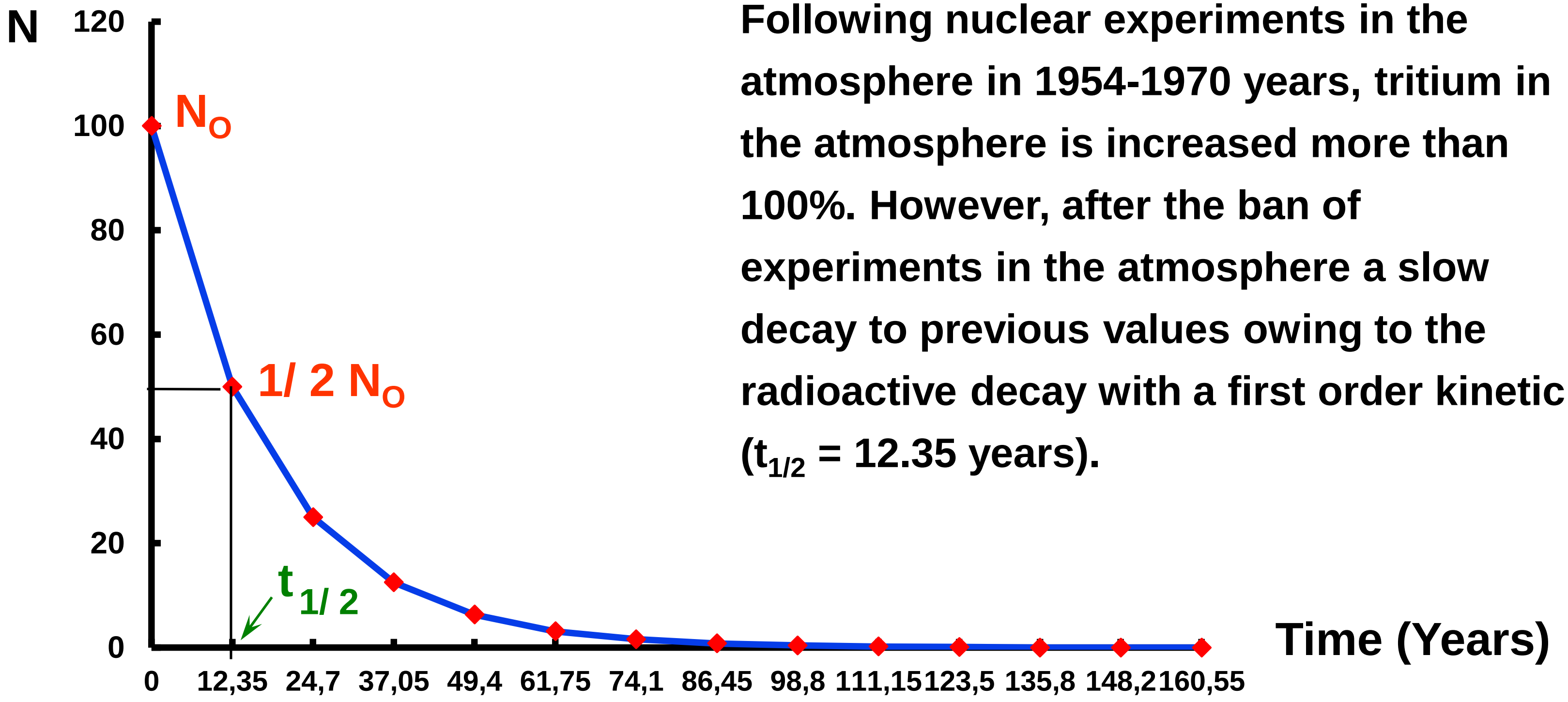


Atomic Properties of Hydrogen, and
Isotopes Deuterium and Tritium.

Property	H	D	T
Isotopic abundance (%)	99.98	0.0156	10^{-18}
Relative atomic mass /u.m.a.	1.007825	2.014102	3.016049
Nuclear spin quantic number	1/2	1	1/2
Magnetic moment n./(magnetons)[a]	2.79270	0.85738	2.9788
NMR frequency (at 2.35 tesla)/MHz	100.56	15.360	104.68
NMR rel. sensitivity (at cost. field)	1.000	0.00964	1.21
Quadrupole moment n./(10^{-28} m^2)	0	2.766×10^{-3}	0
Radioactive stability	Stable	Stable	β^- $t_{1/2}$12.35 y

[a'] Nuclear magneton μ_N = $eh/2m_p$ = 5.0508 × 10^{-27} J T^{-1}. [b]) $E_{maximum}$ = 18.6 keV; E_{mean} = 5.7 keV.

Kinetic Law of Exponential Decay of Tritium.



Following nuclear experiments in the atmosphere in 1954-1970 years, tritium in the atmosphere is increased more than 100%. However, after the ban of experiments in the atmosphere a slow decay to previous values owing to the radioactive decay with a first order kinetic ($t_{1/2}$ = 12.35 years).

$$\ln \frac{N}{N_0} = -k \cdot t$$

$t_{1/2}$ = half life

Physical Properties of H_2 Molecule and
Isotope molecules D_2 and T_2.

Property [(a)]	Hydrogen	Deuterium	Tritium
M.p. */K*	13.957	18.73	20.62
B.p. */K*	20.39	23.67	25.04
Heat of fusion */kJ mol^{-1}*	0.117	0.197	0.250
Heat of evaporation */kJ mol^{-1}*	0.904	1.226	1.393
Critical temperature */K*	33.19	38.35	40.6 (calc.)
Critical pressure */atm*	12.98	16.43	18.1 (calc.)
Bond Energy */kJ mol^{-1}* (a 298 K)	435.88	443.35	446.9
Zero point Energy */kJ mol^{-1}*	25.9	18.5	15.1
Internuclear distance */pm*	74.14	74.14	(74.14)

(a') Data rifer to H_2 of natural isotopic composition. All data concern mixtures of *orto* and *para* forms at equilibrium at R.T..

Ionized Forms of Hydrogen.

HYDROGEN CATION (PROTON) and OXONIUM ION

IONIZATION POTENTIAL $\mathbf{H^{\bullet}(g) \rightleftarrows H^{+}(g) + e^{-}}$ **I.P. = 1311 *kJ·mol*$^{-1}$**

(r = 1.5 *pm*)

***PROTON AFFINITY* :** $\mathbf{H^{+}\,(g) + H_2O\,(g) \rightleftarrows H_3O^{+}\,(g)}$ **- ΔH ≅ 720 *kJ·mol*$^{-1}$**

***HYDRATION ENERGY* :**

$\mathbf{H^{+}\,(g) \overset{H_2O_{(l)}}{\rightleftarrows} H_3O^{+}\,(aq)}$ **- ΔH ≅ 1090 *kJ·mol*$^{-1}$**

HYDRIDE ANION

***ELECTRON AFFINITY* :** $\mathbf{H\,(g) + e^{-} \rightarrow H^{-}\,(g)}$ **- ΔH_{calc} ≅ 72 *kJ·mol*$^{-1}$**

Hydride ion exists only combined with very electropositive cations, NaH, CaH_2, $LiAlH_4$.
Ionic hydrides are powerful reducing compounds: $\mathbf{NaH + H_2O \rightarrow NaOH + H_2}$

MOLECULAR HYDROGEN CATION

$\mathbf{H_2\,(g) \rightarrow H_2^{\bullet +}\,(g) + e^{-}}$ **$E_{leg.}$ = 255 *kJ·mol*$^{-1}$ (436)**

r = 106 *pm* (74.2)

Hydrogen Combined Sources on Earth.

- Hydrogen gas is very rare in the Earth's atmosphere (1 *ppm* by volume) because of its light weight, which enables it to escape from Earth's gravity more easily than heavier gases. However, hydrogen is the third most abundant element on the Earth, mostly on the surface and in the earth’s crust in the form of chemical compounds:
  - water (H_2O)
  - organic matter, a wide variety of molecules which combine C-H and C-C bonds in living organisms (fats, sugars, proteins, etc.) or in dead organisms (petrol, natural gas, coal)

Hydrogen is not a Source of Energy - Need to be Produced.

- **The world Hydrogen capacity is ~ 58 Mtons/year (650 bn Nm^3/year)**
- **Not one of top 50 chemicals by industrial tonnage (sulfuric acid is first, at 295 Mton worldwide in 2013)**
- **If compare by moles, the output is 29000 billion moles H_2 to 3010 billion moles H_2SO_4.**

$$\boxed{\text{moles} = \frac{\text{Mass in gram}}{\text{Molecular weight}}}$$

$$MW_{H_2} = 2.02 \text{ u.m.a.}$$

$$MW_{H_2SO_4} = 98.08 \text{ u.m.a.}$$

- The energy density per unit *volume* of both liquid hydrogen and compressed hydrogen gas at any practicable pressure is significantly less than that of traditional fuel sources, although the energy density per unit fuel *mass* is higher.

Preparation, Production, Purification.

⇨ **Laboratory** : Metal (M) + Acid (HX) → $M^{n+} + n\,X^{-} + H_2$ E° < 0-0.4 *V*

Metal (M) + Hydroxide (XOH) → $M(OH)_n^{-} + X^{+} + H_2$ [M = Al]

$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$

⇨ **Industrial production** (“steam creaking” of oil at 400°C):

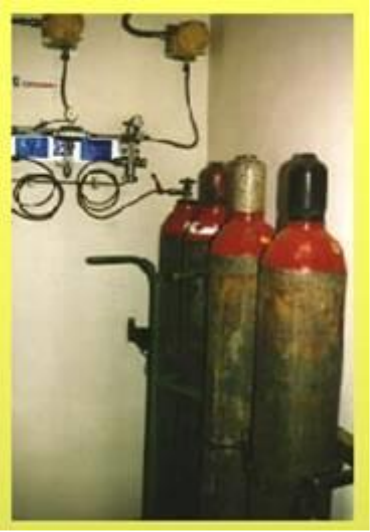
i) $CH_4 + H_2O \xrightarrow{1100°C} CO + 3\,H_2$ ΔH° = + 183.6 *kJ·mol*$^{-1}$

ii) $C + H_2O \xrightarrow{1000°C} CO + H_2$ ΔH° = + 131.3 *kJ·mol*$^{-1}$ (water gas)

and $CO + H_2O \xrightarrow[\text{"Co"}]{400°C} CO_2 + H_2$ ΔG° = - 19.9 *kJ·mol*$^{-1}$

or ***Water electrolysis*** when high purity need (> 99.95%)

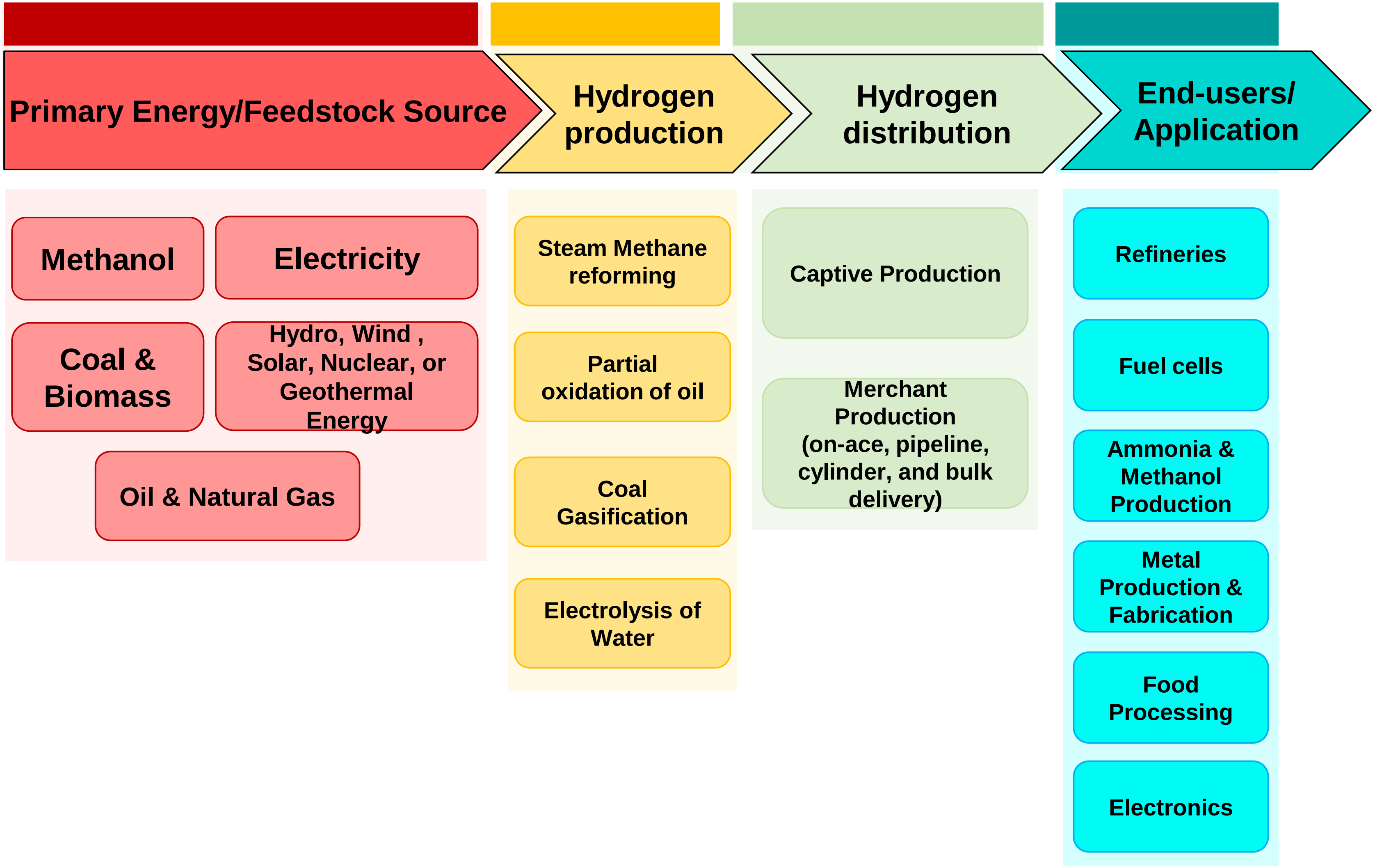
$$H_2O \xrightarrow[OH^- / H^+]{\text{Electric current}} 1/2\,O_2 + H_2$$ (or through NaCl)



⇨ **Purification** : Adsorption on molecular sieves

Diffusion through metallic membranes (Pd)

Hydrogen Generation Ecosystem.



Primary Energy/Feedstock Source

- Methanol
- Electricity
- Coal & Biomass
- Hydro, Wind , Solar, Nuclear, or Geothermal Energy
- Oil & Natural Gas

Hydrogen production

- Steam Methane reforming
- Partial oxidation of oil
- Coal Gasification
- Electrolysis of Water

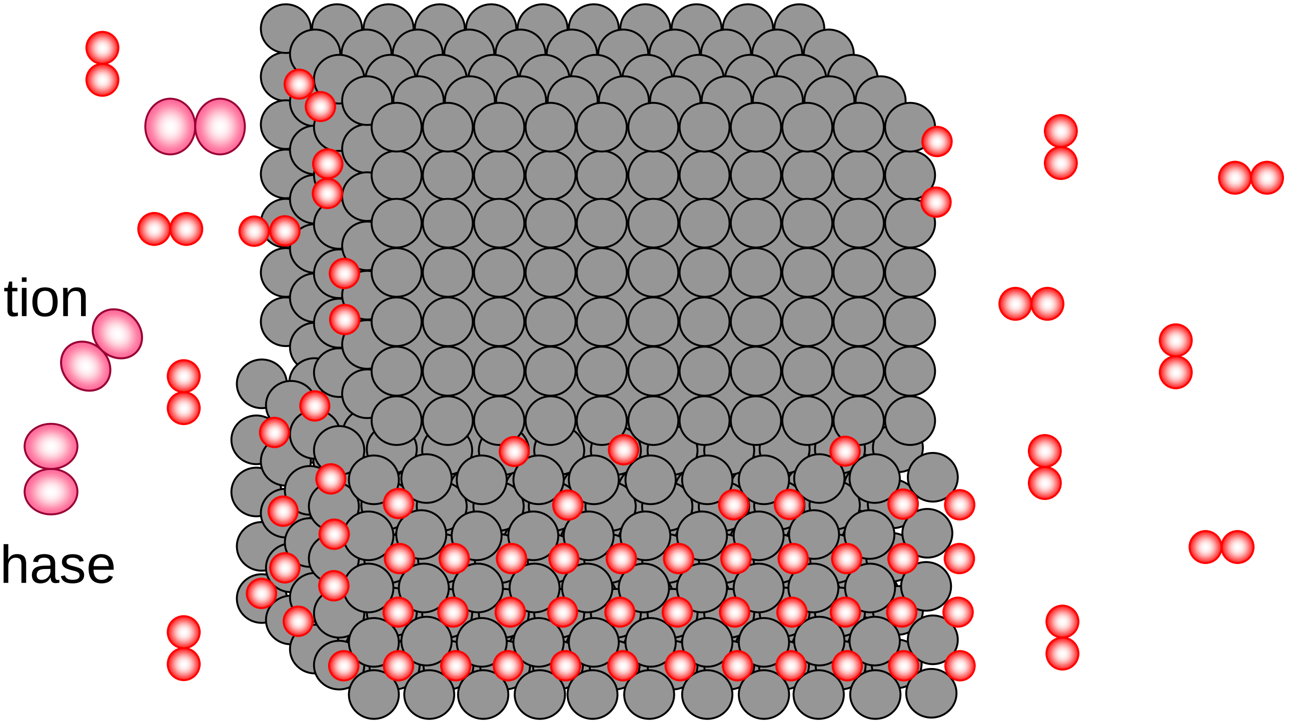
Hydrogen distribution

- Captive Production
- Merchant Production (on-ace, pipeline, cylinder, and bulk delivery)

End-users/ Application

- Refineries
- Fuel cells
- Ammonia & Methanol Production
- Metal Production & Fabrication
- Food Processing
- Electronics

Hydrogen Purification by Metallic Membranes.



H_2 gas mixture

Metal and Metal Hydride

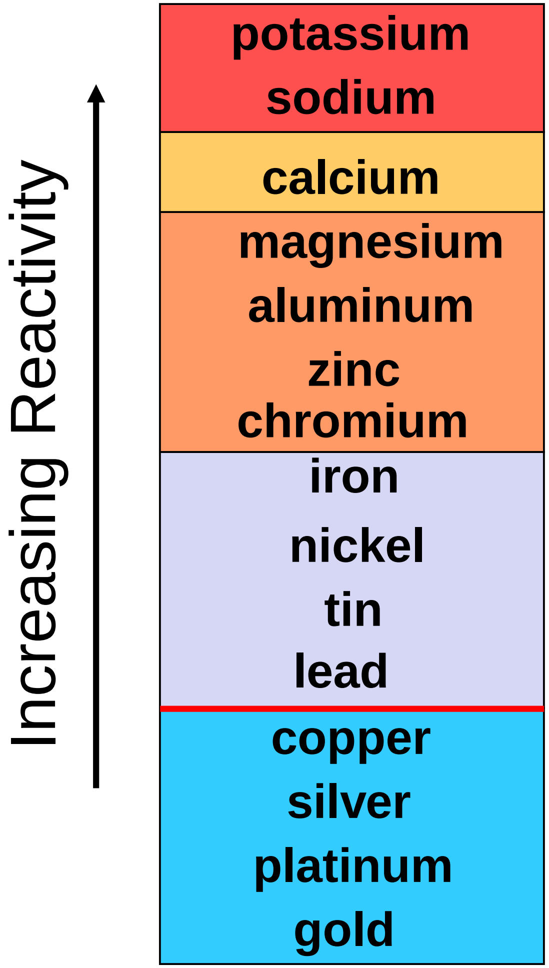
Pure H_2 gas

Hydrogen
adsorbed
on metal

Solid solution
α–phase

Hydride phase
β-phase

Activity Series of Metals Towards H_2O/Acids.



potassium
sodium

calcium

magnesium
aluminum
zinc
chromium

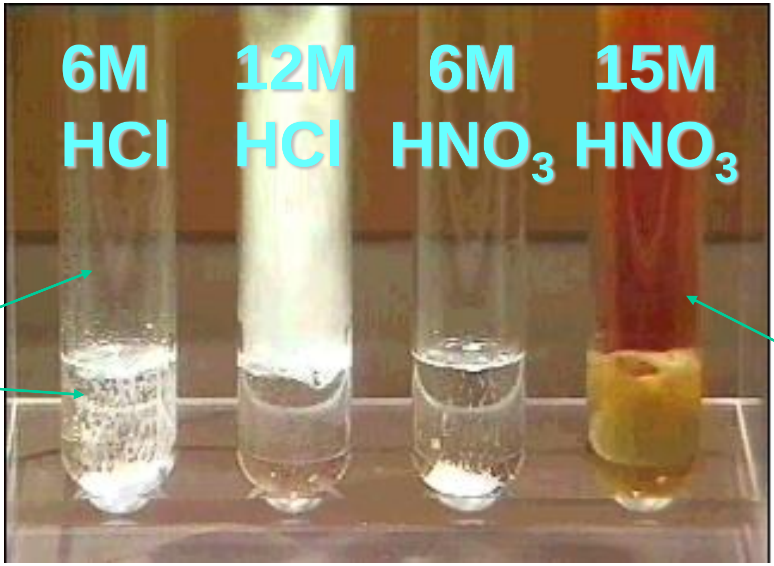
iron
nickel
tin
lead

copper
silver
platinum
gold

- Reacts violently with cold water
- Reacts slowly with cold water
- Reacts very slowly with steam, but quite reactive in acid
- Reacts moderately with high levels of acids
- < HYDROGEN comes here
- Unreactive in acid

Acid Attack on Metal.

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$$



$$Zn + 4\,HNO_3 \longrightarrow Zn^{2+} + 2NO_2 + 2\,NO_3^- + 2\,H_2O$$

ZINC Corrosion by Acids

$$(E°_{Zn/Zn^{2+}} = -\,0.77\ V < E°_{H^+/H_2} = 0.0\ V)$$

$$(E°_{Zn/Zn^{2+}} = -\,0.77\ V < E°_{HNO_3/NO_2} = 0.94\ V)$$

Molecular Hydrogen Properties and Reactivity.

Colorless, odorless, tasteless gas (d = 0.0799 g·ml^{-1}) with low solubility in liquids. Highly combustible, it explodes with air if it is 4–74% concentrated. At RT reacts:

$$H_2 + F_2 \xrightarrow{> -100^\circ C} 2\,HF \qquad\qquad H_2 + PdCl_{2\,(aq)} \xrightarrow{R.T.} Pd_{(s)} + 2\,HCl_{(aq)}$$

At higher temperatures it reacts with all metals to give the corresponding hydrides, and with non metals to give covalent hydrides, frequently under VIII group B metal catalysis (Raney Nickel, Pd/C, Fe, or by thermal and photochemical initiation):

$$x/2\,H_2 + M \rightarrow MH_x \qquad\qquad 3\,H_2 + N_2 \xrightarrow{450^\circ C} 2\,NH_3$$

Photochemical Reaction: UV irradiation (λ = 300 *nm*) or Δ

$$\left.\begin{array}{ll} Cl_2 \xrightarrow{h\nu} 2\,Cl\bullet & \text{Initiation} \\ \left.\begin{array}{l} Cl\bullet + H_2 \rightarrow HCl + H\bullet \\ H\bullet + Cl_2 \rightarrow HCl + Cl\bullet \end{array}\right\} & \text{Propagation} \\ 2\,X\bullet \rightarrow X\text{-}X & \text{Termination} \end{array}\right\} \text{Free radical chain processes}$$

$$Cl_2 + H_2 \rightarrow 2\,HCl \qquad \text{Overall Reaction}$$

Hydrogen Uses.

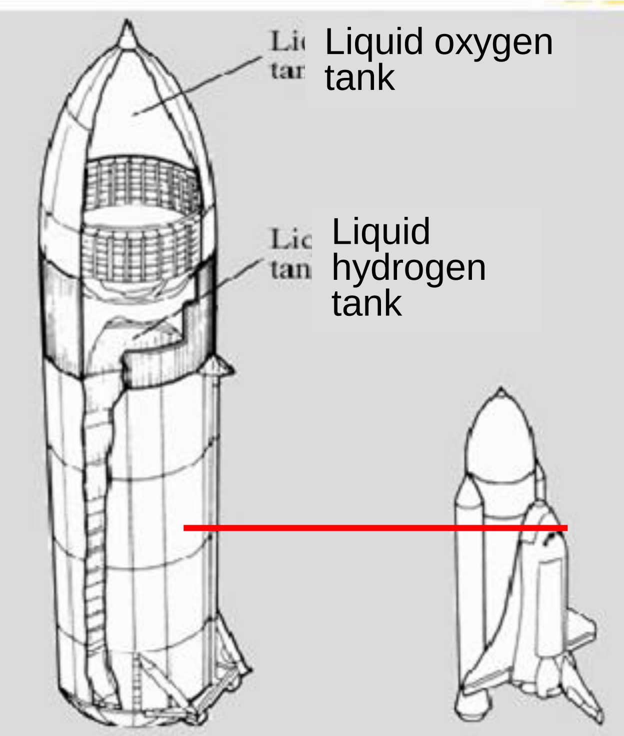
- Synthesis of Ammonia* (10^8 tons/year, Cost: 190 *$/t*).

  $N_{2(g)} + 3\,H_{2(g)} \rightleftarrows 2\,NH_{3(g)}$
- Synthesis of methanol ($CO + 2\,H_2 \rightleftarrows CH_3OH$).
- Catalytic hydrogenation of unsaturated fats (margarine).
- Synthesis of hydrogen chloride (HCl) from elements.
- Chemical reagent for reductions.
- Synthesis of metal hydrides (CaH_2 , $LiAlH_4$, $NaBH_4$, boranes, etc.)
- Metal production by reduction of corresponding oxides (Mo, W)
- Soldering (oxygen and atomic hydrogen torches)
- Rocket fuel
- Fuel cells for energy production.

*N.B. half amount converted into NH_3 via Haber process.

Hydrogen as Fuel and Hydrogen Economy.

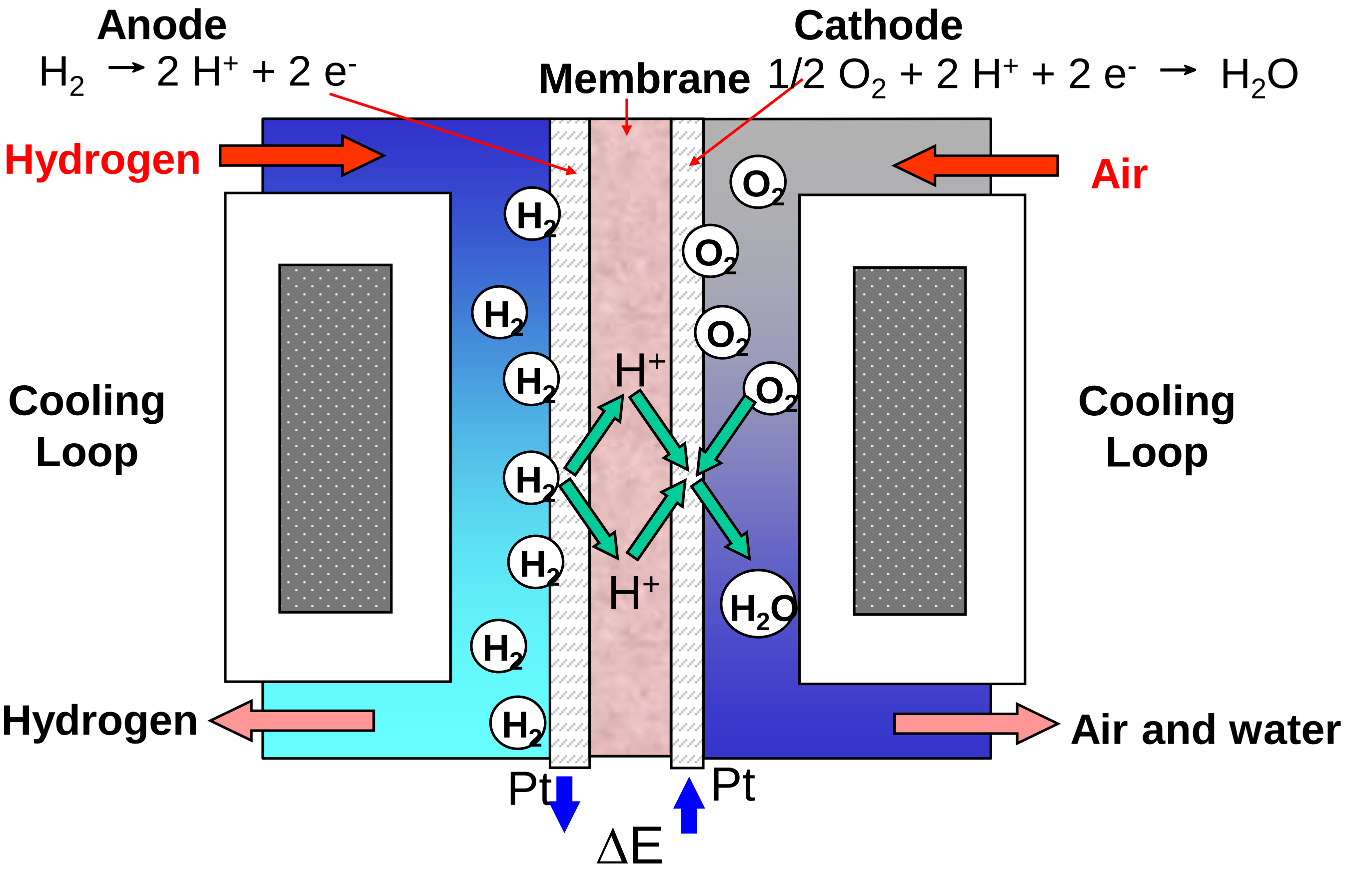
$$\boxed{2\,H_2 + O_2 \rightarrow 2\,H_2O \quad \Delta G = -\,242\ kJ\cdot mol^{-1}}$$



- **Chain reaction with initiation**
- **Highest known specific enthalpy (energy per gram of fuel) - 121 *kJ·g*$^{-1}$**
- **Bulky due to low density (note size of $H_{2(liq.)}$ tank compared to $O_{2(liq.)}$ tank of rocket)**
- **The hydrogen economy consists of an economic system in which energy is supplied by renewable and regenerable resources. Hydrogen can be the medium of energy storage and transport.**

Hydrogen as Electric Energy Carrier – Hydrogen Fuel Cells.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \quad \Delta G = -\,242\ kJ\cdot mol^{-1}$$



Uses of Hydrogen as Chemical Reagent: Hydrogenation - Hydrogenolysis – Desulfurization.

Most unsaturated organic compounds (having double or triple bonds) react with H_2 in the presence of homogeneous (R_3RhH) or heterogeneous (Pd/C, etc.) hydrogenation catalysts, reducing the number of unsaturation :

$$H_2 + R\text{-}CH{=}CH_2 \rightarrow R\text{-}CH_2\text{-}CH_3 \qquad H_2 + R\text{-}C{\equiv}CH \rightarrow R\text{-}CH{=}CH_2$$

Sometimes it undergoes reaction with other molecules (i.e. CO in reactions called hydroformylation) :

$$H_2 + R\text{-}CH{=}CH_2 + CO \xrightarrow{\text{"}Co(CO)_5\text{"}} R\text{-}CH_2\text{-}CH_2CH{=}O \xrightarrow{H_2/Pd} R\text{-}CH_2\text{-}CH_2CH_2OH$$

Hydrogen reduces C-X bonds to C-H (hydrogenolysis) at high T and under catalysis:

$$H_2 + X\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow H\text{-}CH_2\text{-}CH{=}CH_2 + HX \qquad X = Cl, OR, NRR', SR$$

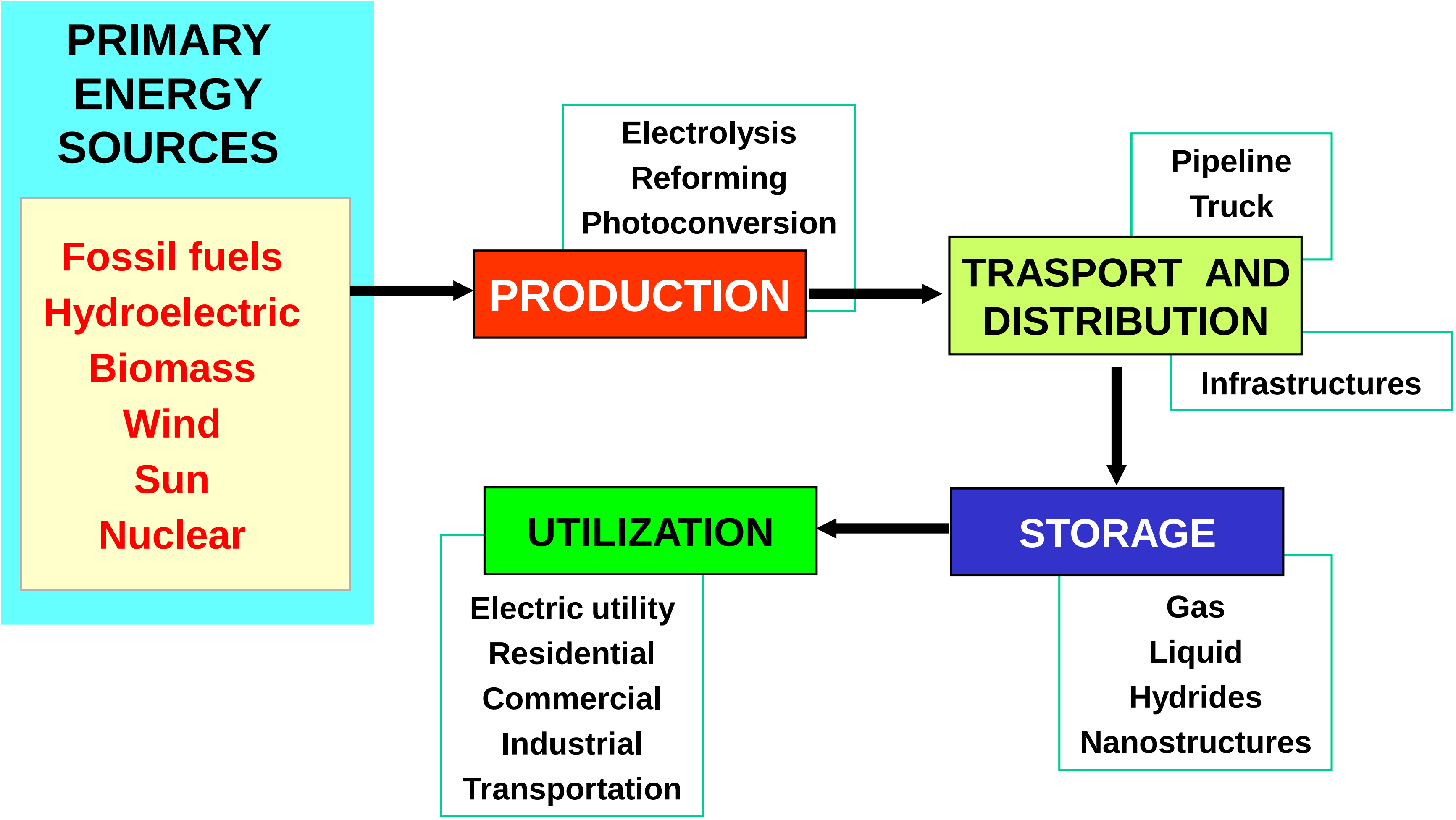
S substitution by H is an important reaction in oil refinery (desulfurization) :

$$C_4H_4S + 4\,H_2 \rightarrow C_4H_{10} + H_2S$$

thiophene butane

Pathway to Hydrogen Economy

(H_2 is a energy carrier not a source!).



PRIMARY ENERGY SOURCES

Fossil fuels
Hydroelectric
Biomass
Wind
Sun
Nuclear

PRODUCTION

Electrolysis
Reforming
Photoconversion

TRASPORT AND DISTRIBUTION

Pipeline
Truck
Infrastructures

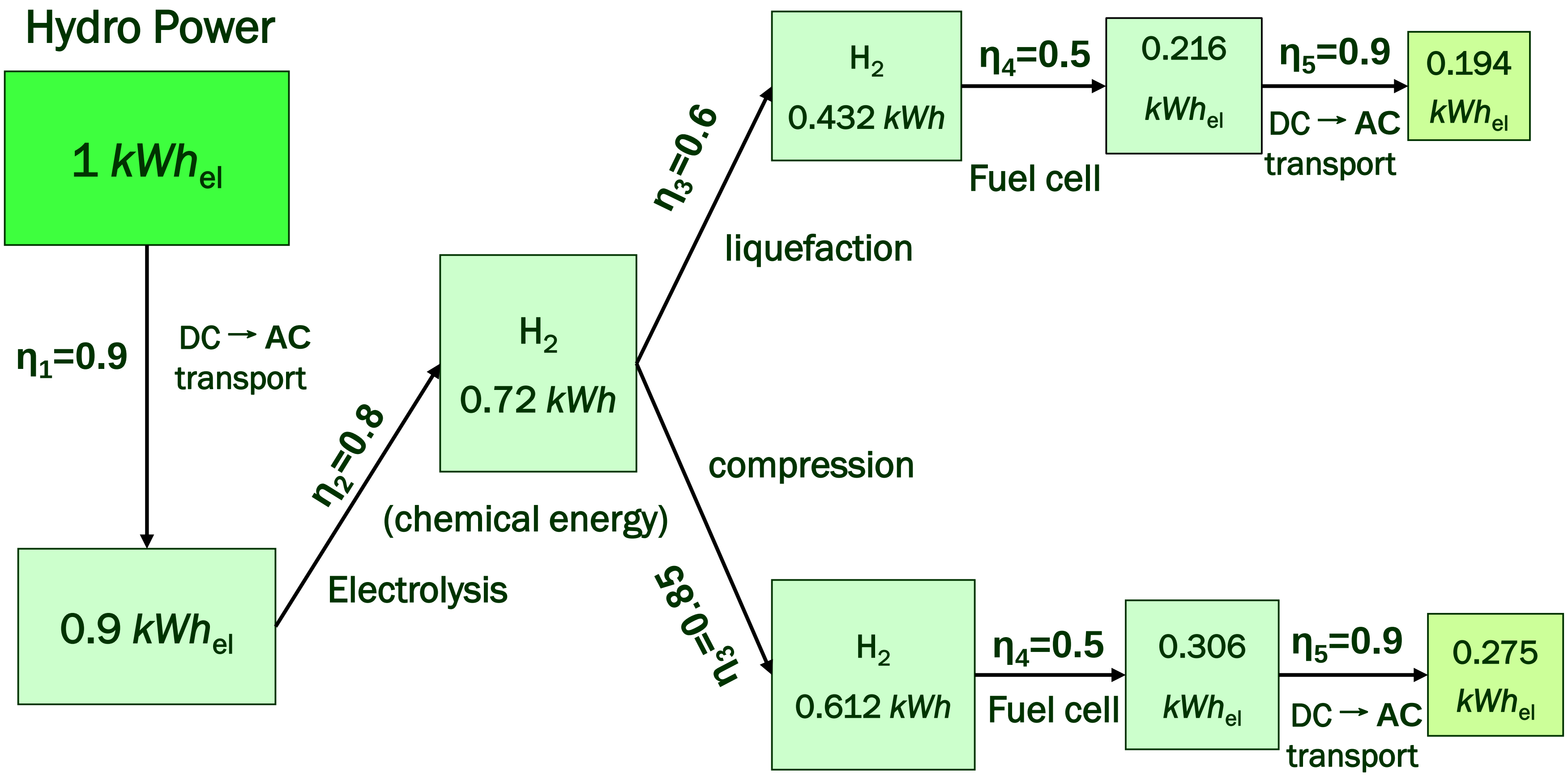
STORAGE

Gas
Liquid
Hydrides
Nanostructures

UTILIZATION

Electric utility
Residential
Commercial
Industrial
Transportation

The Route "Hydropower – HYDROGEN – Fuel Cells".



Hydro Power

$1\ kWh_{el}$

$\eta_1=0.9$

DC → AC transport

$0.9\ kWh_{el}$

$\eta_2=0.8$

Electrolysis

H_2 $0.72\ kWh$

(chemical energy)

$\eta_3=0.6$

liquefaction

H_2 $0.432\ kWh$

$\eta_4=0.5$

Fuel cell

$0.216\ kWh_{el}$

$\eta_5=0.9$

DC → AC transport

$0.194\ kWh_{el}$

compression

$\eta_3=0.85$

H_2 $0.612\ kWh$

$\eta_4=0.5$

Fuel cell

$0.306\ kWh_{el}$

$\eta_5=0.9$

DC → AC transport

$0.275\ kWh_{el}$

$$\eta_{tot} = \eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \eta_4 \cdot \eta_5 = 0.2 \div 0.27$$

Alternatives in the H_2 Production.

Hydrogen from non-renewable sources:

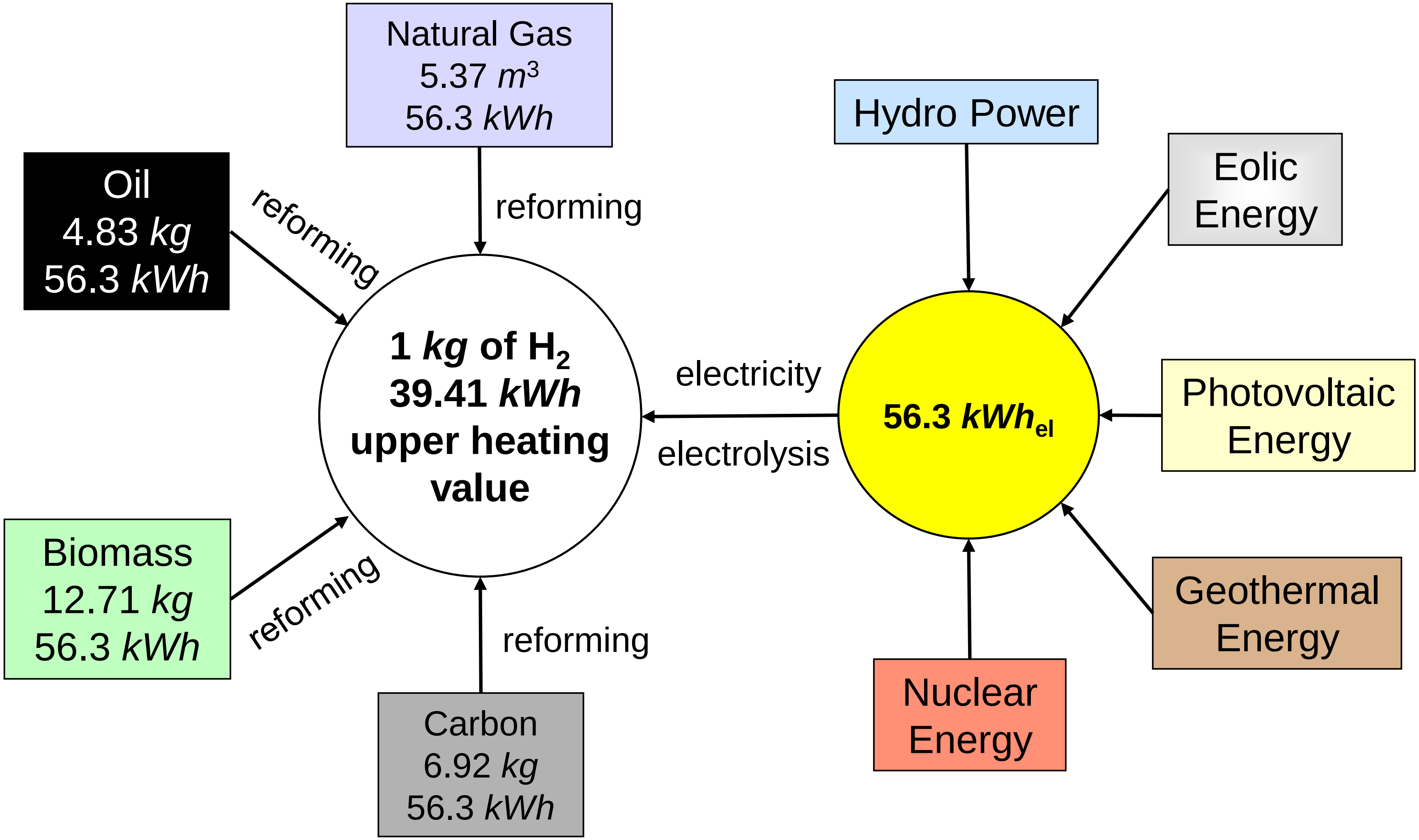
- Hydrogen from carbon (C + $H_2O \rightarrow H_2 + CO$)
- Hydrogen from reforming ($CH_3OH + H_2O \rightarrow 3H_2 + CO_2$)
- Hydrogen by electrolysis (electricity produced from NR sources)

Hydrogen from renewable sources:

- Photovoltaic Hydrogen (PV)
- Hydrogen directly from Sun
- Other routes of Hydrogen Production from Sun
- Biomass

Integrated Hydrogen Production.

(Hypothesis: electrolysis and reforming yield 70%)



Hydrogen Specific Energy Content.

	Content for volume unit		Content for mass unit	
	$[kJ \cdot m^{-3}]$	$[kWh \cdot m^{-3}]$	$[kJ \cdot kg^{-1}]$	$[kW \cdot kg^{-1}]$
Lower heating value	10.800	3	120.000	$33.\bar{3}$
Upper heating value	12.770	3.54	141.890	39.41

Standard Conditions : $T = 273.15\ K$, $P = 1.013\ bar$

Photovoltaic (PV) Hydrogen.

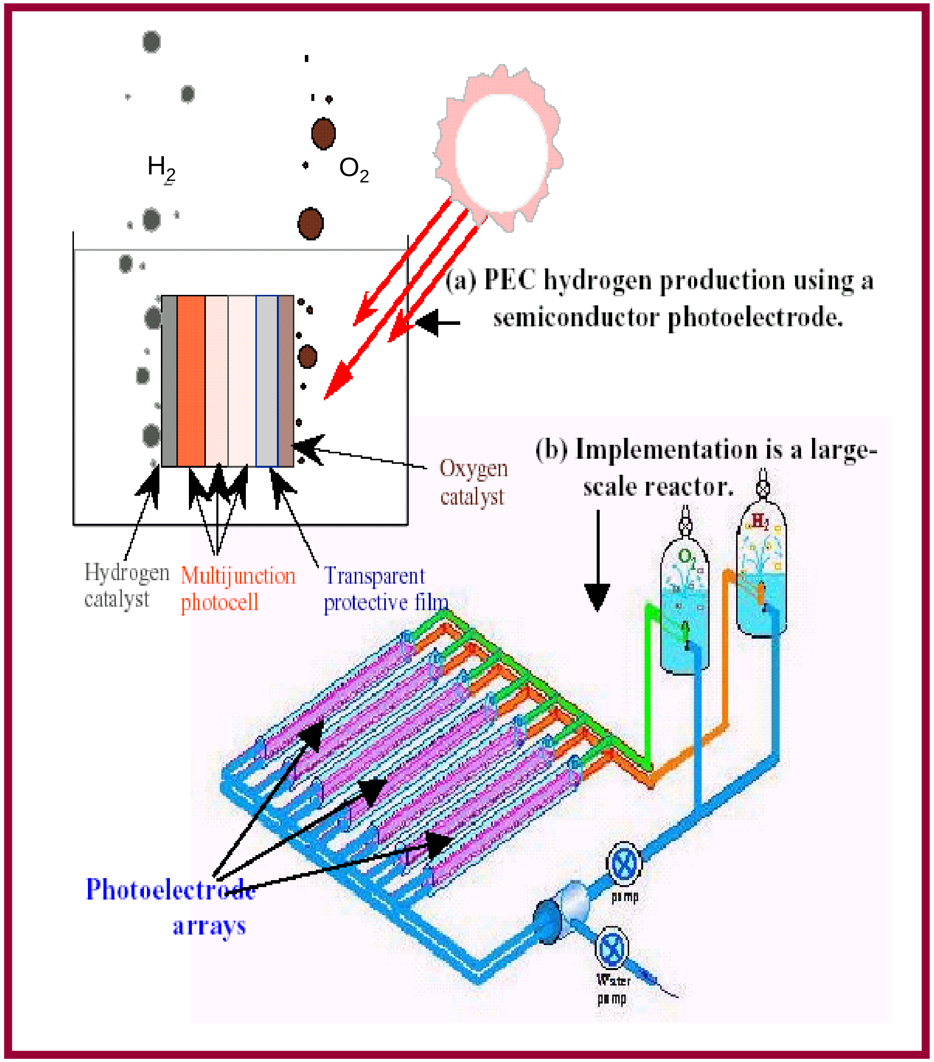
- Stuart Energy Systems P3-1A Fleet Fuel Appliance
  - Installed at SunLine Transit Agency
  - PV system generates 18 *kW* of total 200 needed by electrolyzer (remainder of power is hydroelectric)
  - 1490 SCFH hydrogen produced at 4000 *psig*
  - 67 % overall efficiency.

- Agder College, Norway
  - – 80 *kW* PV array
  - – 50 *kW* electrolyzer
  - – 20 *kW* PEM fuel cell.

Photo-Electrochemical Hydrogen.

- Direct electrochemical production of hydrogen induced by sunlight.
- Potentially more efficient than PV electrolysis.
- Still early in development.

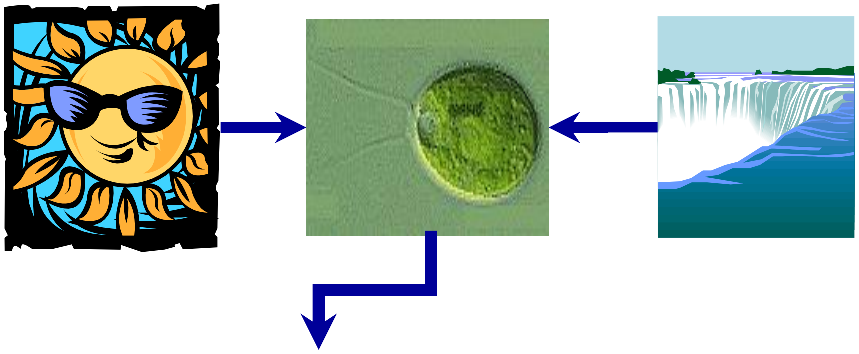
(based on the fact that the overall sun spectral energy is higher than $\Delta G°_f$ of H_2O)



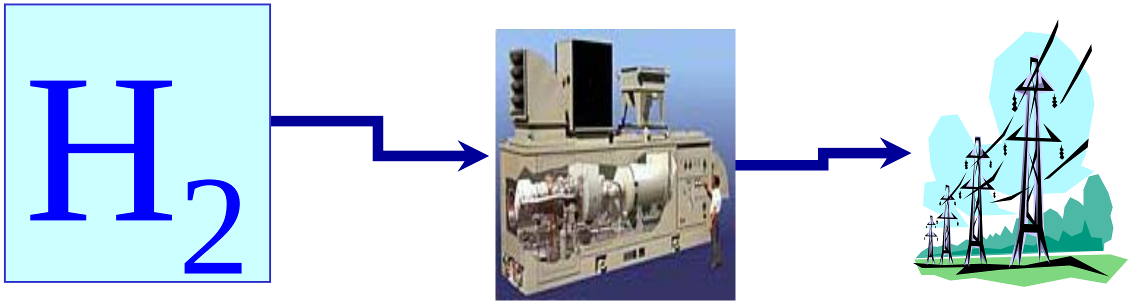
(a) PEC hydrogen production using a semiconductor photoelectrode.

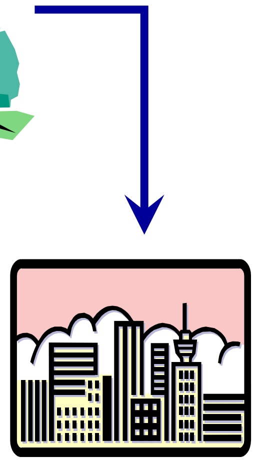
(b) Implementation is a large-scale reactor.

Photo-biological H_2 Production.



Another potentially high efficiency technology for hydrogen production using solar energy. **Based on Algae Modified Metabolism.**



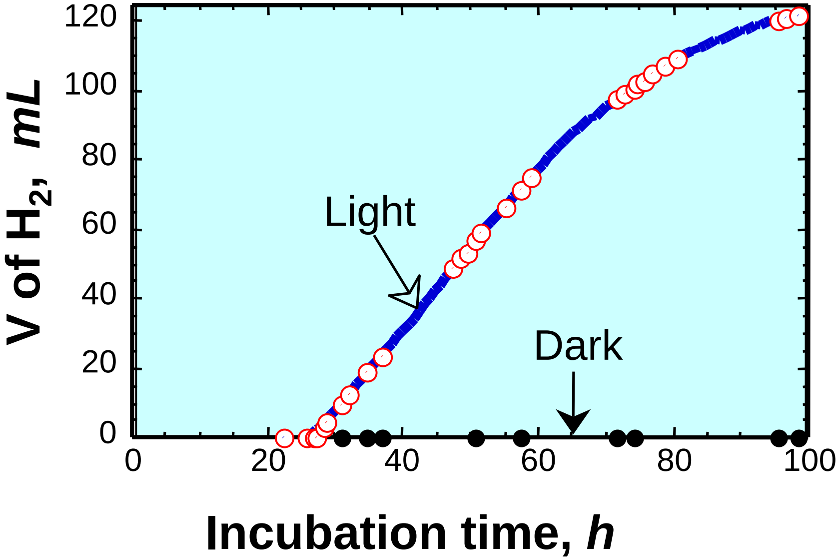


Sun Light + Algae + Water → H_2

Hydrogen + Fuel Cell or Turbine Generator = Electricity

Conditions for H_2 Production.

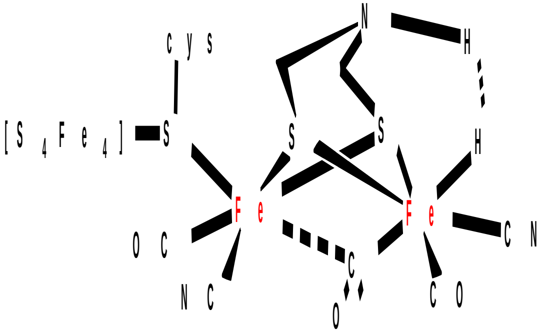
KEY METABOLIC MODIFICATION to induce reversible production of H_2 : sulfur loss from algae.



Algae culture without sulfur and normal green. Prof. Melis, UC Berkeley.

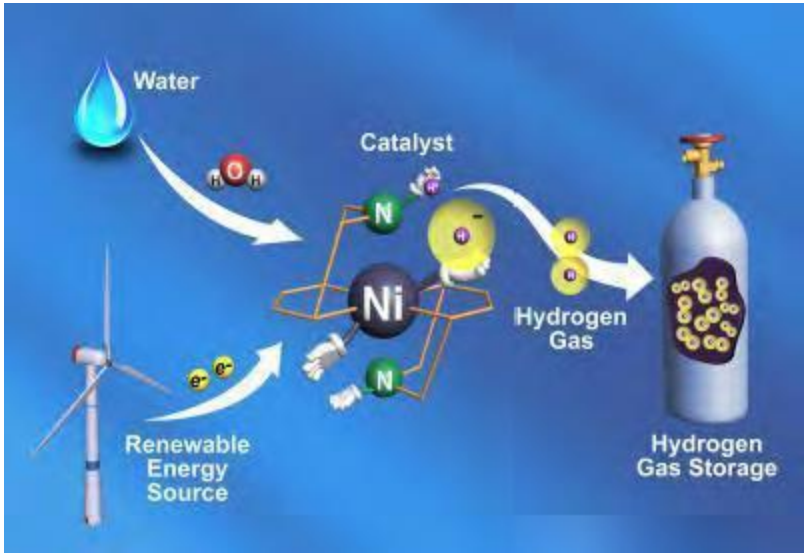
Time sequence in the production of hydrogen in *Chlamydomonas reinhardtii*.

Mimicking Nature for Hydrogen Production.



[FeFe] hydrogenase enzyme motif that catalyzes the formation of H_2 from H_2O

Synthetic mimic

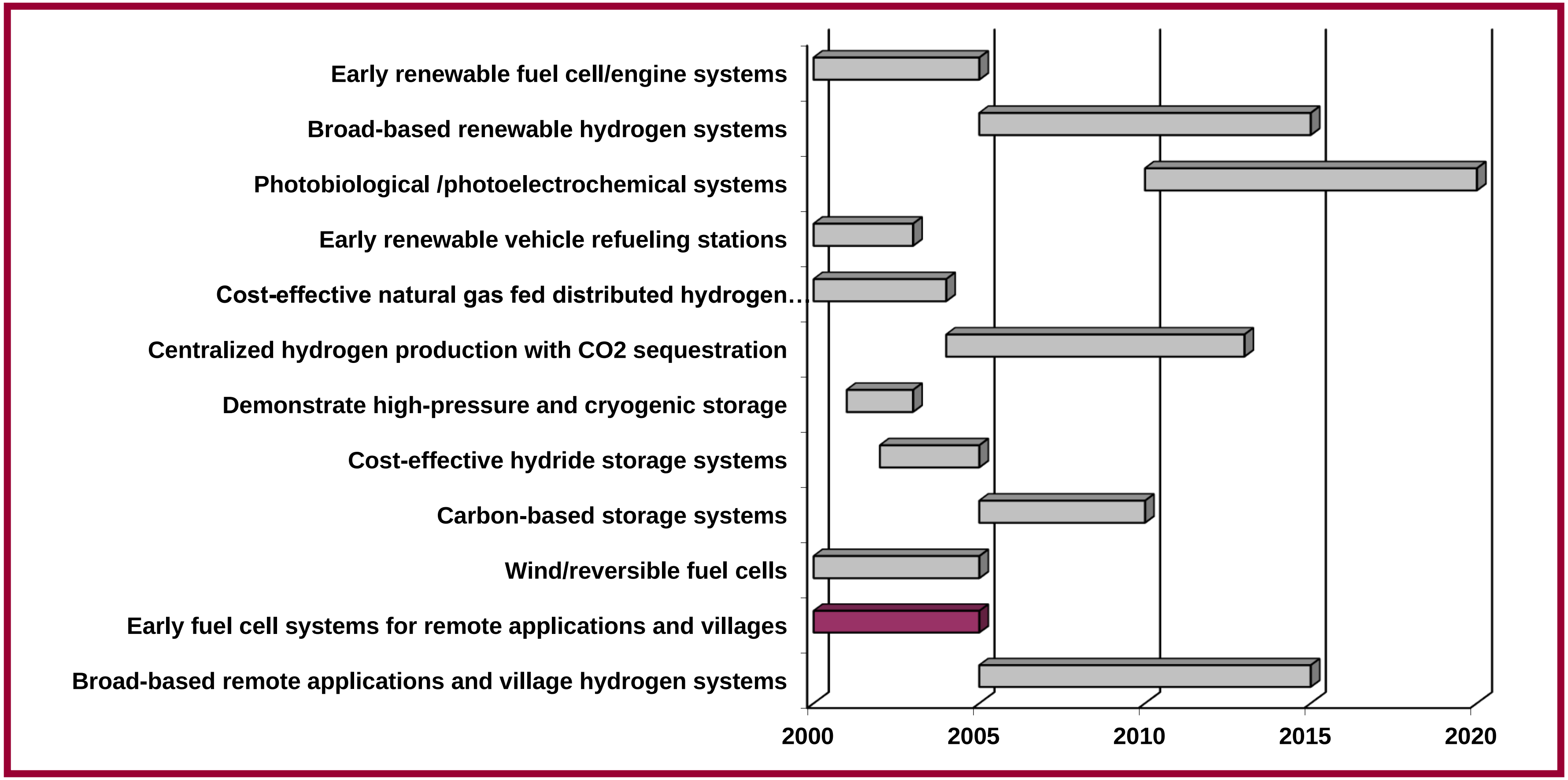


100,000 molecules of H_2 per second

M L Helm et al. Science 2011; 333: 863-866

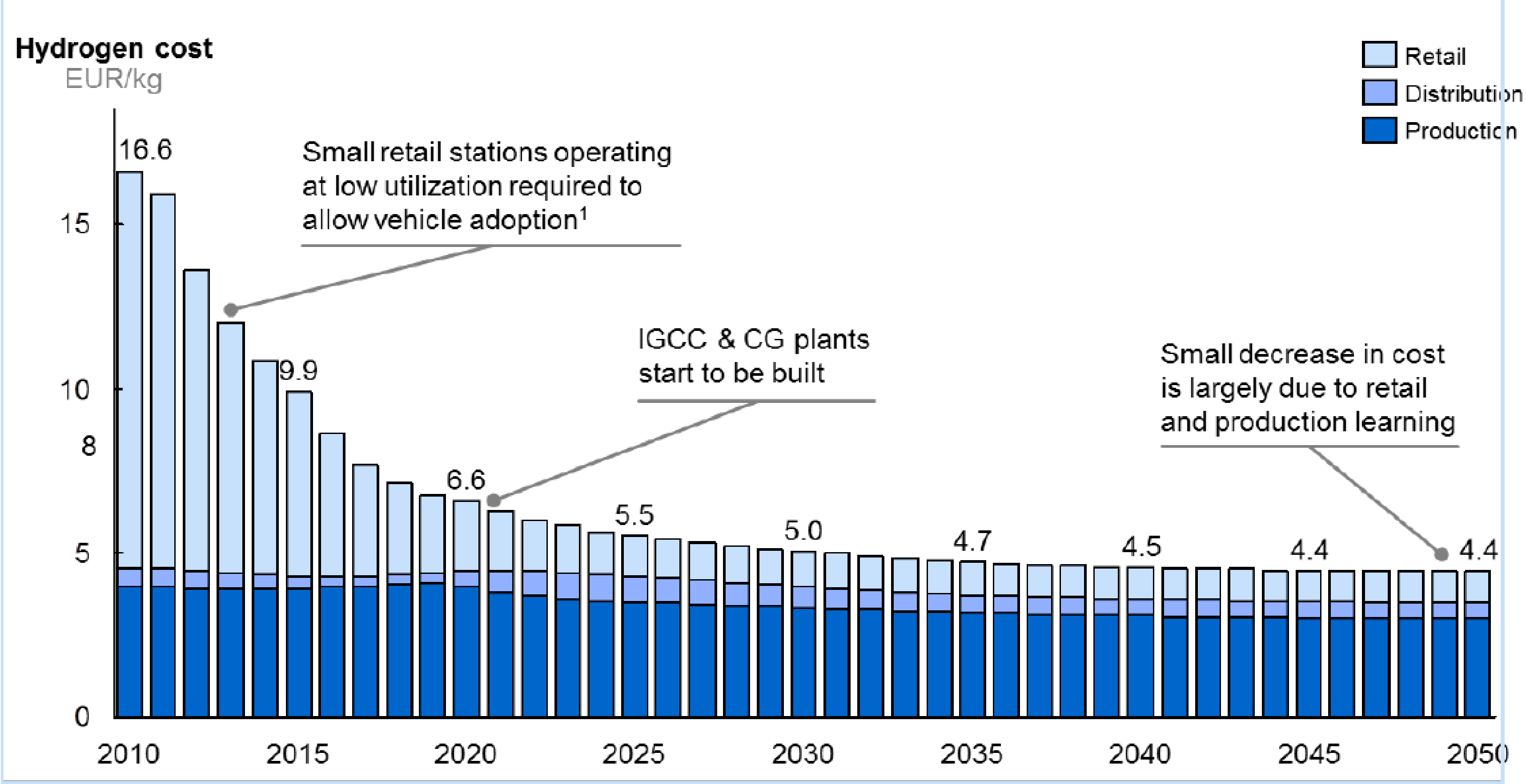
The Hydrogen Economy.

DOE Timeline for development of key hydrogen energy systems (2012).



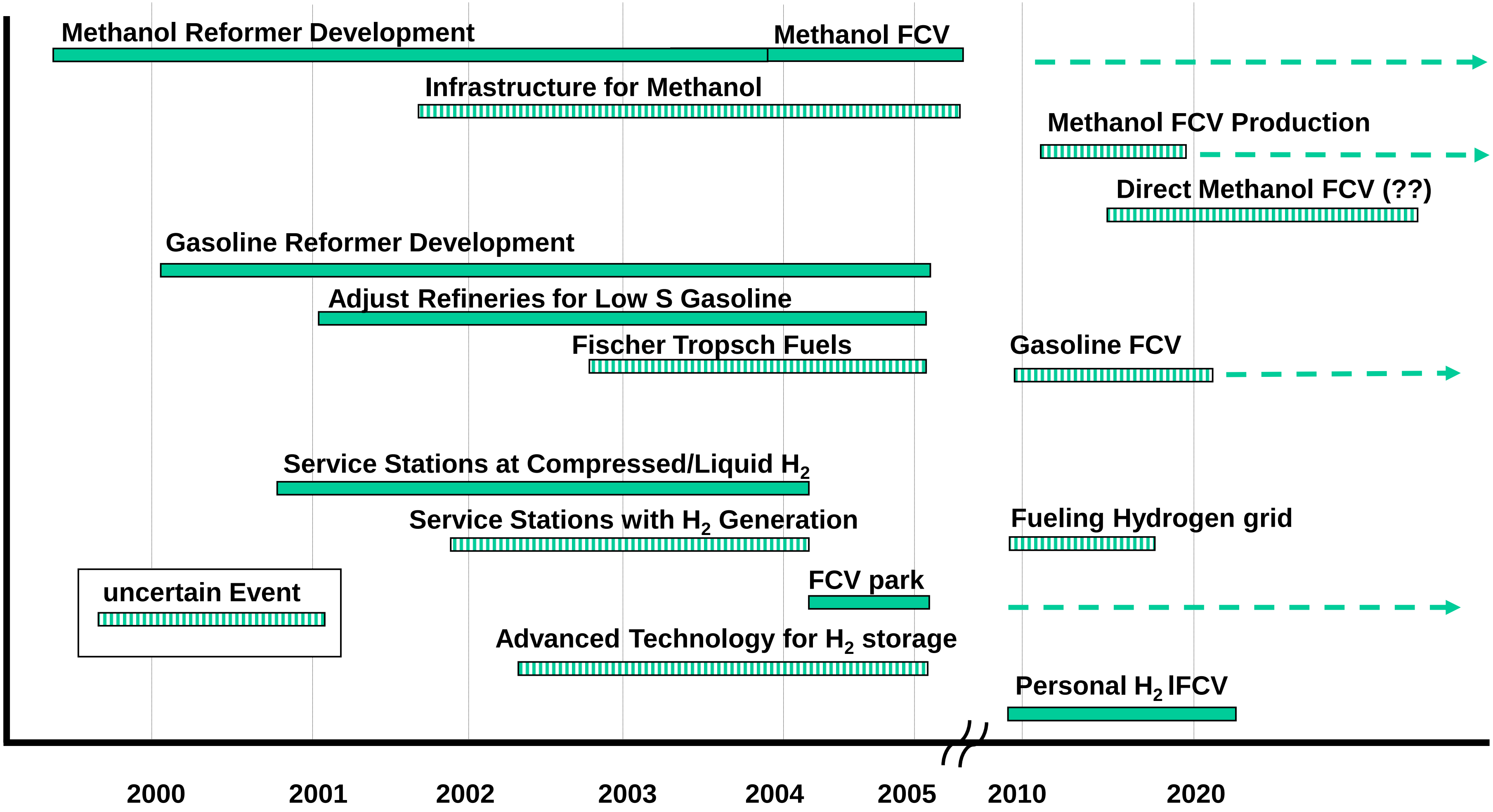
Cost of Hydrogen Delivered at Pump.

Delivered at pump, w/o taxes or excises

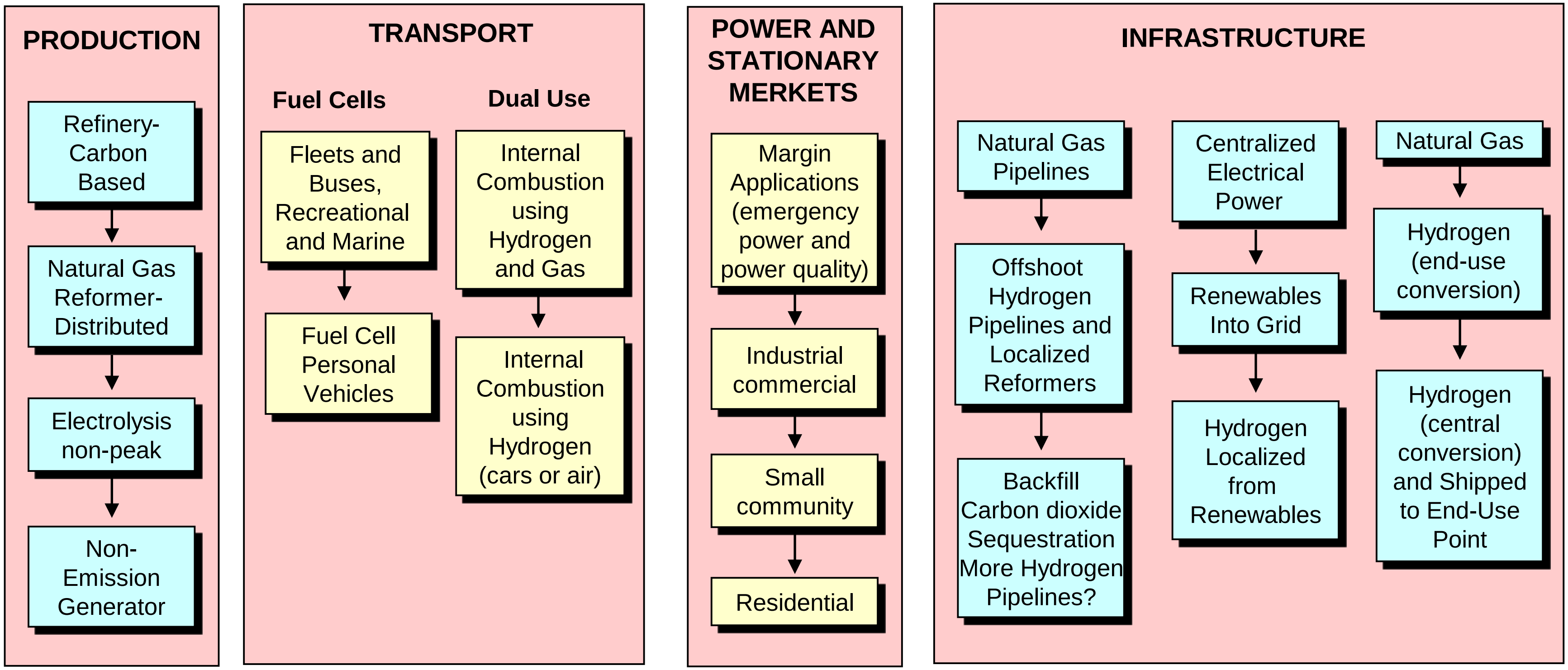


Source: A portfolio of power-trains for Europe (McKinsey 2011)

Possible Routes to FCV Commercialization.



Transition to Hydrogen Economy.



PRODUCTION

- Refinery-Carbon Based
- Natural Gas Reformer-Distributed
- Electrolysis non-peak
- Non-Emission Generator

TRANSPORT

Fuel Cells

- Fleets and Buses, Recreational and Marine
- Fuel Cell Personal Vehicles

Dual Use

- Internal Combustion using Hydrogen and Gas
- Internal Combustion using Hydrogen (cars or air)

POWER AND STATIONARY MERKETS

- Margin Applications (emergency power and power quality)
- Industrial commercial
- Small community
- Residential

INFRASTRUCTURE

- Natural Gas Pipelines
- Offshoot Hydrogen Pipelines and Localized Reformers
- Backfill Carbon dioxide Sequestration More Hydrogen Pipelines?

- Centralized Electrical Power
- Renewables Into Grid
- Hydrogen Localized from Renewables

- Natural Gas
- Hydrogen (end-use conversion)
- Hydrogen (central conversion) and Shipped to End-Use Point

Fuel Cells – The Cutting Edge.

Fuel Cell Type	Operating Temperature	Efficiency	Fuel
Metal-air "half cells"	Ambient	?	Zn, Al
Polymer Electrolyte	80 °C	40 – 45 %	H_2
Direct Methanol	50 – 100 °C	30 – 40 %	MeOH
Phosphoric Acid	160 – 220 °C	40 – 45 %	H_2
Alkaline	120 – 250 °C	60 %	H_2
Molten Carbonate	600 – 650 °C	50 %	Syngas
Solid Oxide	700 –1000 °C	50 – 55 %	CH_4, syngas

Pros and Cons of Fuel Cells.

Pros

- High efficiencies
- Good at part load
- Low emissions
- Good maintenance characteristics
- Few moving parts
- Low noise characteristics
- Distributed power generation can be used with cogeneration

Cons

- Lifetimes unknown
- Loss of efficiency with time
- High investment costs
- Low development status
- Low availability
- Few technology providers
- Absence of fuel infrastructure for most applications

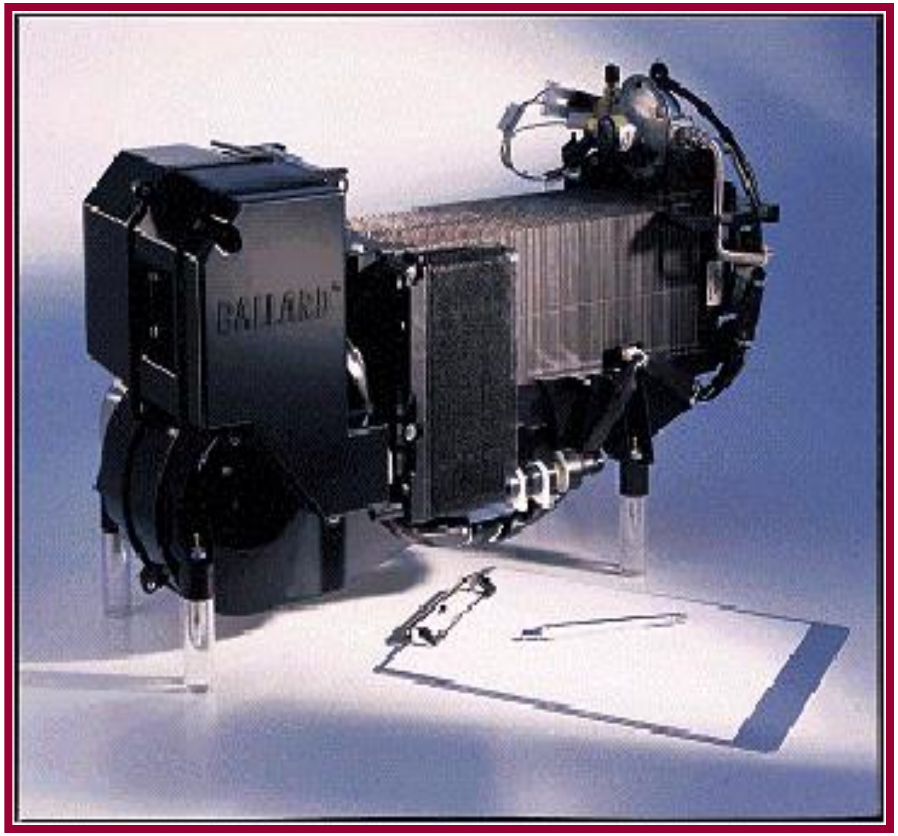
Low-Temperature Fuel Cells.

- ~ 80 – 100 °C Operation
- Applications:

Polymer Electrolyte Membrane Fuel Cells	Direct Methanol Fuel Cells
Automobiles	*Automobiles*
Buses	*Personal Transportation*
Residential and small commercial distributed power generation	*Cell Phones*
Premium power	*Lap Tops*
Telecommunications	*PDAs*

PEM Fuel Cell.

- Ballard NexaTM Power Module
  - 1200W, 26V output at full power
  - Backup or intermittent power
  - CSA, UL certified



Intermediate Temperature Fuel Cells.

- ~ 200 °C Operation
- Applications:

Alkaline Fuel Cells	Phosphoric Acid Fuel Cells
• *Space Power*	• *Baseload Power*
• *Personal Transportation*	• *Cogeneration*
• *Small Watercraft*	
• *Utility Vehicles*	
• *Fleet Vehicles*	

Phosphoric Acid Fuel Cells.

UTC Fuel Cells PC25^{TM}

- 200 kW electrical
- 900,000 Btu/hr. thermal
- 37 % electrical efficiency
- 87 % overall efficiency
- Installation shown is operating on digester gas in Portland, Oregon

High Temperature Fuel Cells.

- ~ 600 – 1000 °C Operation
- Applications

Molten Carbonate Fuel Cell

- *Baseload Power*
- *Cogeneration*
- *Hybrid Power*

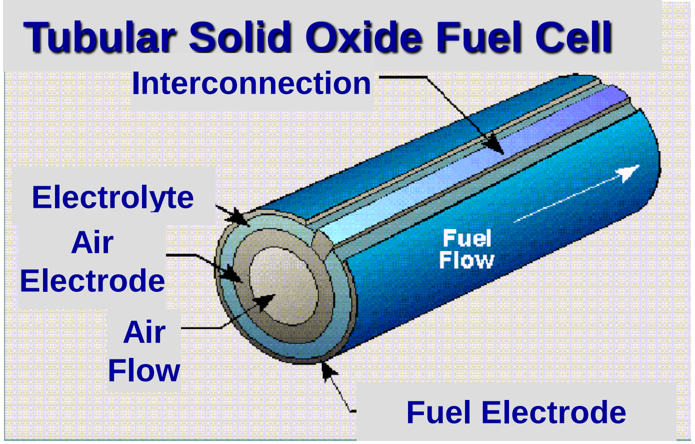
Solid Oxide Fuel Cells

- *Baseload Power*
- *Small-scale Distributed Power*
- *Cogeneration*
- *Hybrid Power*
- *Potential for Future Automotive*
- *use*

Solid Oxide Fuel Cell.

Tubular SOFC

- Typical *Siemens-Westinghouse* design
- Suitable for large scale installations



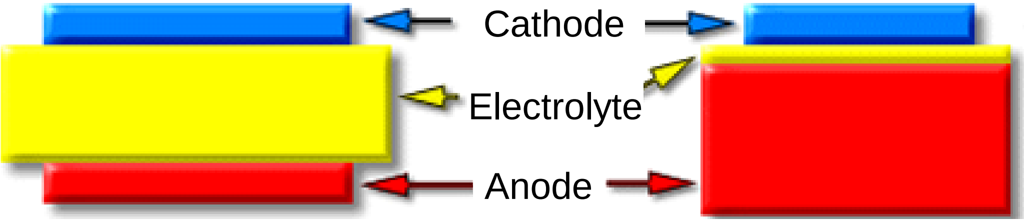
Planar SOFC

- Anode supported design on right
- Lower temperature operation
- Suitable for smaller systems

Single Cell Structure

Conventional flat plate concept
with self-supporting electrolyte to sheet

Anode supported SOFC



0.5 *mm*
1.0 *mm*
0.05 *mm*

Cathode
Electrolyte
Anode

0.05 *mm*
0.01 *mm*
1.5 *mm*

Solid Oxide Fuel Cell.

Siemens/Westinghouse

- – 220 *kW* SOFC/turbine hybrid
- – 200 *kW* tubular fuel cell stack
- – 20 *kW* turbine
- – 55 % electrical efficiency
- – Over 900 hours operational experience
- – Design targeted for eventual 60 – 70 % electrical efficiency

Other Fuel Cell Technologies.

- Applications

Zinc-air Fuel Cells

- *Cars*
- *Hearing aids*
- *Cell Phones*
- *Lap Tops*
- *PDAs*
- *Portable Power*
- *Portable Electronics*

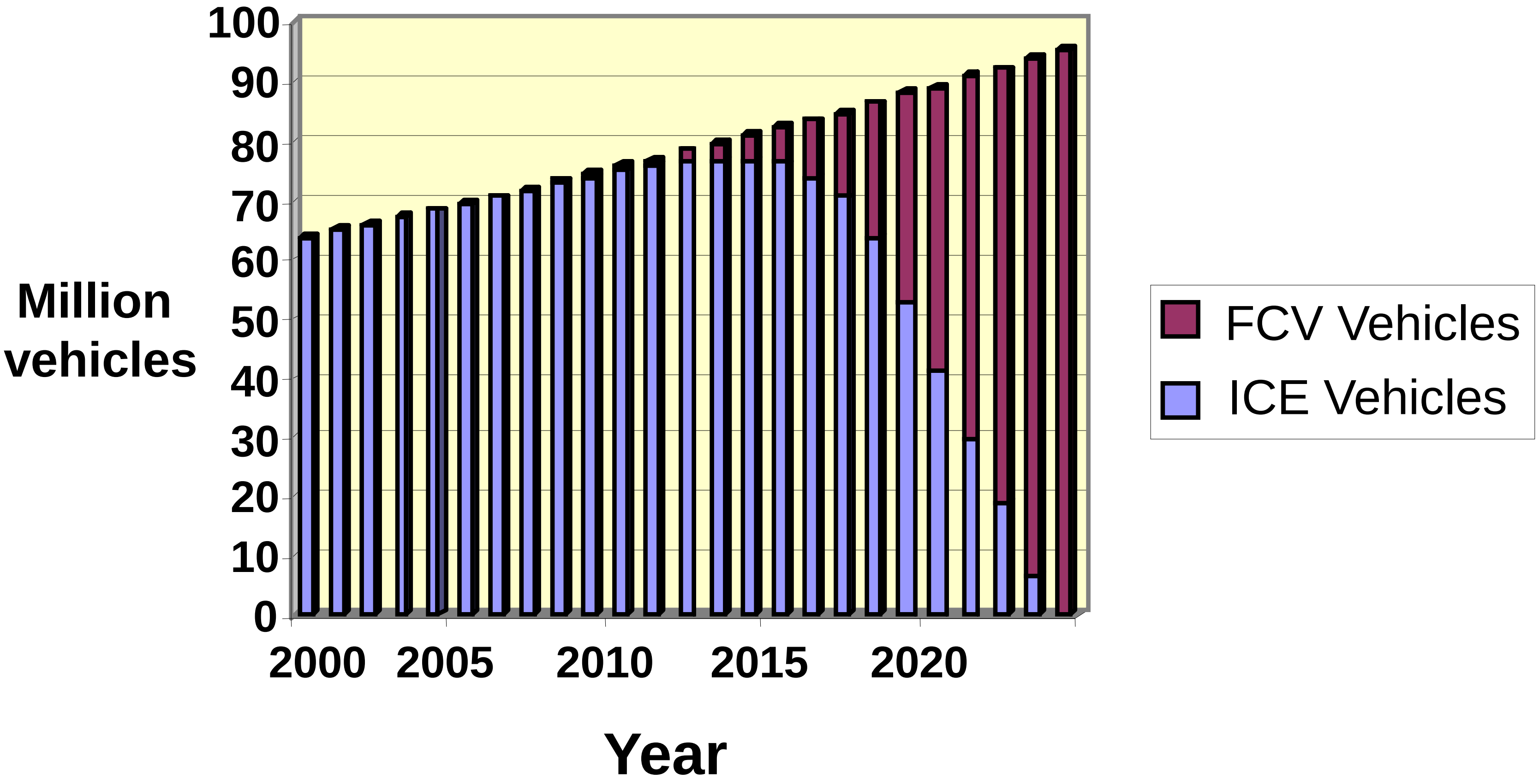
Aluminum-air Fuel Cells

- *Cars*
- *Large-scale Transportation*

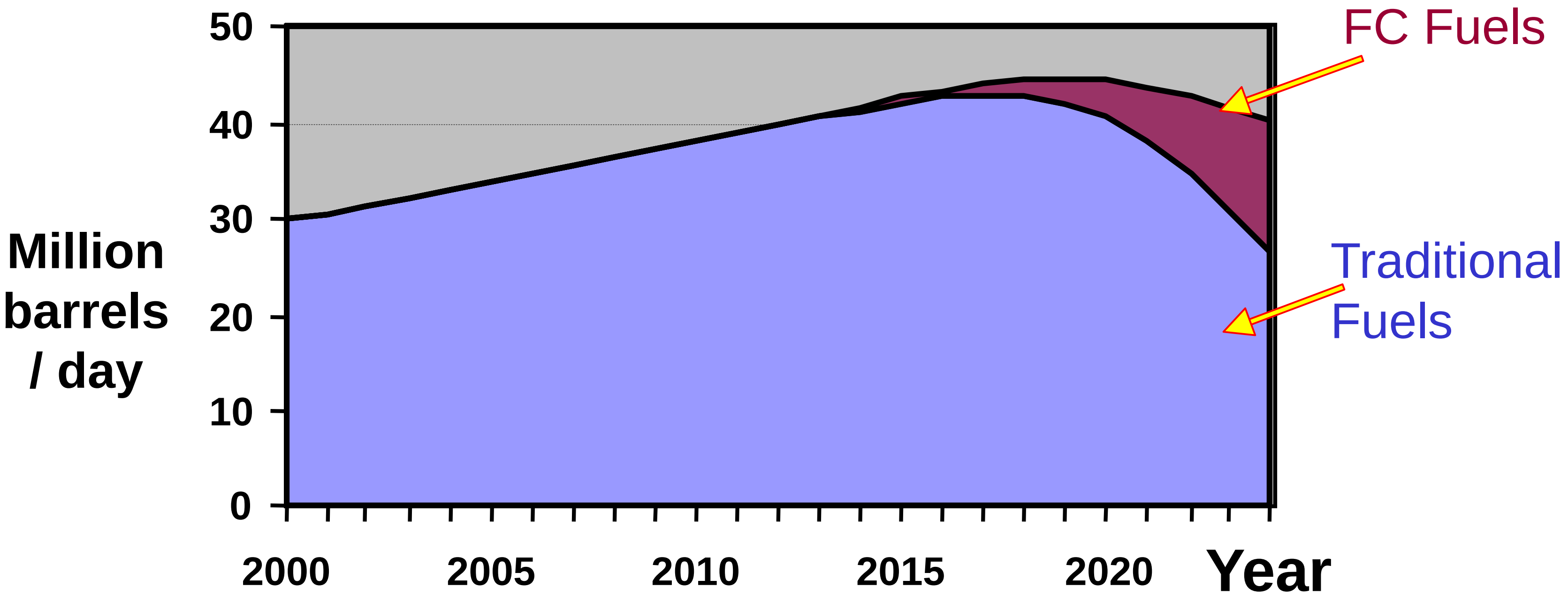
These technologies are challenging to the traditional concept of fuel cells as a part of the hydrogen economy.

Expected Car Production (2000 – 2024).

(More Optimistic market penetration of FCV)



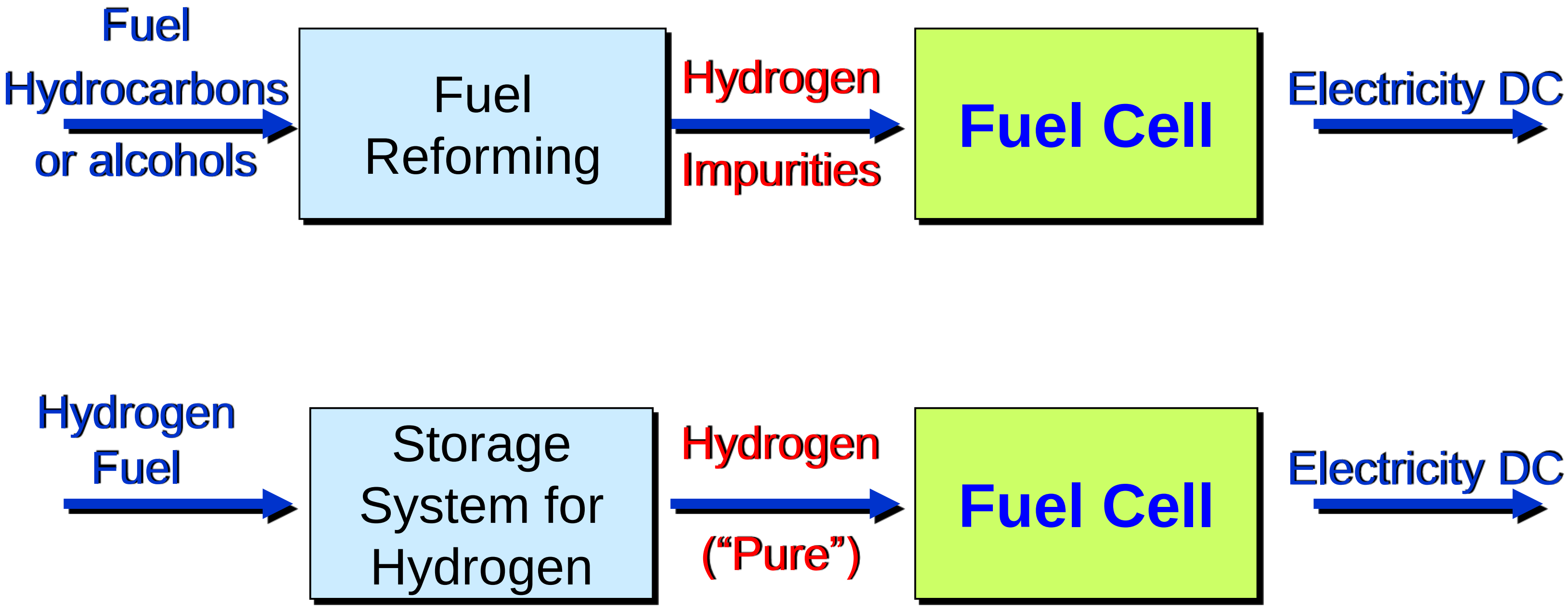
Global Demand of Transport Fuels (more optimistic).



Assumption:

- 2.5% Growing of cars annual sales
- Mean life of vehicles 12 years
- All vehicles are FCV from 2024.

Two Types of H_2 Fuel Systems.

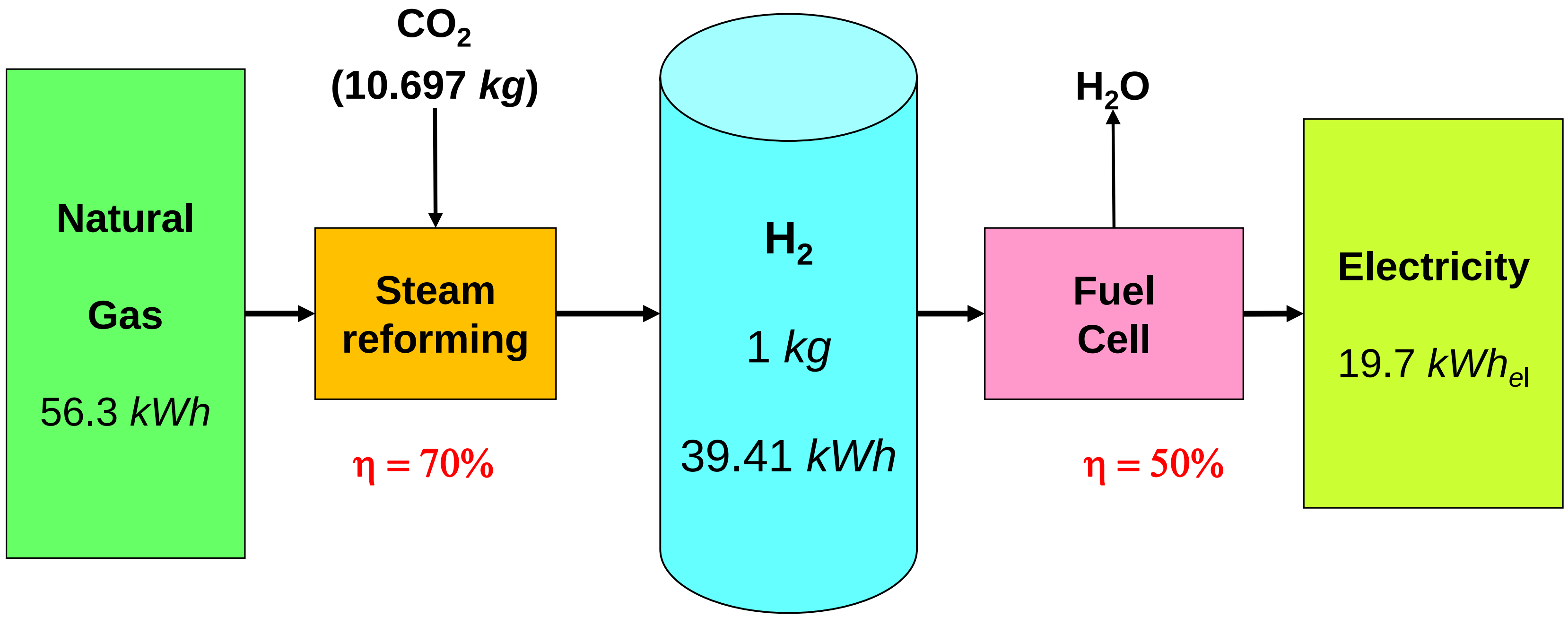


Fuel Hydrocarbons or alcohols → Fuel Reforming → Hydrogen Impurities → **Fuel Cell** → Electricity DC

Hydrogen Fuel → Storage System for Hydrogen → Hydrogen ("Pure") → **Fuel Cell** → Electricity DC

- **Compressed Hydrogen gas**
- **Cryogenic Liquid Hydrogen**
- **Solid Metal Hydrides**
- **Chemical Hydrides in Water**
- **Water**

Natural Gas Steam Reforming.



CO_2

(10.697 *kg*)

Natural

Gas

56.3 *kWh*

Steam reforming

$\eta = 70\%$

H_2

1 *kg*

39.41 *kWh*

H_2O

Fuel Cell

$\eta = 50\%$

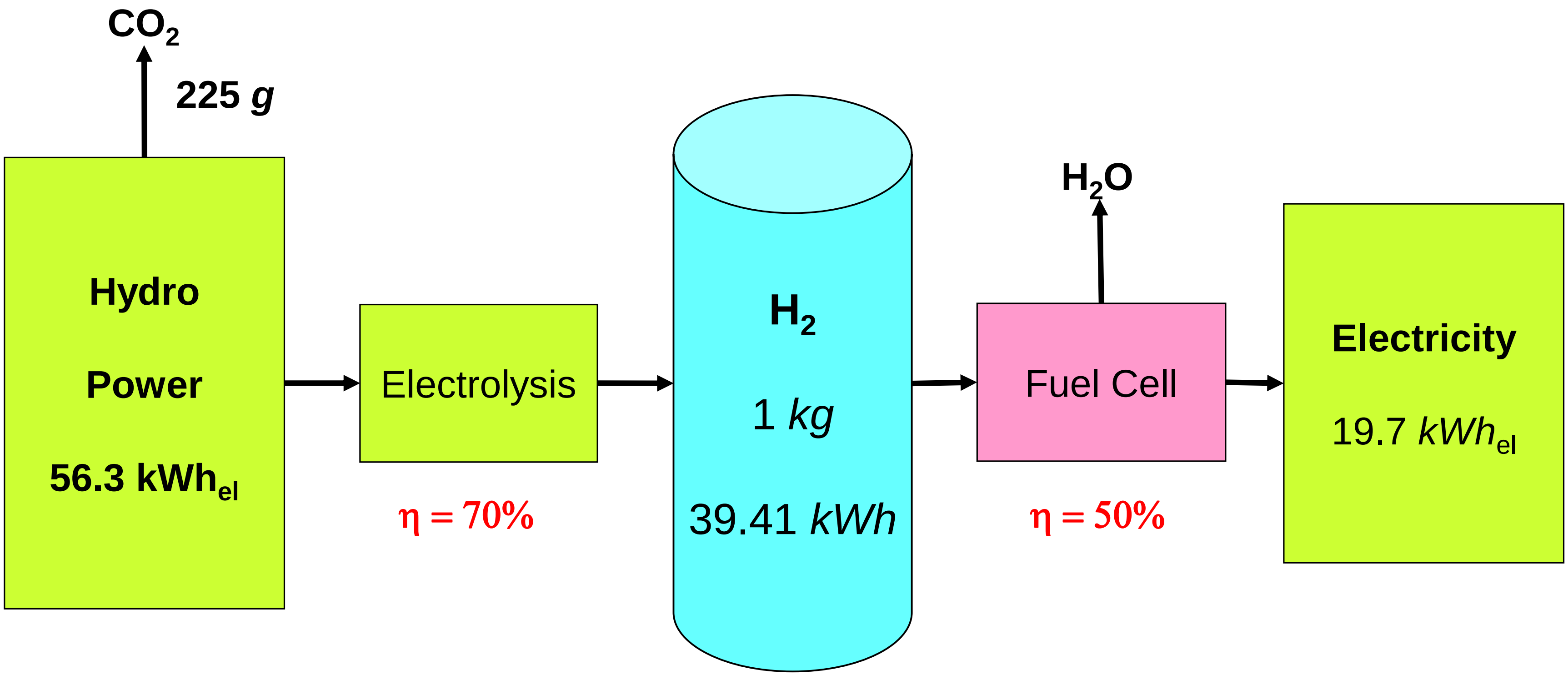
Electricity

19.7 kWh_{el}

Specific emission :

543 $g\ CO_2 / kWh_{el}$

Water Electrolysis with Electric Energy.



CO_2

225 *g*

Hydro

Power

56.3 kWh_{el}

Electrolysis

$\eta = 70\%$

H_2

1 *kg*

39.41 *kWh*

H_2O

Fuel Cell

$\eta = 50\%$

Electricity

19.7 kWh_{el}

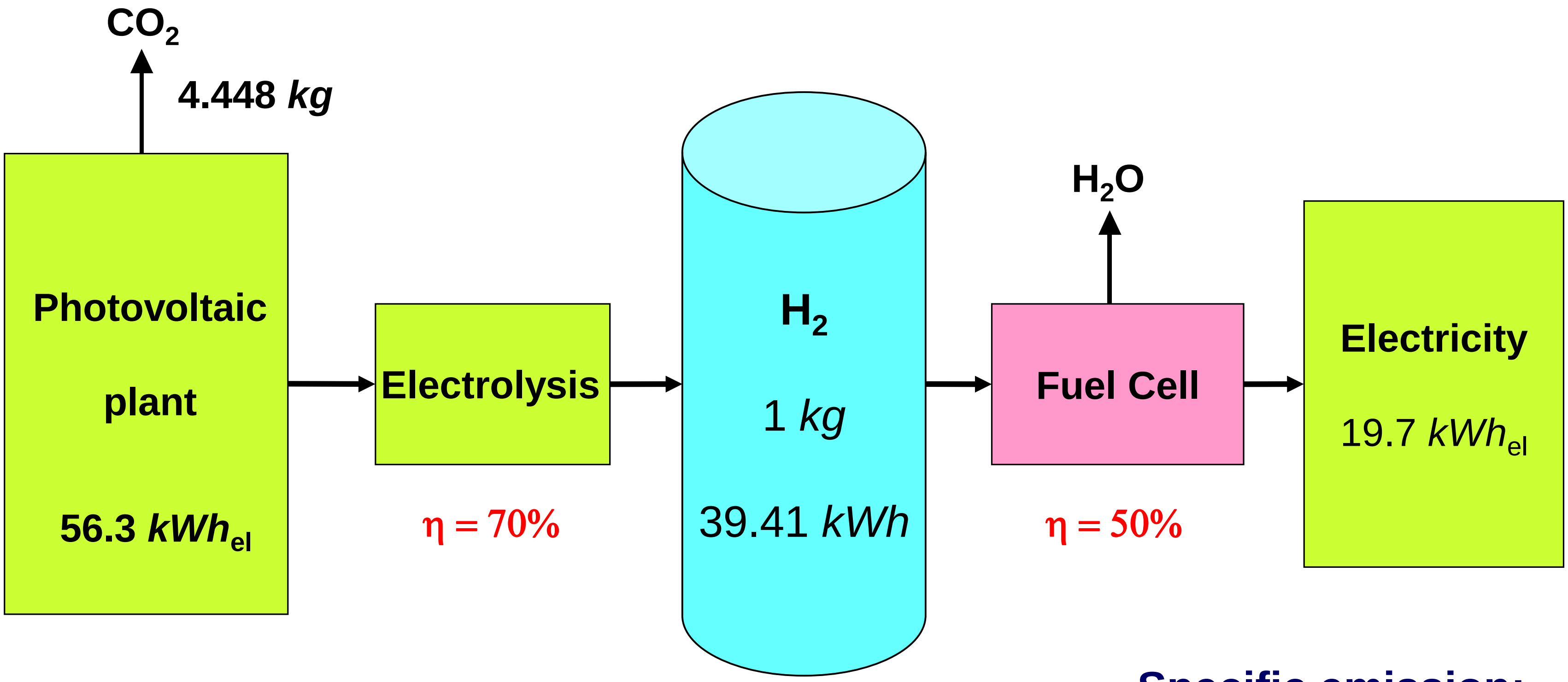
Specific emission :

4 *g* CO_2 / kWh_{el}

Specific emission :

11.4 *g* CO_2 / kWh_{el}

Water Electrolysis with Photovoltaic Electricity.



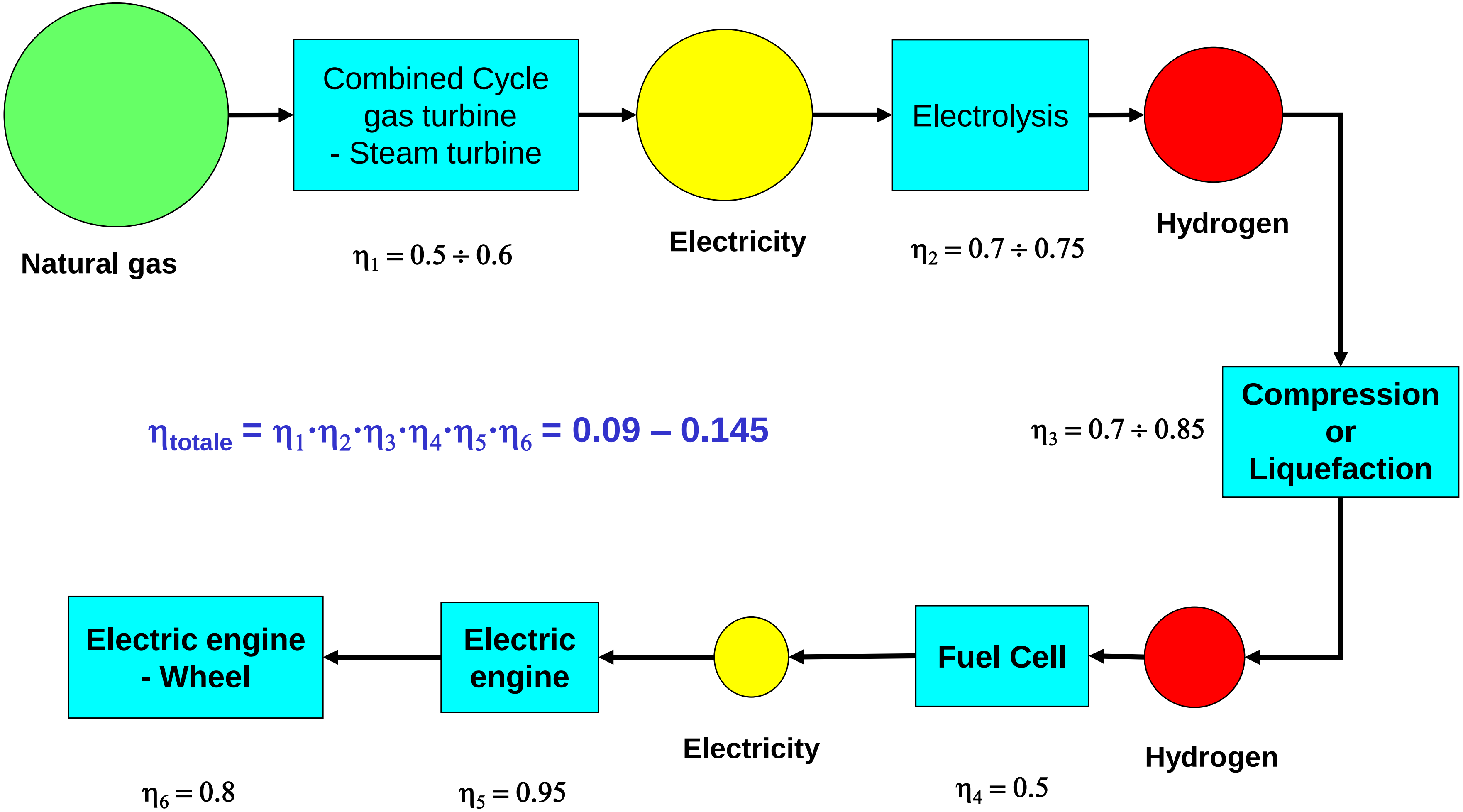
Specific emission:

79 $g\ CO_2 / kWh_{el}$

Specific emission:

225.8 $g\ CO_2 / kWh_{el}$

From Natural Gas to Wheel: (Electrolysis).



Natural gas

Combined Cycle gas turbine - Steam turbine

$\eta_1 = 0.5 \div 0.6$

Electricity

Electrolysis

$\eta_2 = 0.7 \div 0.75$

Hydrogen

Compression or Liquefaction

$\eta_3 = 0.7 \div 0.85$

Hydrogen

Fuel Cell

$\eta_4 = 0.5$

Electricity

Electric engine

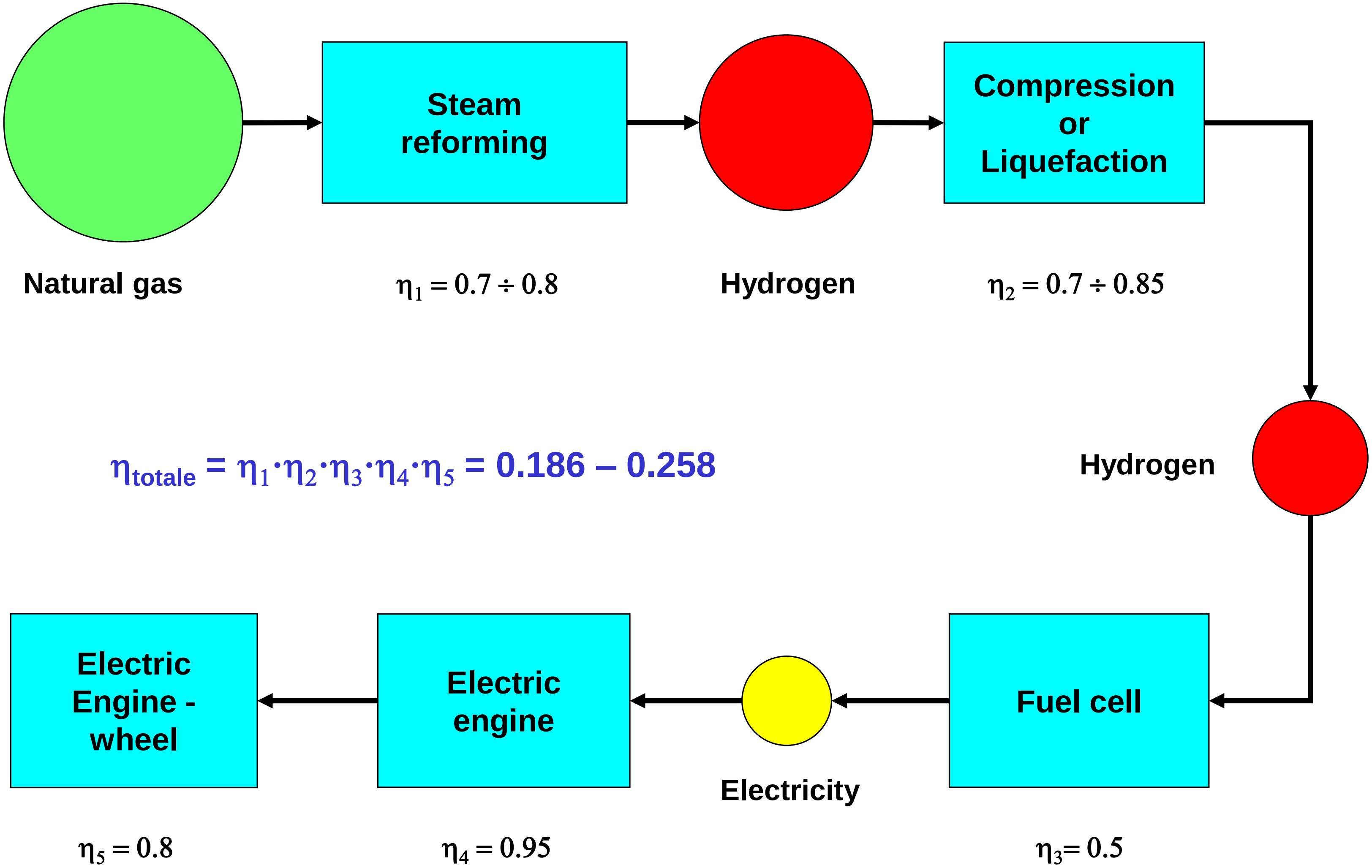
$\eta_5 = 0.95$

Electric engine - Wheel

$\eta_6 = 0.8$

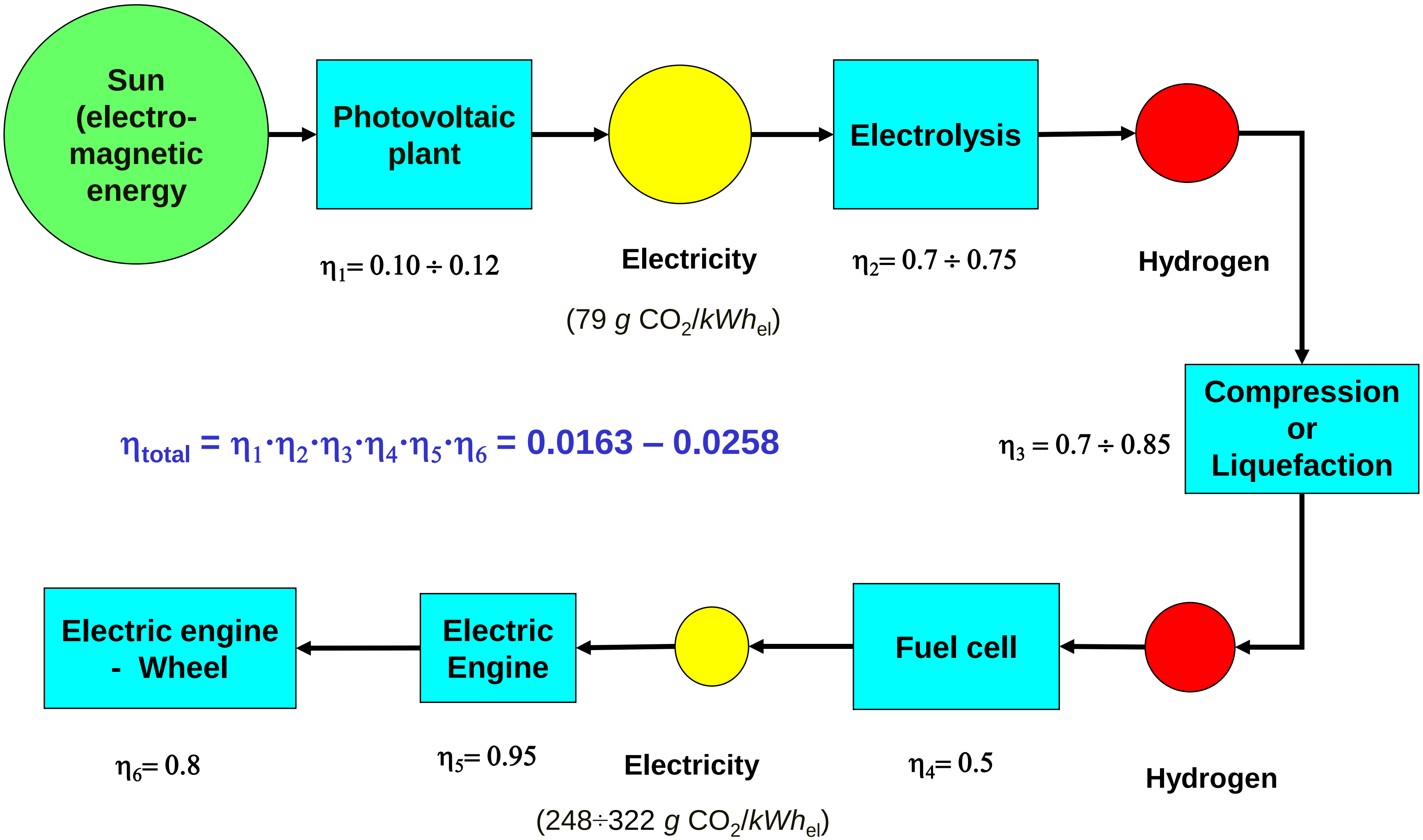
$\eta_{totale} = \eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \eta_4 \cdot \eta_5 \cdot \eta_6 = 0.09 – 0.145$

From Natural Gas to Wheel: (Steam Reforming).



$\eta_{totale} = \eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \eta_4 \cdot \eta_5 = 0.186 - 0.258$

From Solar Energy to Wheel.



Sun (electro-magnetic energy

Photovoltaic plant

$\eta_1 = 0.10 \div 0.12$

Electricity

($79\ g\ CO_2/kWh_{el}$)

Electrolysis

$\eta_2 = 0.7 \div 0.75$

Hydrogen

Compression or Liquefaction

$\eta_3 = 0.7 \div 0.85$

$\eta_{total} = \eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \eta_4 \cdot \eta_5 \cdot \eta_6 = 0.0163 – 0.0258$

Hydrogen

Fuel cell

$\eta_4 = 0.5$

Electricity

($248 \div 322\ g\ CO_2/kWh_{el}$)

Electric Engine

$\eta_5 = 0.95$

Electric engine - Wheel

$\eta_6 = 0.8$

Specific Emissions and Sustainability: Electric Energy Production.

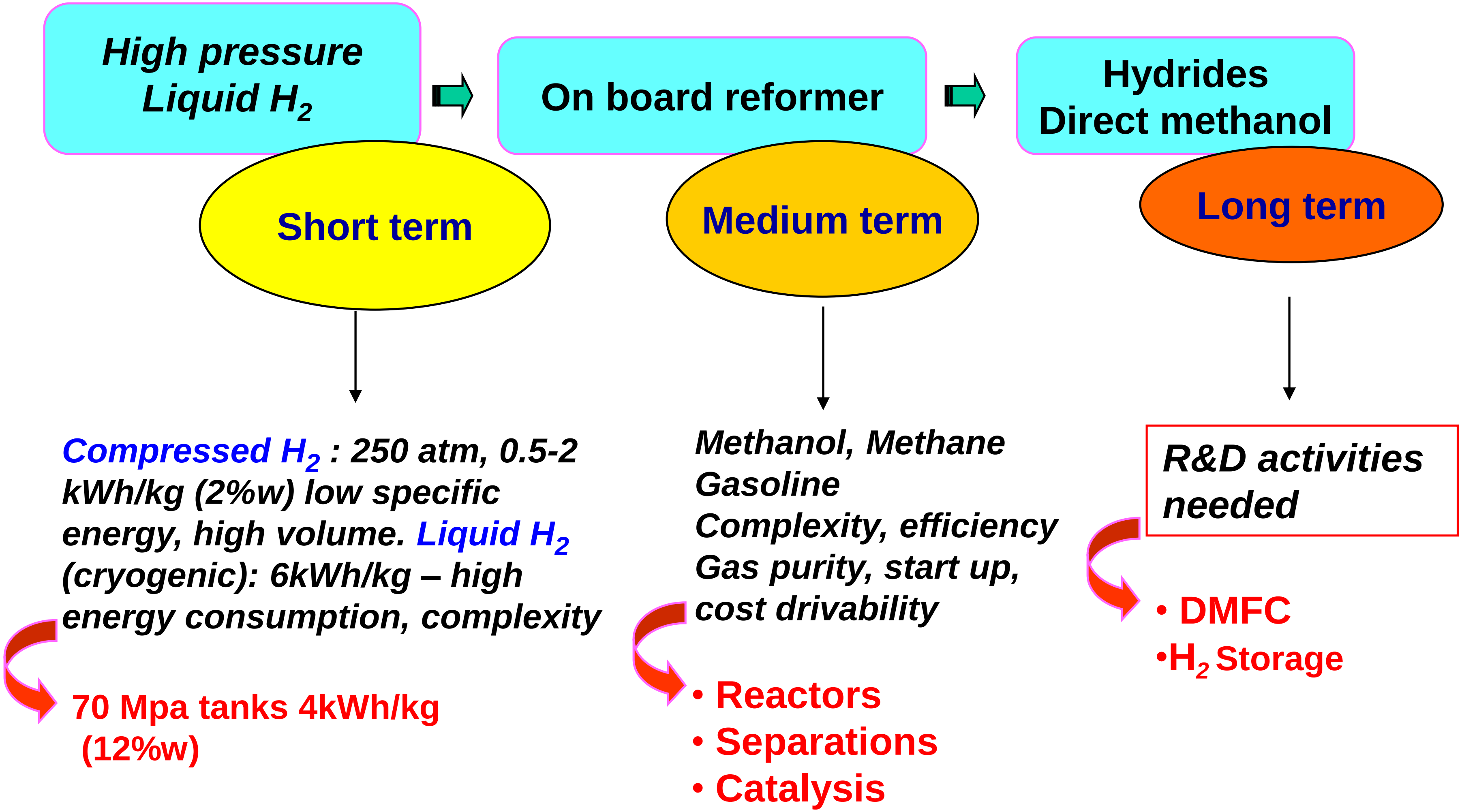
Emissions and sustainability Technology	Specific Emission $[gCO_2/kWh_{el}]$	Sustainable development		
		ecological aspect	economic aspect	social aspect
COAL - combustion, Carnot cycle (η = 40%) - reforming, compressed H_2, fuel cell - combustion, electrolysis, compressed H_2, fuel cell	826 1100 2200	- - - - - - - - -	+ + + + -	- - -
METHANE - combustion, combined cycle - reforming, compressed H_2, fuel cell - combustion, electrolysis, compressed H_2, fuel cell	317 633 760	- - - - -	+ + + + -	+ + +
HYDRO POWER - Electricity Production - Electrolysis, compressed H_2, fuel cell	4 13	+ + + + + + +	+ + + +	+ + +
NUCLEAR ENERGY - Electricity Production - Electrolysis, compressed H_2, fuel cell	8 27	+ + +	+ + + +	+ +
PHOTOVOLTAIC ENERGY - Electricity Production - Electrolysis, compressed H_2, fuel cell	79 263	+ + + -	- - - - - - -	+ + +
EOLIC ENERGY - Electricity Production - Electrolysis, compressed H_2, fuel cell	36 120	+ + +	- - -	+ + +

On-Board Hydrogen Storage Challenge.

- The low volumetric density of gaseous fuels requires a storage method which densifies the fuel.
  - This is particularly true for hydrogen because of its lower energy density relative to hydrocarbon fuels
  - 3 *MJ/L* (5000 *psi* H_2), 8 *MJ/L* (LH_2) vs. 32 *MJ/L* (gasoline)
- Storing enough hydrogen on vehicles to achieve greater than 300 miles driving range is difficult.
- Storage system adds an additional weight and volume above that of the fuel.

How do we achieve adequate stored energy in an efficient, safe and cost-effective system?

Factors Affecting FCV Development.



High pressure
Liquid H_2

On board reformer

Hydrides
Direct methanol

Short term

Medium term

Long term

Compressed H_2 : 250 atm, 0.5-2 kWh/kg (2%w) low specific energy, high volume. Liquid H_2 (cryogenic): 6kWh/kg – high energy consumption, complexity

70 Mpa tanks 4kWh/kg (12%w)

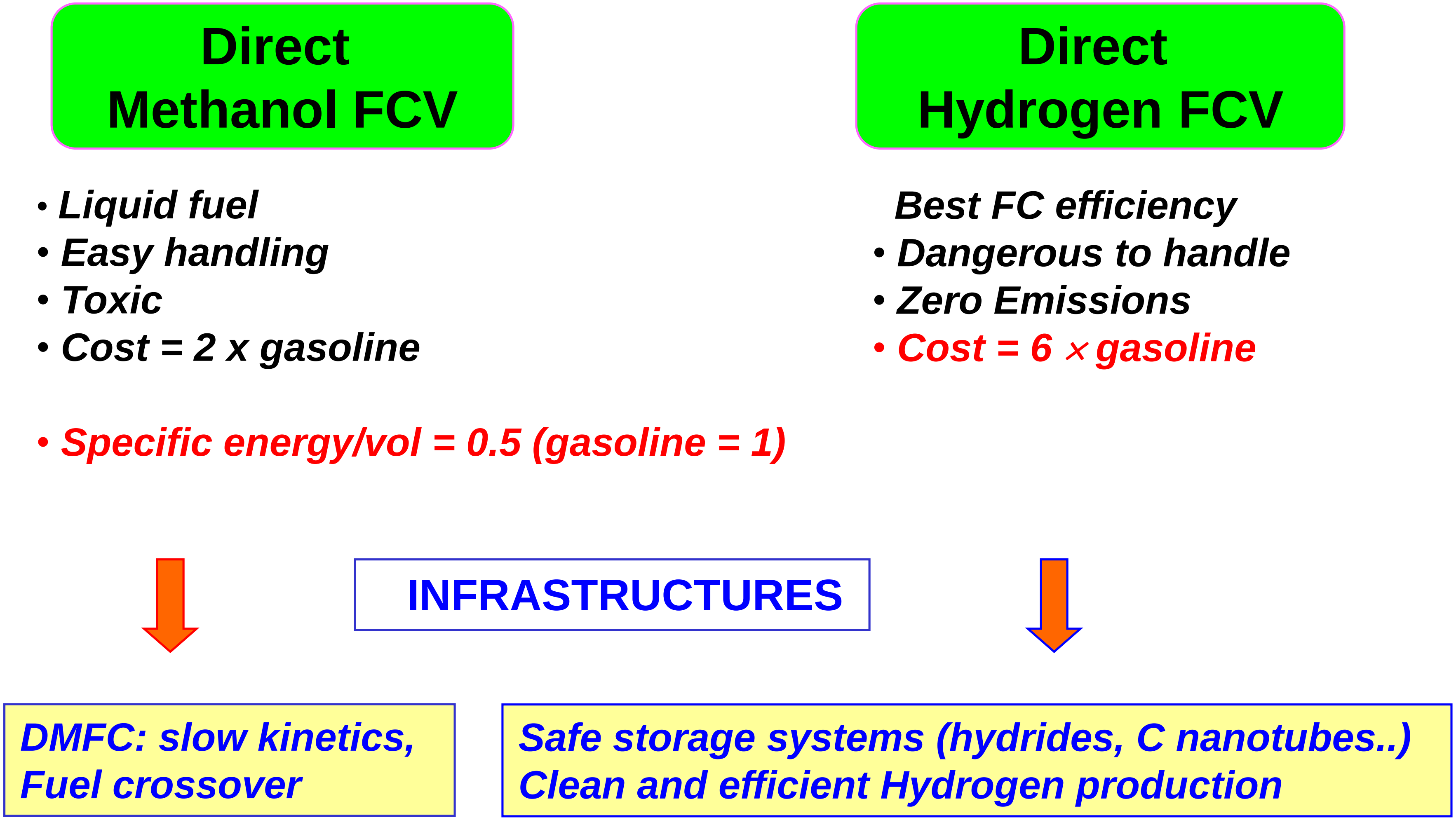
Methanol, Methane
Gasoline
Complexity, efficiency
Gas purity, start up, cost drivability

- Reactors
- Separations
- Catalysis

R&D activities needed

- DMFC
- H_2 Storage

Critical Issues for Next Generation DFCV.



Direct Methanol FCV

- *Liquid fuel*
- *Easy handling*
- *Toxic*
- *Cost = 2 x gasoline*

Direct Hydrogen FCV

Best FC efficiency
- *Dangerous to handle*
- *Zero Emissions*
- *Cost = 6 × gasoline*

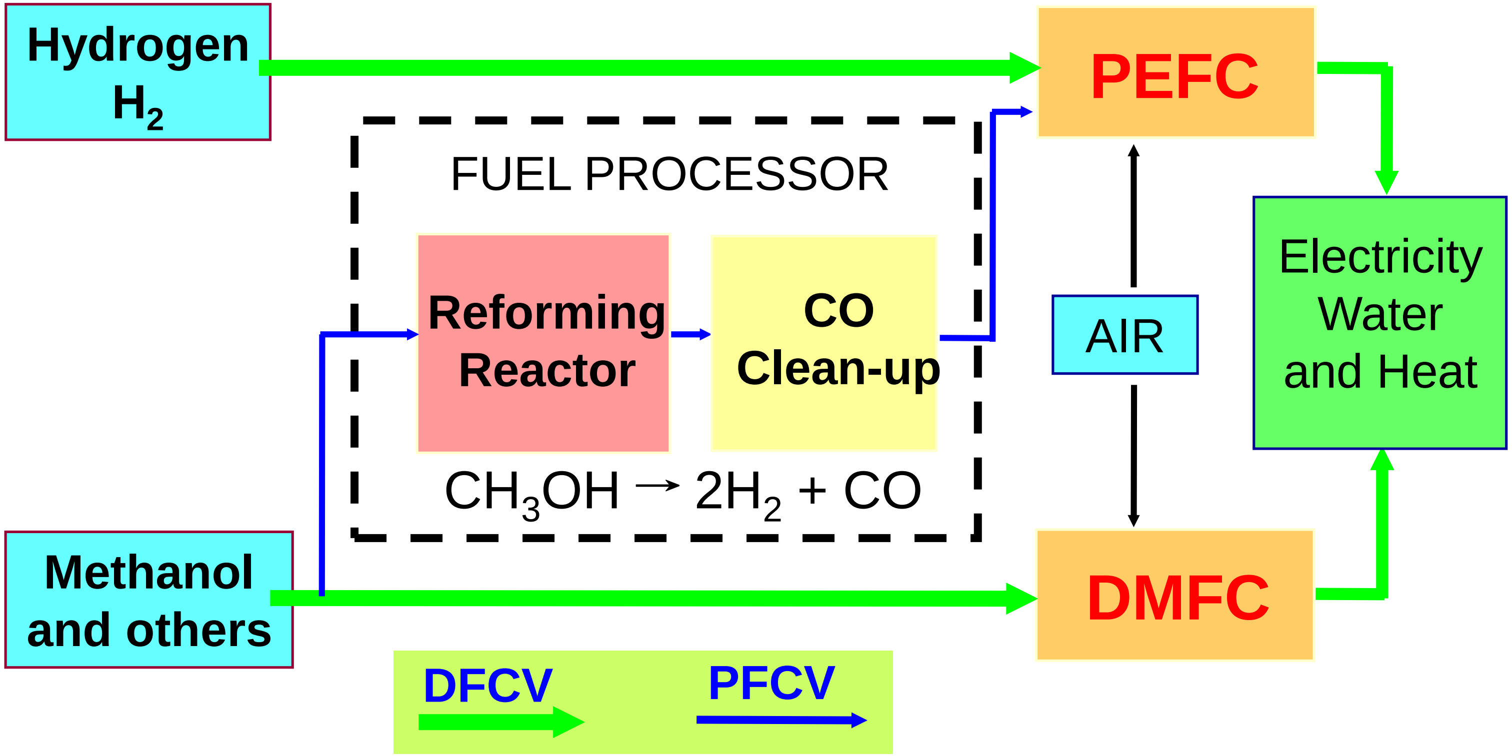
- *Specific energy/vol = 0.5 (gasoline = 1)*

INFRASTRUCTURES

DMFC: slow kinetics,
Fuel crossover

Safe storage systems (hydrides, C nanotubes..)
Clean and efficient Hydrogen production

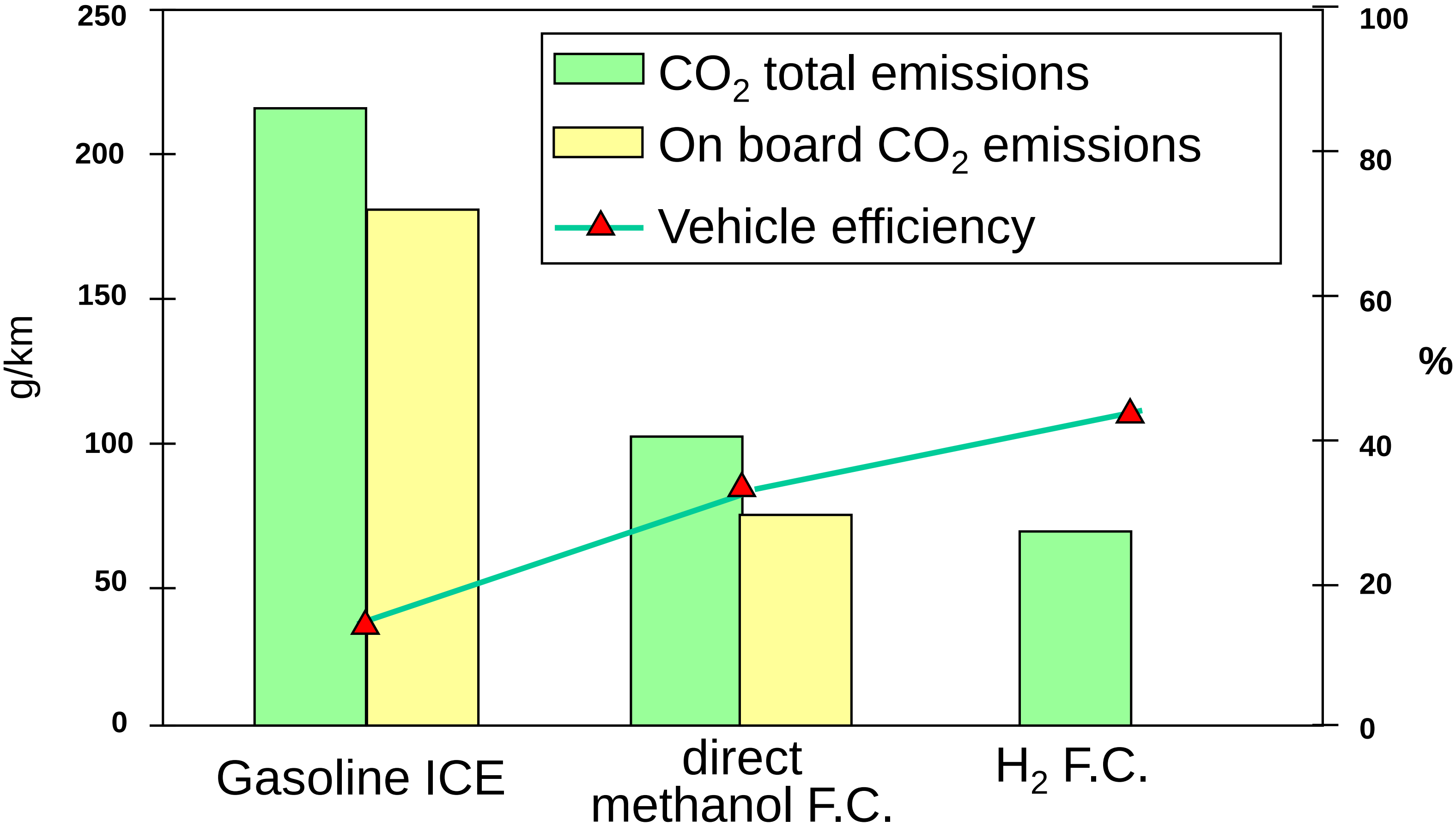
Schemes for Fuel Cells Vehicles.



DFCV = Direct Fuel Cell Vehicle

PFCV = Processed Fuel Cell Vehicle

CO_2 Emissions and DFCV Efficiency.

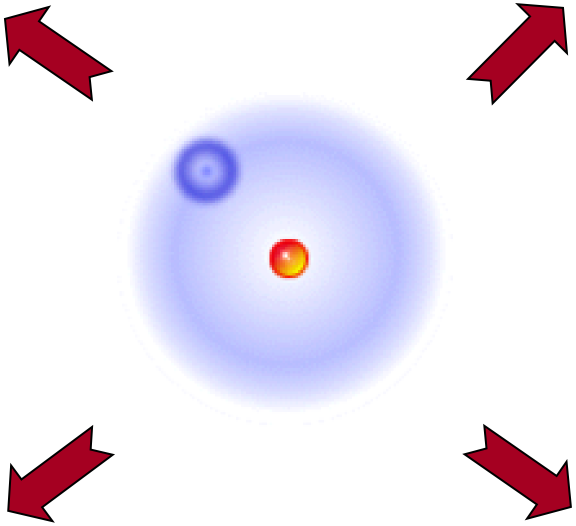


G. Cacciola et al. *J. of Power Sources* 100, 67 (2001)

Hydrogen Storage Technical Barriers: General.

- **Weight and Volume**. The weight and volume of hydrogen on-board storage systems are presently too high, resulting in inadequate vehicle range compared to conventional petroleum fueled vehicles.
- **Efficiency.** Energy efficiency is a challenge for all hydrogen storage approaches.
- **Durability**. Durability of hydrogen storage systems is inadequate. Materials and components are needed that allow hydrogen storage systems with a lifetime of 1500 cycles
- **Refueling Time**. Refueling times are too long.
- **Safety, Codes & Standards**. Standardized hardware and operating procedures, applicable codes and standards, and ensuring that storage systems meet safety requirements and crash-worthiness, are required
- **Life Cycle, Environmental Impact, and Efficiency Analyses**. There is a lack of analyses of the full life-cycle cost, environmental impact, and efficiency for hydrogen storage systems.
- **Cost**. The cost of hydrogen storage system is too high.

Options in Hydrogen Storage.



Pressurized gas

Condensed
liquid state
(20K)

**Hydrogen
storage
technologies**

Metal hydrides
(irreversible decomposition with water or chemo-adsorption at high temperature)

Covalent
nanostructures
(physic-adsorption at low temperature)

H_2 Storage: FCV Requirements.

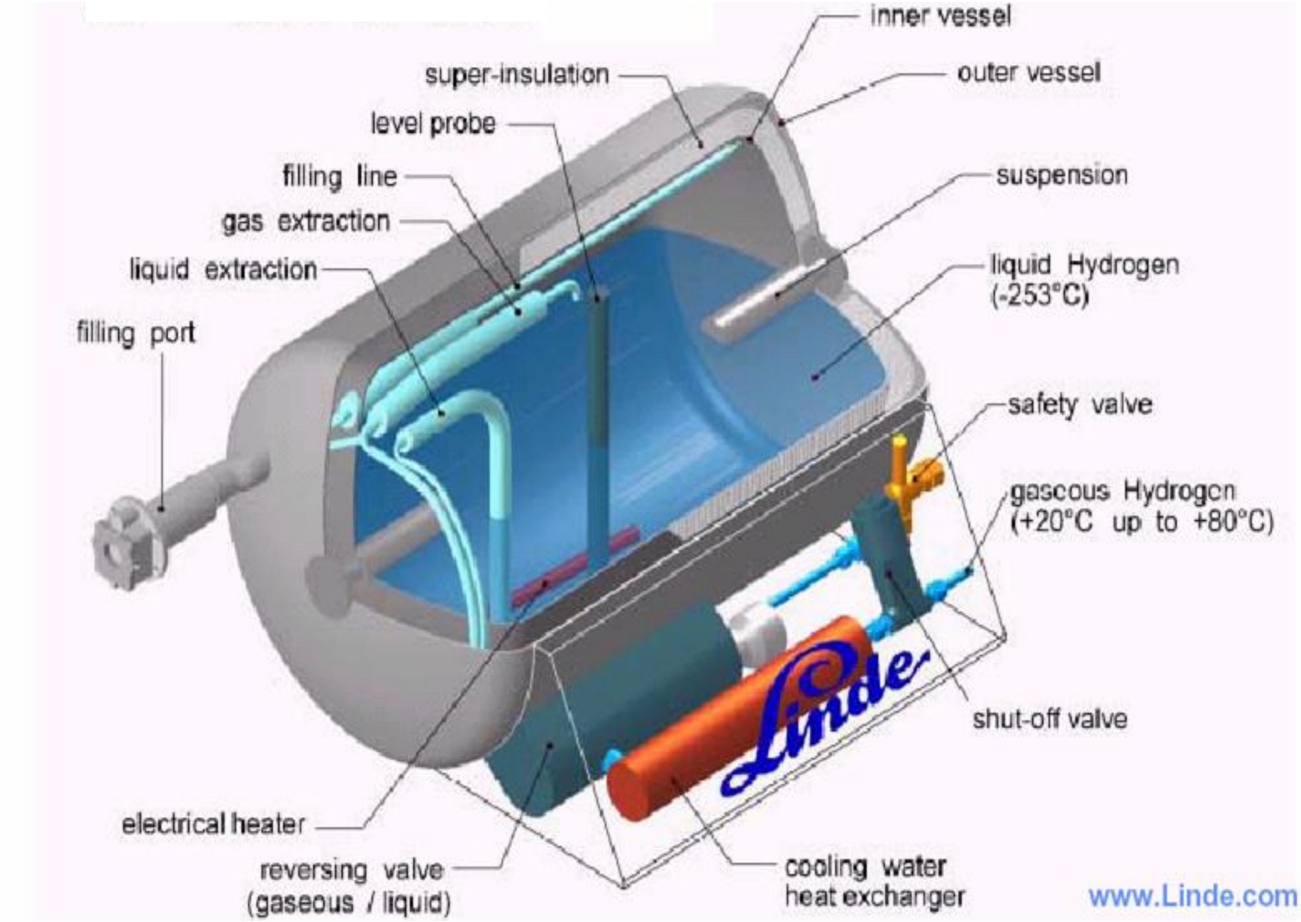
100 *kg* fuel tank – range 500 *km*

Hydrogen capacity: 5 *kg*	(DOE 6.5% wH_2)
Peak consumption: ~1-3 *g/s*	(DOE 1.8% wH_2/*h*)
Reversibility: > 1000cycles	(DOE at least 5000 cycles)
Density:	(DOE 62 *kg* H_2/m^3)
Cost ?	

Wide Range of Hydrogen Storage Materials.

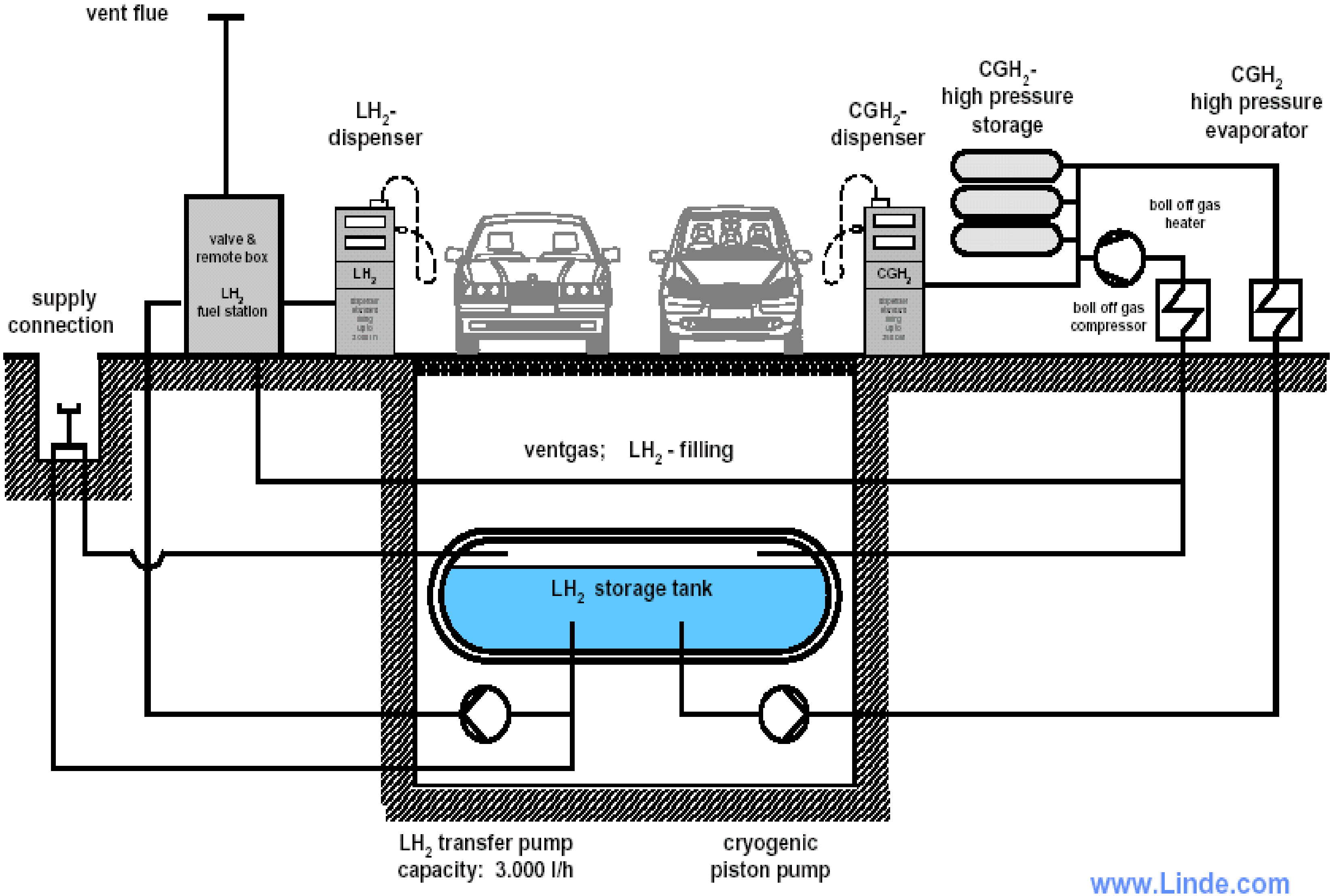
- metal hydrides
- complex hydrides
- chemical hydrides
- Carbohydrates
- Clathrates
- inorganic nanotutes
- organic materials
- MOFs
- carbon materials
- Liquid density 70.8 kg/m^3 $^{\text{at}}$ NTP.

Liquid Hydrogen Storage Tank.



- Liquefying H_2 requires substantial energy
- Boil-off is an issue for non-pressurized insulated tanks

Refueling System with Liquid H_2.



www.Linde.com

Hydrogen Storage with Hydrides (Physisorption Methods).

on board reversible hydrides

- (interstitial, covalent metal hydrides, amides and borohydrides

off board regenerable hydrides

- (hydrocarbons, ammonia borane, alane)

- The highest 99.5 mg/g at 56 bar and 77 K and 164 mg/g at 77K 70 bar (176 mg /g highest reported so far).
- symbolic many metal framework of Zn(II), Cu(II) Mn(III), Cr(III),La(III).

Materials with High Formula Weight for Hydrogen.

Formula	Formula wt.% Hydrogen
CH_4	25
H_3BNH_3	19.5
$LiBH_4$	18.3
$(CH_3)_4NBH_4$	18
NH_3	17.7
$Al(BH_4)_3$	16.8
$Mg(BH_4)_2$	14.8
LiH	12.6
CH_3OH	12.5
H_2O	11.2
$LiAlH_4$	10.6
$NaBH_4$	10.6
AlH_3	10.0
MgH_2	7.6
$NaAlH_4$	7.4

Irreversible Chemical Hydrides - Hydrogen Generation by Sodium Borohydride.

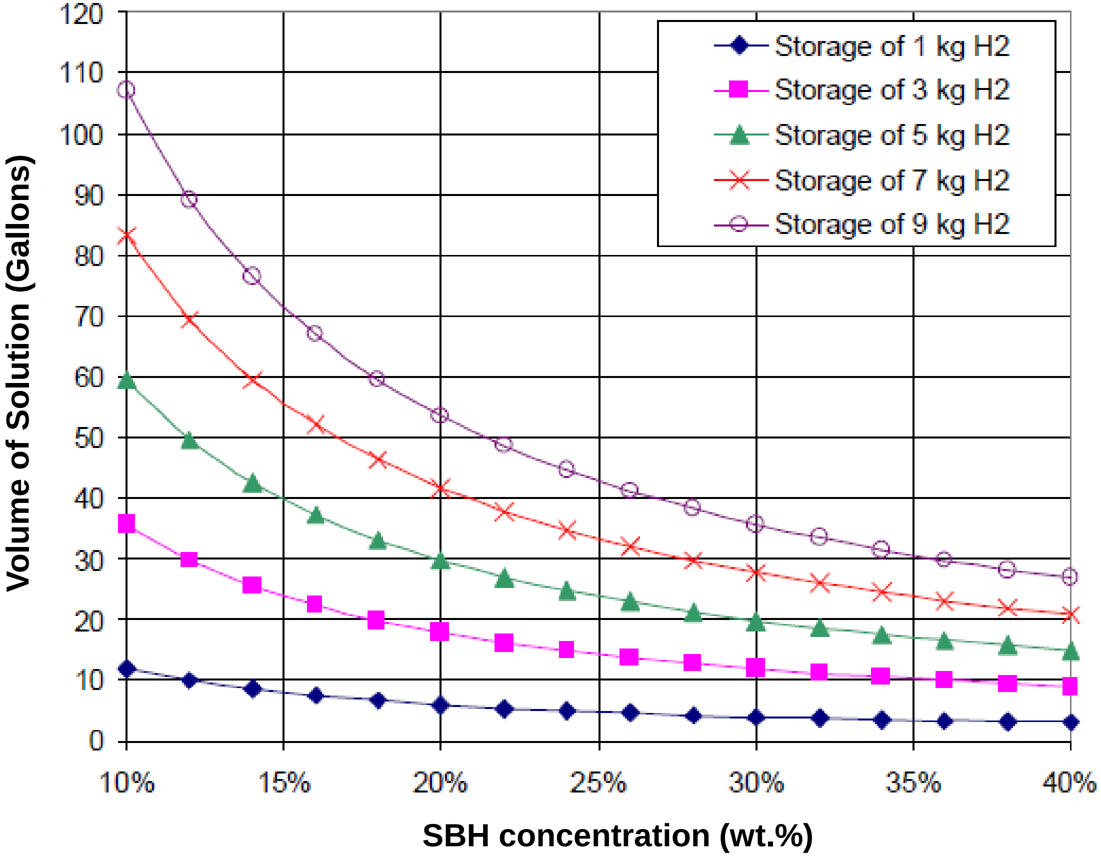
On board Hydrogen Generation System:

$$\underbrace{NaBH_4 \quad + \quad 2\,H_2O}_{\substack{\text{Water based fuel} \\ \text{(20-35\% sol.} \\ \text{stabilized with} \\ \text{1-3\% NaOH)}}} \quad \underbrace{\rightarrow}_{\substack{\text{Catalyst induces} \\ \text{rapid } H_2 \\ \text{production}}} \quad \underbrace{NaBO_2}_{\substack{\text{Borate remains} \\ \text{dissolved in water} \\ \text{(can be recycled)}}} \quad \underbrace{+\ 4\,H_2}_{\substack{\text{Humid pure } H_2 \\ \text{is send to the} \\ \text{fuel cell}}} \ + \ \overset{\substack{\text{Exothermic} \\ \text{reaction}}}{218\ kJ\cdot mol^{-1}}$$

- Exothermic and irreversible reaction: dehydrogenation kinetics are fast.
- The starting solution is liquid at room temperature and pressure.
- Hydrogen capacity is high at around 10% hydrogen (100% purity with 100% relative humidity, no CO, S present).
- Sodium borate solution is “ecologically acceptable” but regeneration costs are a major issue.

Volumetric Storage Efficiency.

Volume of SBH Fuel Solution Required To Store Varying Amounts of Hydrogen



Volumetric storage efficiency of 30 wt.% fuel = ~63 g H_2/L

For comparison:

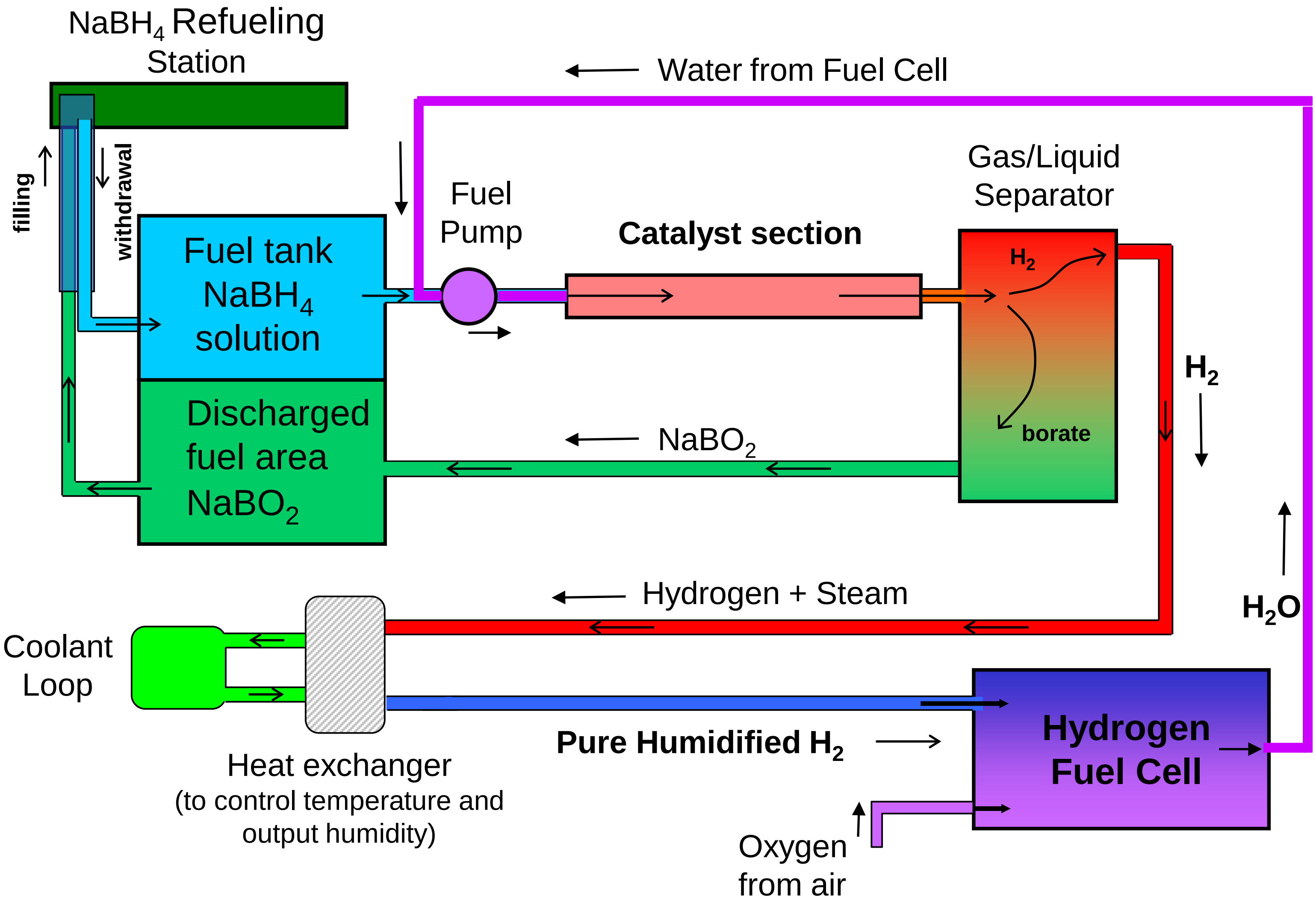
Liquid H_2 = ~71 g H_2/L

5,000 psi compressed = ~23 g H_2/L

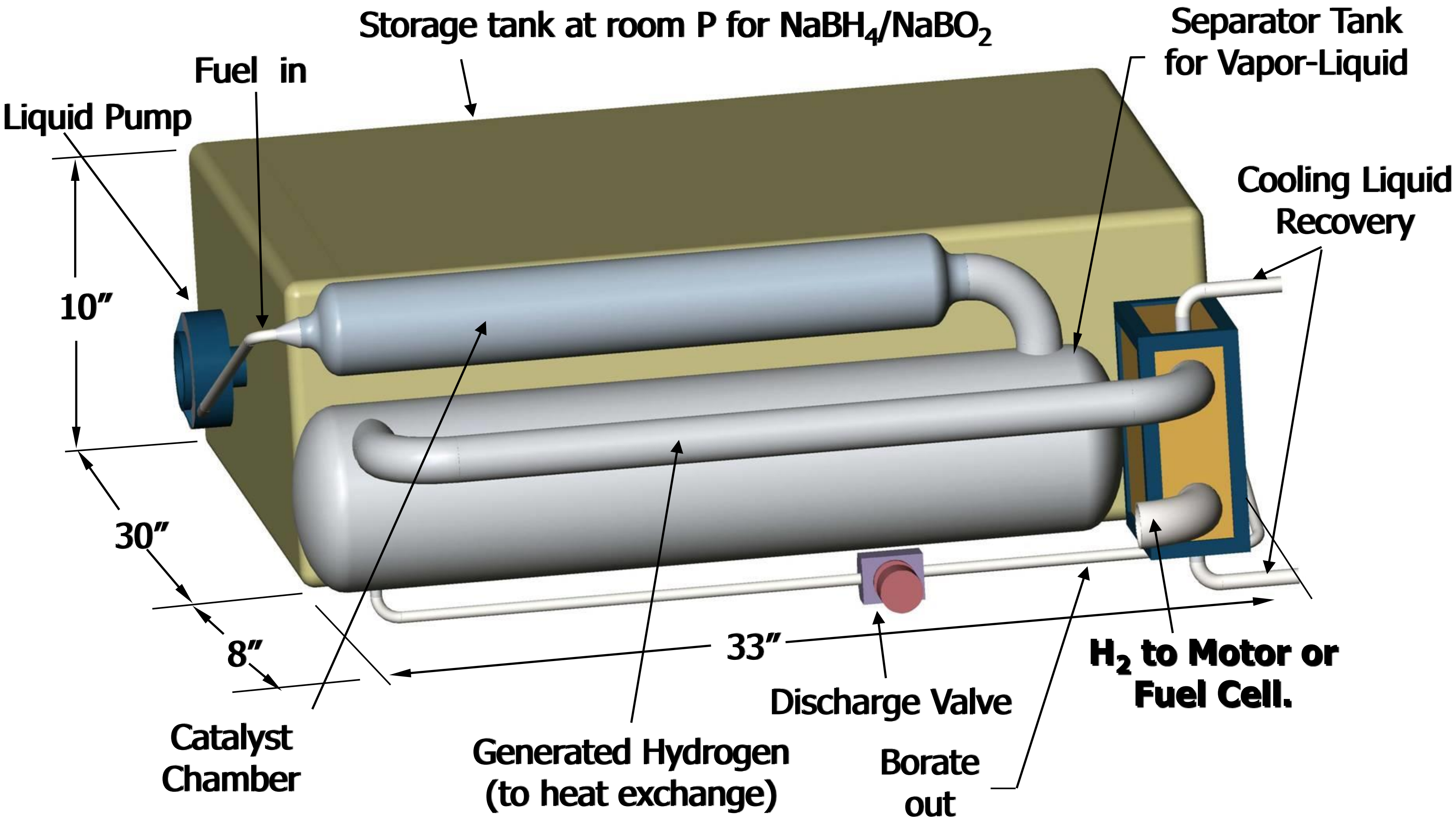
10,000 psi compressed = ~39 g H_2/L

For a practical system, Balance of Plant is key.

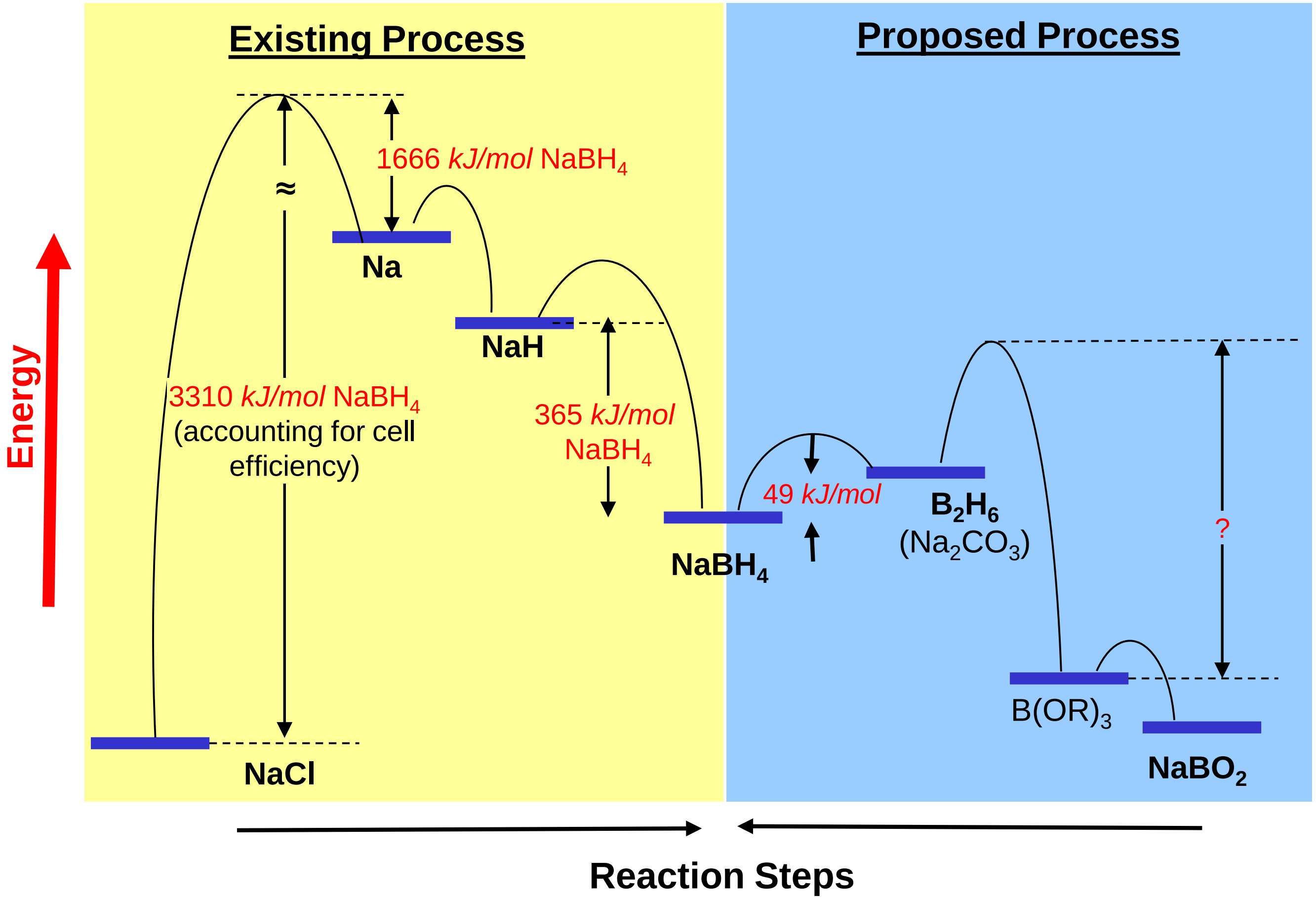
Chemical Hydride Fuel Cycle.



Hydrogen Generation System from $NaBH_4$.



Can B_2H_6 be better than NaH as an Intermediate?



- Production of Na is < 50% energy efficient
- Further energy losses to convert Na to $NaBH_4$

- Utilize alternative intermediate B_2H_6.
- Need appropriate energy input to efficiently produce B_2H_6.

Cost Reduction of Borohydride.

- **Now, $NaBH_4$ is available, but is expensive**
  - Product mainly used for the synthesis of specialty chemicals
  - Available at about € 63/*kg* of H_2
  - Manufactured at a scale not sufficient per energetic uses

- **New process technology could make the compound competitive with gasoline if**:
  - Big plants of 2,500 tons $NaBH_4$/day
  - Serve 900,000 vehicles with fuel cells
  - Produce fuel equivalent to € 2.34/*kg* H_2
  - Total installed costs below 200 million €

Safe Hydrogen Storage.

Hydrides*

- *AB_5*
- *AB_2*
- *AB*
- *A_2B*
- *Complex compounds*
- *Mg Alloys*
- *Mix. other Intermetallic compounds*
- *Solid Solution Alloys*

Already in the market but optimization of properties is required.

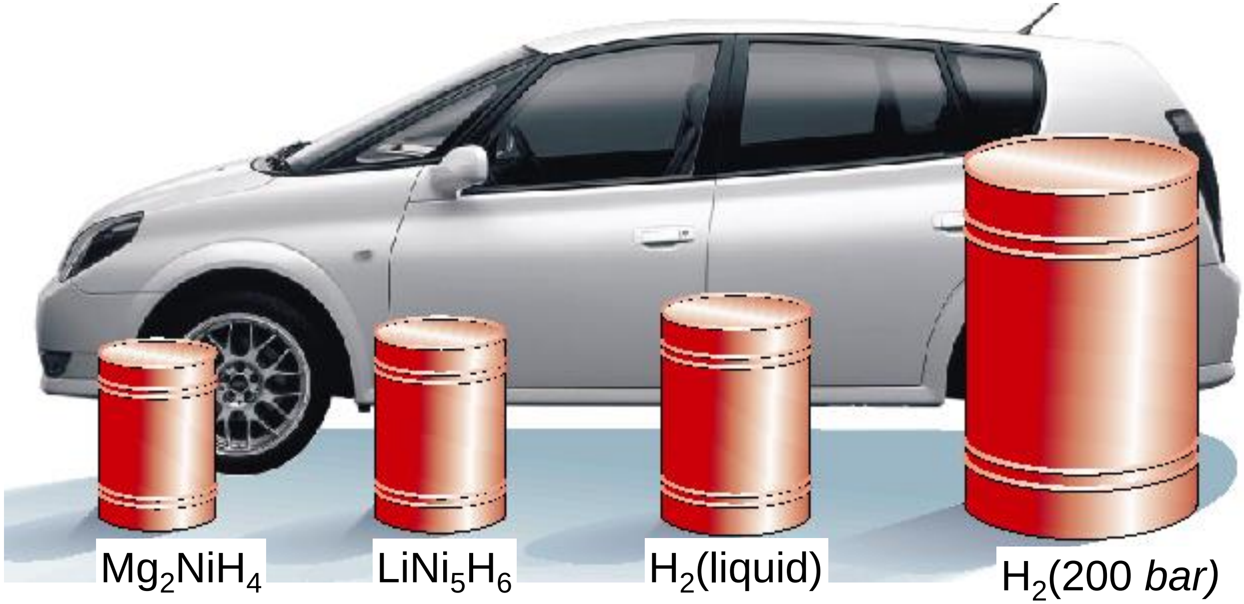
Carbon Nanostructure

- ***graphite nanofibers***
- ***fullerenes***
- ***nanotubes***
- ***activated carbons***

Challenging scientific research
Need for a breakthrough
Still at research level.

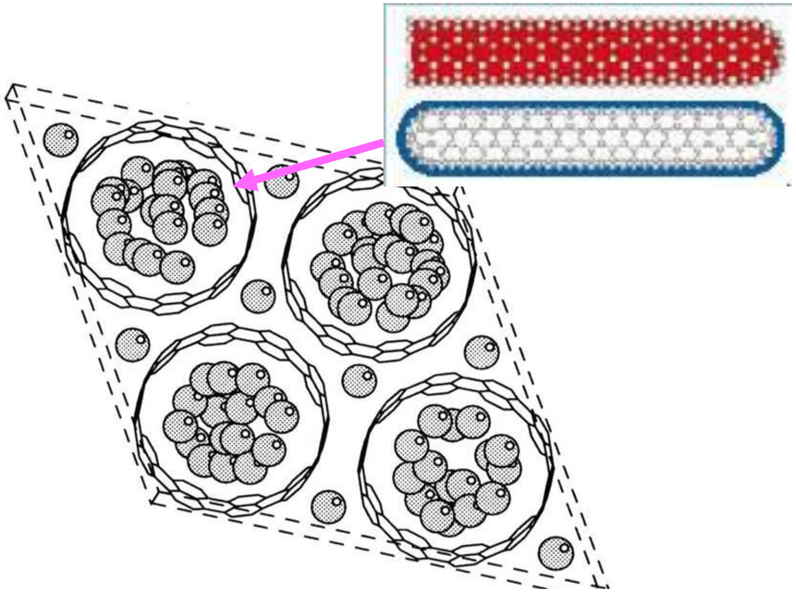
* http://146.246.239.9:591/AB5List.html

Volume Comparison for4 Kg Vehicular Hydrogen Storage.

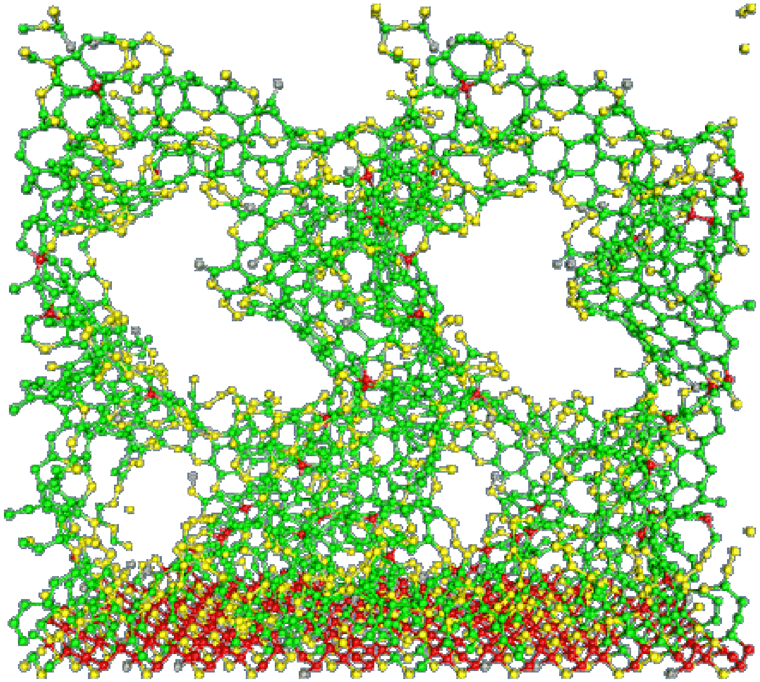


Volume of 4 kg of H_2 compacted in different ways, with relative size to the size of a car. At ambient PT, H_2 displays a volume of 45 m^3, equivalent to a ball with 5 m of diameter — unpractical.

Carbon Nanostructures.

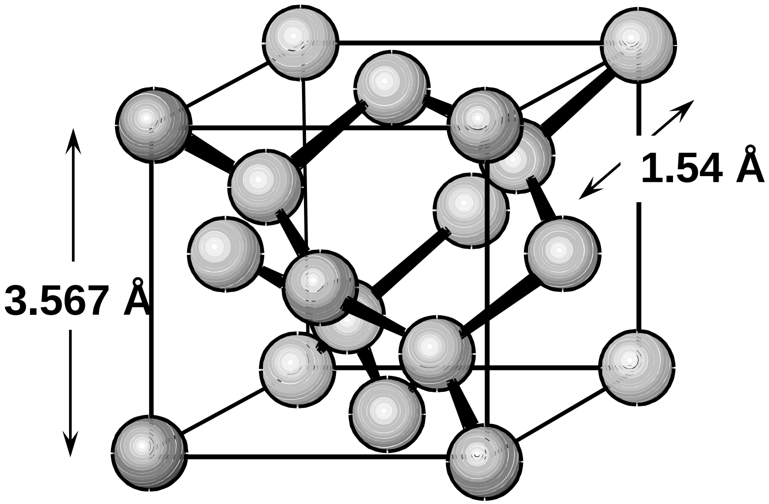


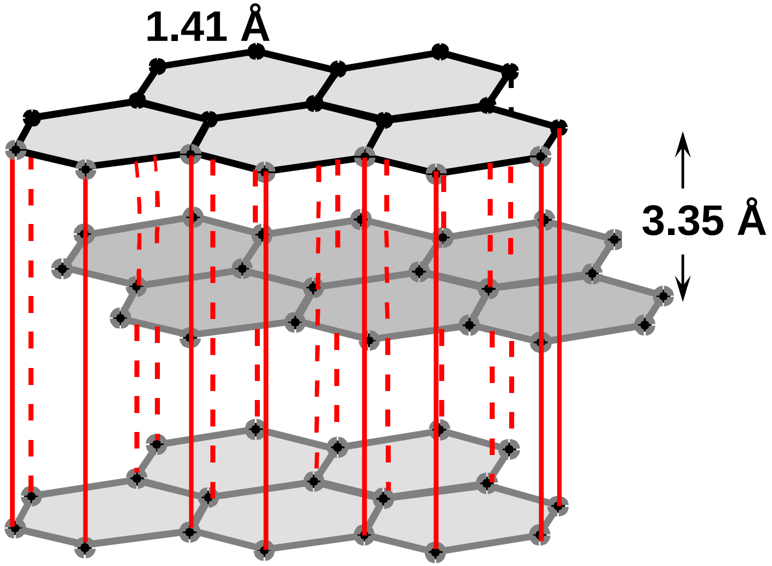
Typical arrangement of H_2 molecules adsorbed on triangularly packed carbon nanotubes.



- **Reversibly stored H is physic-adsorbed upon C-graphitic structures.**
- **Chemisorption can occur upon defects or included metallic particles.**

Allotropic Forms of Carbon.





	Diamond ($\Delta H°_f$ = 1.90 *kJ·mol*$^{-1}$)	**Graphite** [ABAB]
density/g·cm^{-1}	3.5	2.23 – 1.48 (2.27 ideal)
hardness	10	< 1
m.p. /°C	4100	4100

sp^3 hybridized C (angle 109°)
hard, insulating, transparent

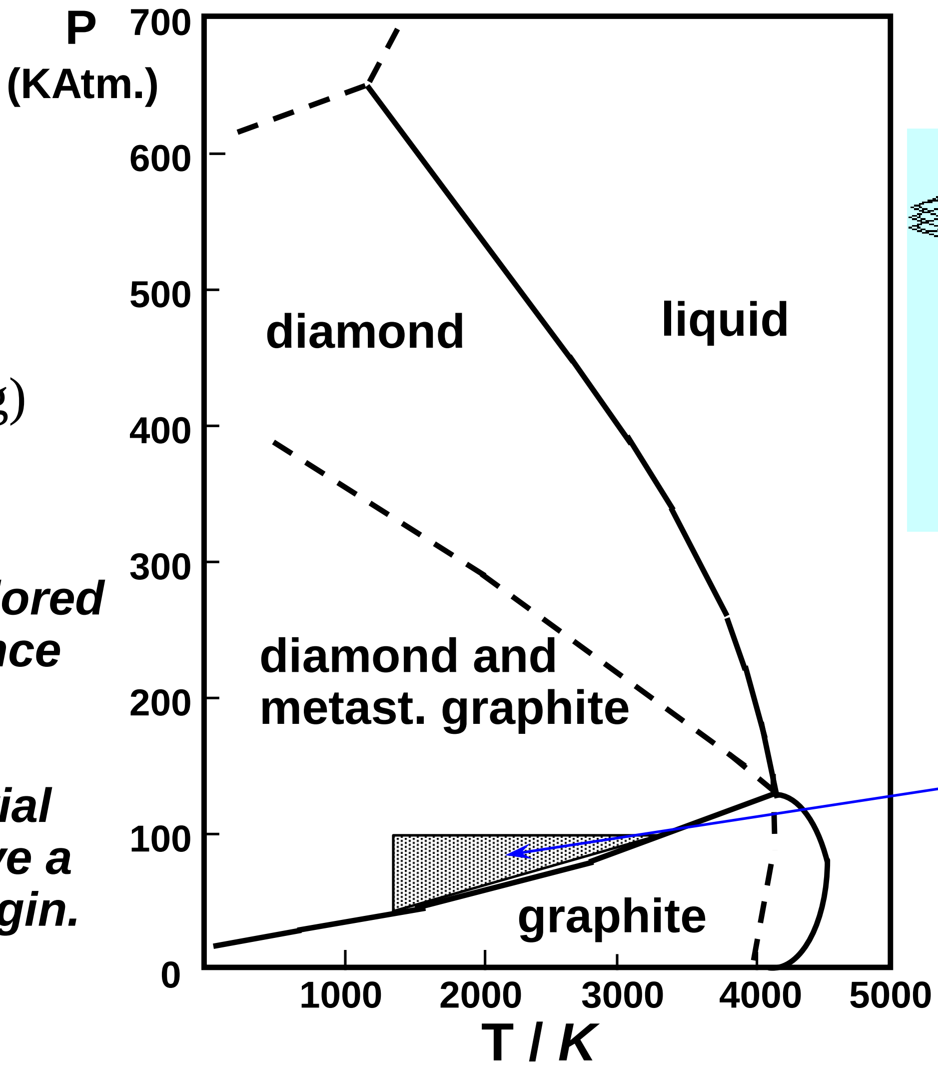
sp^2 hybridized C (angle 120°)
soft, conductor, metallic/black

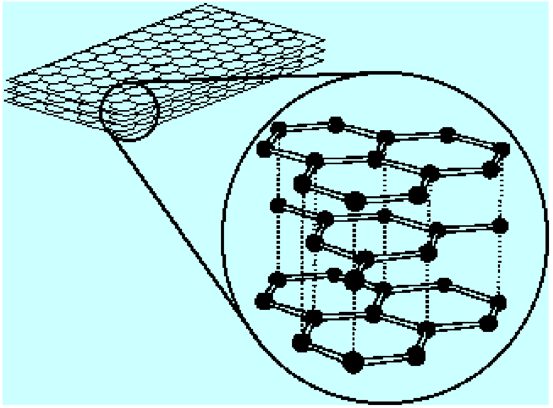
[Available also the β-rhombohedral form] ABCABC

Phase Diagram of Carbon.

(1 Carat = 0.2g)

Diamond becomes colored in the presence of metal impurities. Most industrial diamond have a synthetic origin.

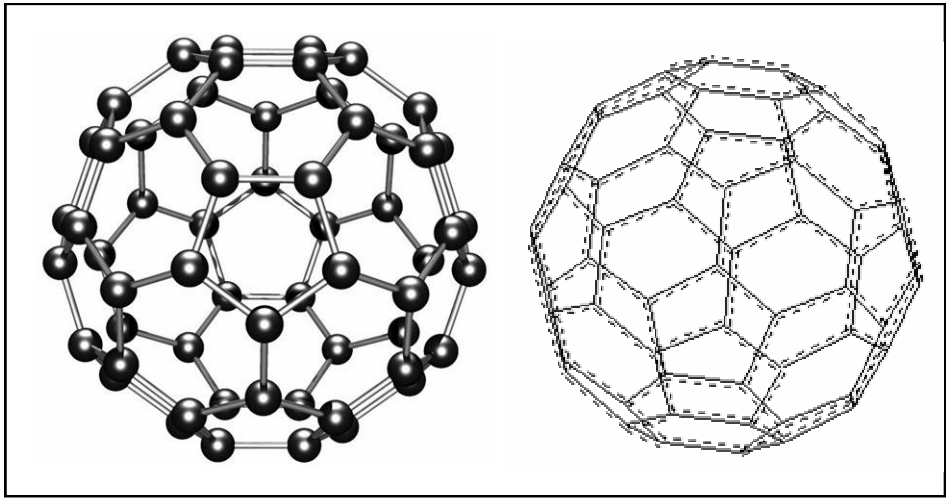


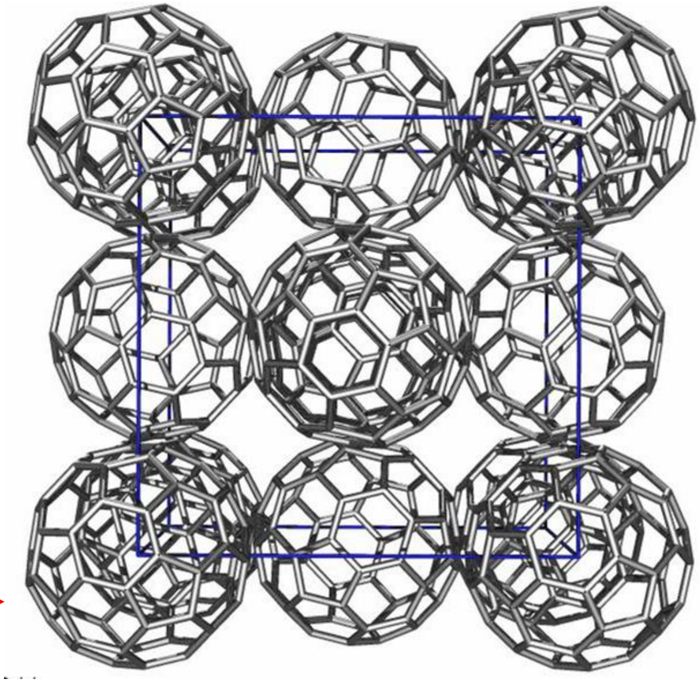


area where the conversion of $C_d – C_g$ is more favorable. The transformation is catalyzed by Cr, Fe, Pt.

Fullerenes and C-60 Fullerene.

A fullerene is any cyclic molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called buckyballs, cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings. Can be obtained by graphite by arc pyrolysis. They are less stable than graphite. Fullerenes have found extensive applications.





Cubic lattice

Fullerenes and Derivatives.

Preparation: Depolymerization of C ($\Rightarrow C_2, C_3, C_4, ...$):

Via electric arc with Graphite electrodes at 100 *mbar* under He, Ar:

Fullerene + other materials: extraction with C_6H_6, CCl_4, and chromatographic separation

Properties: Yellow-brown to dark-brown crystals, stable to air and H_2O,

Sublime under vacuum at 300°C.

Insoluble in H_2O, soluble in C_6H_6, C_6H_{12}, CCl_4, CS_2 (C_{60}: 5 *g/L* C_6H_6)

Conductibility: no metallic conductibility – different from Graphite)

Isolated: C_{60}, C_{70}, C_{76} , C_{78} (2 Isomers: C_{2v} o D_3 symmetry), C_{84}

as in Graphite 3 *sp*^{2} localized and 1 bond π delocalized:

Slowly converted into graphite:

C_{60} (s) {1500°C} $\rightarrow C_{Graphite}$ (stable) ($\Delta G < 0$)

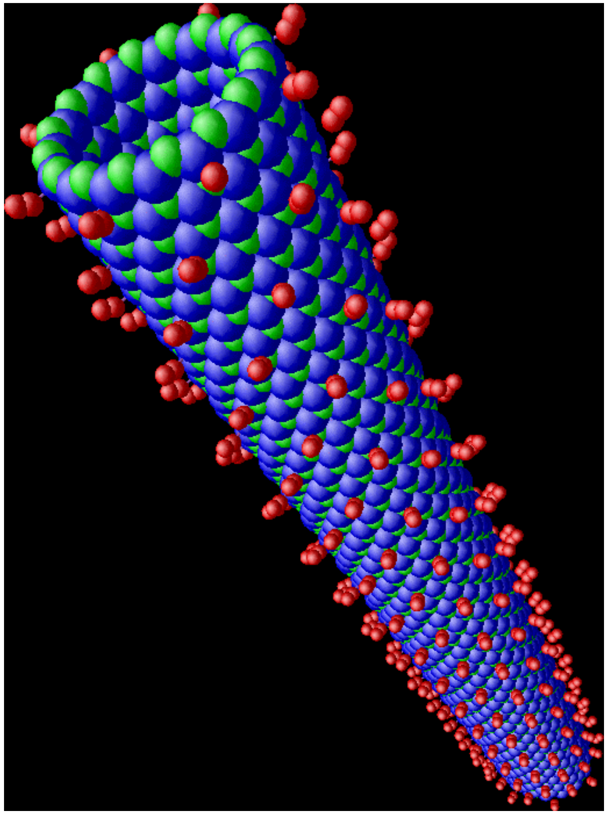
Reactions:

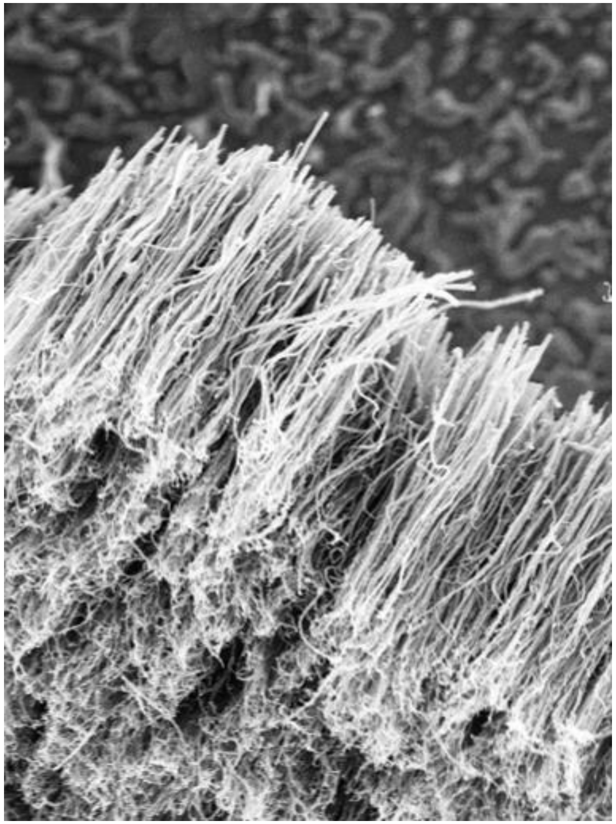
$C_{60} + F_2 \rightarrow C_{60}F_6$ (brown) $\rightarrow C_{60}F_{42}$ (brown) $\rightarrow C_{60}F_{60}$ (colorless)

$C_{60} + H_2$ (native) $\rightarrow C_{60}H_{36}$ (colorless); $C_{60} + Br_2 \rightarrow C_{60}Br_{24}\cdot 2Br_2$

Approach to non Covalent Storage of H_2 by Carbon Nanotubes.

- Synthesis of materials with bond energy and nanostructures designed to storage and release significant amount of hydrogen.
- Selection of appropriate prototypes for storage systems.





Timetable of CNT Development.

1904

Gas adsorption experiments (Dewar)

1991

Nanotube discovery (Iijima)

1993

Single Wall Carbon Nanotubes

1997

First report on H_2 Storage

1999

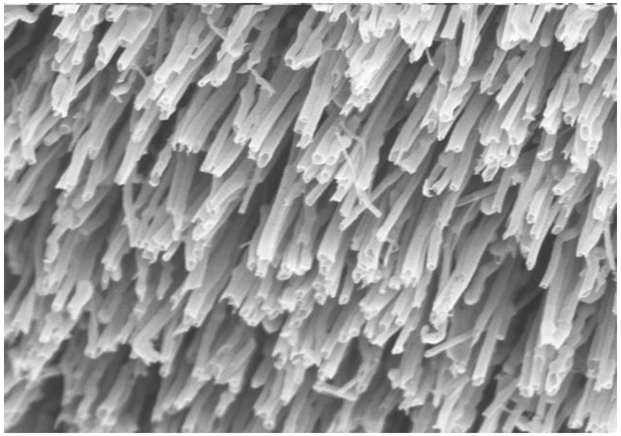
NREL experiments

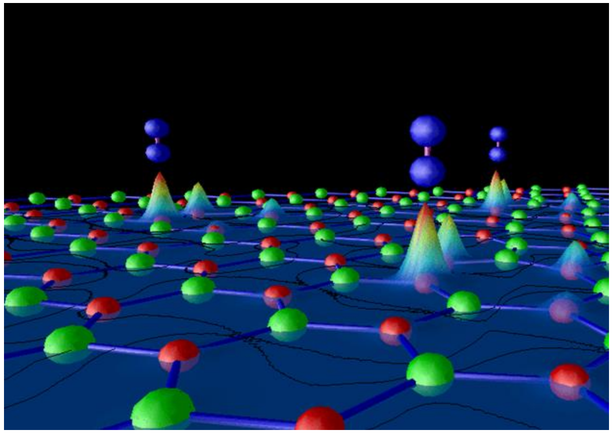
2001

Storage of cryogenic Hydrogen

2002

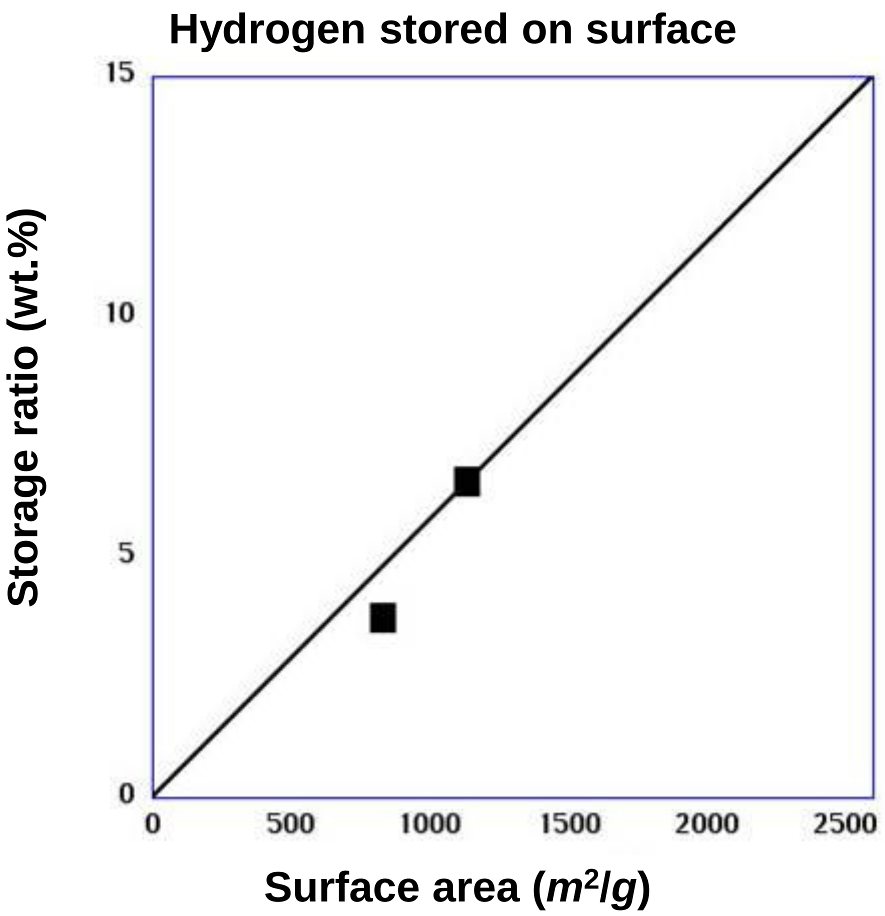
First examples of H_2 storage systems

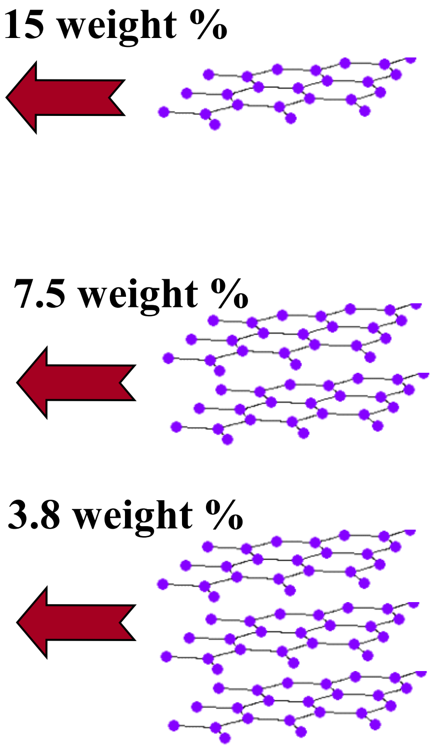




The US DOE target for hydrogen storage materials by 2015 is 6 wt.% and CNT are the most promising.

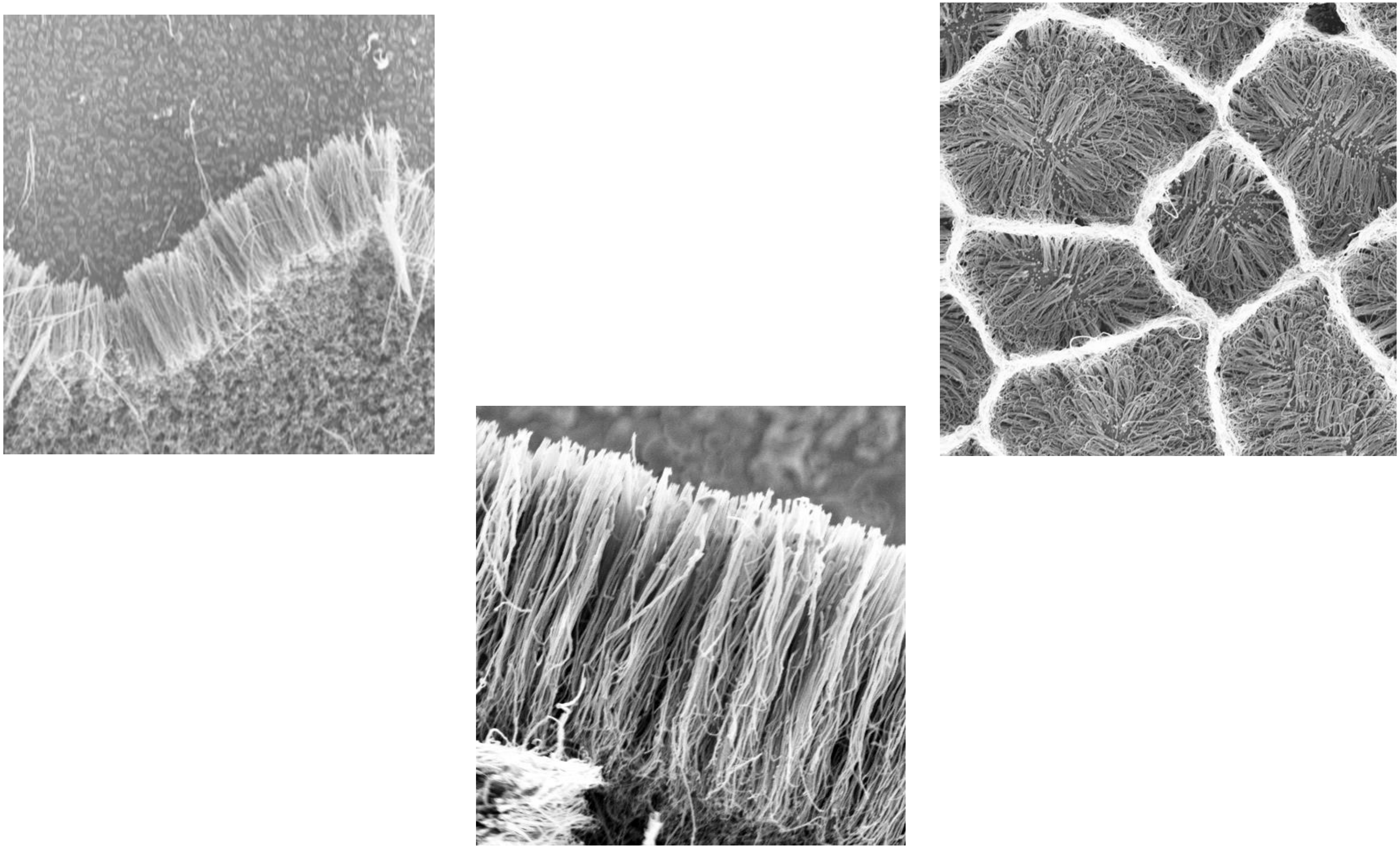
Storage Capacity vs. Material Quality.



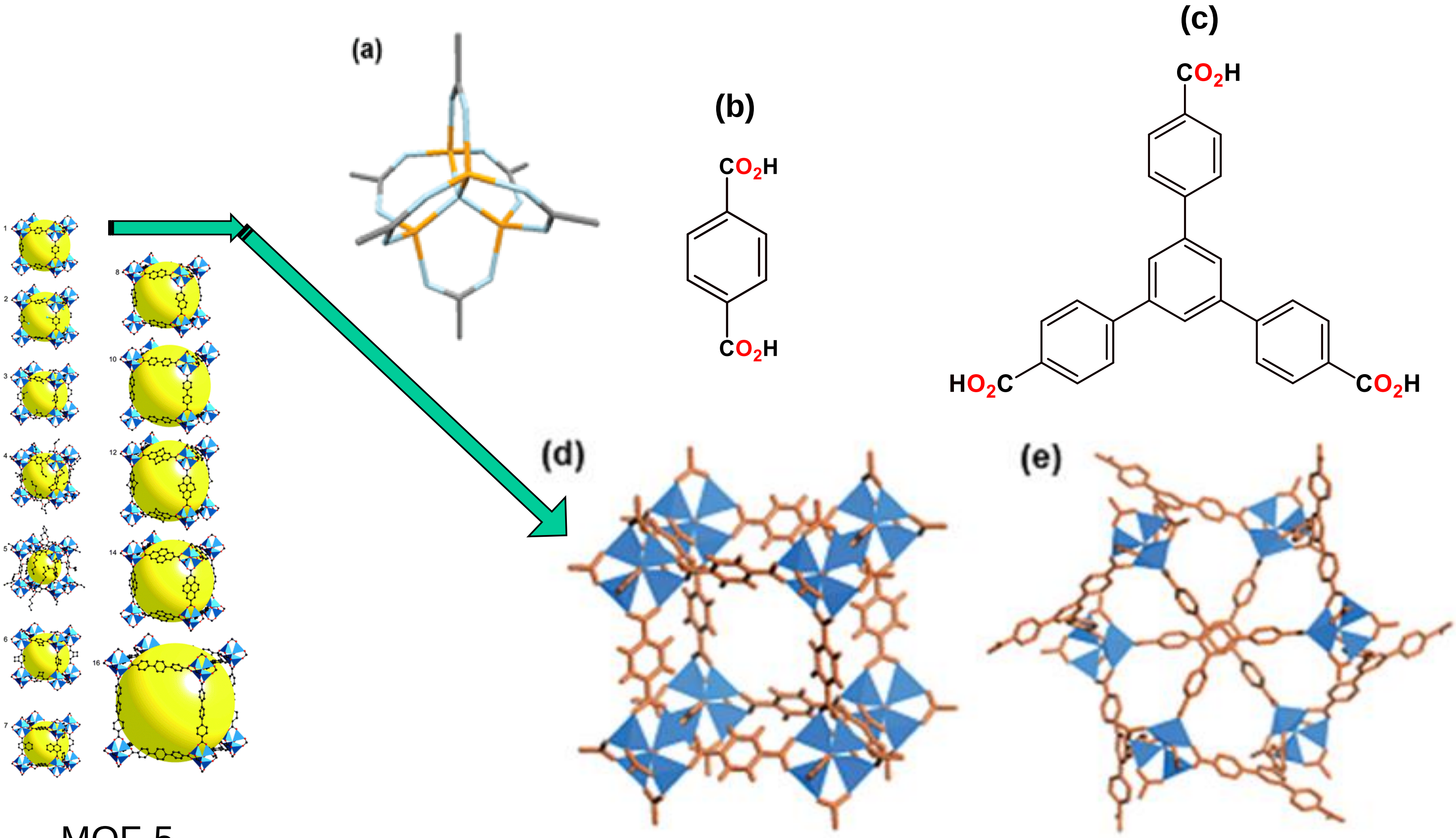


N.B. In 2014 the SWCNT best performance is 5.5 %.

Covalent Materials.



Metal Organic Frameworks (MOF) for Hydrogen Storage.



MOF-5

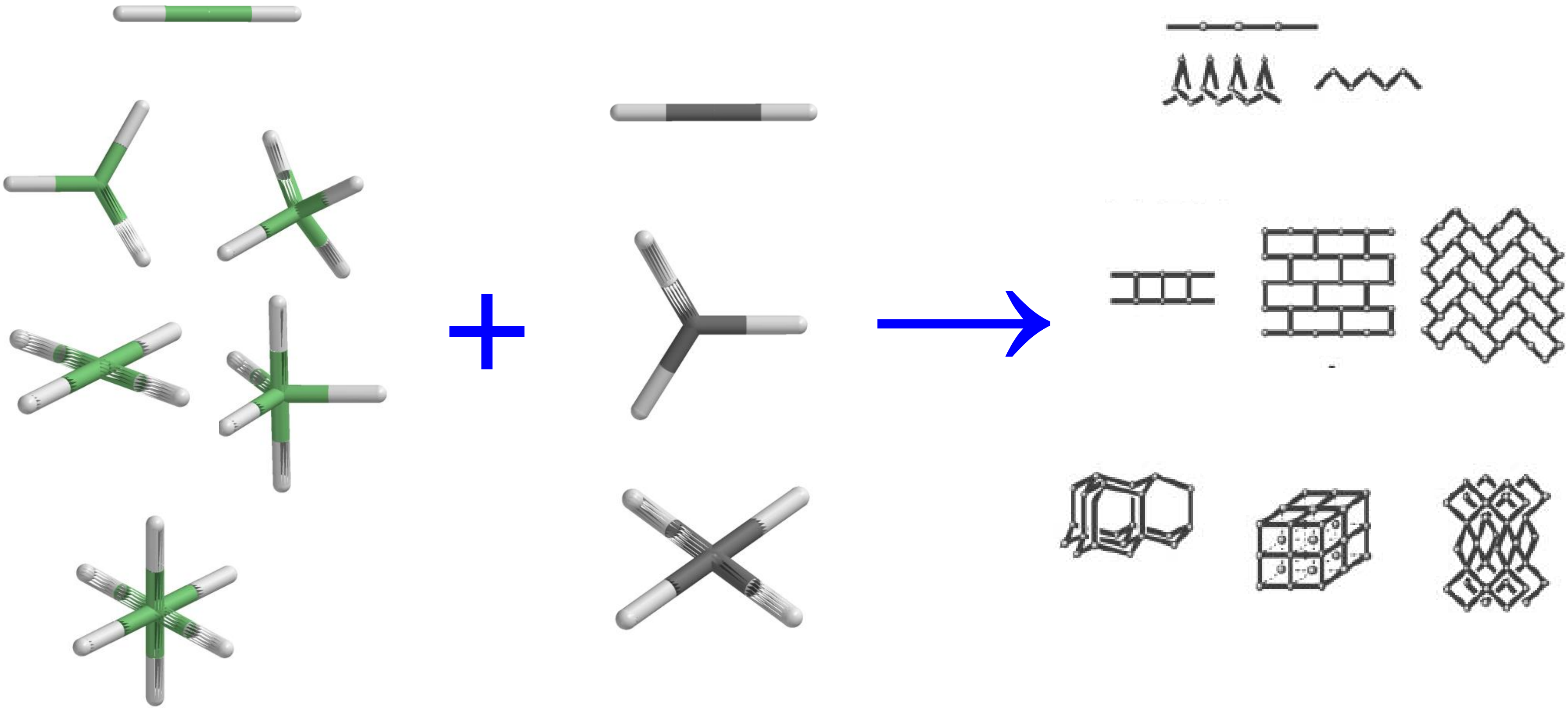
(a) [Zn$_4$O]SBU. The carboxylic acids used in the synthesis of (b) MOF-5 and (c) MOF-177. The structure of (b) MOF-5 and (c) MOF-177.

MOF basics: MOF= Metal Organic Frameworks; organic-inorganic hybrid materials.

Metal center or
cluster
(inorganic part)

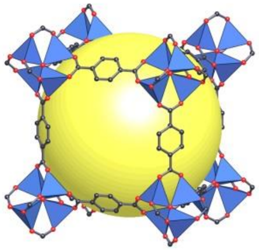
Linker
(organic part)

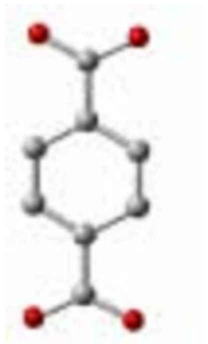
Metal Organic
Framework
(coordination polymer)



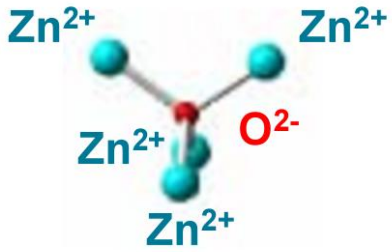
Synthesis of MOF.

$$4\,Zn^{2+} + 3\,H_2L + H_2O \xrightarrow[\text{DEF}]{\text{100°C 18h}} Zn_4O(L)_3$$





+

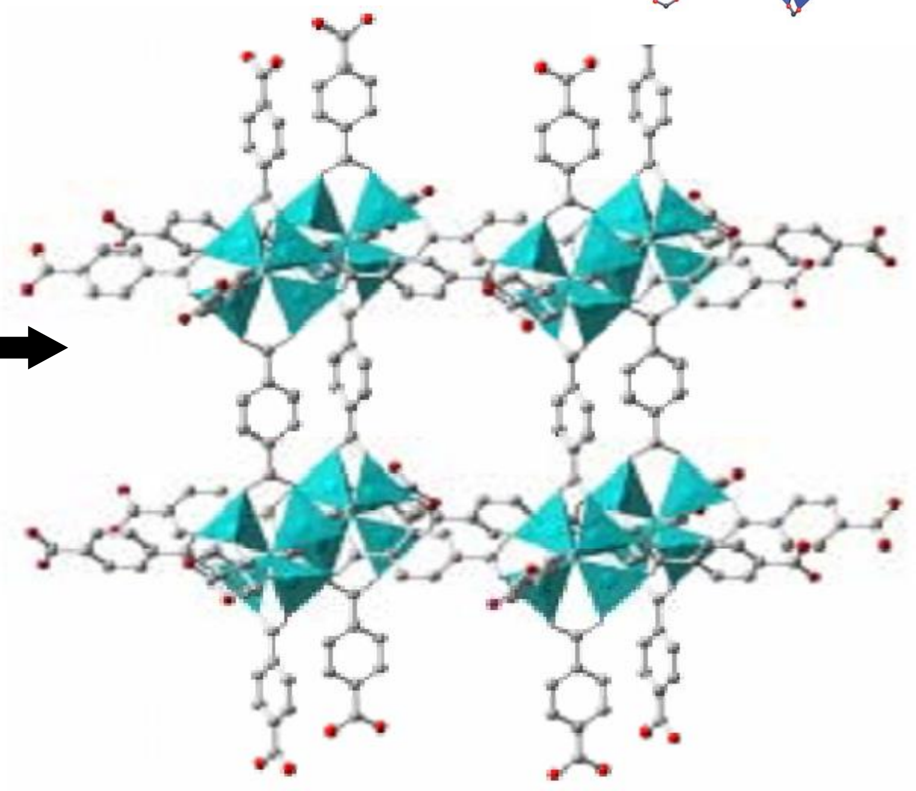


Linker

Terephthalic Ac.

SBU

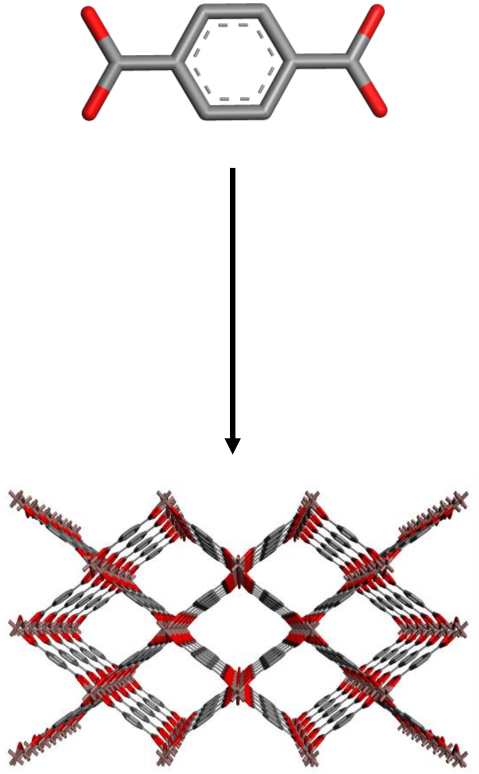
ZnO_4 Cluster



3D-Network (MOF-5)

MOFs Examples.

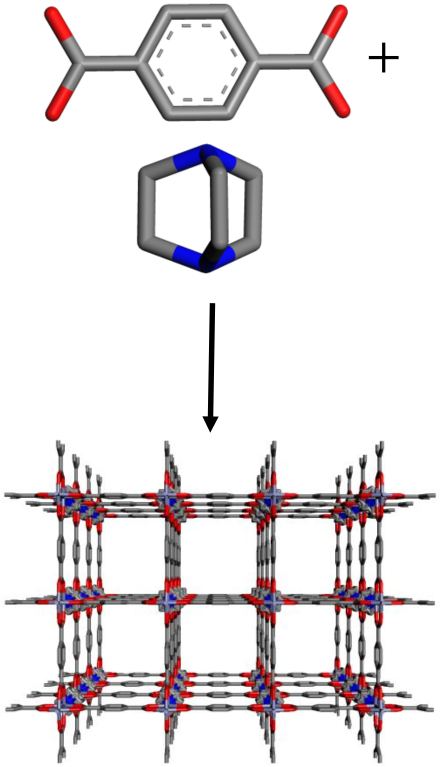
$AlCl_3$ +



USO-1-Al
(MIL-53)

1300 m^2/g

$Ni(NO_3)_2$ +

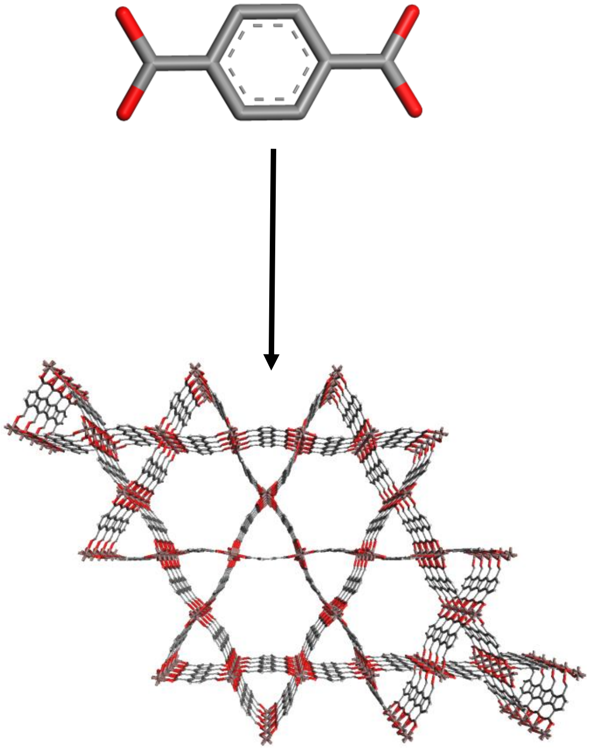


+

USO-2-Ni

1925 m^2/g

$InCl_3$ +



USO-3-In
(MIL-68)

930 m^2/g

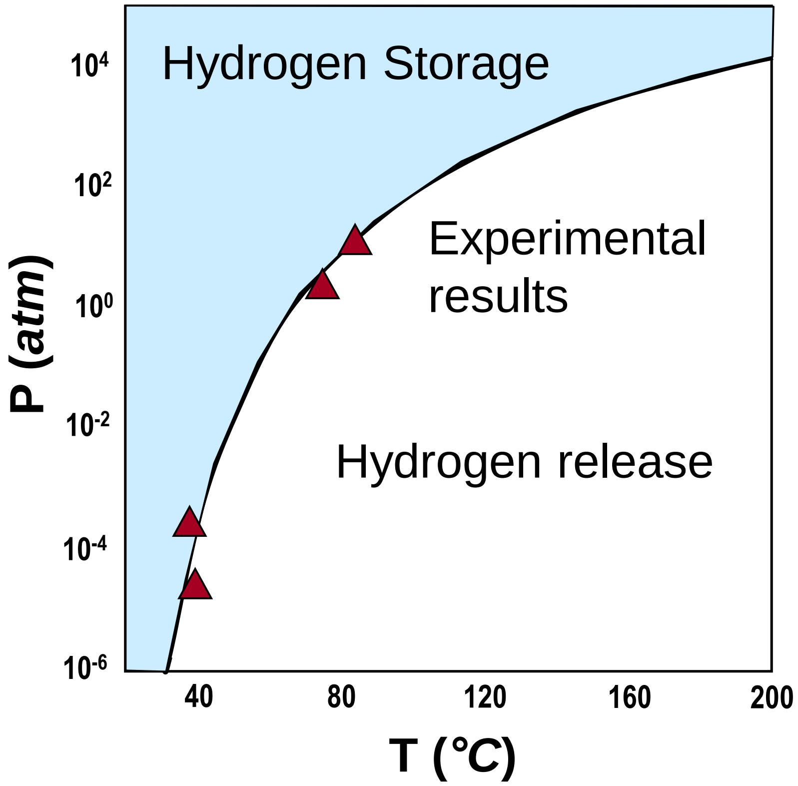
H_2 absorption Capacities of MOFs - Embedded with Palladium Nanoparticles.

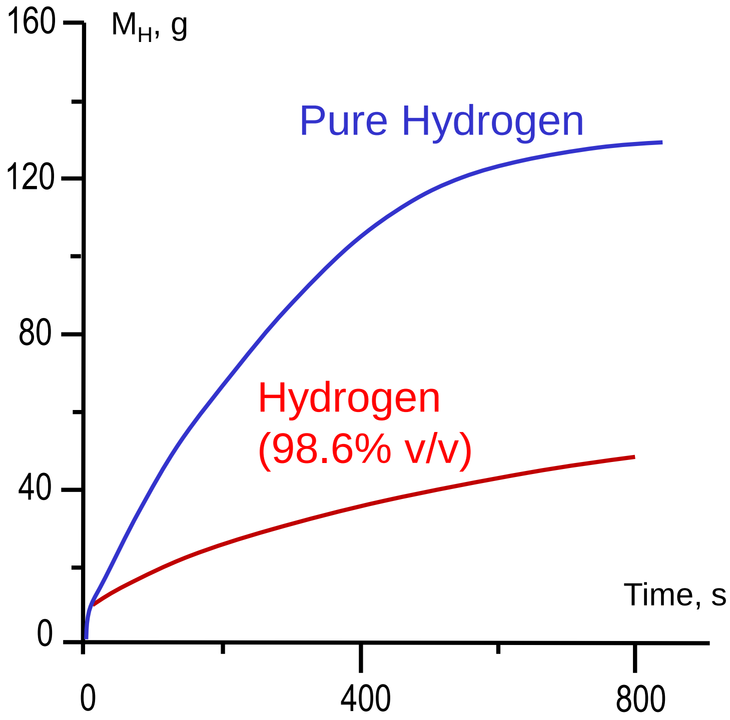
Sample	amount of Pd NPs, wt. %	Condition	H_2 uptake amount, wt.%
PdNPs@SNU-3	0	77 K, 1 bar (298 K, 95 bar)	1.03 (0.13)
	1.70/5 min[a]	77 K, 1 bar	0.35
	2.60/10 min[a]	77 K, 1 bar	0.20
	2.94/30 min[a]	77 K, 1 bar (298 K, 95 bar)	1.48 (0.3)
	3.20/60 min[a]	77 K, 1 bar	1.10
MIL-100 (Al)	0	77 K, 4 MPa (298 K, 4 MPa)	3.1 (0.19)
MIL-100 (Al)/Pd	9.7	77 K, 4 MPa (298 K, 4 MPa)	1.3 (0.35)

[a] In the MeCN solution of 1.0 × 10^{-3} M $Pd(NO_3)_2 \cdot 2H_2O$ with a 1:1 mol ratio of Pd^{II}/MOF.

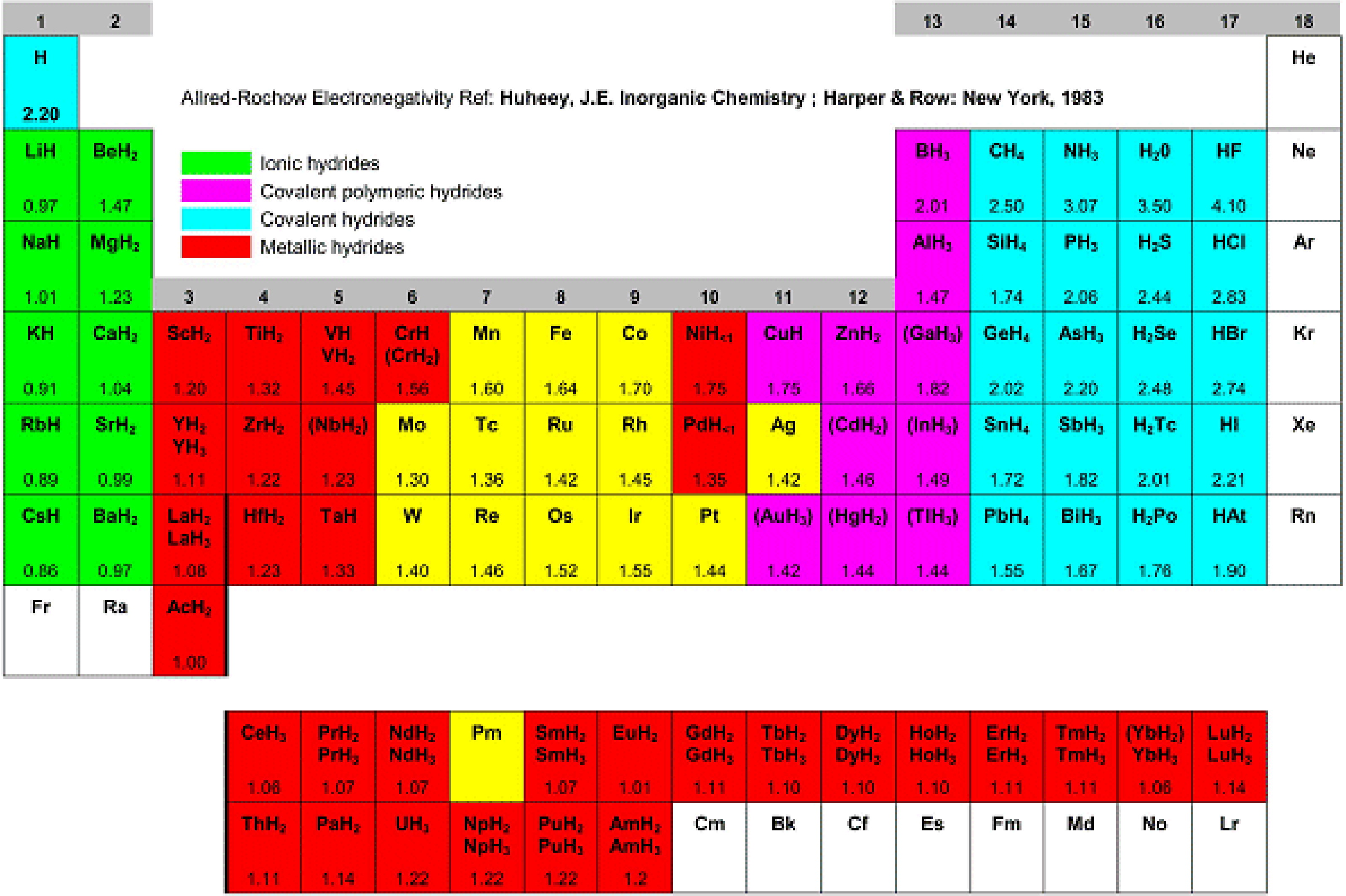
H_2 Storage: Thermodynamic and Kinetic.

Hydrogen absorption follows van’t Hoff equation, but non-absorbable impurities dramatically decrease efficiency of hydrogen systems affecting kinetics, heat and mass transfer, refueling time and energy conversion efficiency in fuel cells.





Hydrides of Elements.



Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

- 🟩 Ionic hydrides
- 🟪 Covalent polymeric hydrides
- 🟦 Covalent hydrides
- 🟥 Metallic hydrides

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
🟦 H 2.20																	He
🟩 LiH 0.97	🟩 BeH_2 1.47											🟪 BH_3 2.01	🟦 CH_4 2.50	🟦 NH_3 3.07	🟦 H_20 3.50	🟦 HF 4.10	Ne
🟩 NaH 1.01	🟩 MgH_2 1.23											🟪 AlH_3 1.47	🟦 SiH_4 1.74	🟦 PH_3 2.06	🟦 H_2S 2.44	🟦 HCl 2.83	Ar
🟩 KH 0.91	🟩 CaH_2 1.04	🟥 ScH_2 1.20	🟥 TiH_2 1.32	🟥 VH VH_2 1.45	🟥 CrH (CrH_2) 1.56	🟨 Mn 1.60	🟨 Fe 1.64	🟨 Co 1.70	🟥 $NiH_{<1}$ 1.75	🟪 CuH 1.75	🟪 ZnH_2 1.66	🟪 (GaH_3) 1.82	🟦 GeH_4 2.02	🟦 AsH_3 2.20	🟦 H_2Se 2.48	🟦 HBr 2.74	Kr
🟩 RbH 0.89	🟩 SrH_2 0.99	🟥 YH_2 YH_3 1.11	🟥 ZrH_2 1.22	🟥 (NbH_2) 1.23	🟨 Mo 1.30	🟨 Tc 1.36	🟨 Ru 1.42	🟨 Rh 1.45	🟥 $PdH_{<1}$ 1.35	🟨 Ag 1.42	🟪 (CdH_2) 1.46	🟪 (InH_3) 1.49	🟦 SnH_4 1.72	🟦 SbH_3 1.82	🟦 H_2Te 2.01	🟦 HI 2.21	Xe
🟩 CsH 0.86	🟩 BaH_2 0.97	🟥 LaH_2 LaH_3 1.08	🟥 HfH_2 1.23	🟥 TaH 1.33	🟨 W 1.40	🟨 Re 1.46	🟨 Os 1.52	🟨 Ir 1.55	🟨 Pt 1.44	🟪 (AuH_3) 1.42	🟪 (HgH_2) 1.44	🟪 (TlH_3) 1.44	🟦 PbH_4 1.55	🟦 BiH_3 1.67	🟦 H_2Po 1.76	🟦 HAt 1.90	Rn
Fr	Ra	🟥 AcH_2 1.00															

🟥 CeH_3 1.08	🟥 PrH_2 PrH_3 1.07	🟥 NdH_2 NdH_3 1.07	🟨 Pm	🟥 SmH_2 SmH_3 1.07	🟥 EuH_2 1.01	🟥 GdH_2 GdH_3 1.11	🟥 TbH_2 TbH_3 1.10	🟥 DyH_2 DyH_3 1.10	🟥 HoH_2 HoH_3 1.10	🟥 ErH_2 ErH_3 1.11	🟥 TmH_2 TmH_3 1.11	🟥 (YbH_2) YbH_3 1.08	🟥 LuH_2 LuH_3 1.14
🟥 ThH_2 1.11	🟥 PaH_2 1.14	🟥 UH_3 1.22	🟥 NpH_2 NpH_3 1.22	🟥 PuH_2 PuH_3 1.22	🟥 AmH_2 AmH_3 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Reversible Solid-State Material Storage Systems.

Hydrogen Capacity and Reversibility.

Hydrogen capacity and reversibility are inadequate at practical operating temperatures and pressures and within refueling time constraints. Adequate cycle life of these systems has not been demonstrated.

Maximum values of 3.3 % were reported for graphene sheets at R.T. and of 6.7% at 50 bar (1% Pd) and 7.1 at 60 bar (5% Pd).

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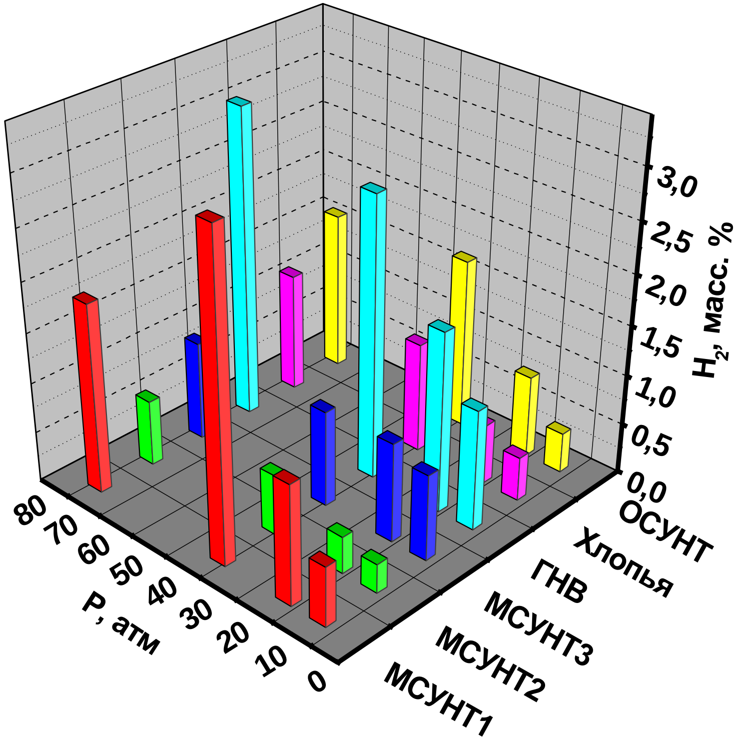
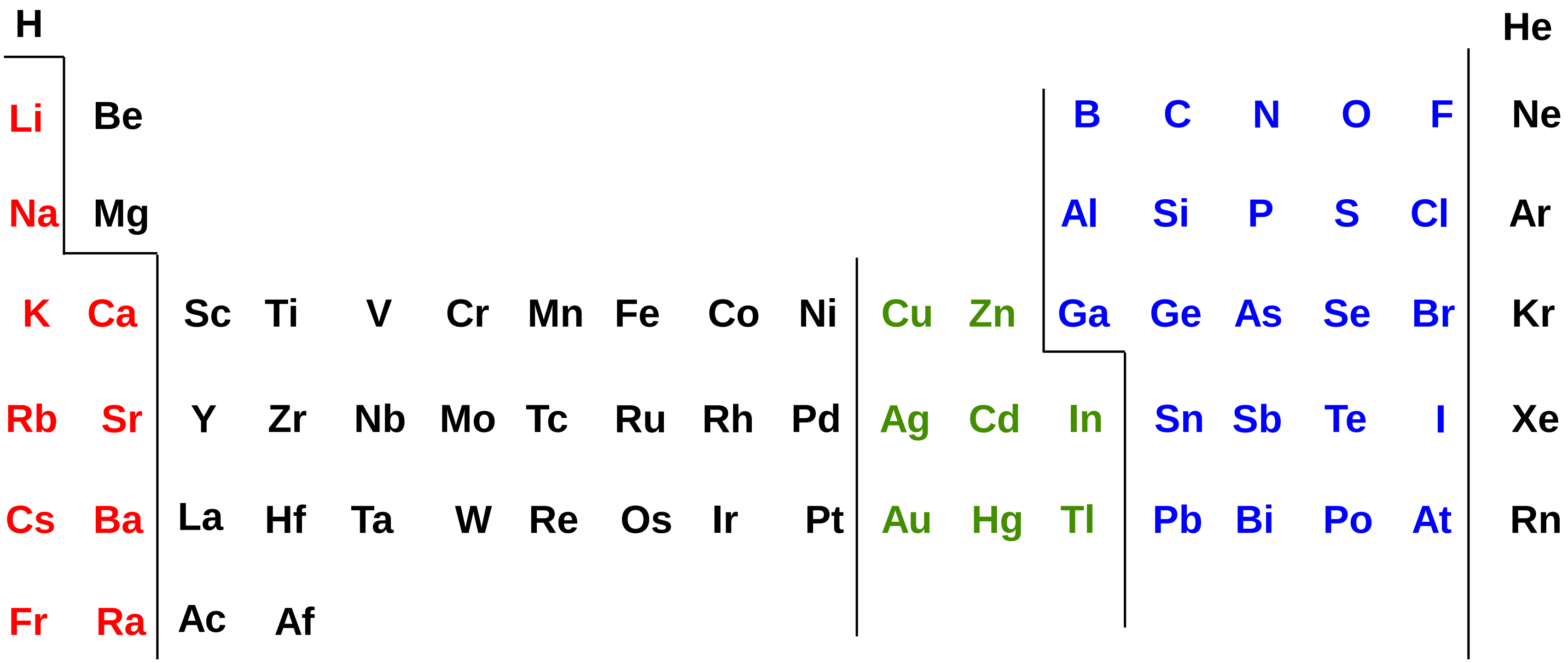


Reversible capacity of carbon nanostructures (nanotubes, nanofibers, nanoflakes) at 20°C.

Binary Hydrides of Elements.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Af														

Ionic Hydrides

Transition Metal Hydrides

Intermediate Hydrides

Covalent Hydrides

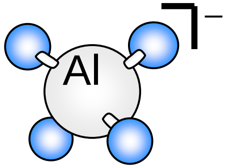
Ionic Hydrides: Preparation and Properties.

- **Prepared from elements at 300-700°C; if metal is finely dispersed can react at lower temperature;**
- **Crystalline solids with limited thermal stability (to reach 10 mmHg need 550°C for LiH, 210°C for NaH and KH, 170°C for Rb-H, 885°C for CaH_2, 585°C for SrH_2, 230 for BaH_2, and 85°C for MgH_2);**
- **Dissolve in fused alkaline salts;**
- **Being strong reducing species [E°(H_2/H^-) = - 2.25 *V*], they react efficiently with water generating hydrogen and absorb easily oxygen in very exothermic reactions;**
- **Only LiH can be melted without decomposition; this compound shows moreover low sensitivity for oxygen, chlorine and HCl at R.T.;**
- **MgH_2 reacts with water slowly enough to allow the use as dehydrating agent for solvents and gaseous species;**
- **They are used to prepare complex hydrides ($NaBH_4$ and $LiAlH_4$).**

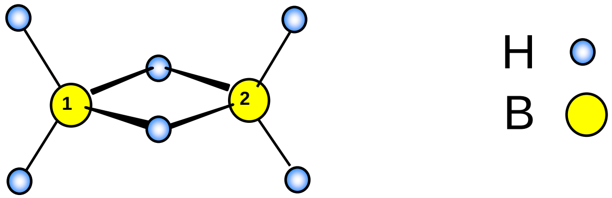
More Covalent Hydrides.

- **Aluminum forms the solid AlH_3 which exists in at least six different solid phases; the compound is useful and selective reducing agent in organic chemistry; it behaves as a Lewis acid reacting with LiH to give complex anions (tetrahydroaluminate):**

$$LiH + AlH_3 \rightarrow LiAlH_4$$



- **Boron affords a quite complex series oh hydrides starting from diborane (B_2H_6), all having three center two electron bonds (banana bonds)**



- **IV-V group hydrides are covalent, volatile, molecular, not very reducing compounds (in particular hydrocarbons C_nH_{2n+1}), soluble in apolar solvents, and having complex chemistry.**

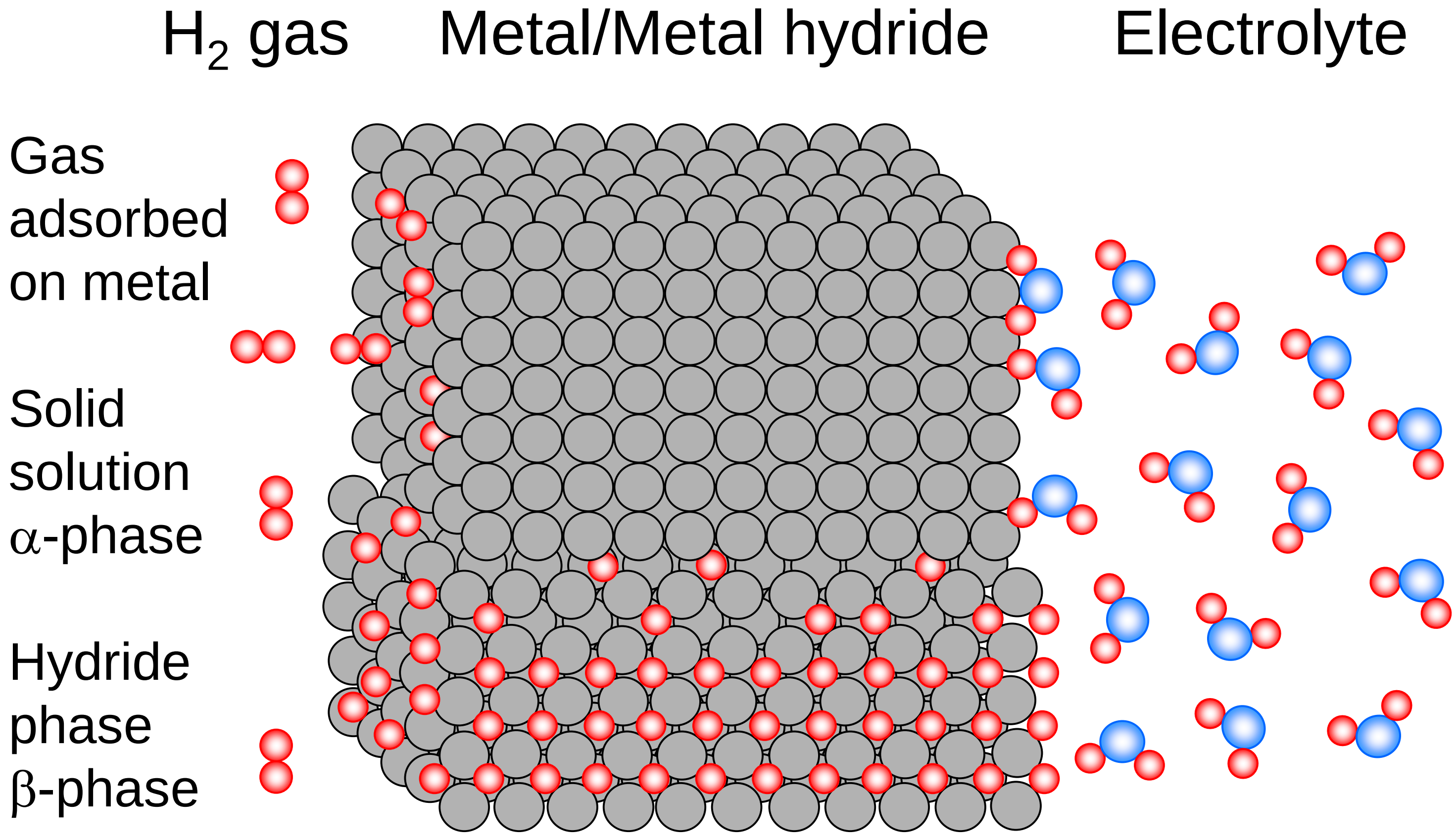
Transition Metal Hydrides.

- Compounds with non ionic structure, existing frequently in several different phases with a quite variable stoichiometry;
- Show a typical band structure of not covalent solids, which determine their properties and behavior;
- Block "d" hydrides are relatively unstable, they are grey-black solids very similar in reactivity to the corresponding metals. Are generally stable to air, but react on heating with air or acids. Ti, Zr, and Hf react exothermically with hydrogen giving non stoichiometric hydrides (i.e. $TiH_{1.7}$). Pd, Pt, and Ni hydrides are quite stables and are frequently used in catalysis;
- block "f" hydrides (lanthanides and actinides) are easily formed; they are black non stoichiometric solids with ionic structure. Uranium forms an UH_3 hydride, reactive and relevant intermediate for enrichment of ^{235}U.

Hydrides: Basic Classes.

AB_5: $LaNi_5H_{6.5}$, $LaNi_{4.7}Al_{0.3}H_{6.5}$	poor capacity (max 2%w), life cycle
AB: $FeTiH_2$	poor capacity (max 1.9%w), loss after cycling
AB_2: $ZrV_2H_{5.5}$	poor capacity (max 3%w), activation
A_2B: Mg_2NiH_4	3.6%w, slow kinetics, high T_{des}, activation
MgH_2	7.6%w, slow kinetics, high T_{des}, activation
Layer phases	Ca Al X (X = Si), 5%w, not reversible
Composites	Eutectic, destabilized nanostructured alloys
Complex hydrides ($NaAlH_4$ - $LiAlH_4$)	high capacity, not reversible

Metal with Interstitial Hydrogen and Hydride Phases used in Fuel Cells.



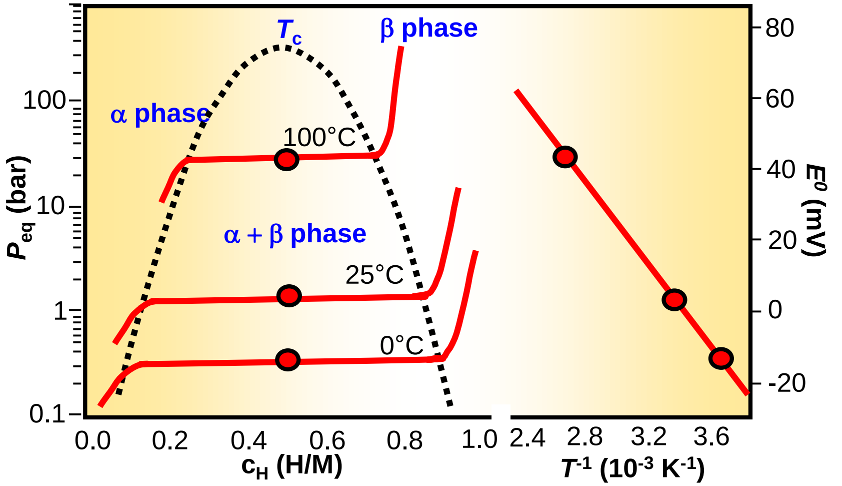
Hydrides: Basic Properties (1).

Two main issues :

- Thermodynamic stability of Hydride - strictly dependent upon M-H bonding properties

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Van't Hoff Equation



$\Delta S = 130\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

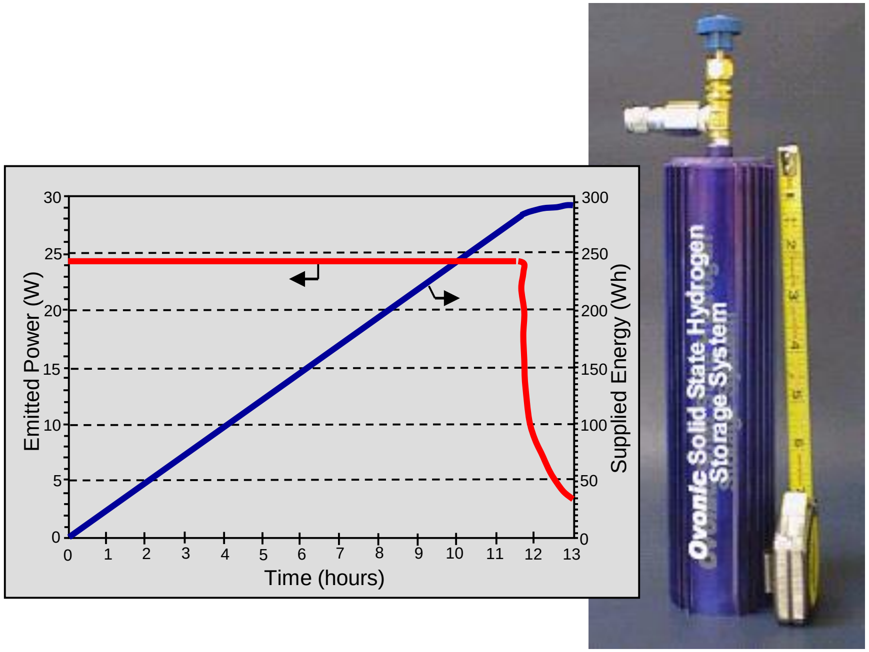
- Kinetics: First order Arrhenius-like

$K = A{\cdot}e^{-E/KT}$

A,E dependent upon a number of surface and structural parameters

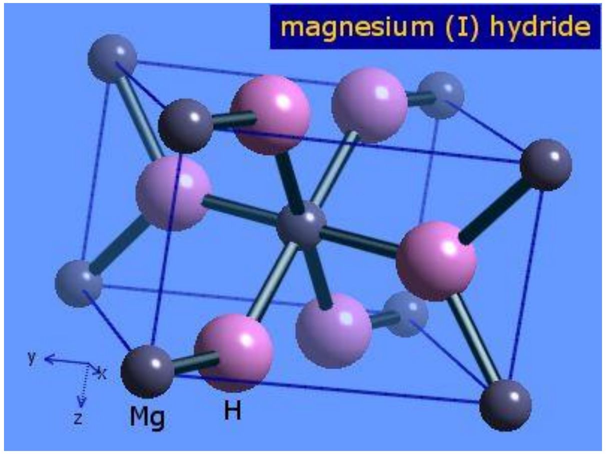
NiMH Cells Technology.

- High Power –1000 $W \cdot kg^{-1}$ (HEV)
- High Energy Density– 80 $Wh \cdot kg^{-1}$ (EV)
- Excellent Life Cycle – >50,000 PNGV Cycles 100 *Wh*



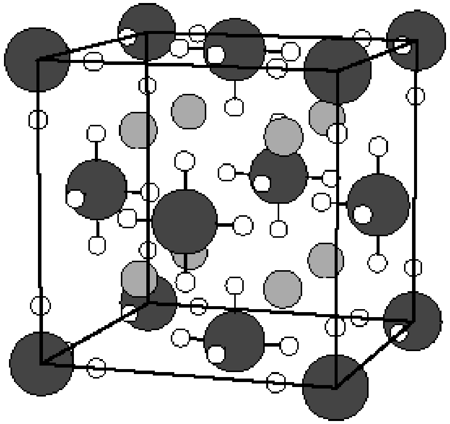
Hydrides: Basic Properties (2).

- Bulk H-uptake involving phase transitions
- Large volume change and Enthalpy are observed.



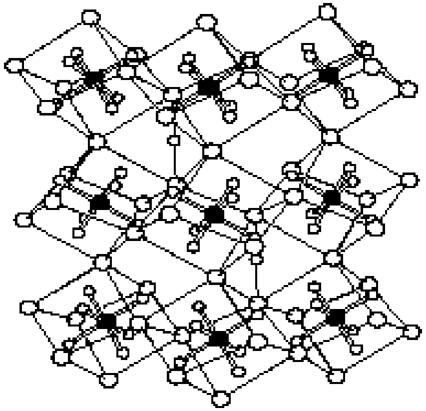
7.7 %w

Mg_2NiH_4



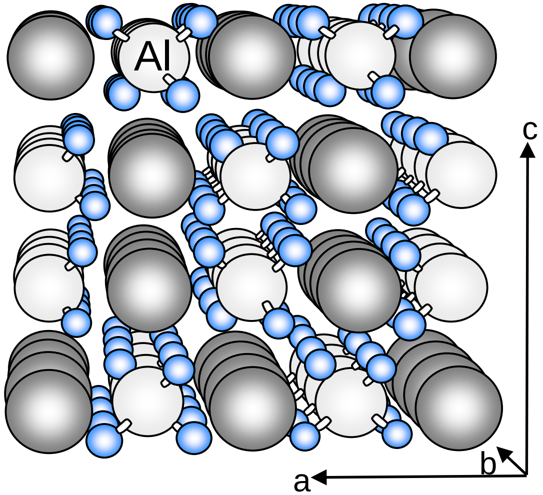
3.6 %w

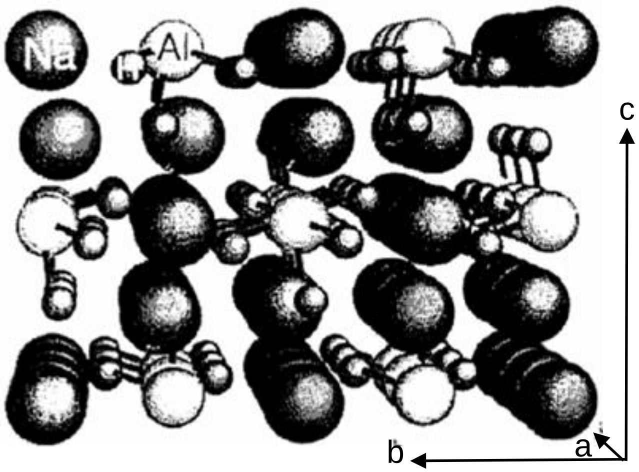
Mg_3MnH_7



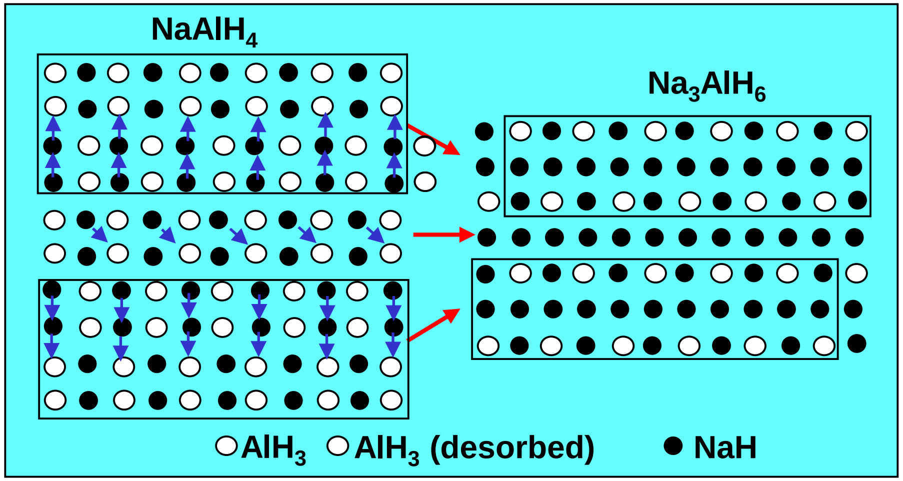
5.2 %w

Hydrides: Basic Properties (3).



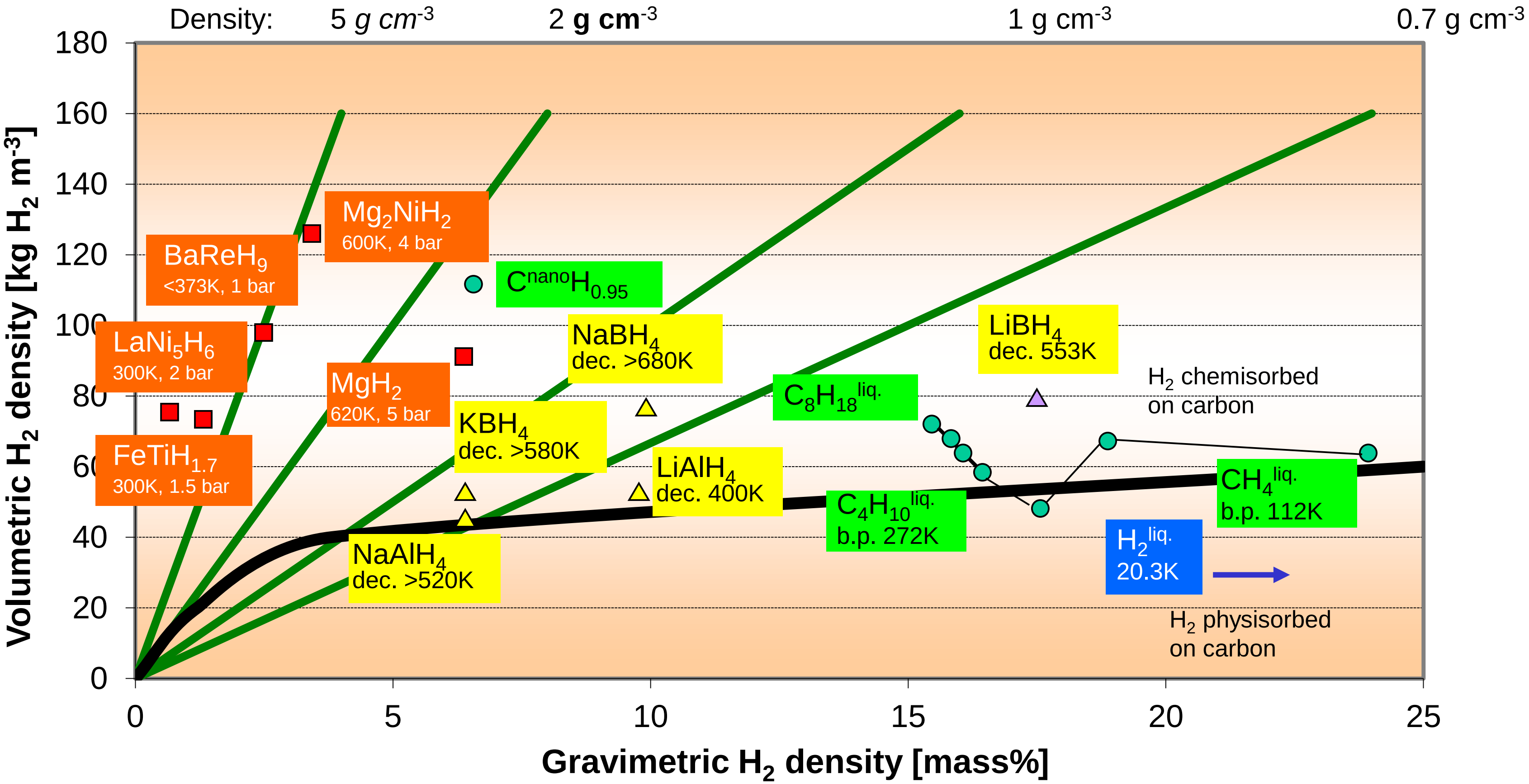


$$3\ NaAlH_4 \longrightarrow Na_3AlH_6 + 2\ Al + 3\ H_2$$

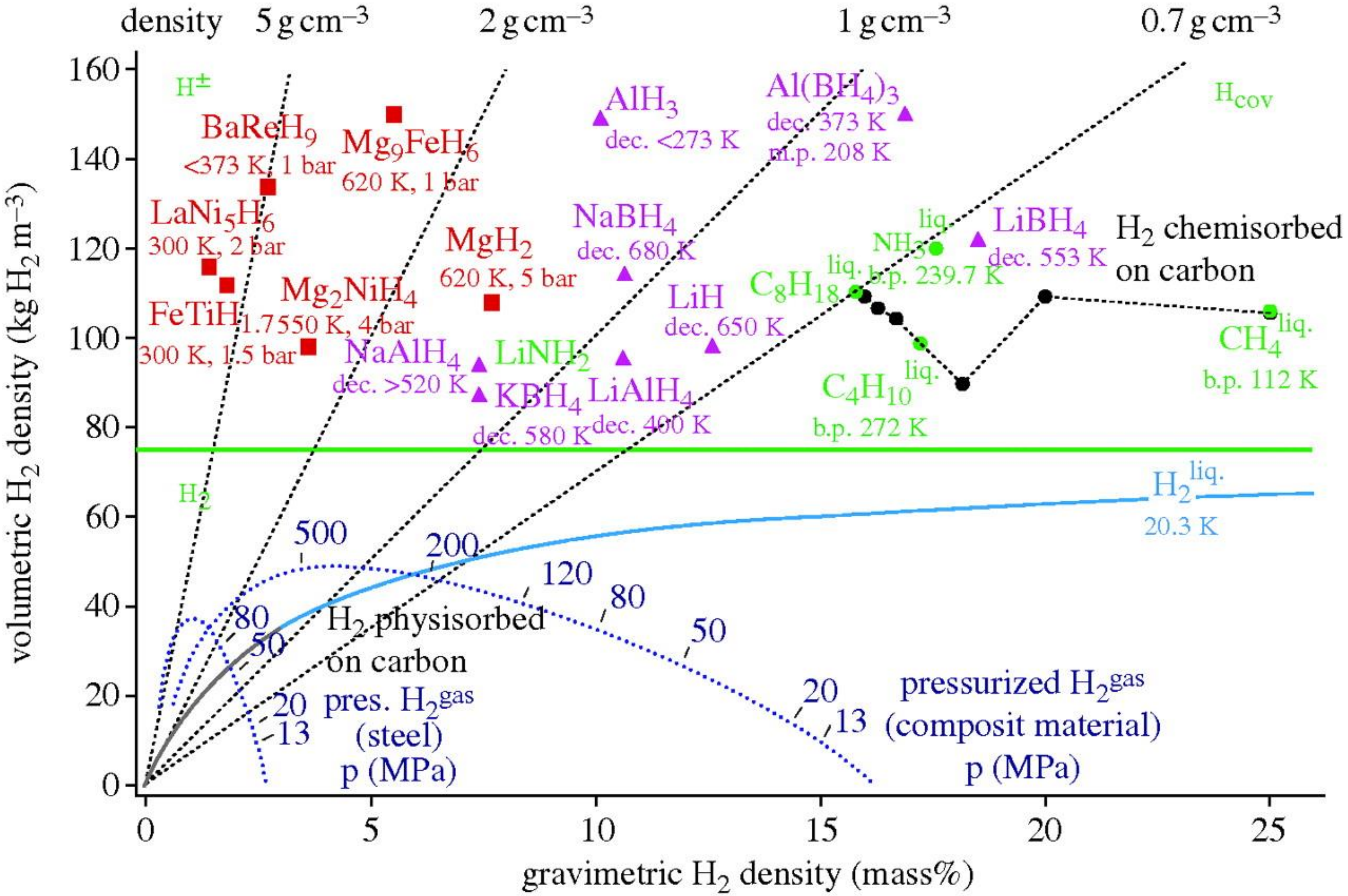


Structure transformation and phase transition

Comparison of H_2 Stored by Mass and by Volume for Different Species.



Trend in Volumetric vs. Gravimetric H_2 Density.



Hydrides: Magnesium Alloys.

Mg based Systems :

Mg_2Ni 3.6%, activation, slow kinetic, high T (300°C)

Mg 7.6%, activation, slow kinetic, high T (300°C)

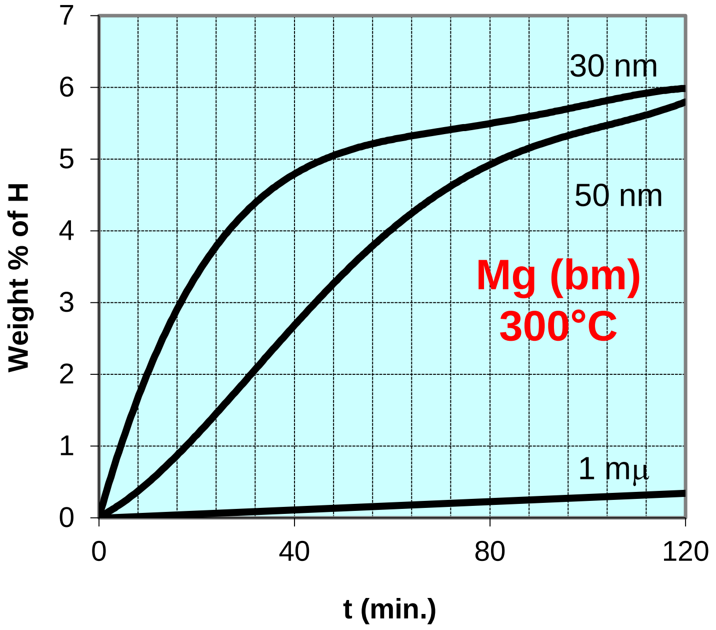
High enthalpy of hydride formation (–74 $kJ \cdot mol^{-1}$)

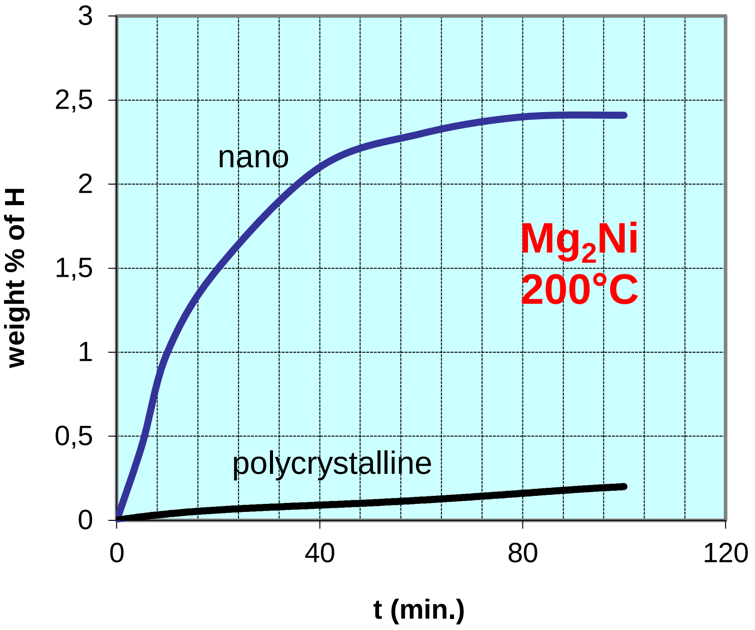
→ High T dehydrating

- novel synthesis
- nanostructure control
- nanoscale catalysis
- nanocomposites
- functional nanocomposites

NanoScale Structures (10^{-9})

Grain Size, Specific Surface Areas.





Reduced grain size = increased absorption and desorption kinetics

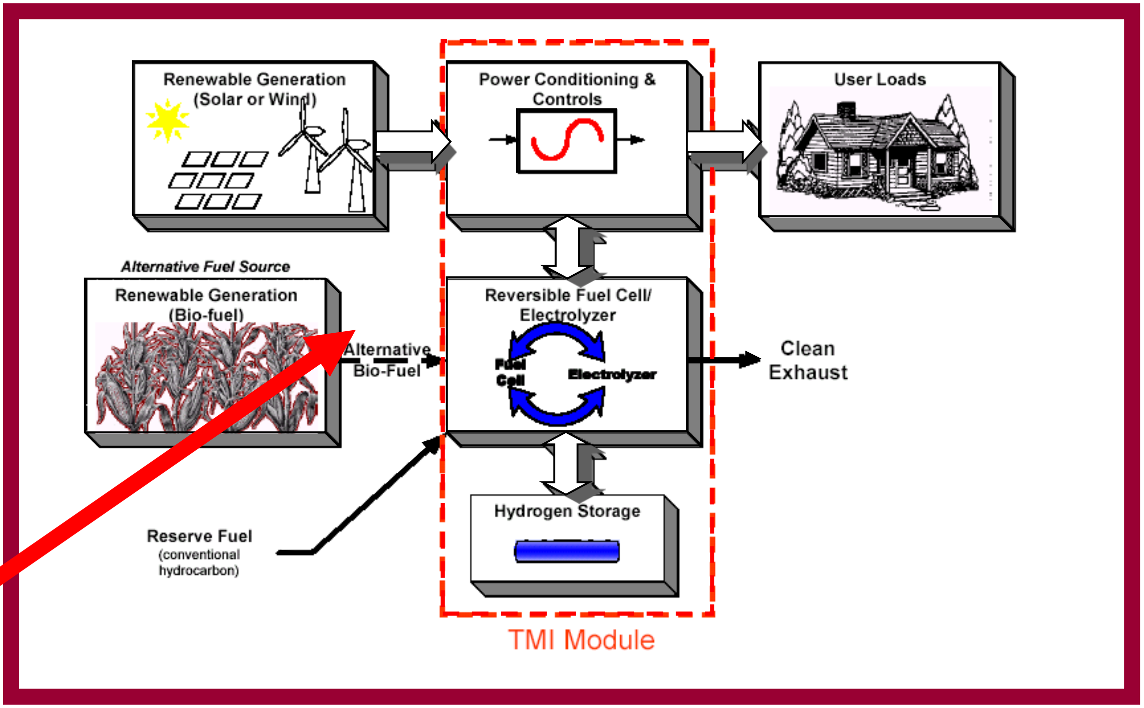
Reduced grain size = increased hydrogen absorption capacity

Ball-milling

- Large grain boundaries = paths for hydrogen diffusion
- Low grain size, high surface/volume = hydrogen access
- mechanical destabilization, defects = active sites

Reversible Fuel Cell.

- Hydrogen replaces batteries used on conventional renewable energy systems:
  - Higher storage energy density
  - Potentially higher efficiency
  - Eliminates “deep discharge”

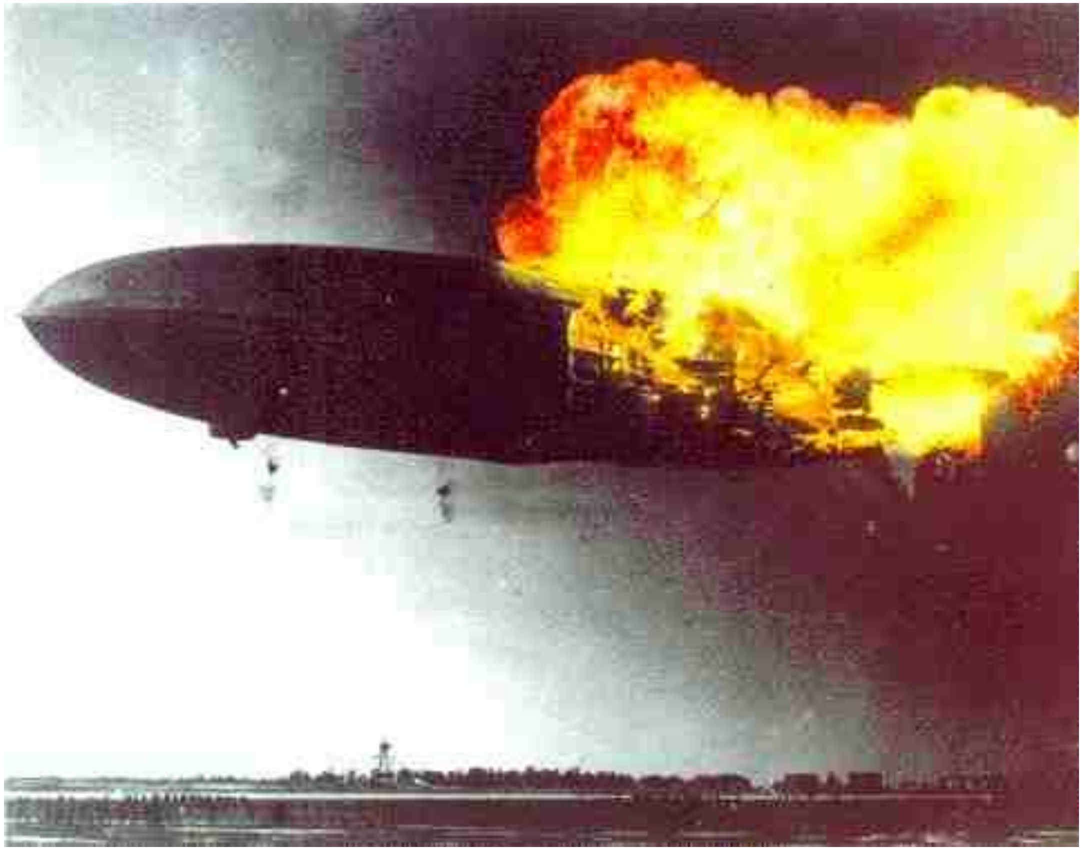


- **Very much like conventional FC**
  - The distinction is replacement of the electrolyzer and fuel cell with a “reversible fuel cell

- Efficiency is likely to be lower, but capital costs can in principle be reduced significantly.

Hydrogen Safety
The Zeppelin *The Hindenburg*.

- Contained 0.198 million m^3 of hydrogen
- Burned and crashed in Lakehurst NJ on 6 May 1937
- 62 survivors
- 35 dead
  - One was burned
  - 34 jumped or fell



Cause of fire has now been attributed to the cellulose acetate/aluminum coating on the skin of the aircraft

Hydrogen Safety.

- **Properties of hydrogen and other fuels:**

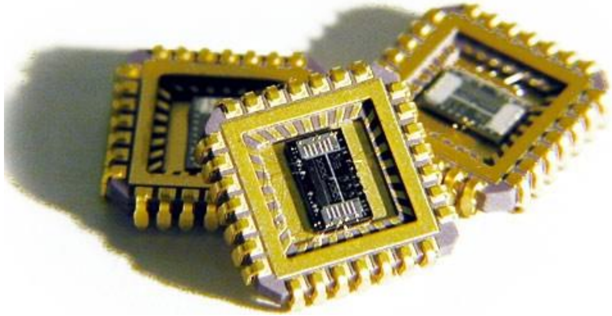
Property	Gasoline	Methane	Hydrogen
Flammability limits in Air (vol %)	1.0 - 7.6	5.3 - 15.0	4.0 - 75.0
Ignition Energy in Air (*MJ*)	0.24	0.29	0.02
Ignition Temperature (°C)	228 - 471	540	585
Flame Temperature in Air (°C)	2197	1875	2045
Explosion Energy (g-TNT/*kJ*)	0.25	0.19	0.17
Flame Emissivity (%)	34 - 43	25 - 33	17 - 25

Hydrogen Safety.

- Effective detection also key to safe use of hydrogen
- Adequate sensor technology still lacking
  - Existing technology not specific to hydrogen
  - Detects other combustible gases
    - Carbon monoxide
    - Natural gas
    - Automobile exhaust
  - “False positive” readings
- Innovative new technologies offer promise.

Hydrogen Safety.

Hydrogen Sensors

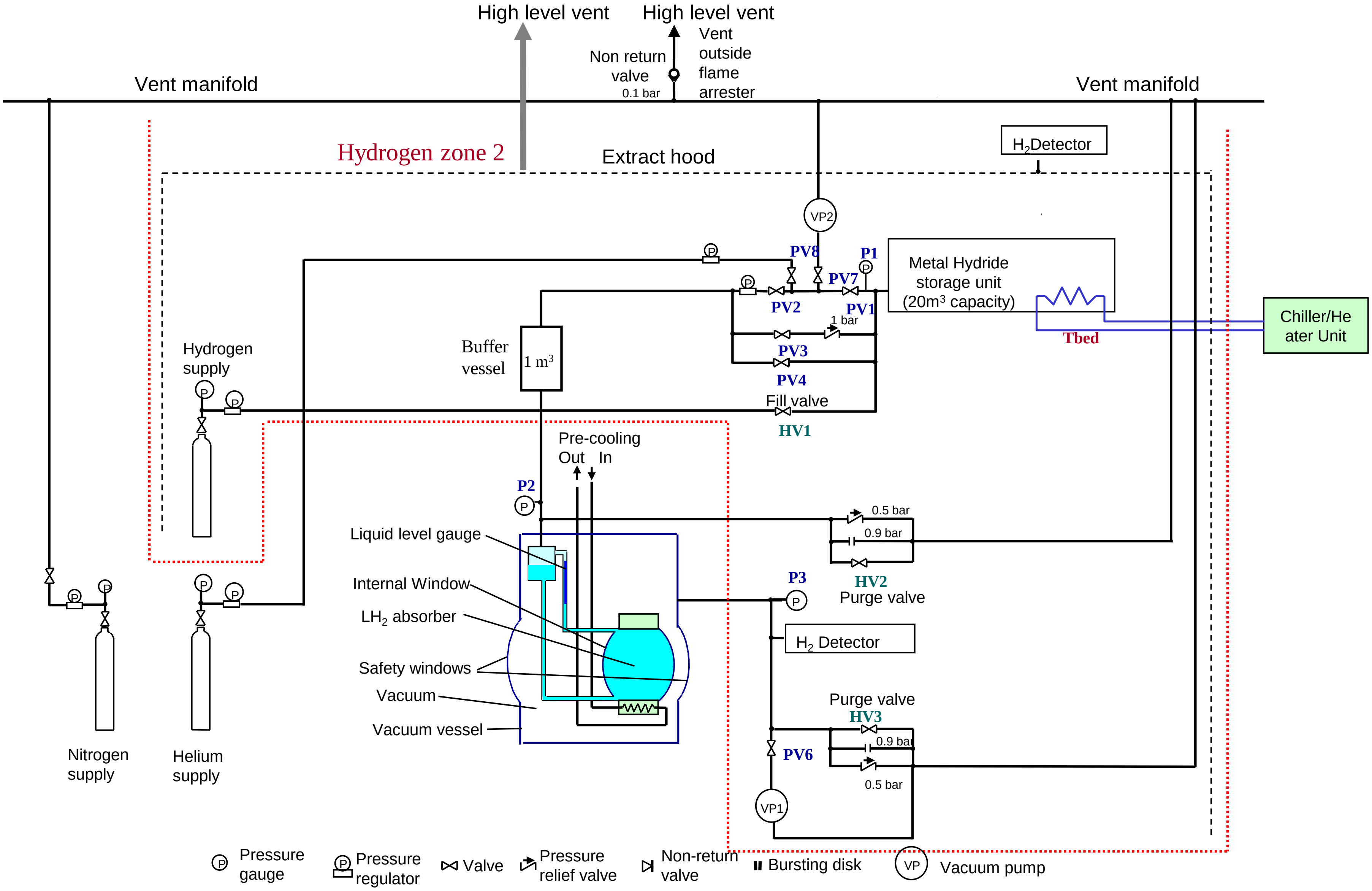


- **DCH Technology Inc. H2Scan**
  - Platinum filament resistivity sensor
  - Highly selective to hydrogen

- **OptiSense HydroSafe optrodes**
  - Transition metal complex embedded in porous glass matrix
  - Hydrogen-specific
  - Color change from yellow to blue

New sensor technologies may be critical for both automotive and distributed power fuel cell introduction.

MICE Hydrogen System.



Protective Measures.

- ✓ There should be no open flames or smoking in areas where hydrogen is used.
- ✓ Work in an area with plenty of ventilation. If possible, work in a fume hood or use a canopy hood as fugitive vapors, if not captured, may collect near the ceiling.
- ✓ Ground all equipment and piping used with hydrogen, and make sure that you are properly grounded before working with hydrogen. Rubber soled shoes prevent you from being grounded, so you should touch a grounded object to discharge built up static electricity before beginning work.
- ✓ Wear appropriate lab safety gear for the work being performed: safety glasses/ goggles, lab coat, gloves and preferably a face shield.
- ✓ If working with liquid hydrogen you must have appropriate insulated gloves and protective shoes in addition to the appropriate safety gear. (Cryogenic liquid hydrogen can cause severe burns to the skin due to the extremely low temperature.) Presently, there is no known liquid hydrogen use at UCB. If you plan to use or are using liquid hydrogen you must first check with EH&S and the Campus Fire Marshall.
- ✓ Remove electrical equipment or electronic devices from the vicinity of hydrogen gas unless the device is certified "intrinsically safe". Even invisible small sparks from electronic devices could ignite hydrogen.
- ✓ Use metal piping with hydrogen. Do not use non-conductive or plastic tubing. Be sure to dissipate static charge when flowing hydrogen gas by electrically bonding and grounding the cylinder, metal piping and apparatus being used.

Storage and Handling.

- ✓ Hydrogen cylinders must be stored with valve's protective cap in place. If the cap has been removed, the cylinder must be stored upright and secured with noncombustible straps or chains.
- ✓ Hydrogen cylinders must be stored more than 20 feet away from cylinders of O_2 or other oxidizers, e.g., Br_2, Cl_2, F_2 or be separated by a noncombustible wall extending not less than 18" above and to the sides of the stored material.
- ✓ Never open the cylinder valve before making sure all your connections are secure as the static discharge from flowing gas may cause hydrogen to be ignited.
- ✓ NEVER USE ADAPTERS.
- ✓ Be aware of leaks! H_2 has a low viscosity which makes it to have a high leakage rate. A leak as small as 4 micrograms/second can support combustion. Due to low molecular weight, H_2 will diffuse rapidly in a room and will collect near the ceiling. Ventilation need.
- ✓ There must be no more than 1000 cubic feet of flammable gases per fire control area unless there are adequate engineering controls. A standard large cylinder contains about 260 cubic feet of hydrogen. There should be fire sprinklers wherever H_2 is used.
- ✓ All electronic equipment used near hydrogen gas must be grounded.
- ✓ Check that the pressurized system does not leak hydrogen with leak detection solution or pressure sensing.
- ✓ Close the cylinder valve when unused. Do not leave the piping pressurized if not used.

Reactivity of H_2 to be Considered.

- It ignites easily with oxygen, could explode when heated.
- It reacts violently or explosively or forms heat- and/or-shock sensitive explosive mixtures with oxidizers, halogens, halogen compounds, acetylene, bromine pentafluoride, chlorine oxides, fluorine perchloride, oxides of nitrogen (check MSDS for list of incompatibles).
- Mixtures with chlorine may explode on exposure to light.
- Mixtures with oxygen may explode in presence of platinum catalyst.
- It is incompatible with copper(II) oxide, difluorodiazene, iodine heptafluoride, lead trifluoride, liquid nitrogen, lithium perchlorate triidrato, metals, nitrogen trifluoride, nitril fluoride, palladium(II) oxide, palladium trifluoride, potassium tetrafluorohydrazine, xenon hexafluoride.
- It forms hydrides when heated with alkalis, alkaline earth, and some other elements.

https://ehs.berkeley.edu/sites/default/files/lines-of-services/workplace-safety/80hydrogen.pdf

Hydrogen on Internet.

www.hydrogen.org
www.efcf.com/reports
www.psi.ch
www.enea.it
www.eren.doe.gov/hydrogen/
www.diebrennstoffzelle.de
www.fuelcells.com
www.wupperinst.org
www.iefe.uni-bocconi.it
www.lbst.de
www.toyota.com
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