Ειδικά κεφάλαια παραγωγής ενέργειας

Ενότητα 5: HYDROGEN & FUEL CELLS

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Τμήμα Μηχανολόγων Μηχανικών

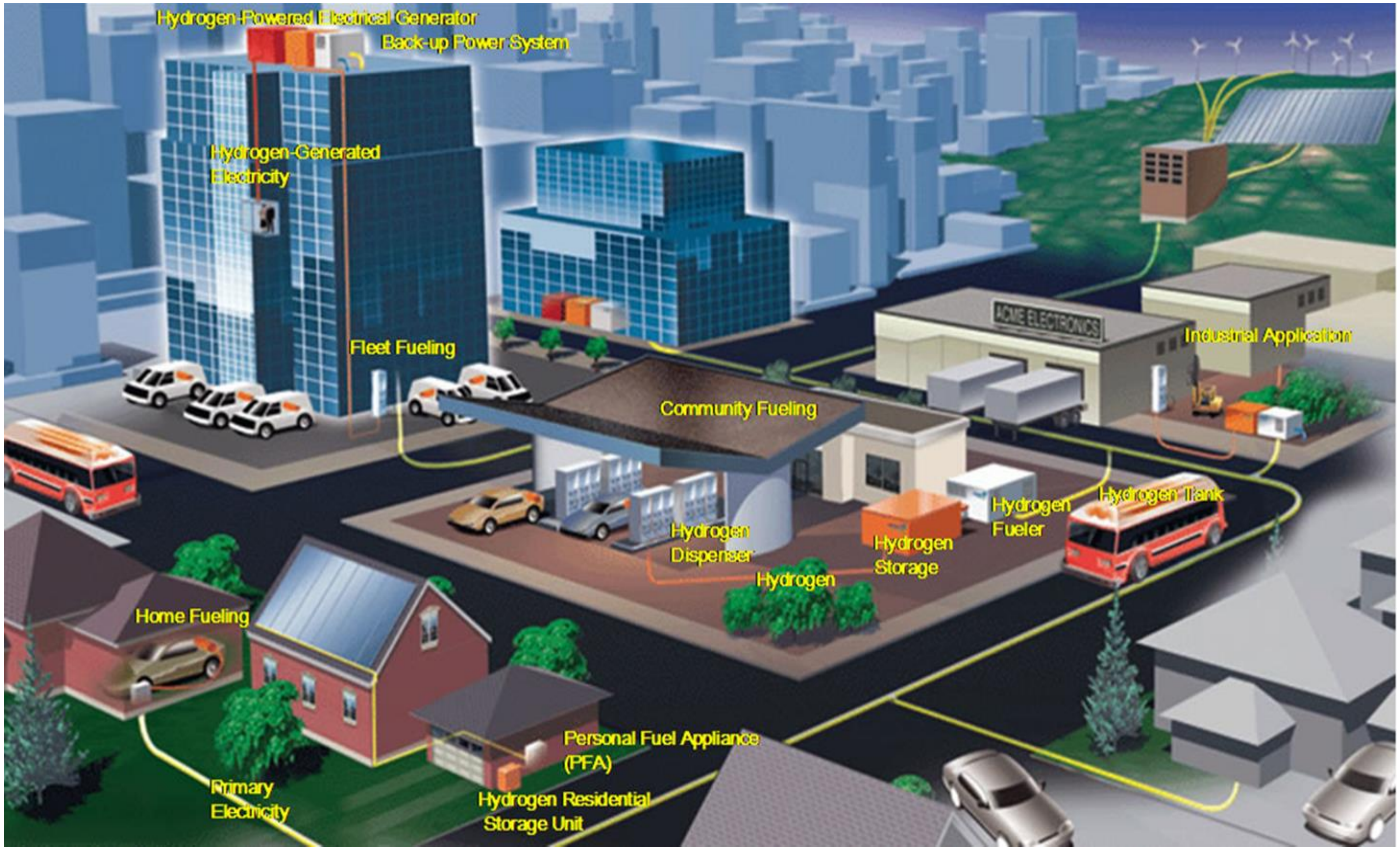
Άδειες Χρήσης

Χρηματοδότηση

- Το παρόν εκπαιδευτικό υλικό έχει αναπτυχθεί στα πλαίσια του εκπαιδευτικού έργου του διδάσκοντα.
- Το έργο «**Ανοικτά Ψηφιακά Μαθήματα στο Πανεπιστήμιο Δυτικής Μακεδονίας**» έχει χρηματοδοτήσει μόνο τη αναδιαμόρφωση του εκπαιδευτικού υλικού.
- Το έργο υλοποιείται στο πλαίσιο του Επιχειρησιακού Προγράμματος «Εκπαίδευση και Δια Βίου Μάθηση» και συγχρηματοδοτείται από την Ευρωπαϊκή Ένωση (Ευρωπαϊκό Κοινωνικό Ταμείο) και από εθνικούς πόρους.

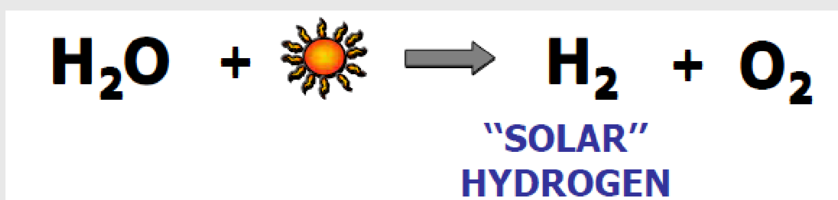
Ευρωπαϊκή Ένωση
Ευρωπαϊκό Κοινωνικό Ταμείο
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ
επένδυση στην κοινωνία της γνώσης
ΥΠΟΥΡΓΕΙΟ ΠΑΙΔΕΙΑΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ
ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ
ΕΣΠΑ 2007-2013
πρόγραμμα για την ανάπτυξη
ΕΥΡΩΠΑΪΚΟ ΚΟΙΝΩΝΙΚΟ ΤΑΜΕΙΟ
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

HYDROGEN & FUEL CELLS



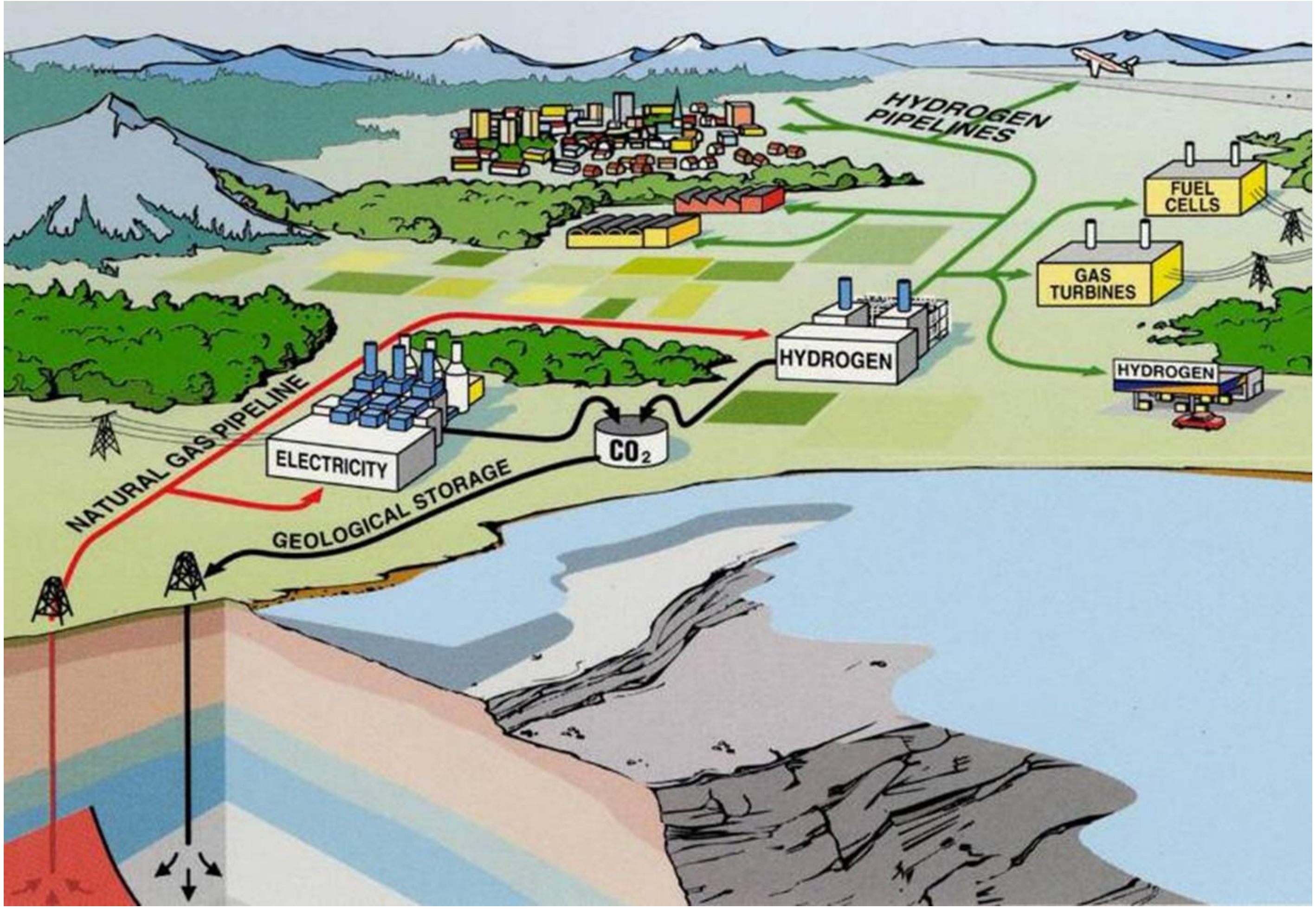
A Vision of a Hydrogen Future

- *"I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. I believe then that when the deposits of coal are exhausted, we shall heat and warm ourselves with water. Water will be the coal of the future."*



Jules Vernes (1870) *L´île mystérieuse*

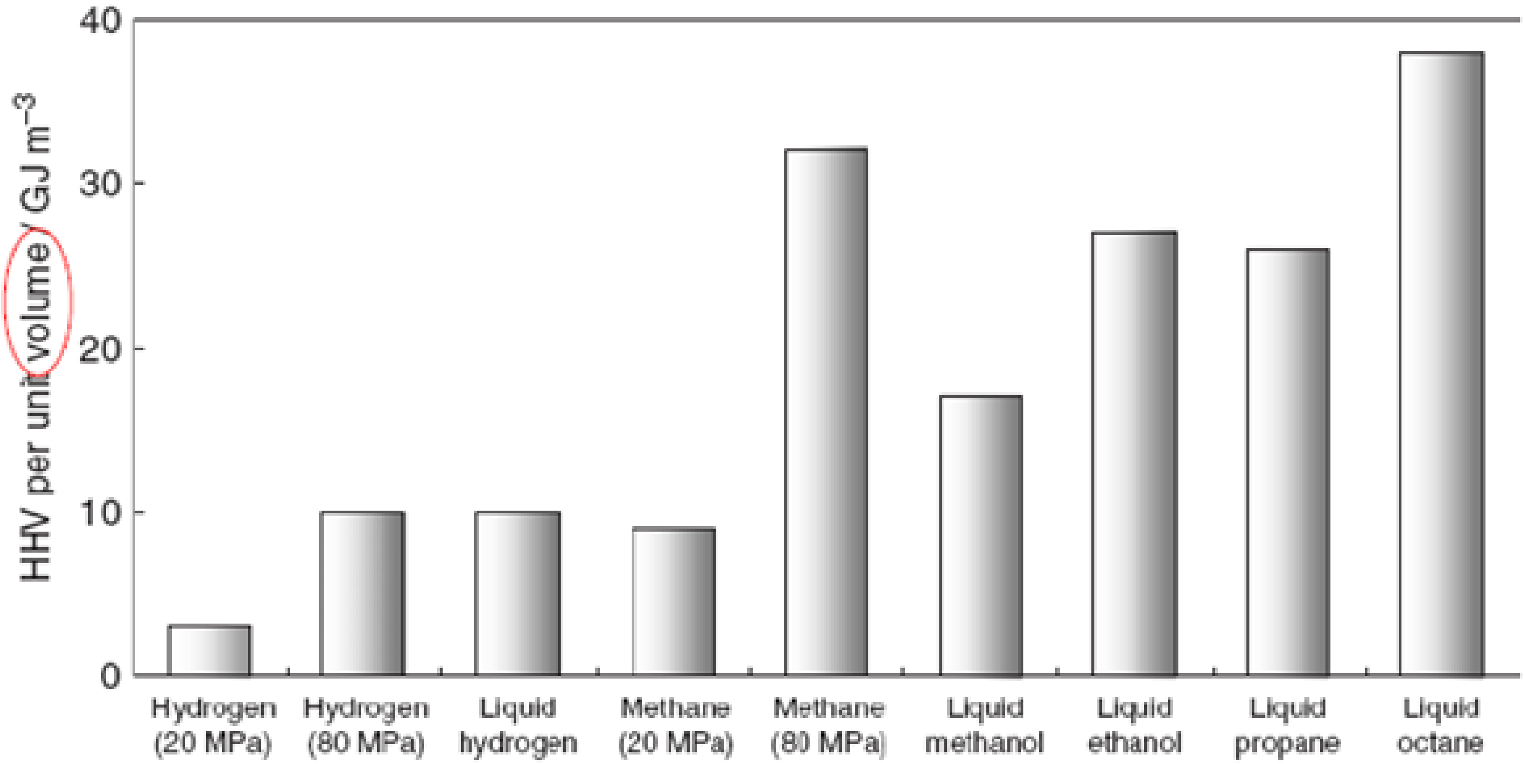
Hydrogen Economy Schematic



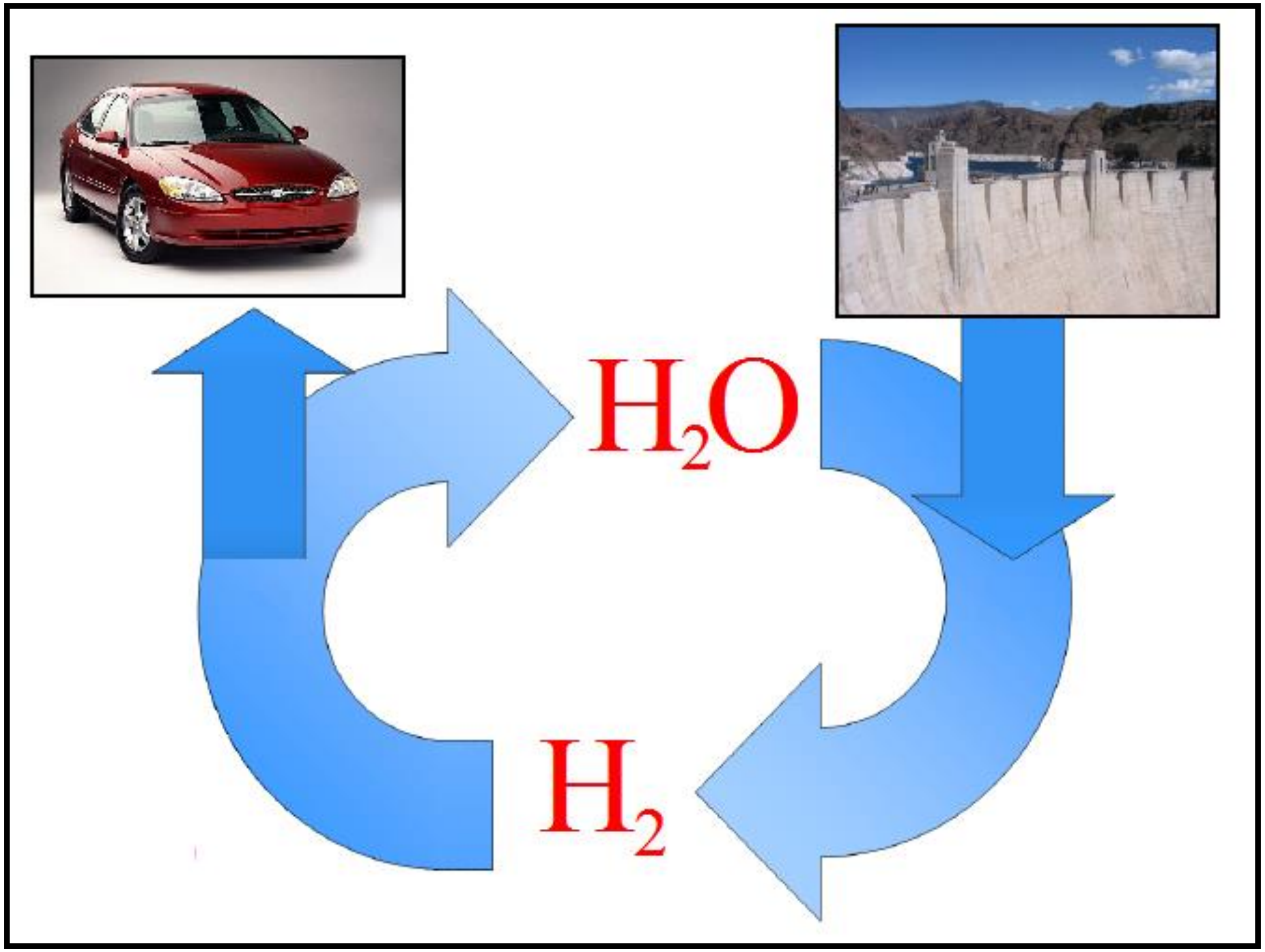
Hydrogen – H_2

Boiling Point	-252.9 oC
Liquid Density @ -253 °C	70.8 kg/m^3
Flammability Limits	4 – 74 %
Ignition Energy	0.005 milli calorie

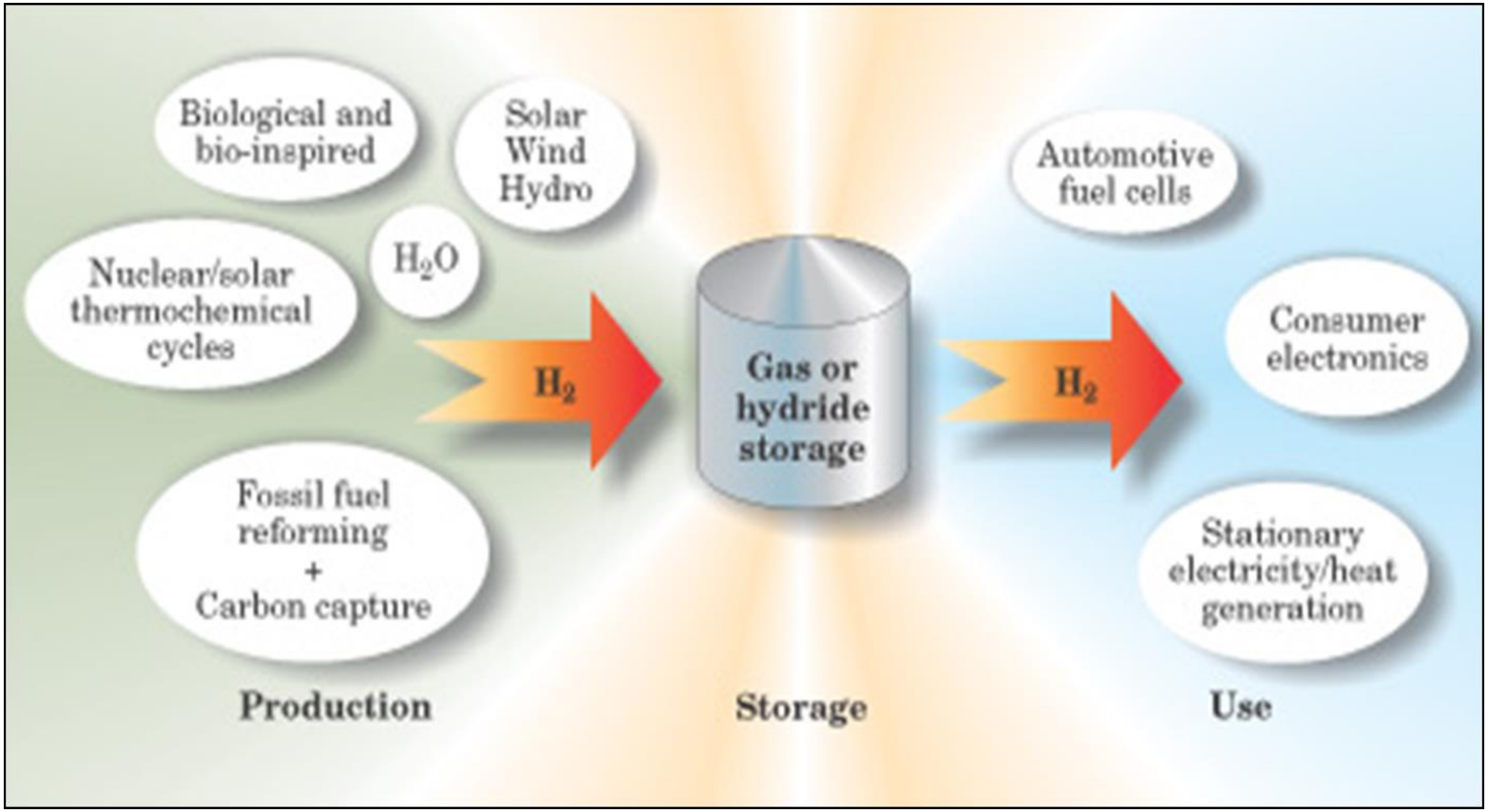
Energy Content of selected "Fuels"



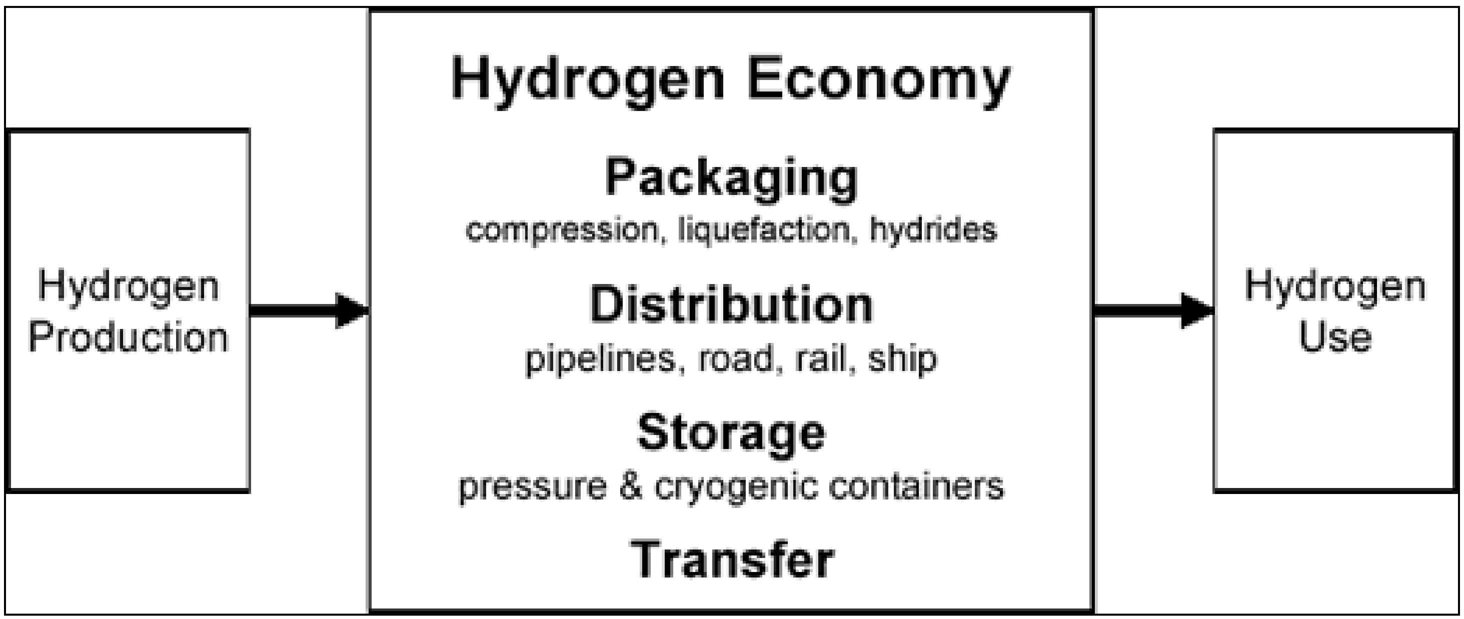
The Ideal Hydrogen Energy Cycle



Hydrogen Economy Cycle



Operating the Hydrogen Economy



Advantages of a Hydrogen Economy

- **Waste product of burning H_2 is water**
- **Elimination of fossil fuel pollution**
- **Elimination of greenhouse gases**
- **Elimination of economic dependence**
- **Distributed production**

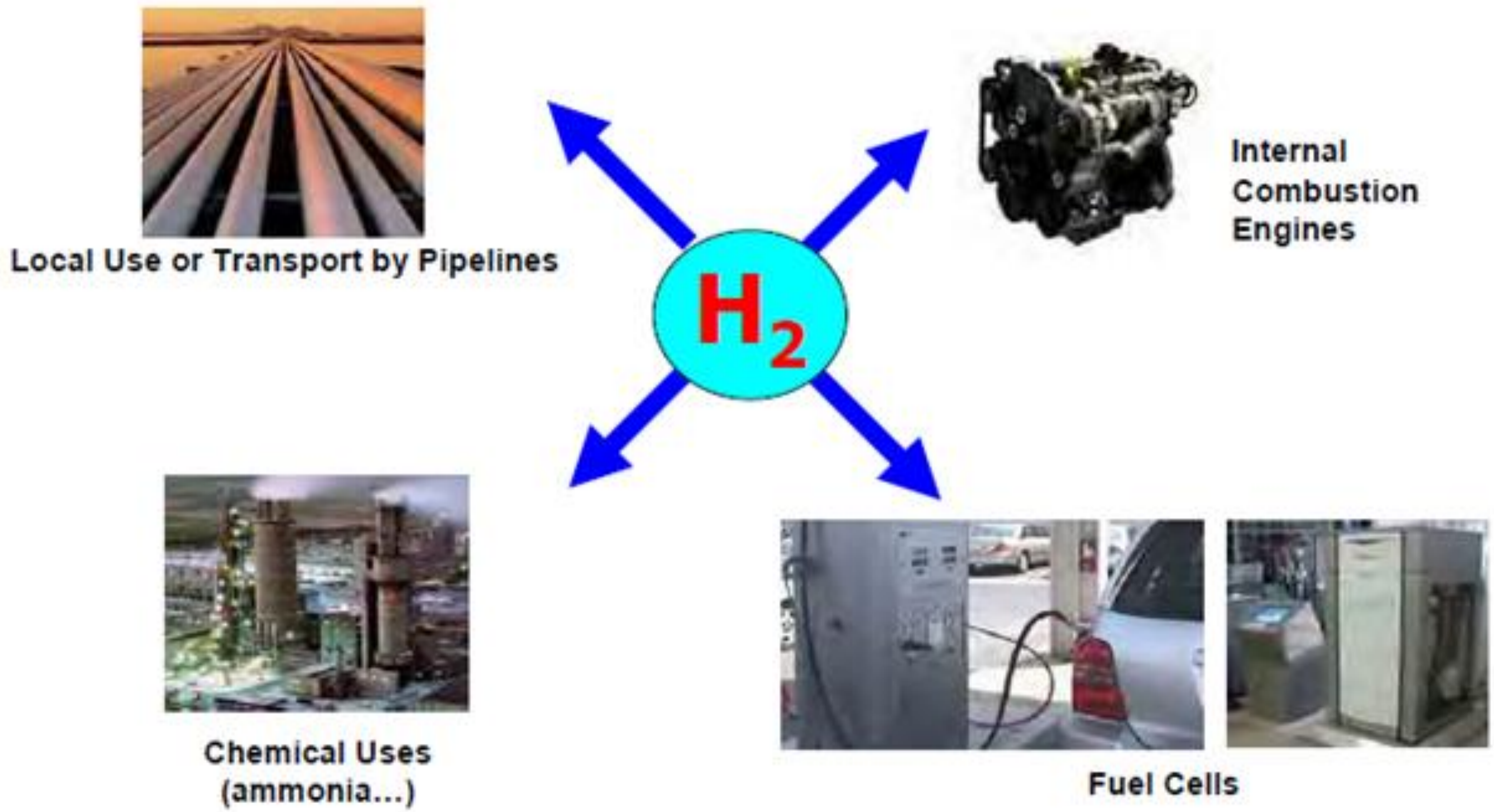
Disadvantages of Hydrogen

- Low energy densities.
- Difficulty in handling, storage, transport.
- Requires an entirely new infrastructure.
- Creates CO_2 if made from fossil fuels.
- Low net energy yields:
  - Much energy needed to create hydrogen.

Issues with Hydrogen

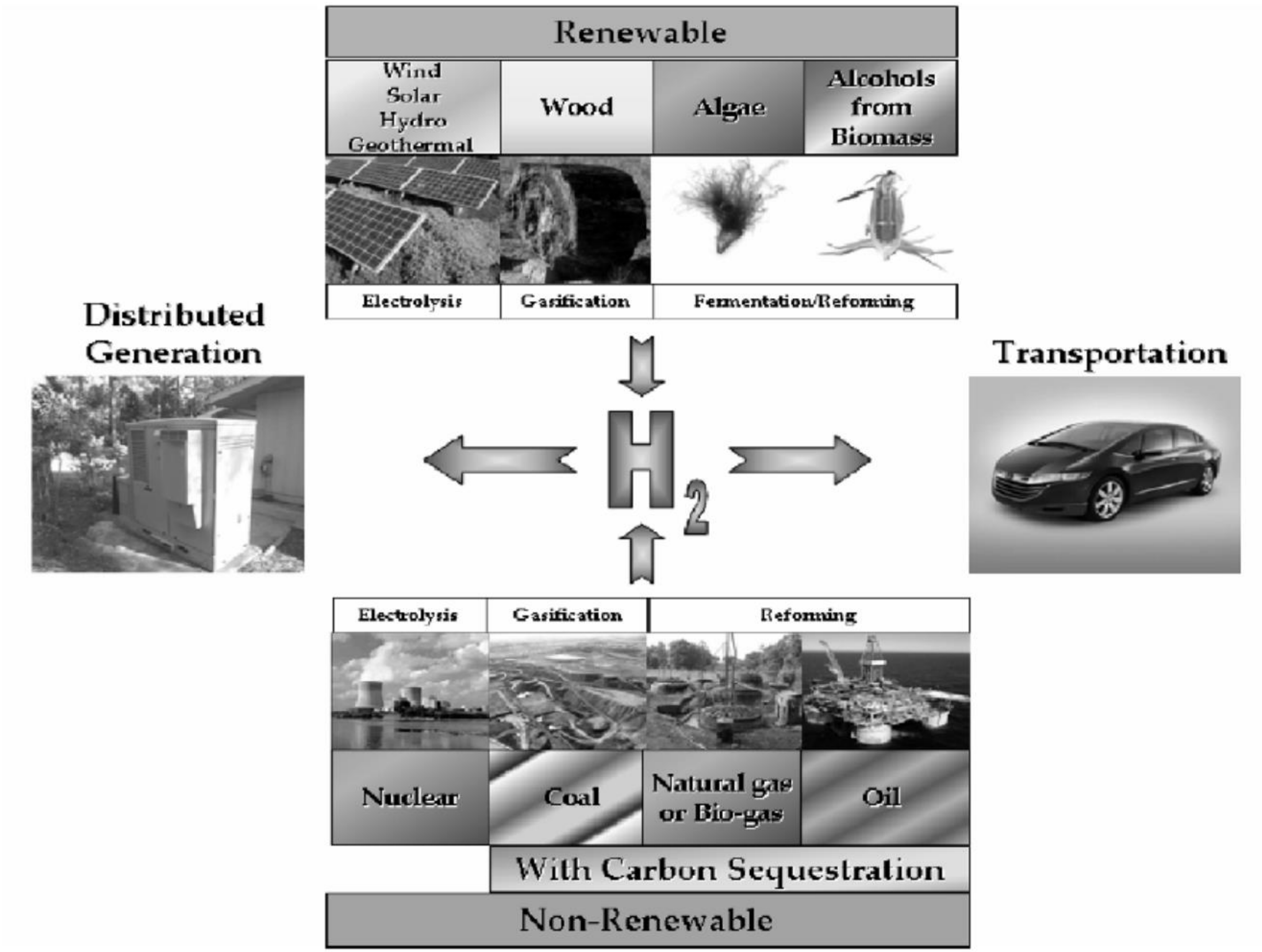
- Not widely available on planet earth.
- Usually chemically combined in water or fossil fuels (must be separated).
- Fossil fuel sources contribute to pollution and greenhouse gases.
- Electrolysis requires prodigious amounts of energy.

Hydrogen Uses



Hydrogen Energy & Air Liquide

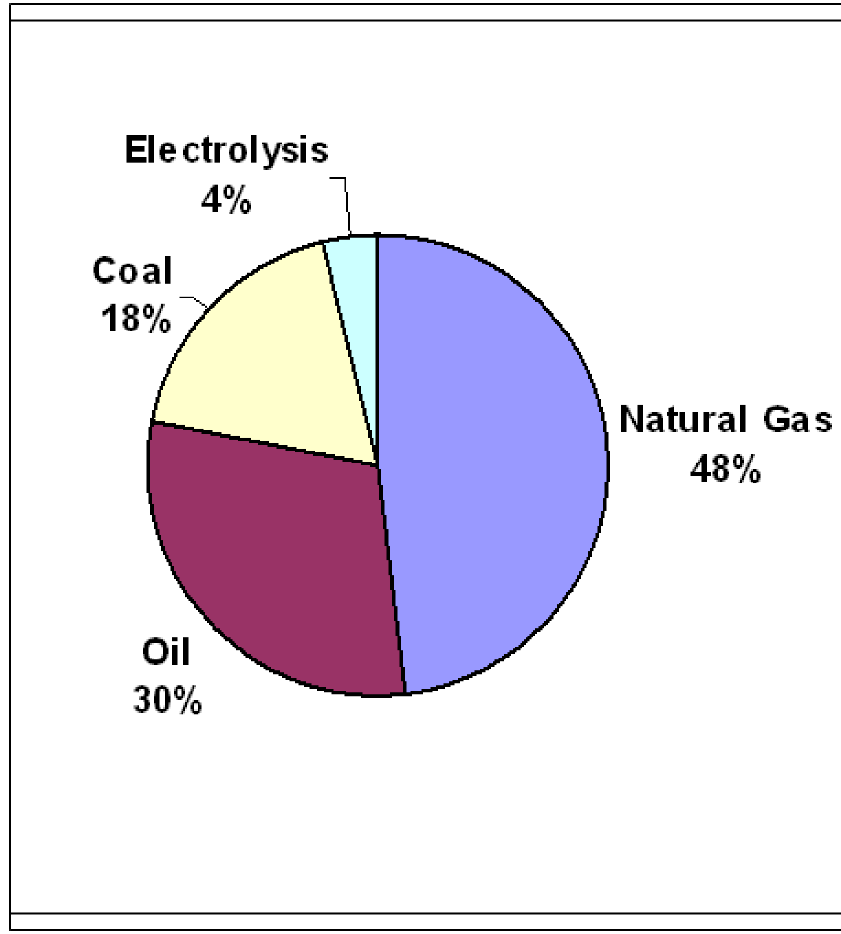
Hydrogen Pathways (1/2)



Current Hydrogen Production

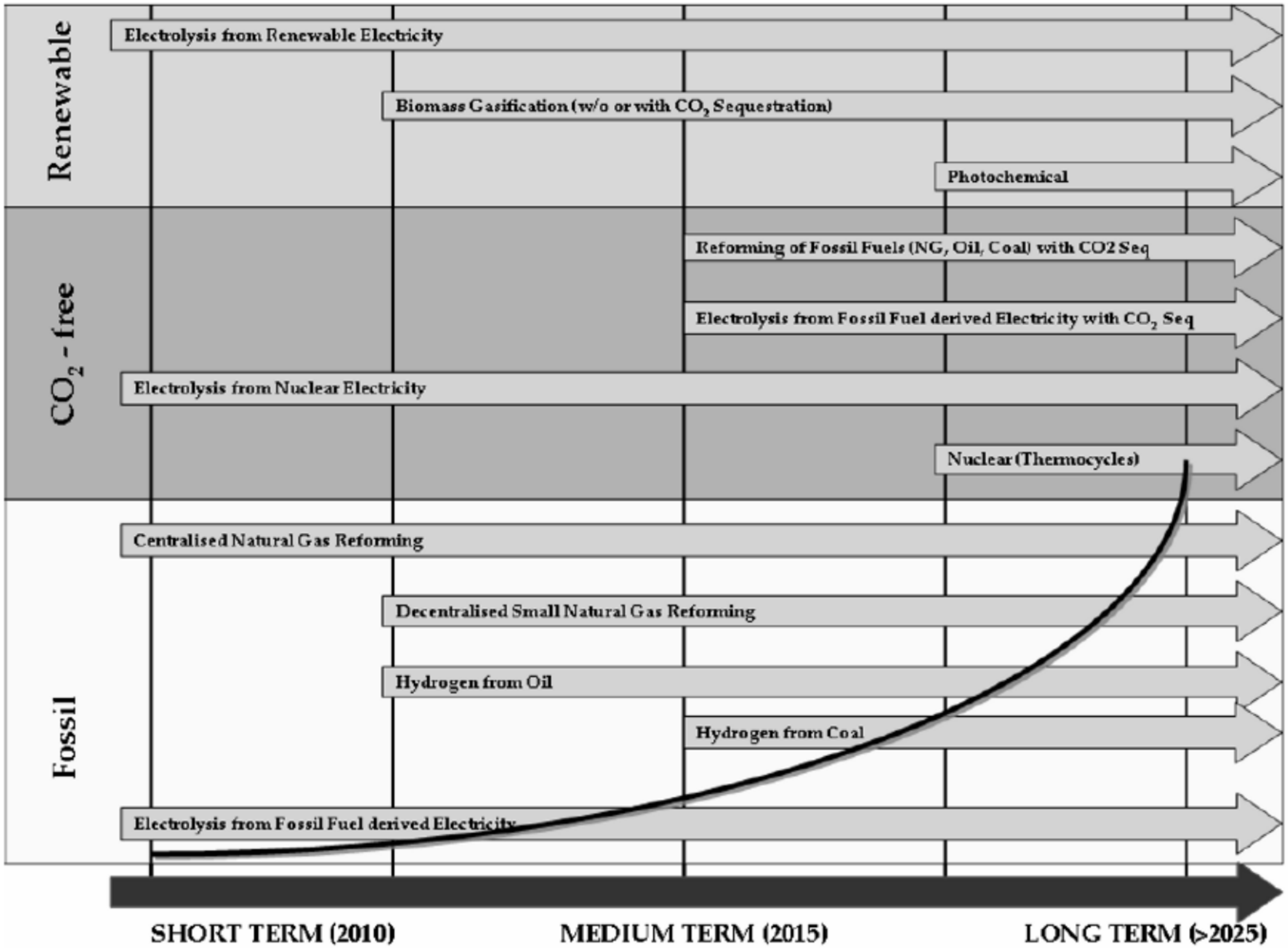
- Current hydrogen production.
  - 48% natural gas.
  - 30% oil.
  - 18% coal.
  - 4% electrolysis.

- Global Production:
  - 50 million tonnes / yr.
  - Growing 10% / yr.



Hydrogen Production

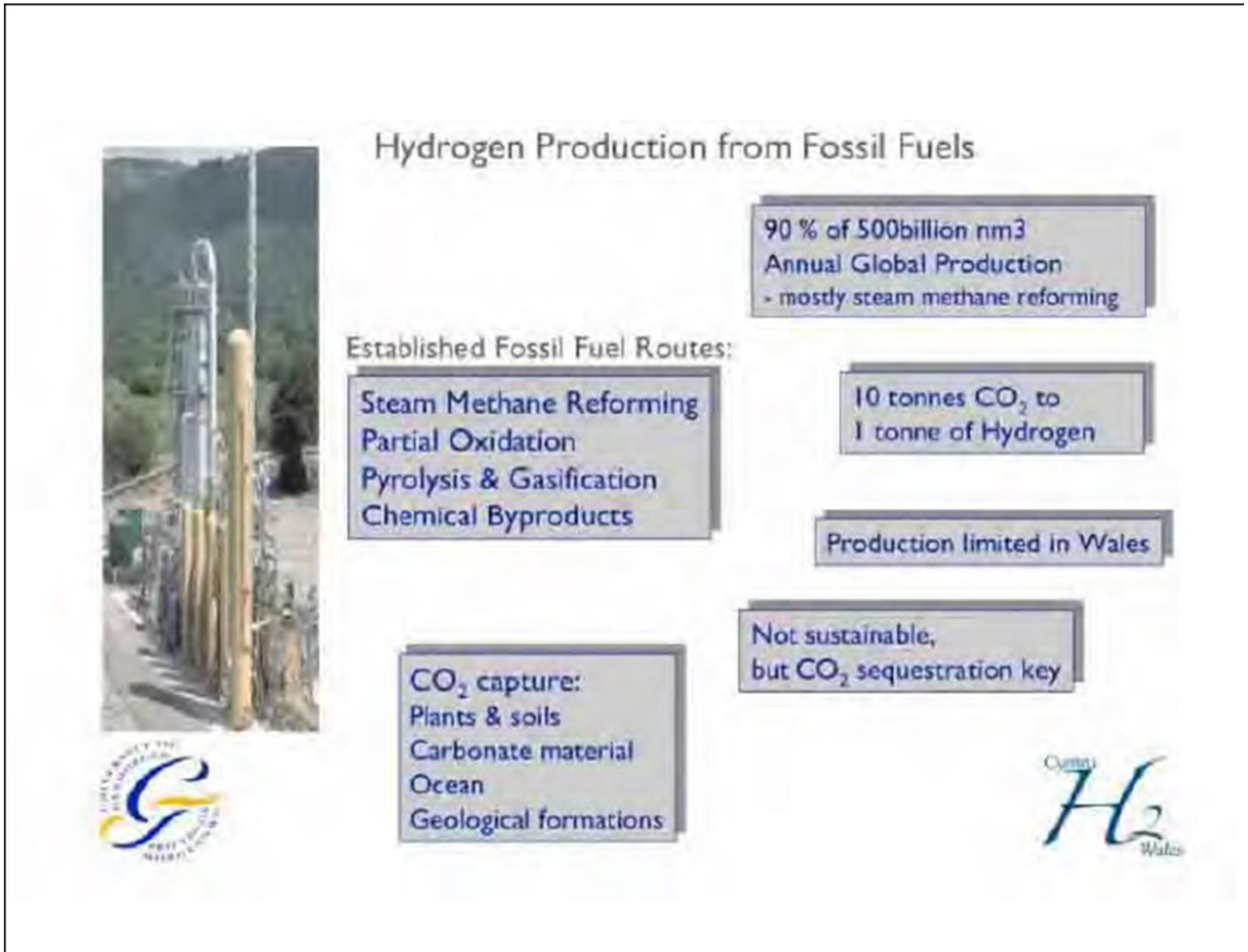
Hydrogen Pathways (2/2)



How is Hydrogen Produced?

- Reforming fossil fuels:
  - Heat hydrocarbons with steam.
  - Produce H_2 and CO.
- Electrolysis of water:
  - Use electricity to split water into O_2 and $H_{2.}$
- High Temperature Electrolysis:
  - Experimental.
- Biological processes:
  - Very common in nature.
  - Experimental in laboratories.

Hydrogen
Production from fossil fuels



Steam Reforming (1/2)

- **From any hydrocarbon**
  - **Natural gas typically used**
- **Water (steam) and hydrocarbon mixed at high temperature (700–1100 °C)**
  - **Steam (H_2O) reacts with methane (CH_4)**
  - **$CH_4 + H_2O \rightarrow CO + 3\ H_2$ - 191.7 kJ/mol**

$$CH_4 + H_2O + heat \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2 + heat$$

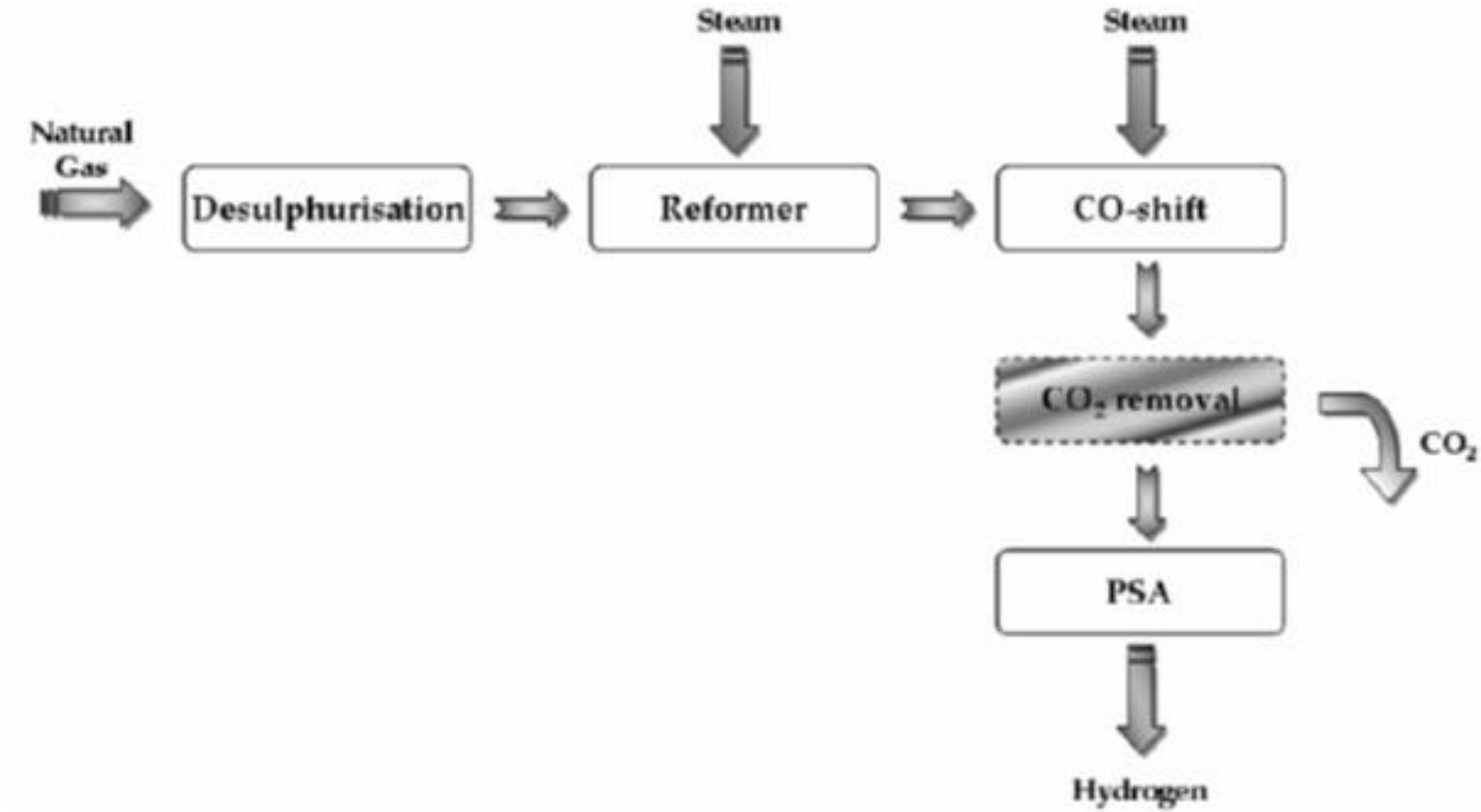
Hydrogen from natural gas reforming (1/4)

Process			H_2/CO
Steam reforming:			
$CH_4 + H_2O$	=	$CO + 3H_2$	3
$C_nH_m + nH_2O$	=	$nCO + (n + \frac{m}{2})H_2$	2-2.5
$CO + H_2O$	=	$CO_2 + H_2$	
CO_2 reforming:			
$CH_4 + CO_2$	=	$2CO + 2H_2$	1
Autothermal reforming (ATR):			
$CH_4 + 1½O_2$	=	$CO + 2H_2O$	(1.8 - 3.8)
$CH_4 + H_2O$	=	$CO + 3H_2$	
$CO + H_2O$	=	$CO_2 + H_2$	
Catalytic partial oxidation (CPO):			
$CH_4 + ½O_2$	=	$CO + 2H_2$	2

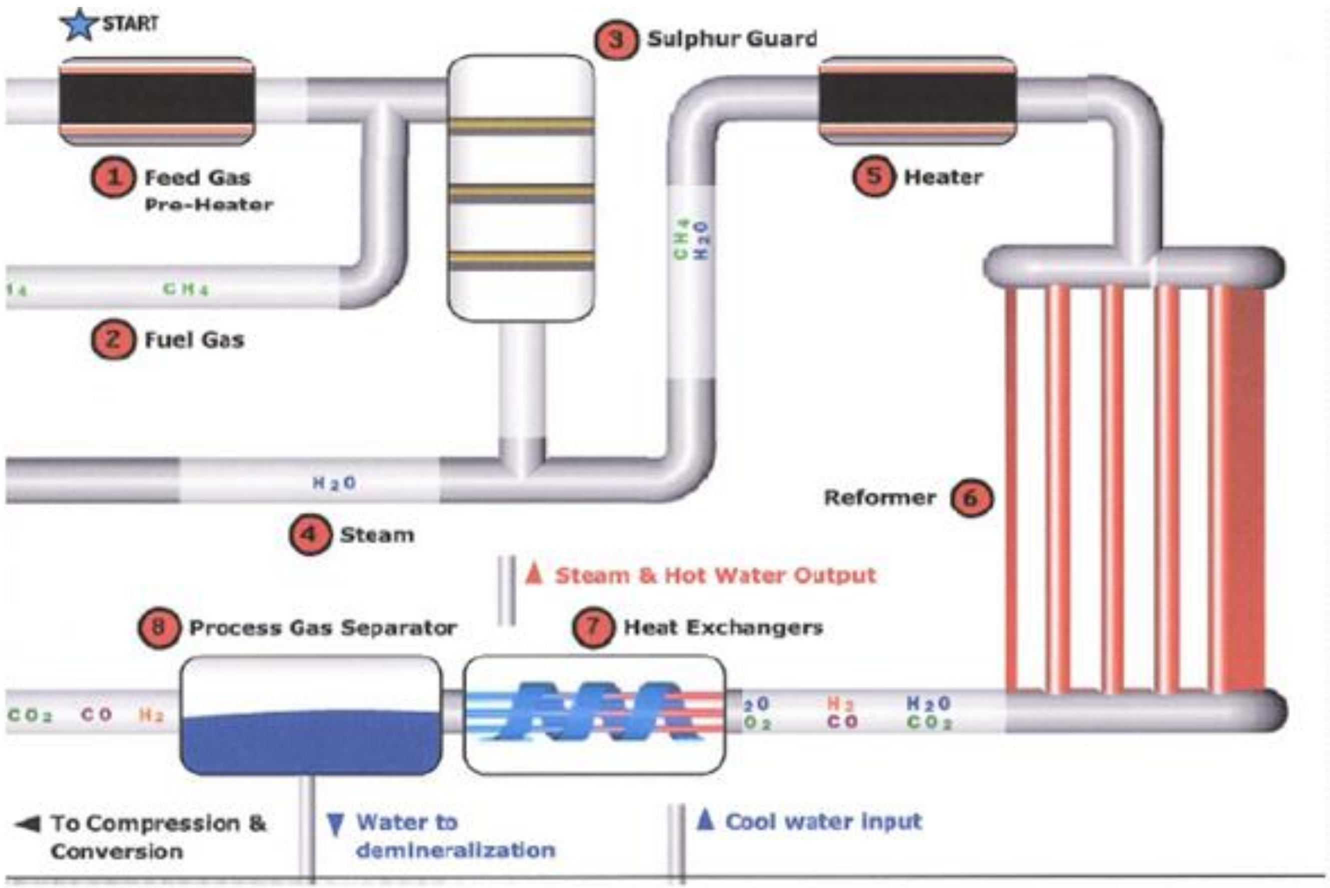
Hydrogen from natural gas reforming (2/4)

	$-\Delta H^0_{298}$ (kJ/mol)
Steam reforming	
$CH_4 + H_2O = CO + 3H_2$	−206
$C_nH_m + nH_2O = nCO + (n + \frac{1}{2}m)H_2$	−1175[a]
$CO + H_2 = CO_2 + H_2$	41
CO_2 reforming	
$CH_4 + CO_2 = CO + 2H_2$	−247
ATR	
$CH_4 + 1\frac{1}{2}O_2 = CO + 2H_2O$	520
$H_2O + CH_4 = CO + 3H_2$	−206
$CO + H_2O = CO + H_2$	41
CPO	
$CH_4 + \frac{1}{2}O_2 = CO + 2H_2$	38

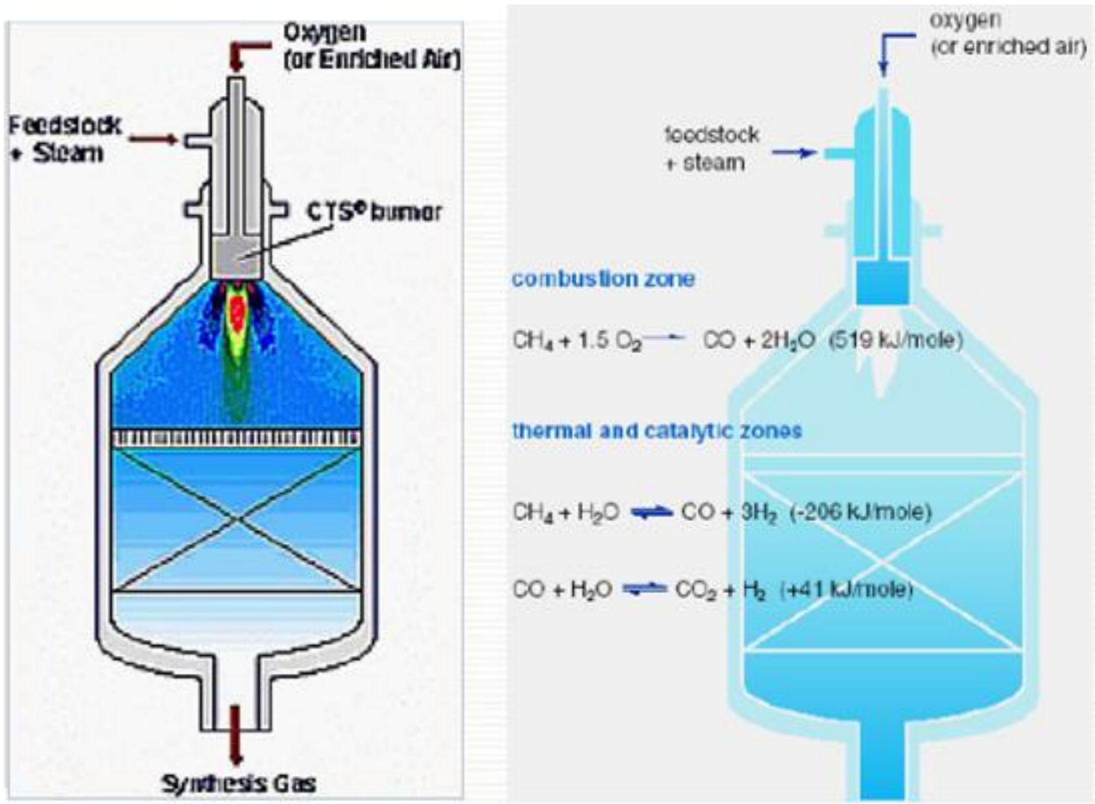
Steam Reforming (2/2)



Hydrogen from natural gas reforming (3/4)

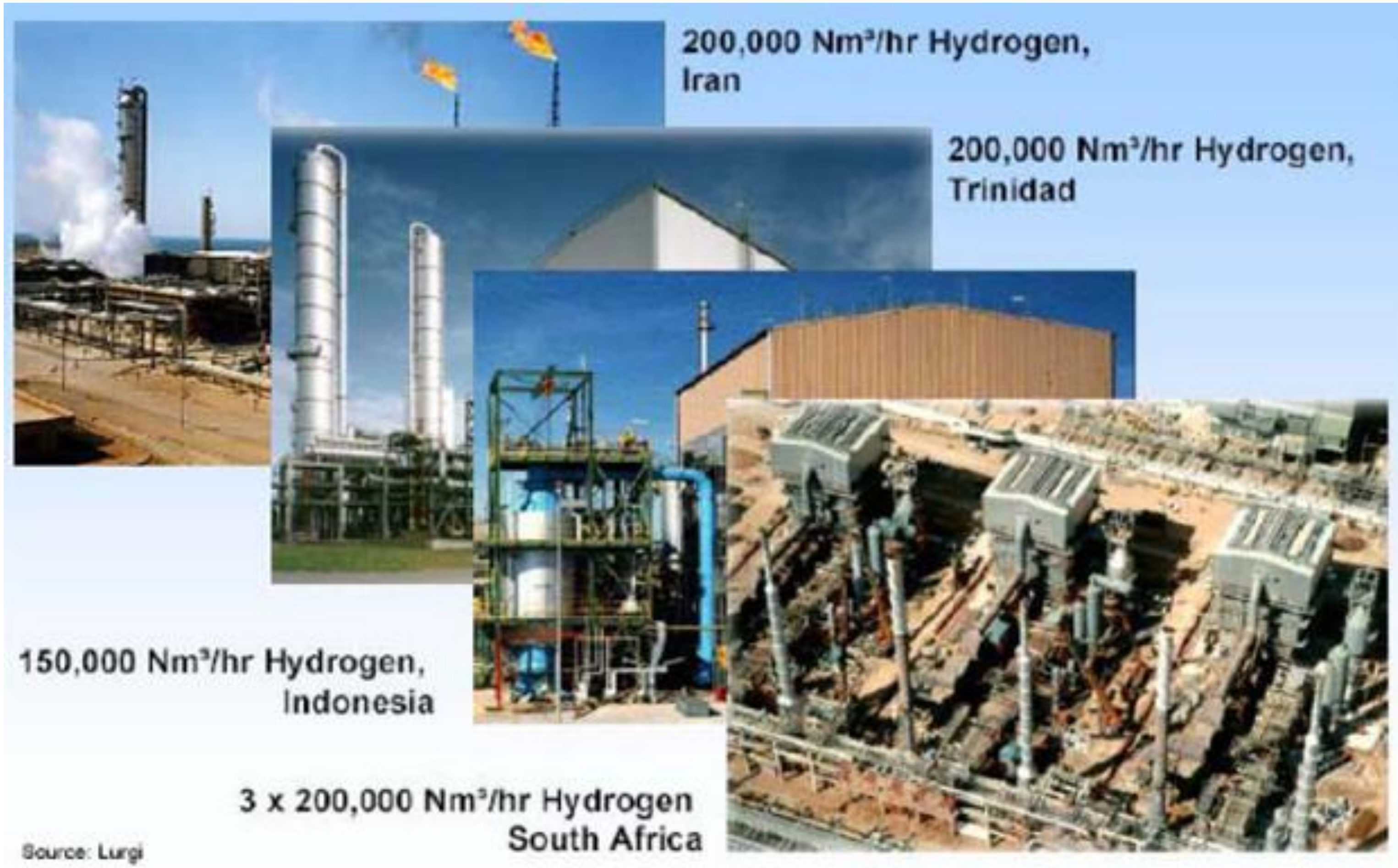


Autothermal Reformer



Steam Reforming Plants

Hydrogen from natural gas reforming (4/4)



Steam Reforming Techno-Economic Data

Table 3.1. Technical and economic data for different SMR options (Stoukides, 2000 and Dreier *et al.*, 2000)

		Small–scale on-site SMR		Large–scale SMR		Solar reformer
		State of the art	Long–term target	State of The art	Long–term target	Long–term target
		TECHNICAL DATA				
Capacity natural gas	kW	4500	4275	405,000	385,000	125,000
Solar heat	kW					47,700
Hydrogen output	Nm^3/h	1000	1000	100,000	100,000	50,000
Pressure	Bar	16	16	30	30	
Efficiency (H_2 LHV)	%	67	70	74	78	87
Lifetime	yr	25	25	25	25	20
Utilisation time	hr/yr	8000	8000	8000	8000	2000
		ECONOMIC DATA				
Investment cost	$€_{2000}/kW_{H2}$	690	655	335	320	370
Fixed cost	%Invest./yr	5	5	2	2	5.5
Variable cost	$€_{2000}/Nm^3$	0.003	0.003	0.003	0.003	0.013

Integrated gasification coal combustion (IGCC)

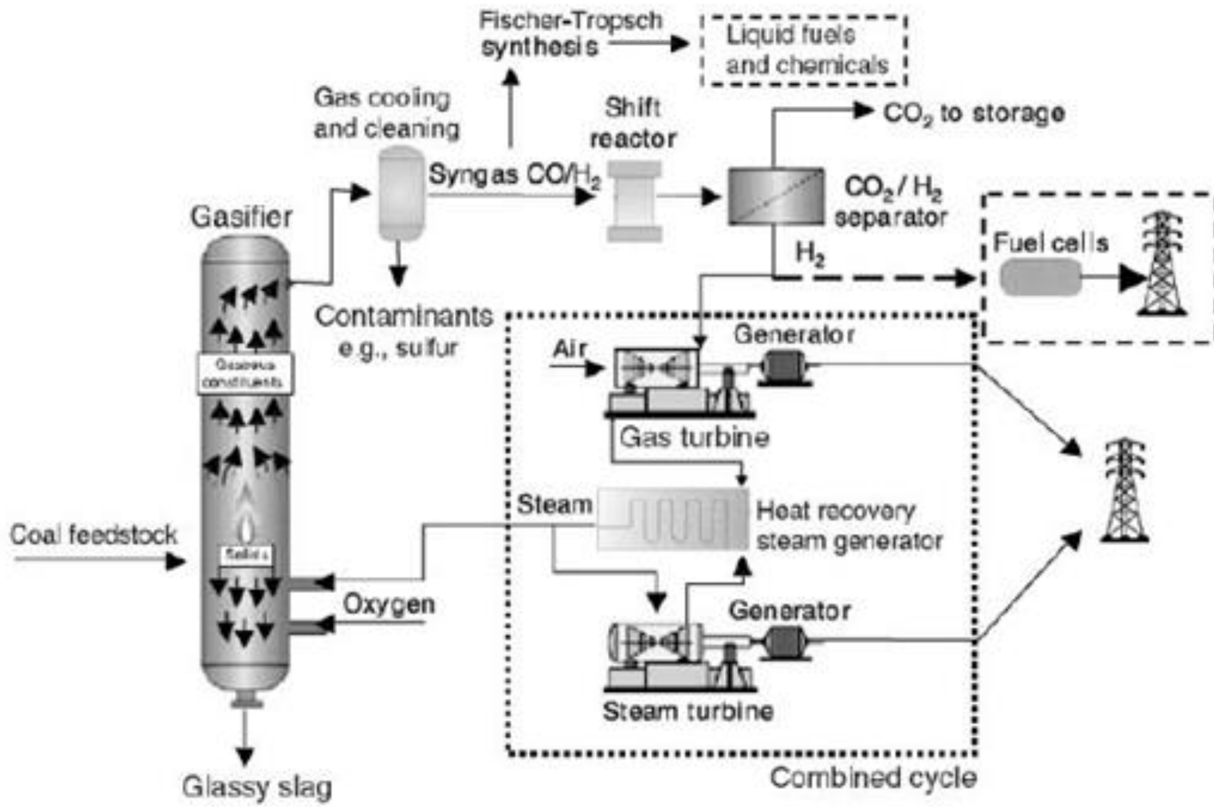
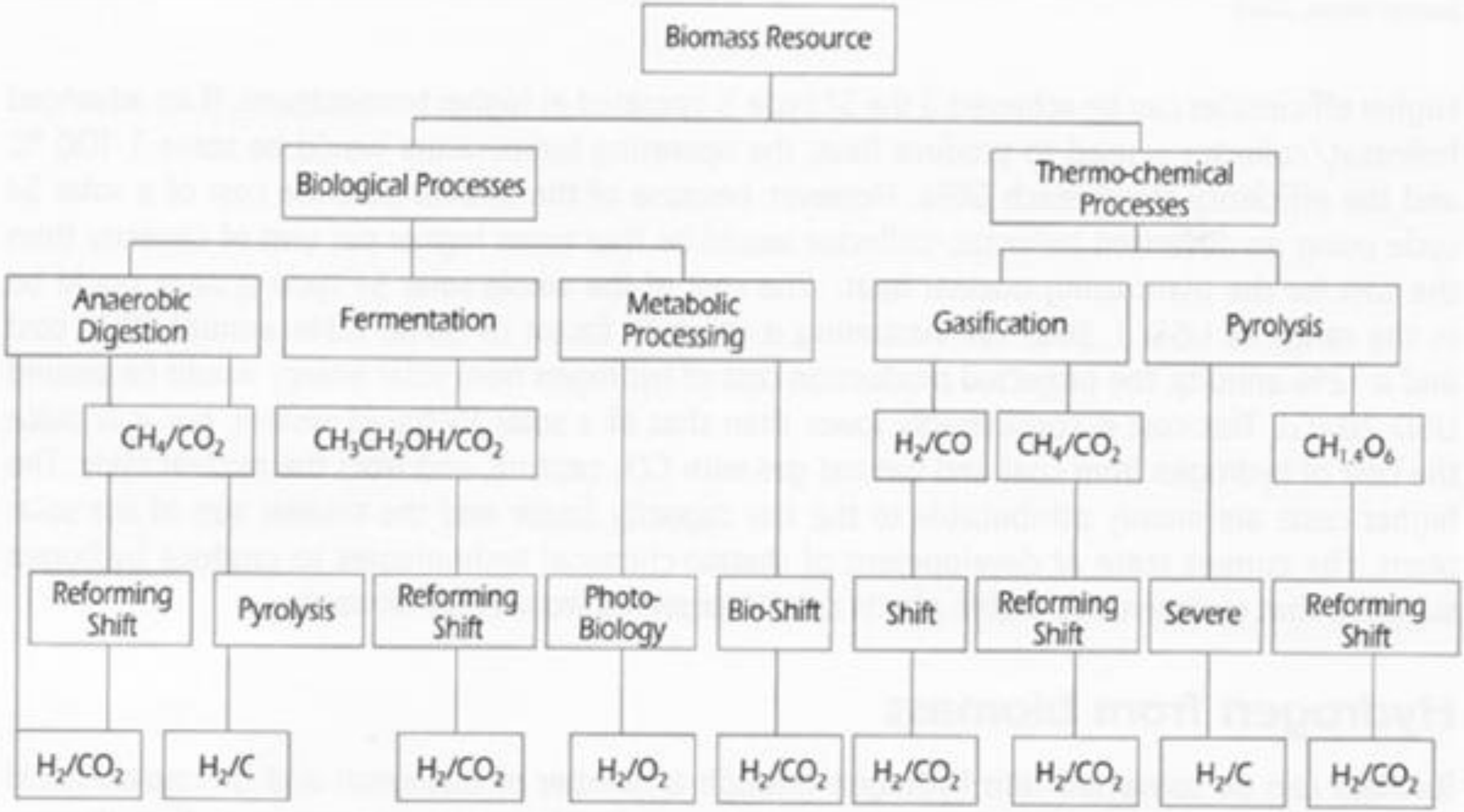


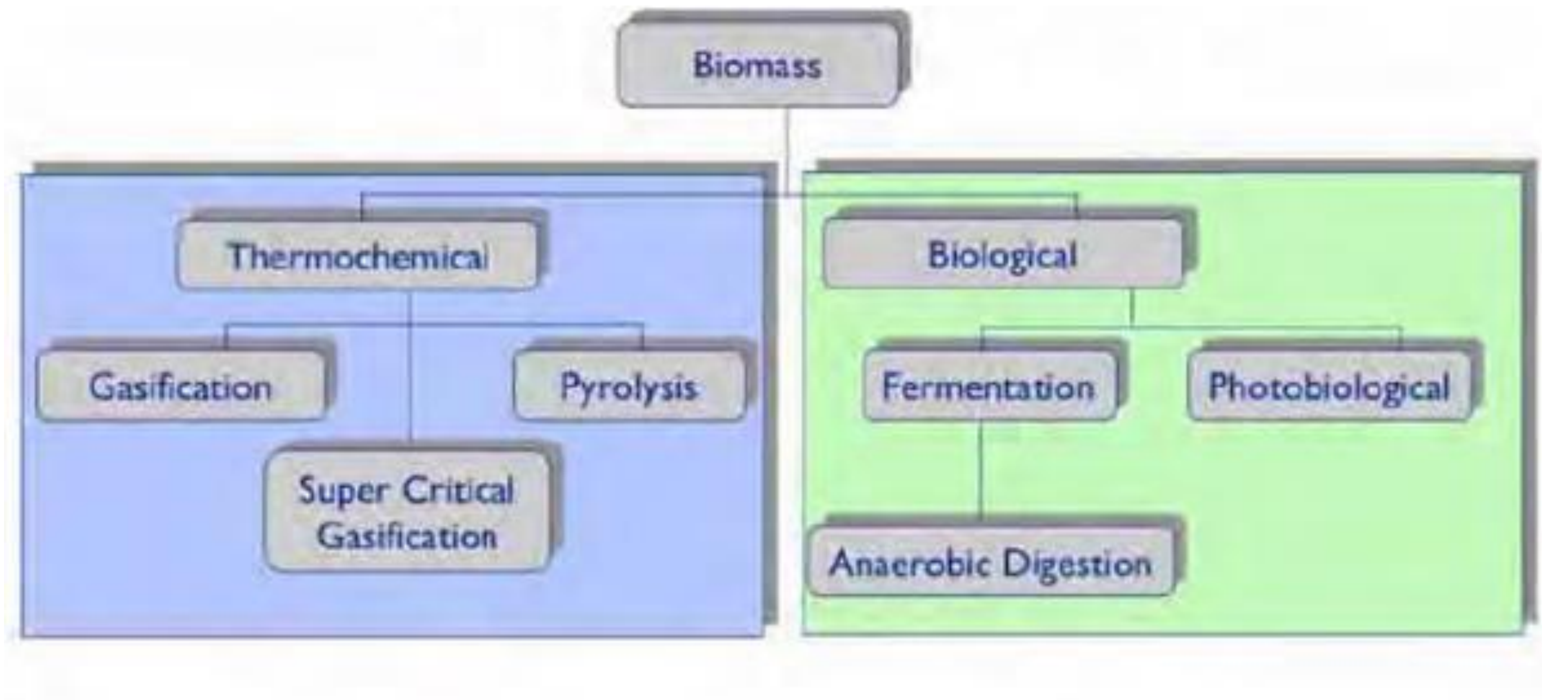
Figure 2.9 Concept of a poly-generation plant based on the IGCC process.

Biomass to H2 Routes

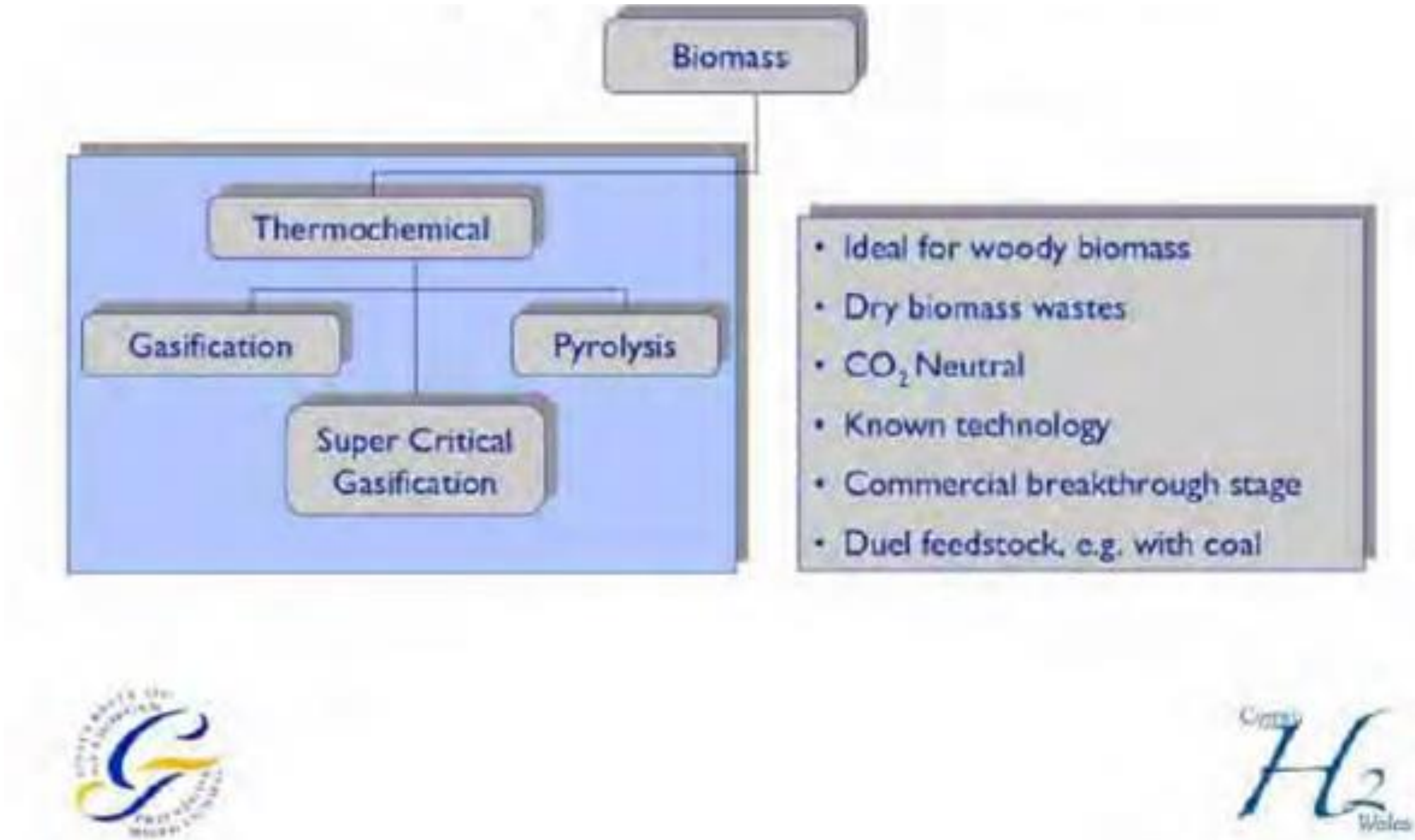


Source: Larsen *et al.*, 2004.

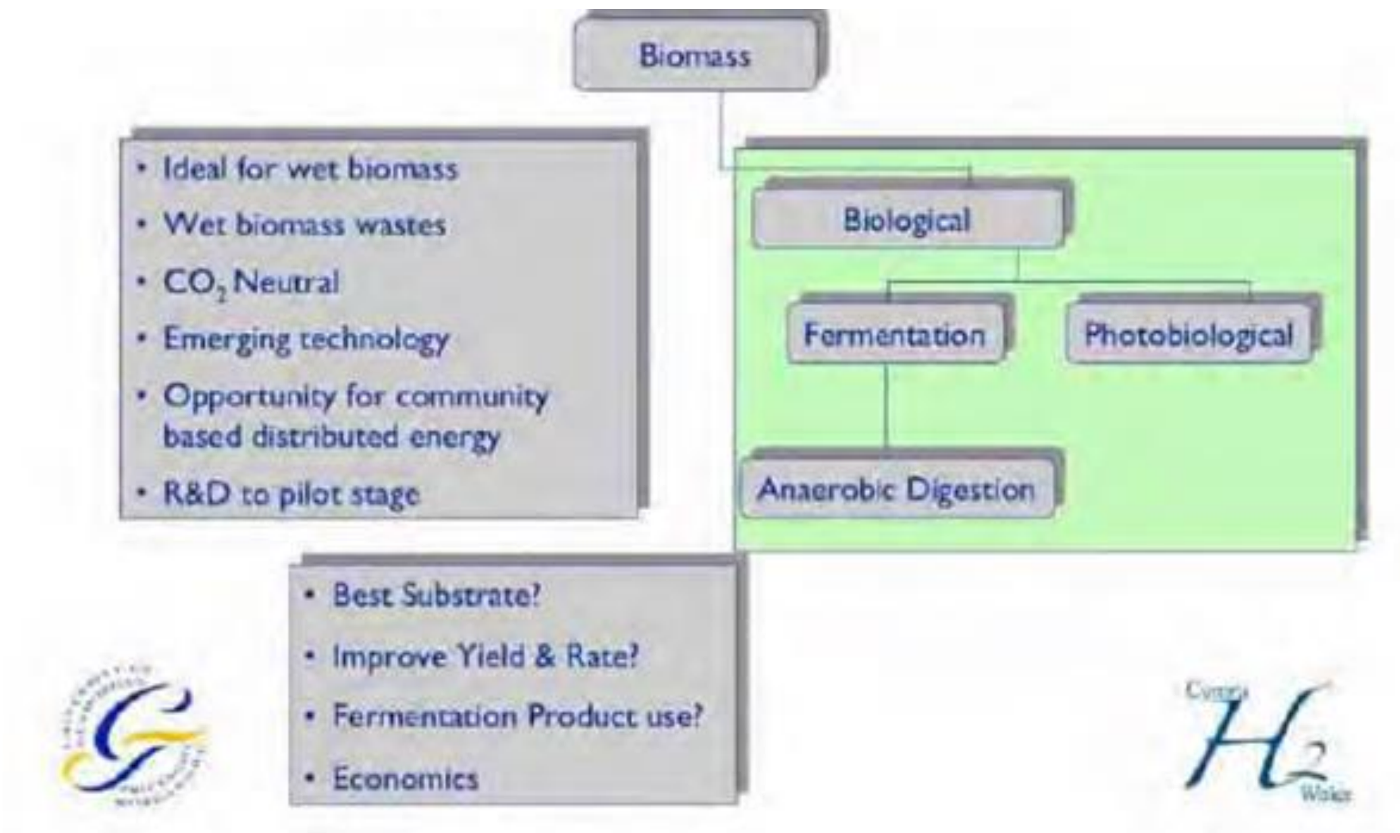
Hydrogen Production from Biomass (1/3)



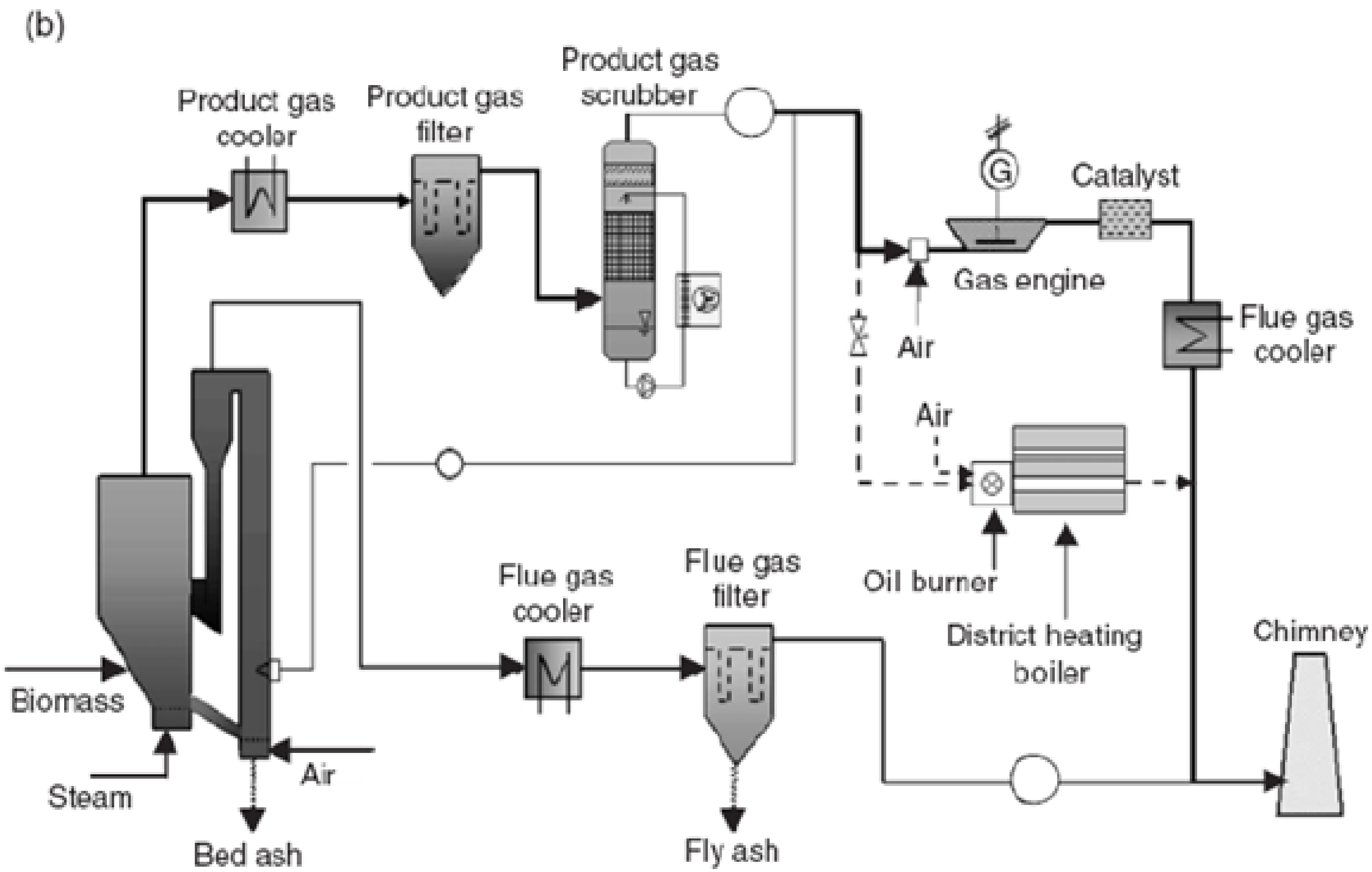
Hydrogen Production from Biomass (2/3)



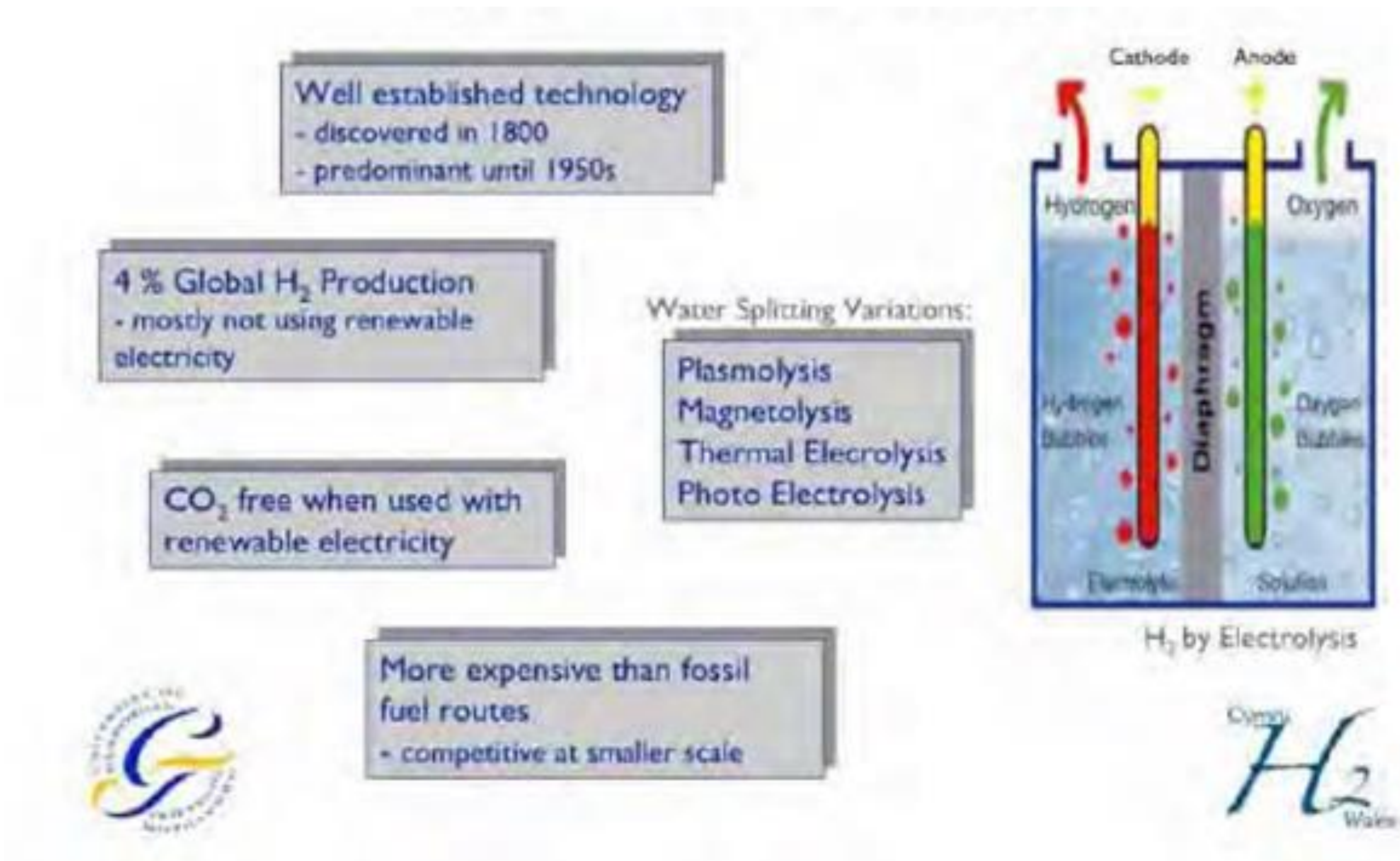
Hydrogen Production from Biomass (3/3)



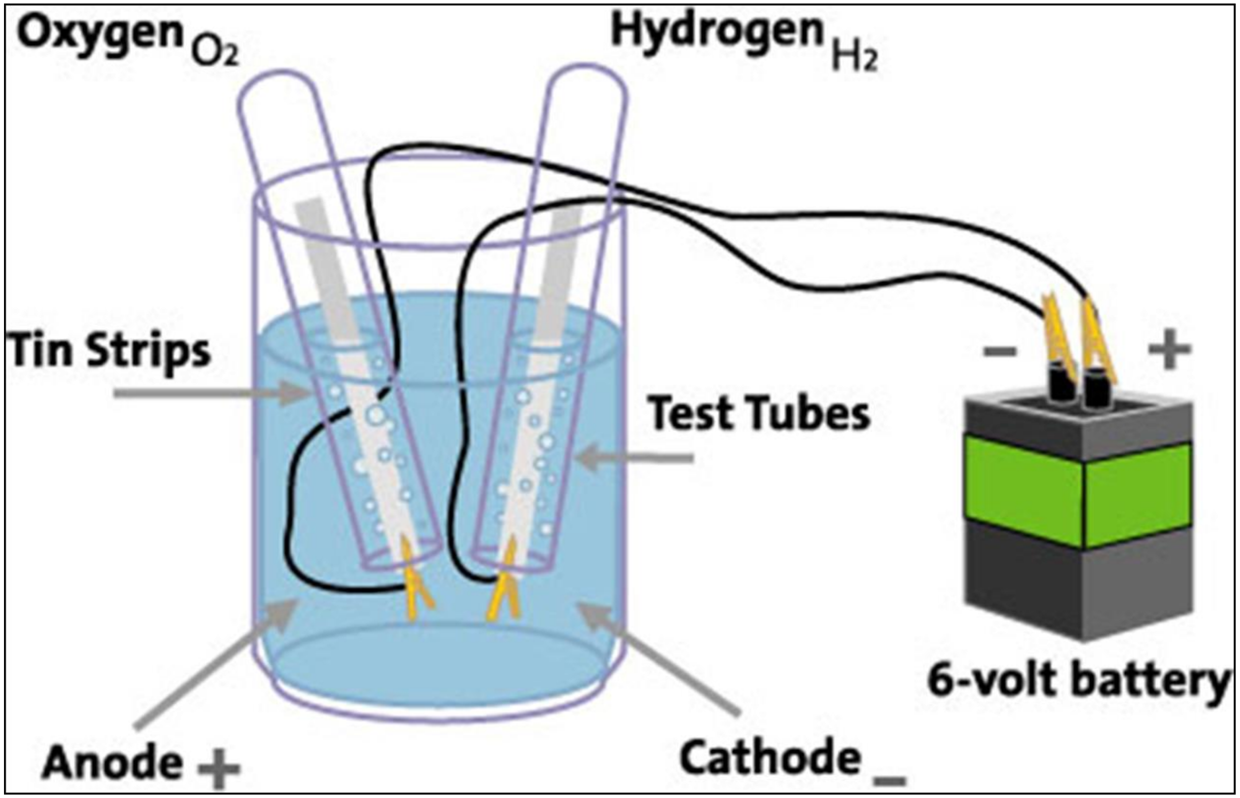
Hydrogen from Biomass



Hydrogen Production by Electrolysis



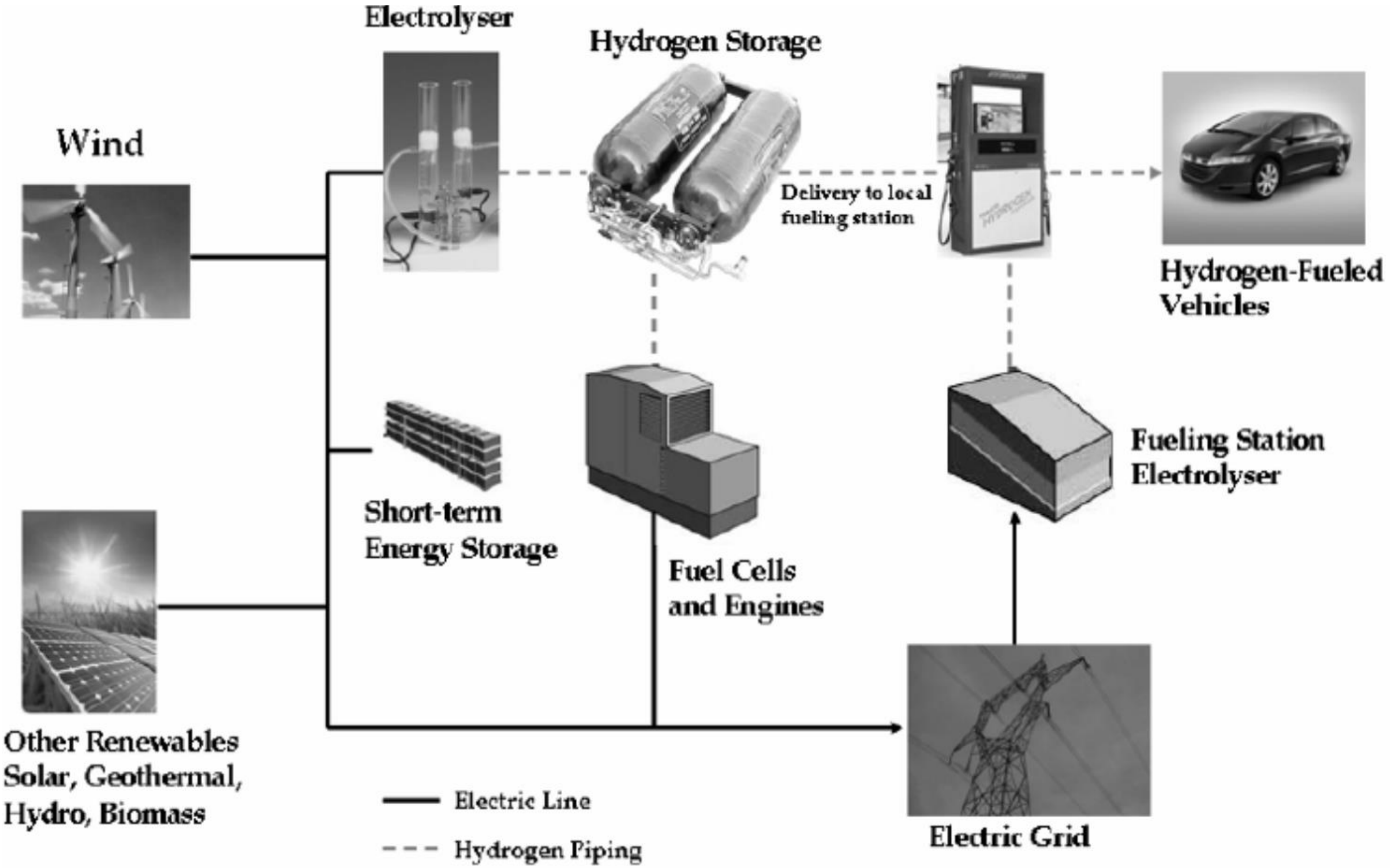
Electrolysis of Water (H_2O)



$$H_2O + electricity \rightarrow H_2 + \frac{1}{2} O_2$$

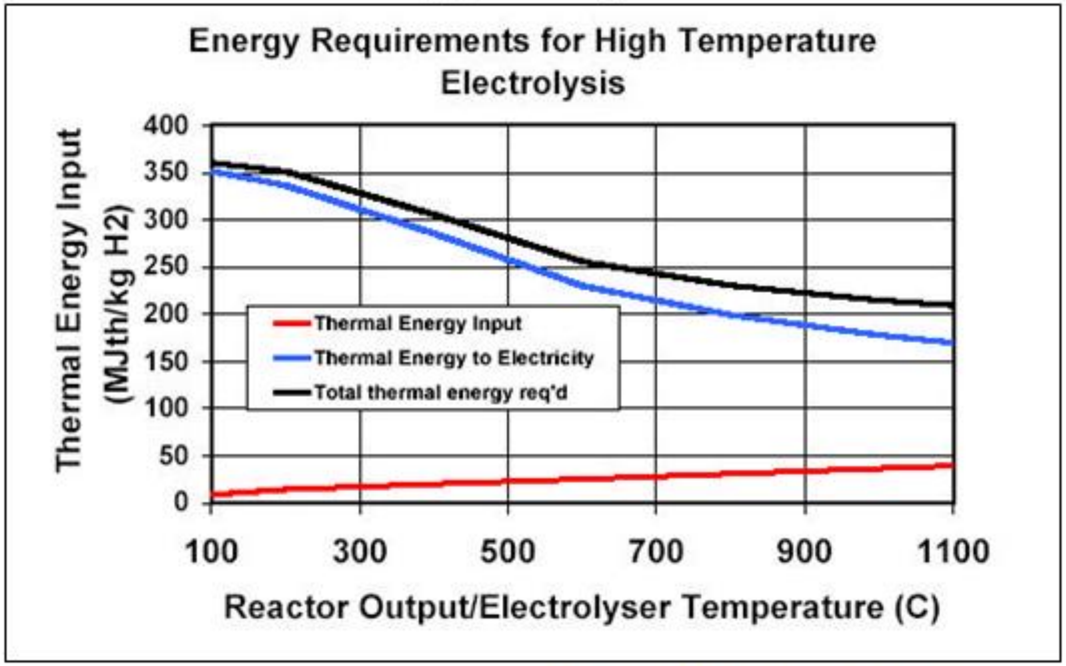
http://www.gm.com/company/gmability/edu_k-12/9-12/fc_energy/make_your_own_hydrogen_results.html

Electrolysis of Water



High Temperature Electrolysis

- **Electrolysis at high temperatures**
- **Use less energy to split water**



http://en.wikipedia.org/wiki/Hydrogen_economy

Electrolysis Techno-Economic Data

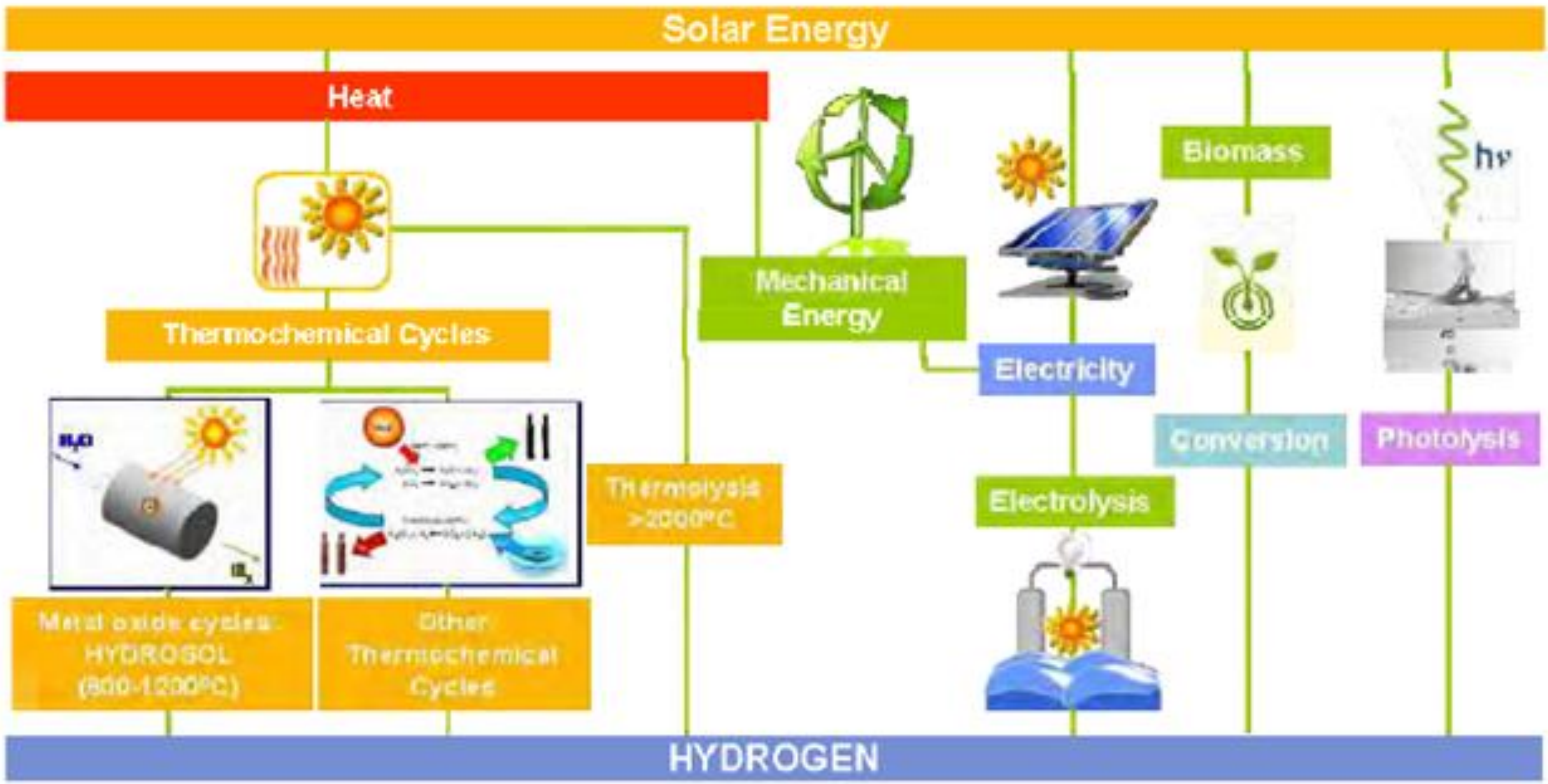
Table 3.3. Technical and economic data of various types of electrolysers

		High–pressure alkaline electrolyser		PEM electrolyser		SOEC
		State of the art	Long–term target	State of The art	Long–term target	Long–term target
		TECHNICAL DATA				
Hydrogen output	N m^3/h	5–50000	5–50,000	10	30	> 10,000
Electricity input	kW/kW$_{H2}$	1.43	1.3	2		1.07
Steam input	kW/kW$_{H2}$					0.2
Pressure	bar	30	100	1.4	400	
Efficiency (H_2 LHV)	%	70	80	50		79
Lifetime	yr	20	20			20
Stack lifetime	yr			3–4	5	9

		ECONOMIC DATA						
		< 5MW$_{el}$		> 5MW$_{el}$				
		SotA	LTT	SotA	LTT			
Investment cost								
Electrolyser	€$_{2000}$/kW$_{el}$	525	450	420	360			
Full system	€$_{2000}$/kW$_{el}$	600	510	480	410	1565		1000
Investment cost								
Electrolyser	€$_{2000}$/kW$_{H2}$	750	560	600	450			
Full system	€$_{2000}$/kW$_{H2}$	860	640	690	510	3130		1270
Fixed cost	%Invest./yr	2	2	2	2	2		2

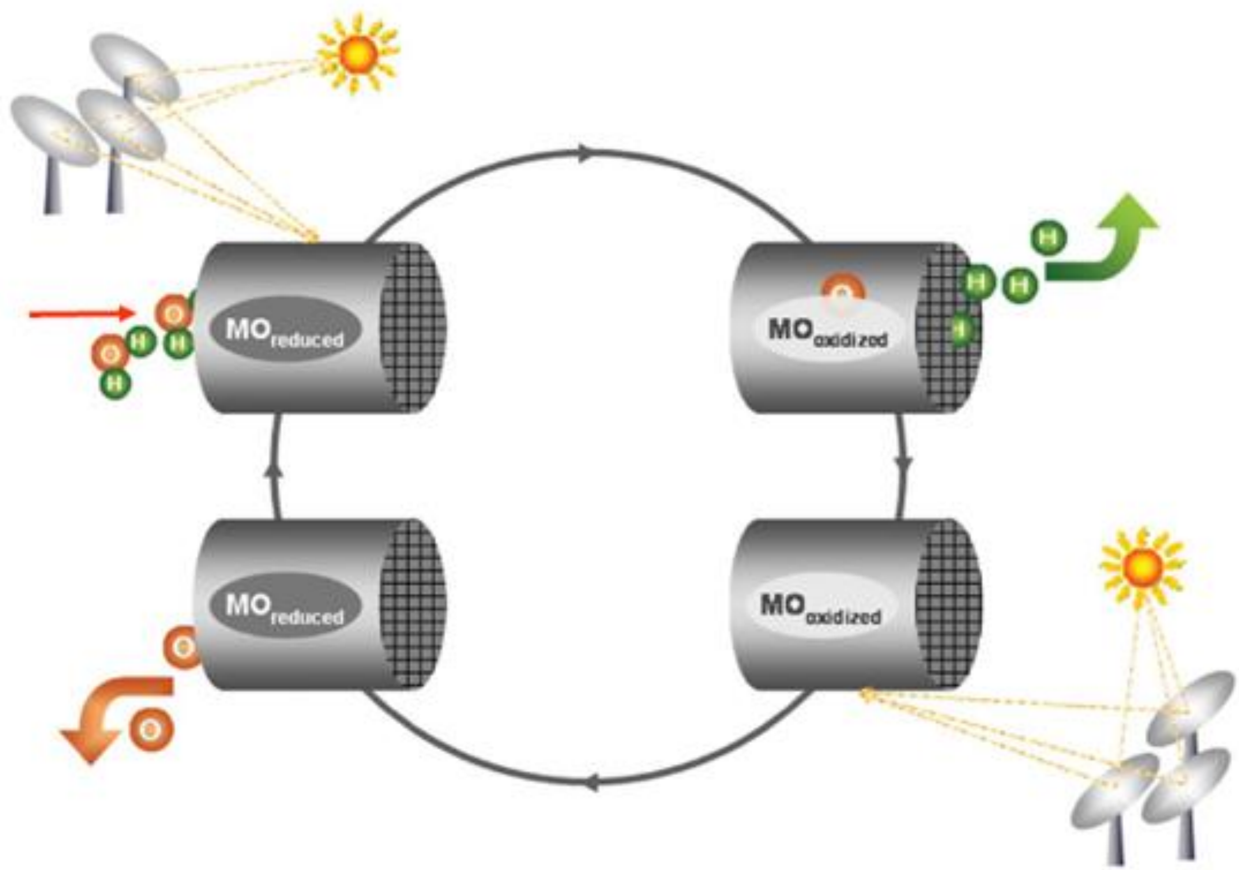
SotA: State of the art; LTT: Long-term target

Renewable Hydrogen Pathways



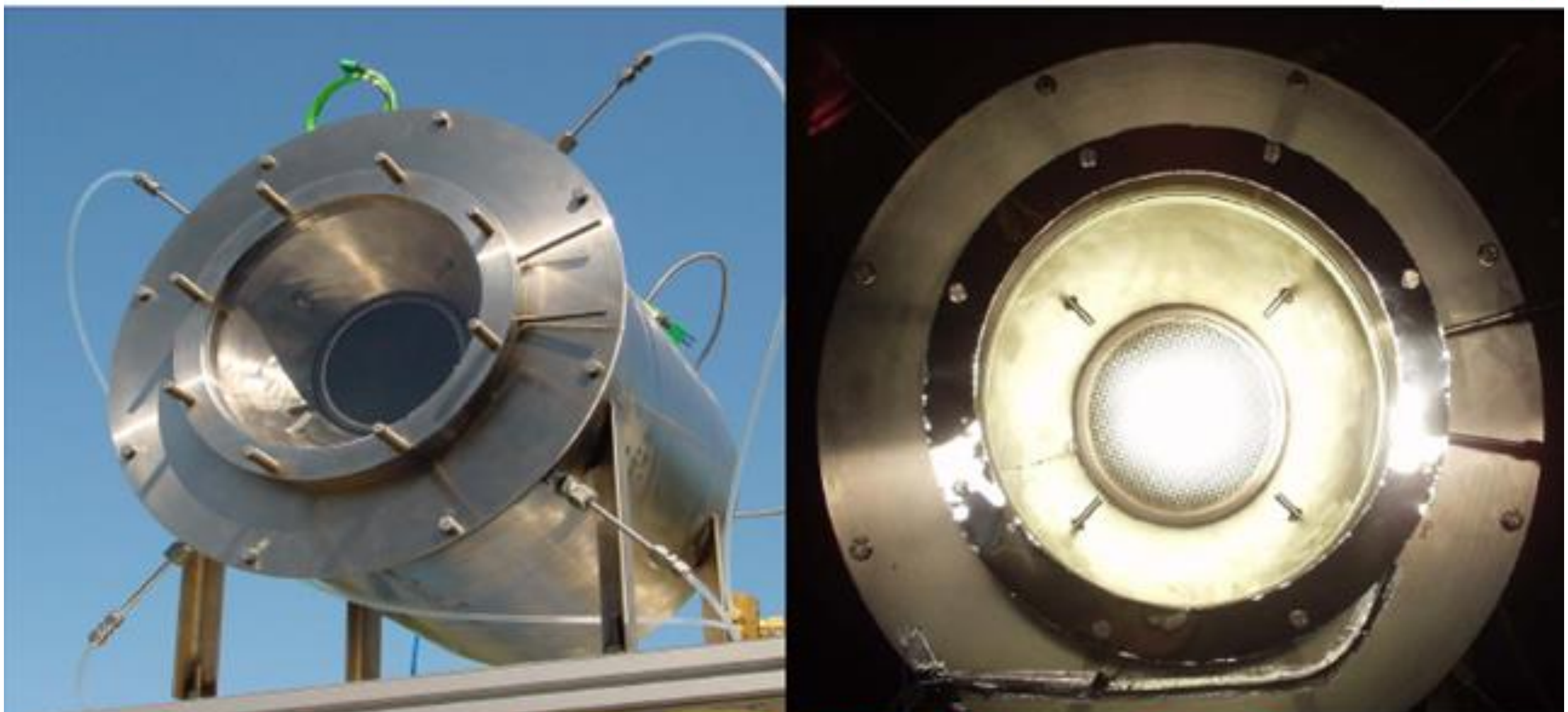
Lorentzou and Konstandopoulos, in Solar Hydrogen and Nanotechnology, Wiley (2009)

Solar Hydrogen: the Hydrosol process



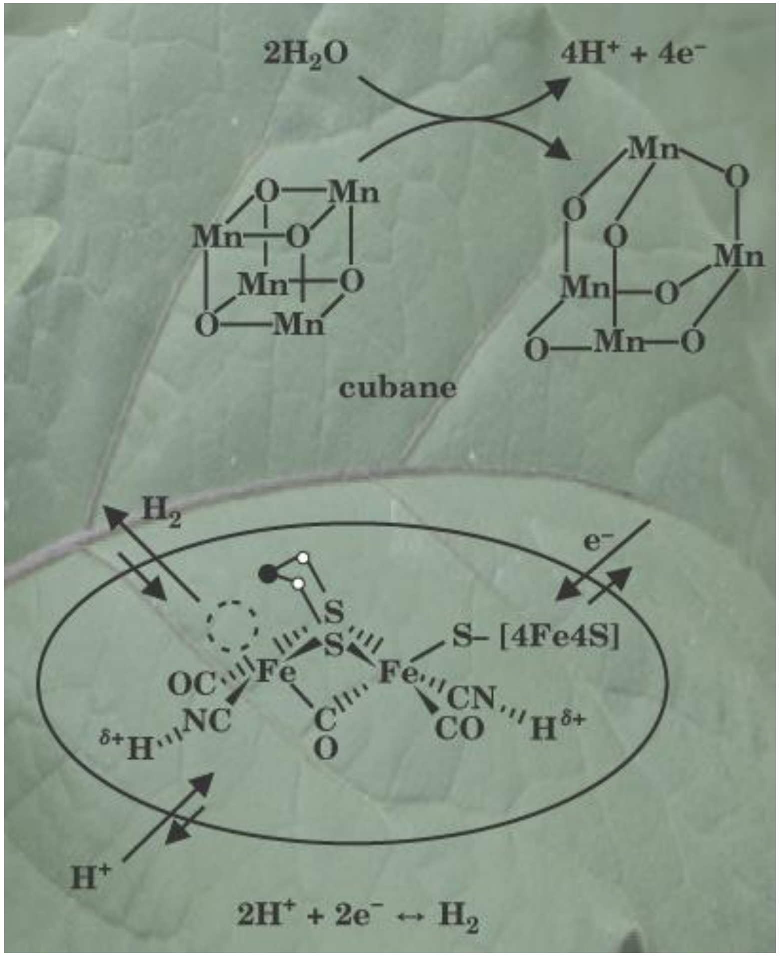
Hydrosol technology evolution

HYDROSOL-I Reactor, 3 kW (2004)



First Solar H_2 production at the DLR, Cologne Solar Furnace

Biological Hydrogen Creation



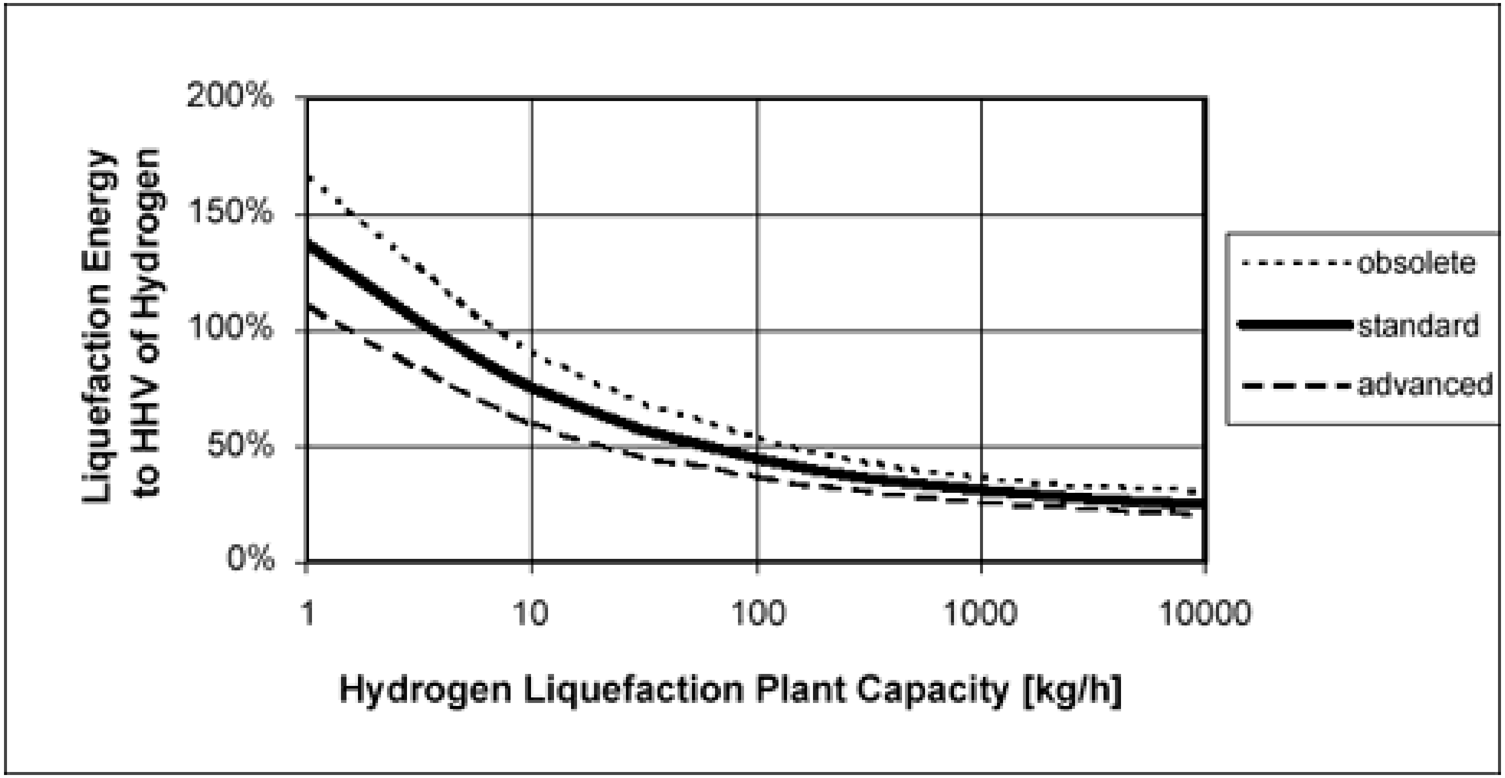
- Nature has very simple methods to split water.
- Scientists are working to mimic these processes in the lab; then commercially.

Crabtree *et al.*, "The Hydrogen Economy," *Physics Today,* Dec 2004

Hydrogen Storage

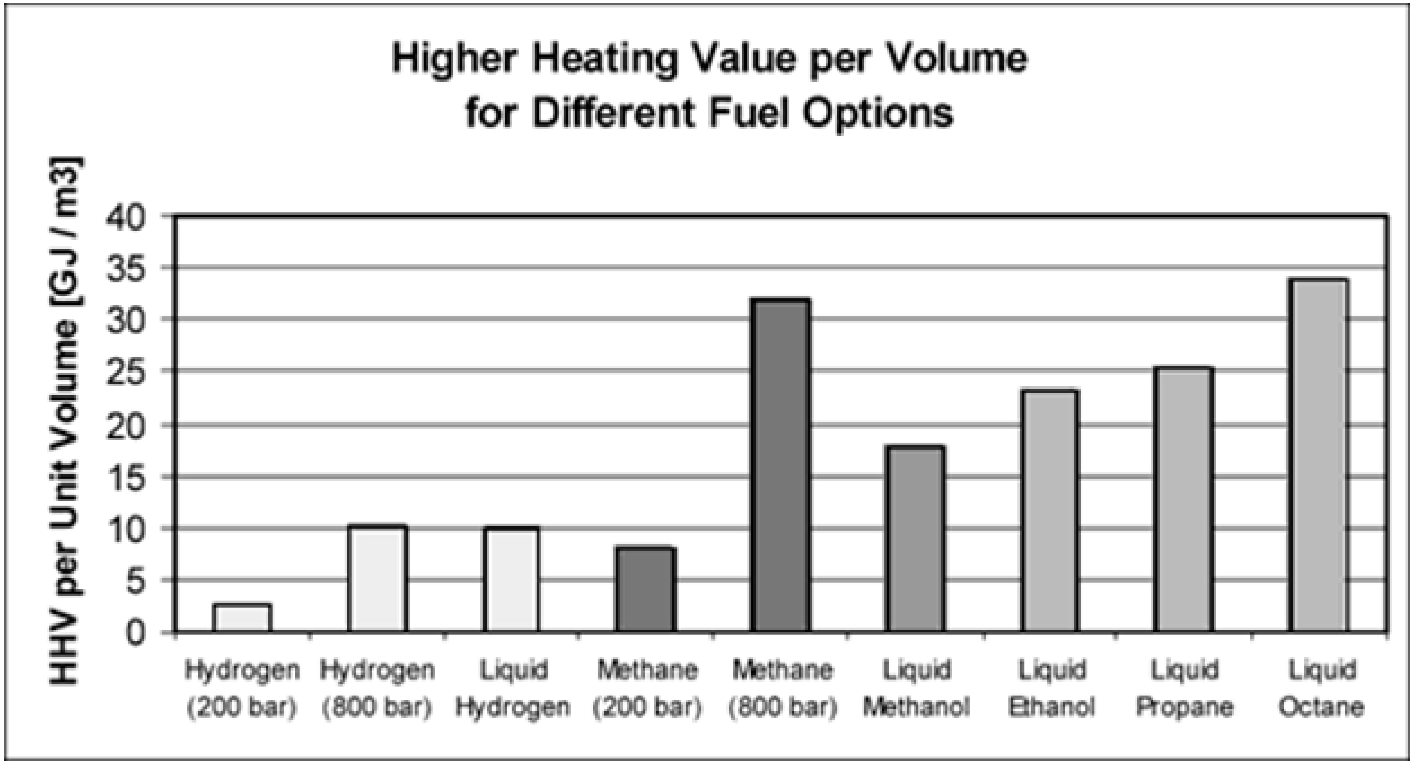
- Storage a major difficulty with hydrogen.
- H_2 has low energy density per volume:
  - Requires large tanks to store.
- H_2 can be compressed to reduce volume:
  - Requires heavy, strong tanks.
- H_2 can be liquefied to reduce volume:
  - Boils at -423 °F (cryogenic).
  - Requires heavily insulated, expensive tanks.
- Both compression and liquefaction require a lot of energy.

Liquifaction Energy vs. Intrinsic Energy



Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?,* Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

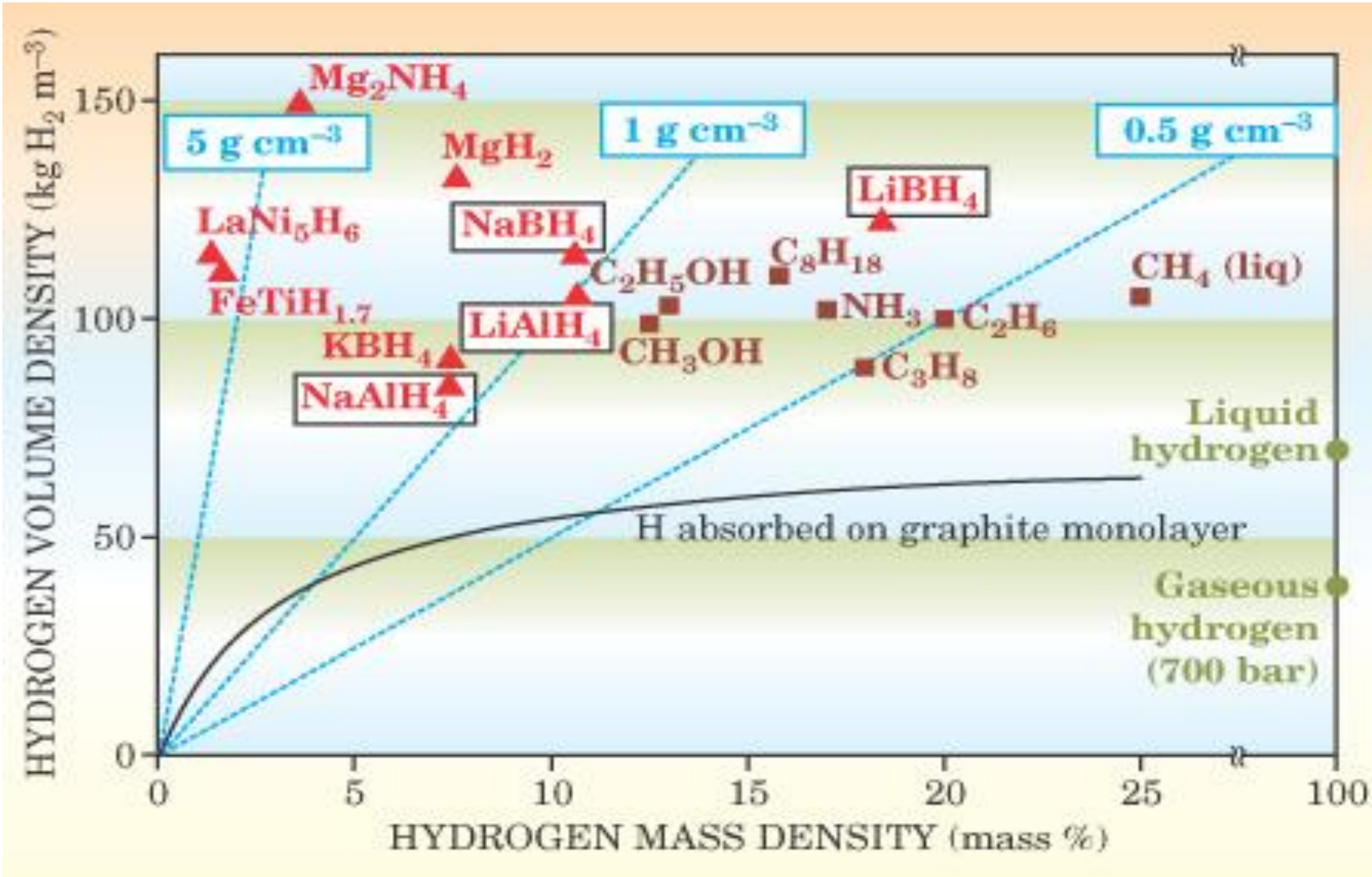
Energy Densities for Various Fuels



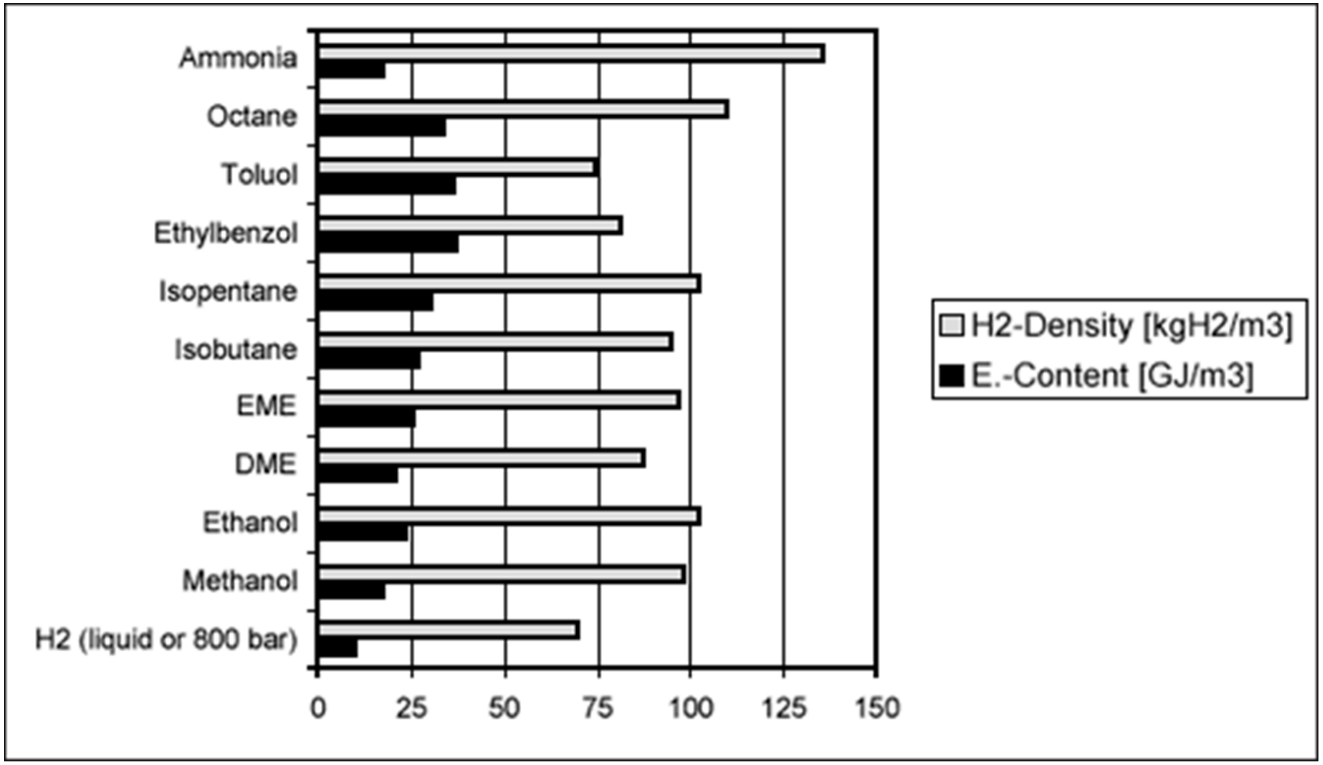
Higher Heating Value (HHV) is a measure of energy

Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?*, Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

Hydrogen Storage Densities



H_2 and Energy Density for Various Fuels



Hydrogen density and HHV energy content of ammonia and selected synthetic liquid hydrocarbon fuels

Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?,* Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

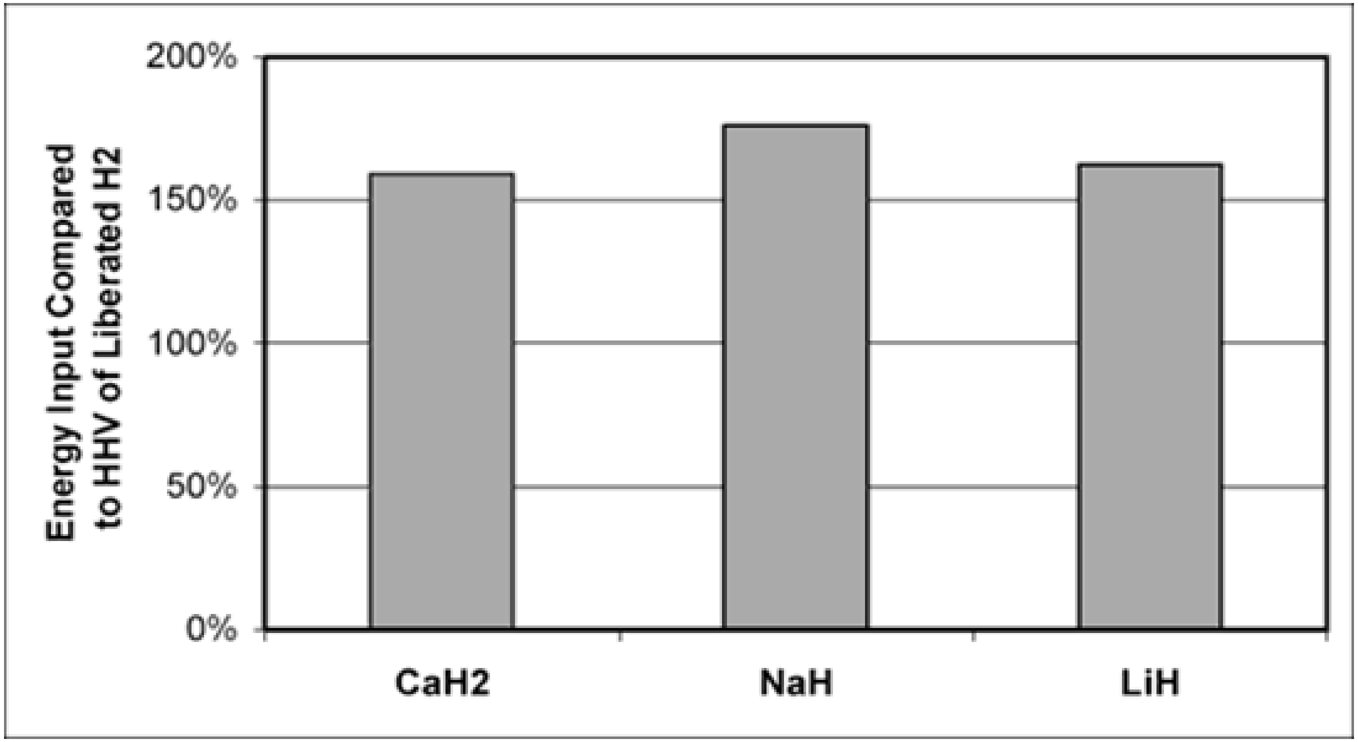
Ammonia Storage

- H_2 can be stored as ammonia (NH_3).
- Exceptionally high hydrogen densities.
- Ammonia very common chemical.
  - Large infrastructure already exists.
- Easily reformed to produce hydrogen.
  - No harmful waste.
- BUT:
  - Ammonia production is energy intensive.
  - Ammonia is a toxic gas.

Metal Hydride Storage

- Metal hydrides can carry hydrogen:
  - Boron, lithium, sodium.
  - Good energy density, but worse than gas.
- Volumes much larger than gasoline:
  - Three times more volume.
  - Four times heavier.
- Hydrides can react violently with water.
- Leading contenders:
  - Sodium Borohydride.
  - Lithium Aluminum Hydride.
  - Ammonia Borane.

Alkali Prod.
Energy vs. Intrinsic Energy



Energy needed to produce alkali metal hydrides relative to the energy content of the liberated hydrogen.

Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?*, Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

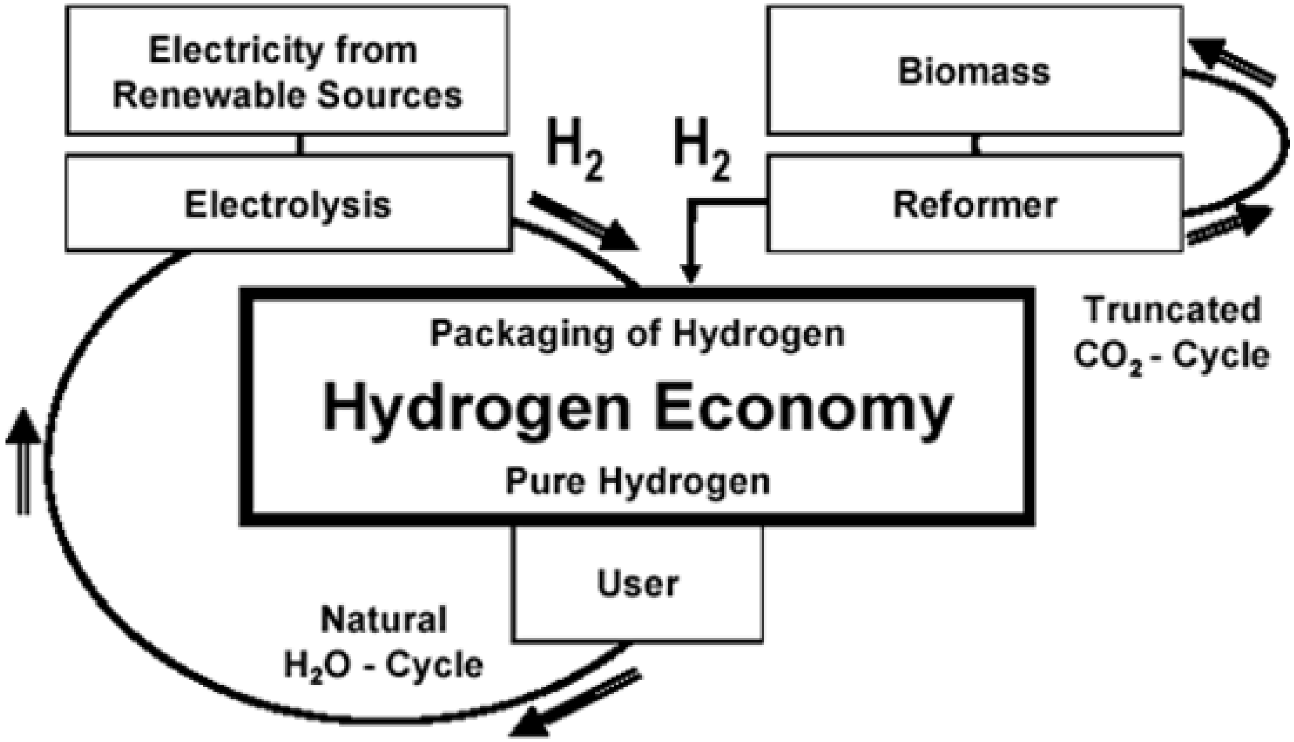
Transporting Hydrogen

Hydrogen Fueling Station

Environmental Concerns

- 48% of hydrogen made from natural gas:
  - Creates CO_2–a greenhouse gas.
- Hydrogen H_2 inevitably leaks from containers:
  - Creates free radicals (H) in stratosphere due to ultraviolet radiation.
  - Could act as catalysts for ozone depletion.

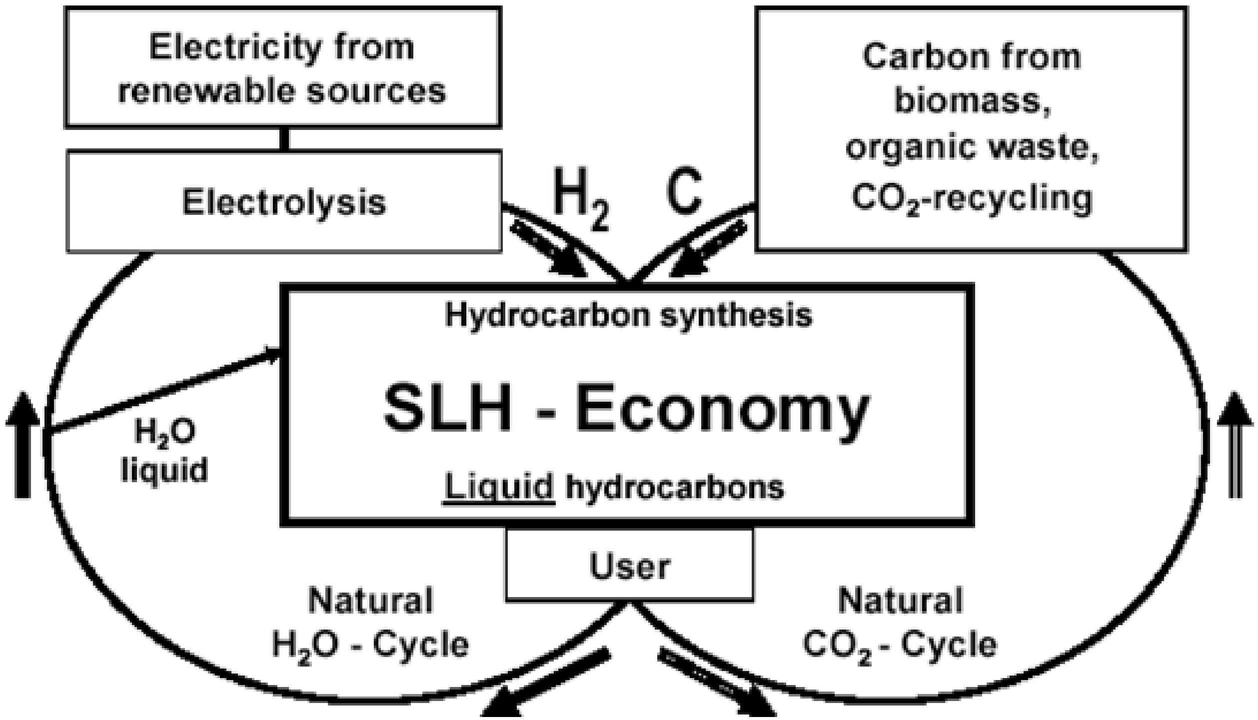
Elemental Hydrogen Economy



Elemental Hydrogen Economy based on the natural cycle of water.
Elemental hydrogen is provided to the user

Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?*, Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

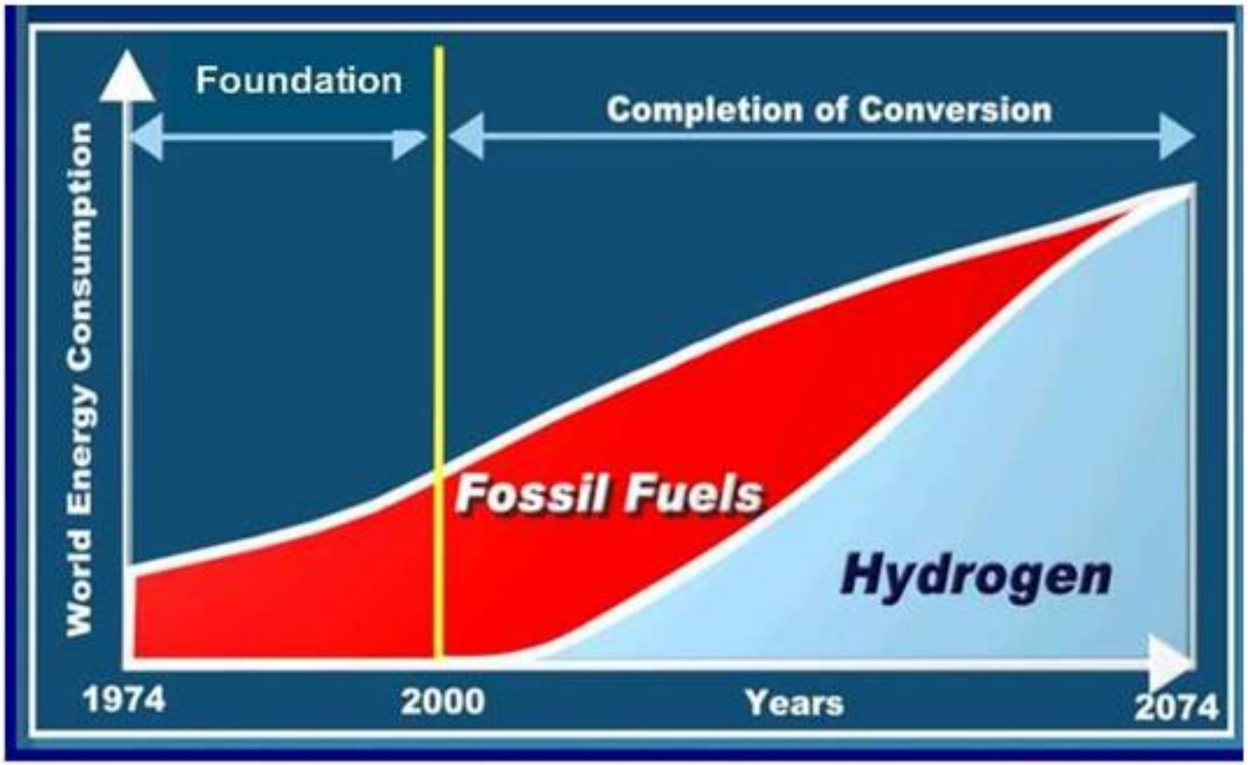
Synthetic Liquid Hydrocarbon Economy



A Synthetic Liquid Hydrocarbon Economy may be based on the two natural cycles of water and carbon dioxide. Natural and synthetic liquid hydrocarbons are provided to the user.

Bossel et al., *The Future of the Hydrogen Economy: Bright or Bleak?*, Oct 28, 2004
http://www.oilcrash.com/articles/h2_eco.htm

UNIDO-ICHET Projection



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
INTERNATIONAL CENTRE FOR HYDROGEN ENERGY TECHNOLOGIES

http://www.unido-ichet.org/ICHET-transition.php

The Iceland Example

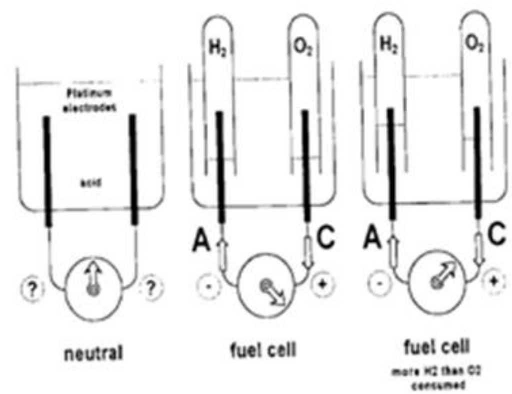
- Iceland committed to be the first hydrogen economy.
  - 2050 goal.
- Will use geothermal resources to create hydrogen.
- Power autos, buses, and fishing fleet with hydrogen.

http://en.wikipedia.org/wiki/Hydrogen_economy

Fuel Cell .... A brief history

The 1st fuel cell was constructed by Sir William Grove in 1839. Before 60's there was no any practical application. However, fuel cell technology was selected instead of nuclear or solar energy to implemented in the Apollo Space Mission.

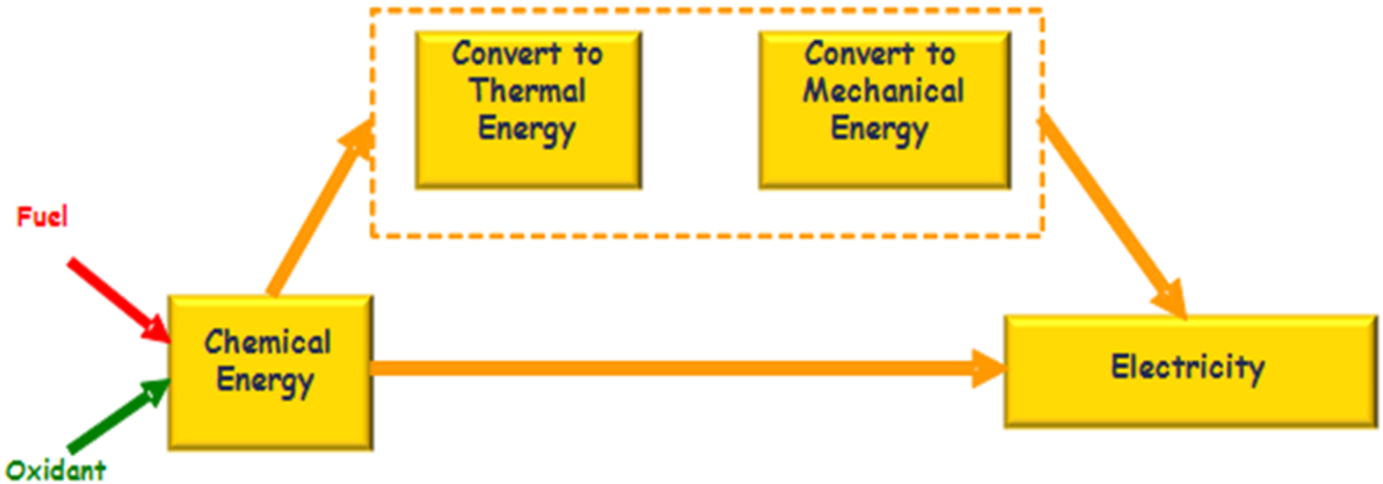
Sir William Robert Grove
(July 11, 1811 - August 1, 1896)
Photo: The Bridgeman Art Library, London (The Royal Institution, London)



Grove's experiment of 1839
Schematic based on information contained in [2]

Fuel Cells vs Thermal Engines

Fuel cells are electrochemical devices that directly convert the chemical energy of a fuel to electricity at higher efficiencies compared to conventional thermal engines.



Comparative Efficiency ...

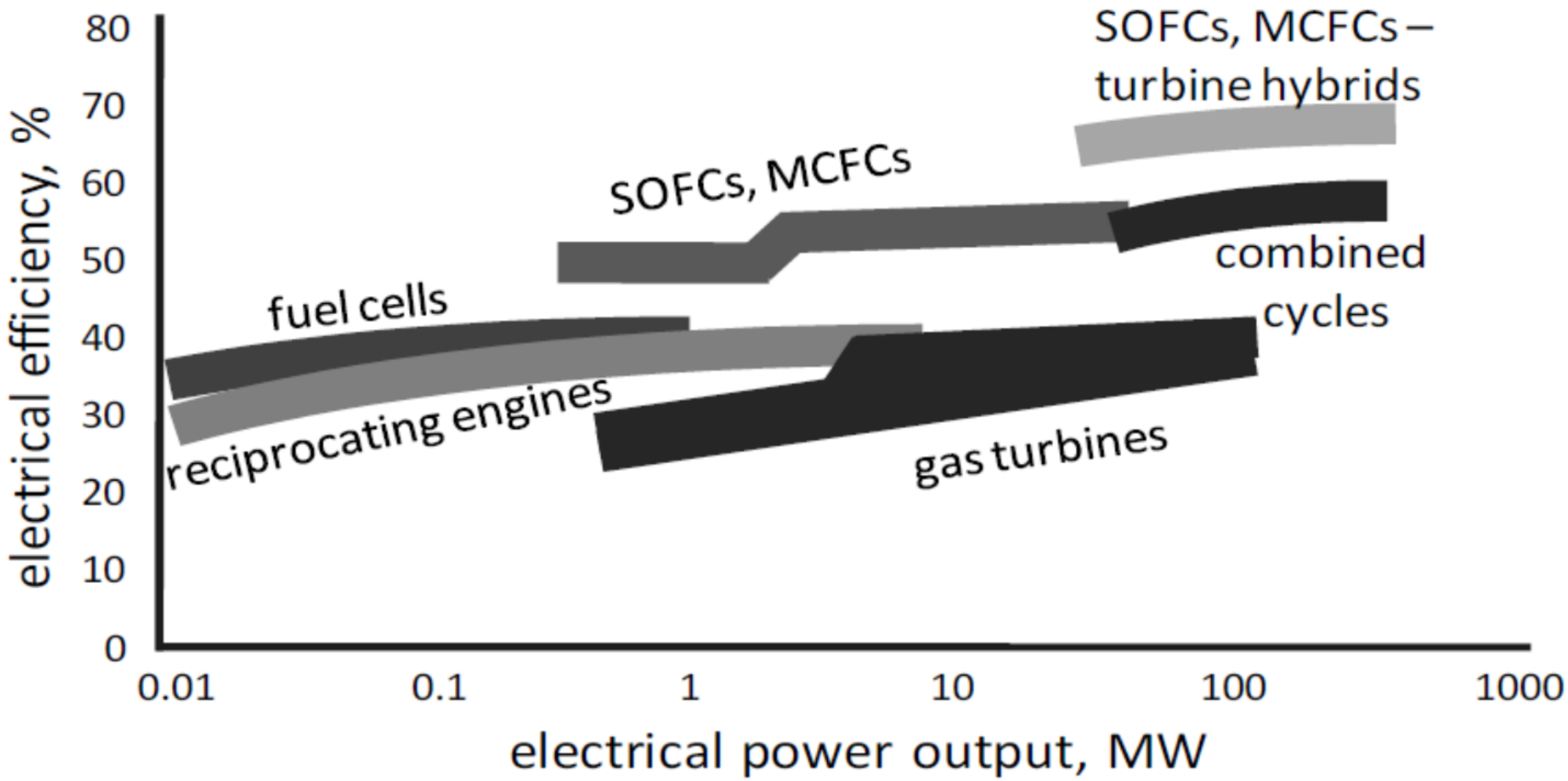
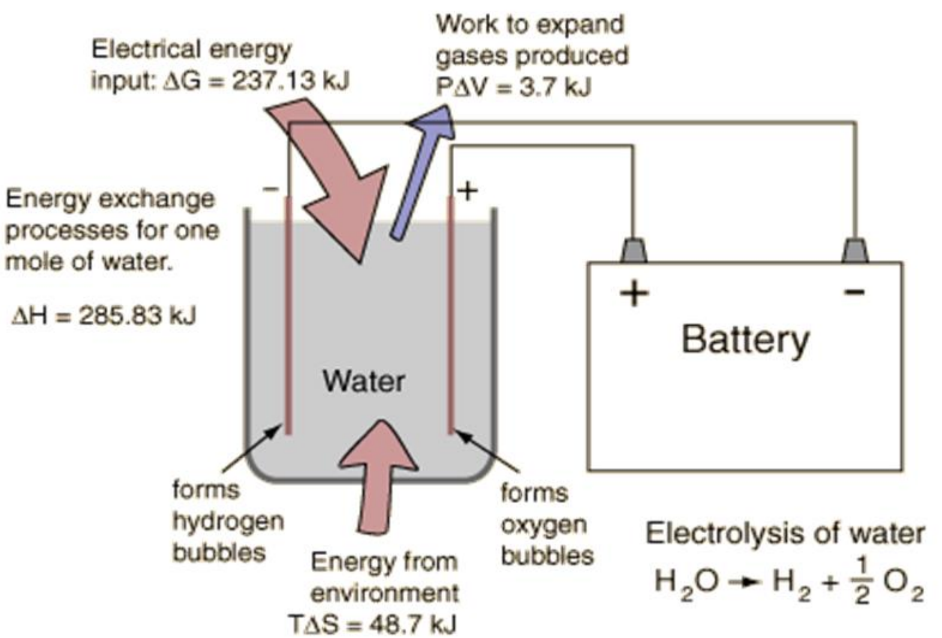
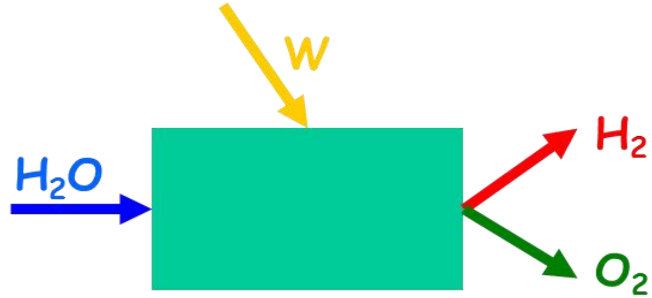


Figure 3.8. Comparative efficiency (% LHV) of power generation systems (US DOE, 2002; IEA, 2005)

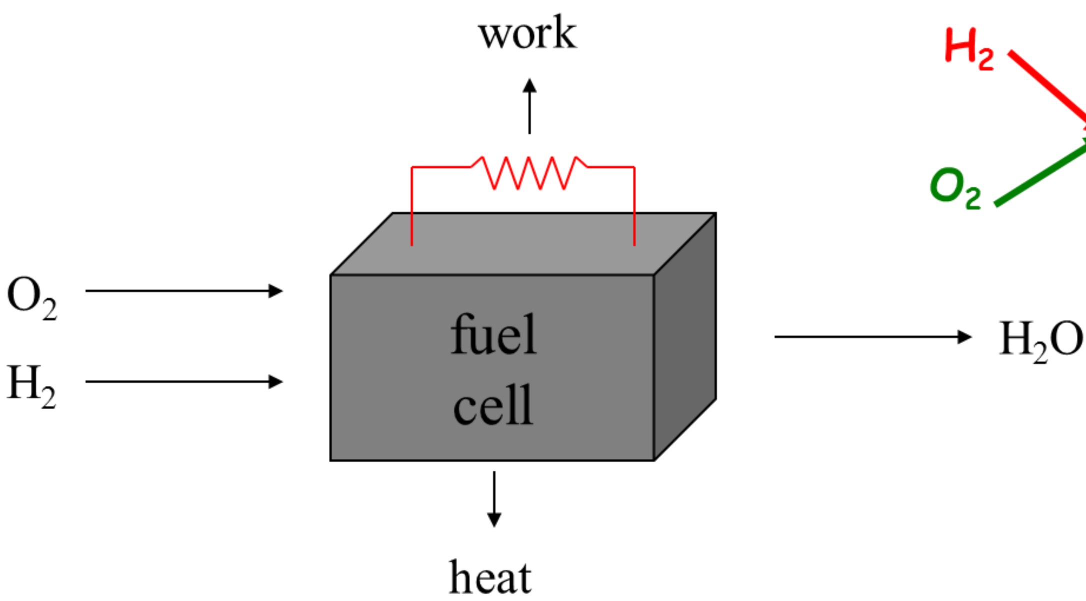
Electrolysis
“How is related with Fuel Cells ?”





Fuel Cell – Operating principle “Reverse Electrolysis”

The well known electrolysis needs work to proceed.
If we reverse electrolysis, work can be produced spontaneously.



Fuel Cell – Operation and Performance (1/3)

The maximum electrical work (W_{el}) of a fuel cell is given by the change in the free energy of the overall (combined anodic and cathodic) electrochemical reaction aA + bB → cC + dD:

$$W_{el} = \Delta G = -nFE \tag{3.18}$$

where n is the number of electrons participating the reaction, F is the Faraday constant (96,487 cb/mole), and E is the reversible potential of the cell (emf). The difference between ΔG and ΔH is proportional to the change in entropy (ΔS):

$$\Delta G = \Delta H - T\Delta S \tag{3.19}$$

Fuel Cell – Operation and Performance (2/3)

where ΔH is the total thermal content of the feed and $T\Delta S$ is the amount of heat produced by a fuel cell operating reversibly. The reversible potential of a fuel cell at temperature T is calculated from the ΔG of the cell reaction, at that temperature:

$$\Delta G = \Delta G^{o} + RT \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad (3.20)$$

so that the reversible potential, becomes:

$$E = E^{o} + \frac{RT}{nF} \ln \frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}} \quad (3.21)$$

The operational cell voltage is the difference between the potentials of the cathode and the anode (as these potentials are altered due to the corresponding activation and concentration losses of each electrode) minus the ohmic losses, of the various stack components:

$$V_{cell} = (E_{cath} - |\eta_{act}^{cath}| - |\eta_{conc}^{cath}|) - (E_{anod} + |\eta_{act}^{anod}| + |\eta_{conc}^{anod}|) - IR \quad (3.22)$$

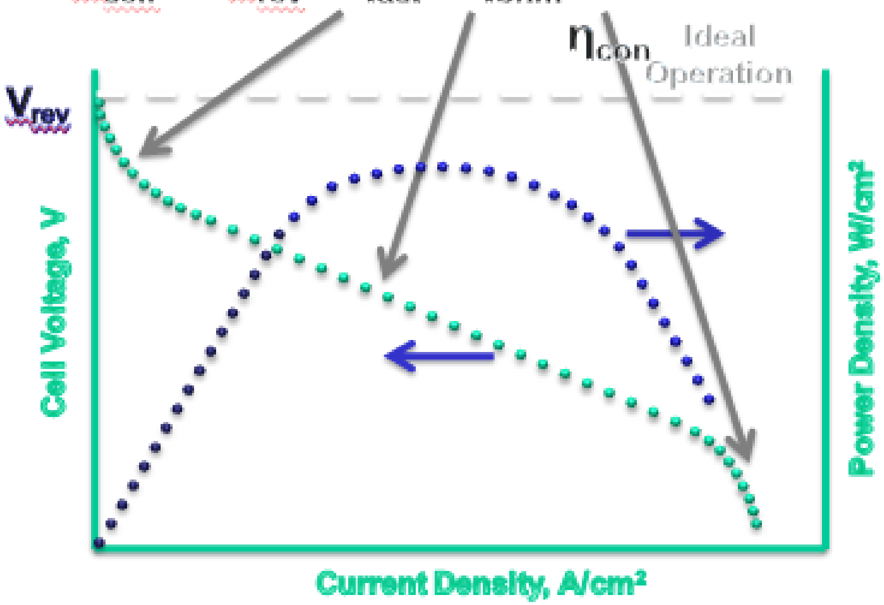
SOFC operation

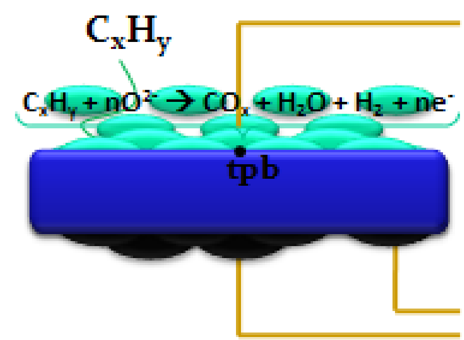
Butler - Volmer

$$V = IR_{ex} = V_{rev} - \underbrace{\left(\frac{RT}{a_c F}\ln\frac{I/A_c}{i_{0,c}} + \frac{RT}{a_a F}\ln\frac{I/A_a}{i_{0,a}}\right)}_{\eta_{act}} - \underbrace{IR_i}_{\eta_{ohm}} - \underbrace{\left(\frac{RT}{nF}\ln\left(1-\frac{I/A_c}{i_{L,c}}\right) + \frac{RT}{nF}\ln\left(1-\frac{I/A_a}{i_{L,a}}\right)\right)}_{\eta_{con}}$$

$$\eta = \eta_{act} + \eta_{ohm} + \eta_{con}$$

$$V_{cell} = V_{rev} - \eta_{act} - \eta_{ohm} - \eta_{con}$$



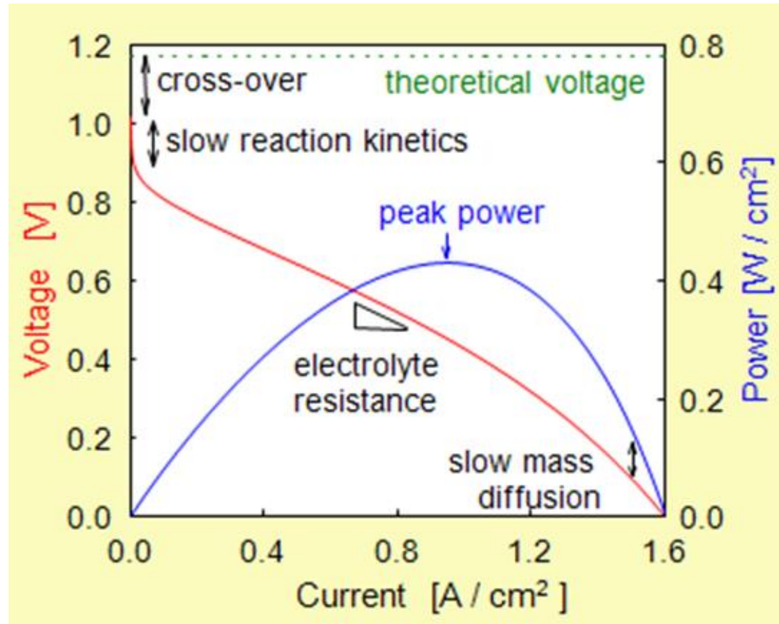


Fuel Cell Performance

$H_2 + ½ O_2 \rightarrow H_2O$.

1.17 Volts (@ no current).

- Voltage losses.
  - Fuel cross-over.
  - Reaction kinetics.
  - Electrolyte resistance.
  - Slow mass diffusion.
- Power = I*V.
- Peak efficiency at low I.
- Peak power at mid I.



Fuel Cell – Operation and Performance (3/3)

as higher heating value). Ideally the electrical work produced in a fuel cell should be equal to the change in Gibbs free energy, ΔG, of the overall reaction, and the ideal efficiency for reversible operation at standard conditions, will be:

$$\eta_{\text{ideal}} = \frac{\Delta G^{\text{O}}}{\Delta H^{\text{O}}} = \frac{-nFE^{\text{O}}}{\Delta H^{\text{O}}} \quad (3.23)$$

The thermal efficiency of an actual fuel cell, operating irreversibly at temperature T, reduces to:

$$\eta_{\text{th}} = \frac{-nFV_{\text{cell}}}{\Delta H^{\text{O}}} = \eta_{\text{ideal}} \frac{-nFV_{\text{cell}}}{-nFE^{\text{O}}} = \eta_{\text{ideal}} \frac{V_{\text{cell}}}{E^{\text{O}}} \quad (3.24)$$

Fuel Cells – Thermodynamics (1/3)

Fuel cells are galvanic cells, where the Gibbs Free Energy of a chemical reaction is converted to electricity (through an electric current).

$$\Delta G = -nF\Delta U_0$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

Thermodynamic properties at 1Atm and 298K

	H_2	O_2	H_2O (l)
Enthalpy (H)	0	0	-285.83 kJ/mol
Entropy (S)	130.68 J/mol·K	205.14 J/mol·K	69.91 J/mol·K

Fuel Cells – Thermodynamics (2/3)

- **Enthalpy Change of the Chemical Reaction:**

$\Delta H = \Delta H_{reaction} = \Sigma H_{products} - \Sigma H_{reactants}$

$= (1mol)(-285.83\ ^{kJ}/_{mol}) - (0) = -285.83\ kJ$

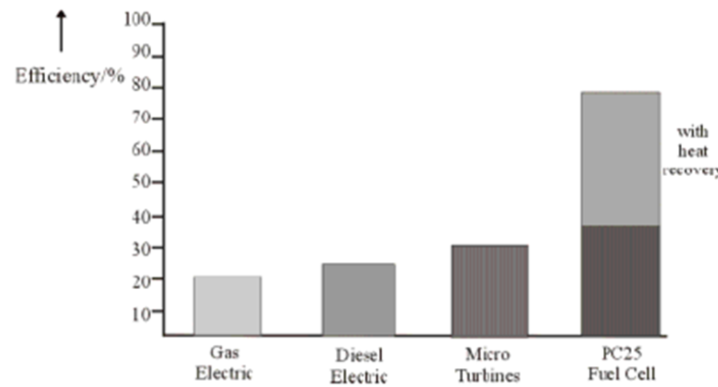
- **Entropy Change of the Chemical Reaction:**

$\Delta S = \Delta S_{reaction} = \Sigma S_{products} - \Sigma S_{reactants} = [(1mol)(69.91\ ^{J}/_{mol \cdot K})] - [(1mol)(130.68\ ^{J}/_{mol \cdot K}) + (½mol)(205.14\ ^{J}/_{mol \cdot K})] = -163.34\ \mathbf{^{J}/_{K}}$

- **Heat of the System:**

$\Delta Q = T\Delta S = (298K)(-163.34\ ^{J}/_{K}) = -48.7\ kJ$

Fuel Cells – Thermodynamics (3/3)



Gibbs Free Energy:

$$\Delta G = \Delta H - T\Delta S$$
$$= (-285.83\ kJ) - (-48.7\ kJ)$$
$$= -237\ kJ$$

Assuming constant temperature and irreversibility.

$$W = \Delta G = -237\ kJ$$

The heat that is transferred to the environment:

$$\Delta Q = T\Delta S = -48.7\ kJ$$

The chemical reaction produces 237 kJ work and 48.7 kJ heat.

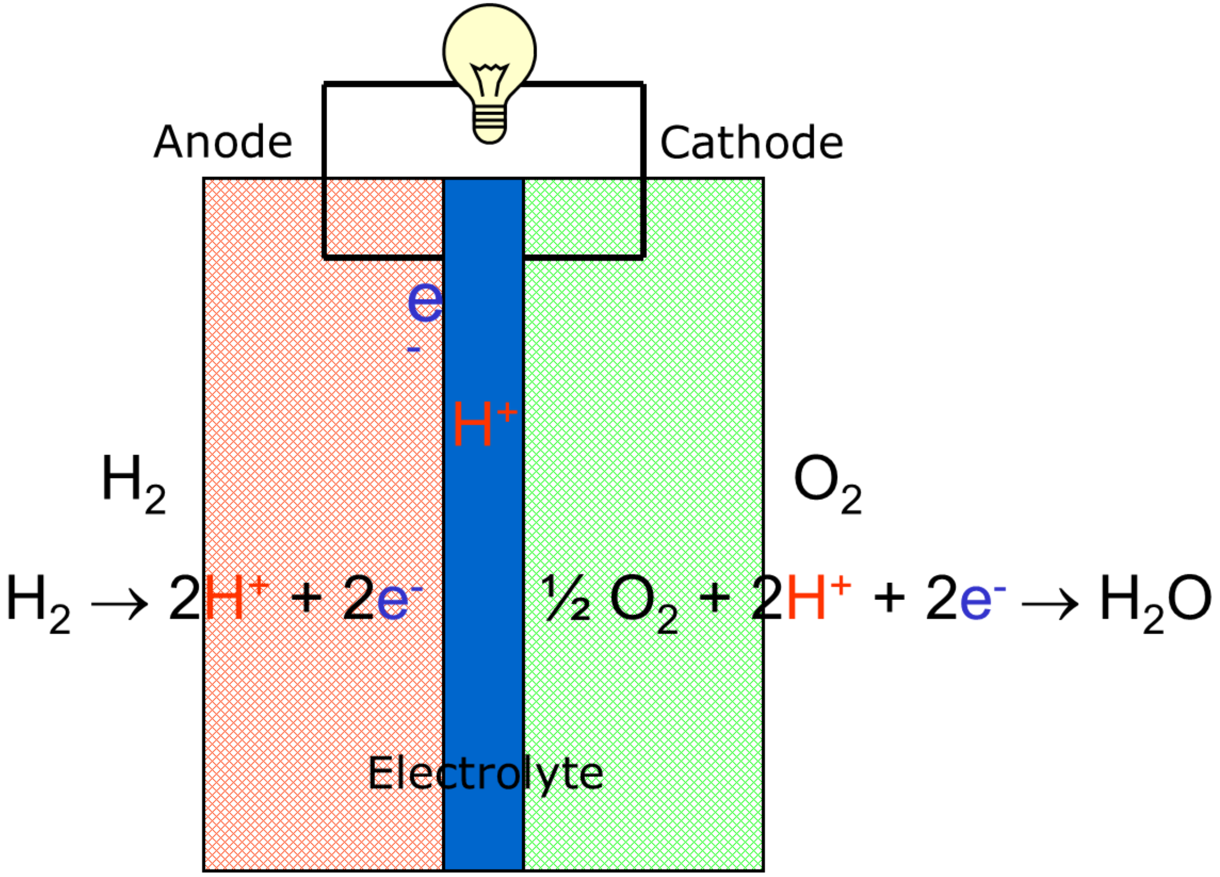
The efficiency of heat engine is equal to: $\varepsilon_r^{\text{thermal}} = \frac{W_r}{(-\Delta H)} = 1 - \frac{T_2}{T_1}$

The efficiency of the fuel cell is equal to: $\varepsilon_r^{\text{cell}} = \frac{W_e}{(-\Delta H)} = \frac{nF\Delta U_0}{(-\Delta H)} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$

Fuel & reactions in fuel cells

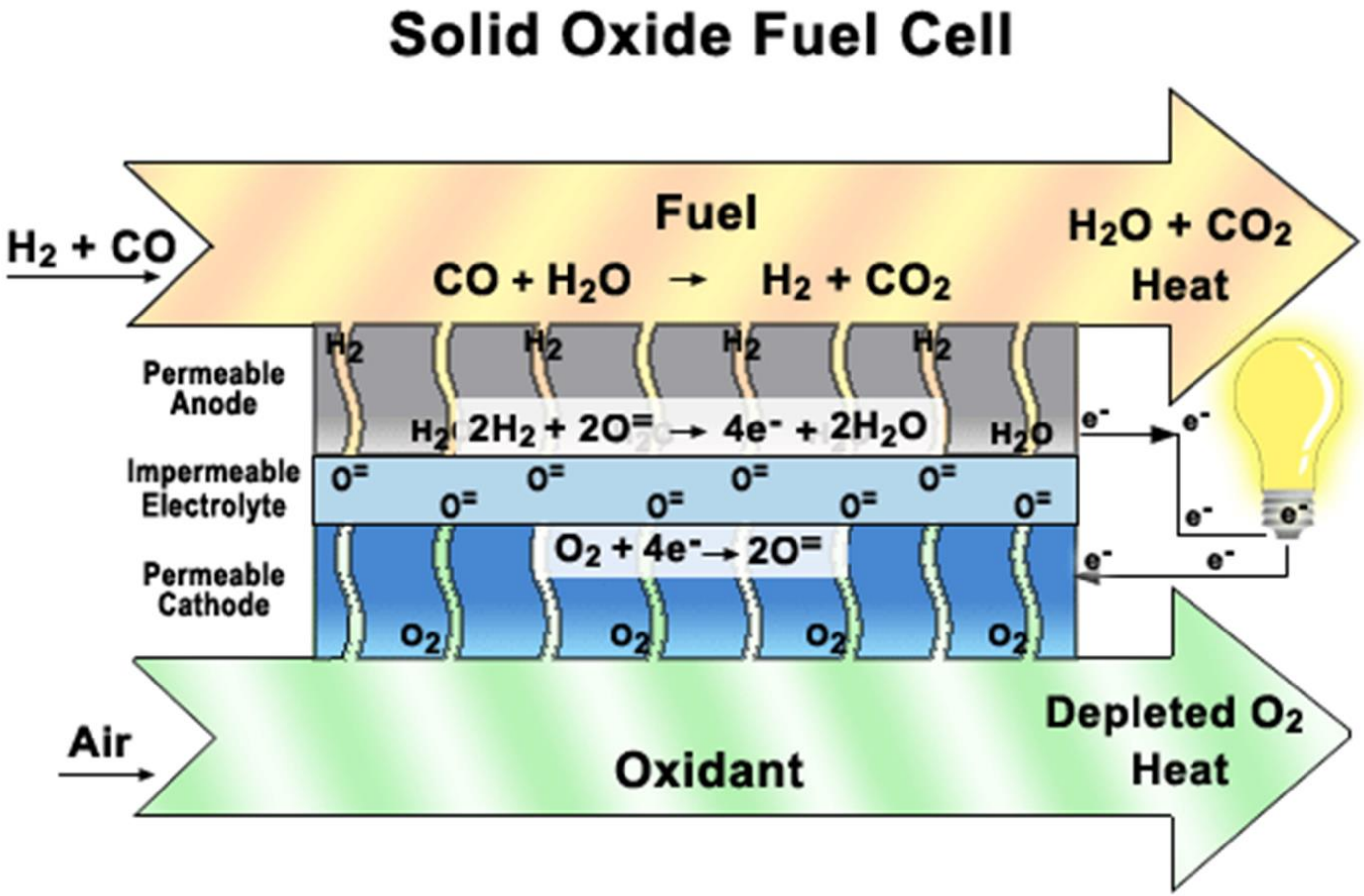
Fuel	Reaction	$-\Delta H_R$ (KJ/mol)	$-\Delta G_R$ (KJ/mol)	E^o (Volt)	%
H_2	$H_2+1/2O_2 \rightarrow H_2O$	286	237,3	1,229	83
CH_4	$CH_4+2O_2 \rightarrow CO_2+ 2H_2O$	890,8	818,4	1,060	91,9
C_3H_8	$C_3H_8+5O_2 \rightarrow 3CO_2+4H_2O$	2221,2	2110,0	1,093	95
CO	$CO+1/2O_2 \rightarrow CO_2$	283,1	257,2	1,066	90,9
C	$C+O_2 \rightarrow CO_2$	393,7	394,6	1,020	124,2
CH_3OH	$CH_3OH+3/2O_2 \rightarrow CO_2+2 H_2O$	726,6	702,5	1,214	96,7
NH_3	$NH_3+3/4O_2 \rightarrow 1/2N_2+3/2 H_2O$	382,8	338,2	1,170	88,4
N_2H_4	$N_2H_4+O_2 \rightarrow N_2+ 2 H_2O$	622,4	602,4	1,560	96,8
$C_{10}H_{22}$	$C_{10}H_{22}+15,5O_2 \rightarrow 10CO_2+11 H_2O$	6832,9	6590,5	1,102	6,5

Fuel Cell: Principle of Operation

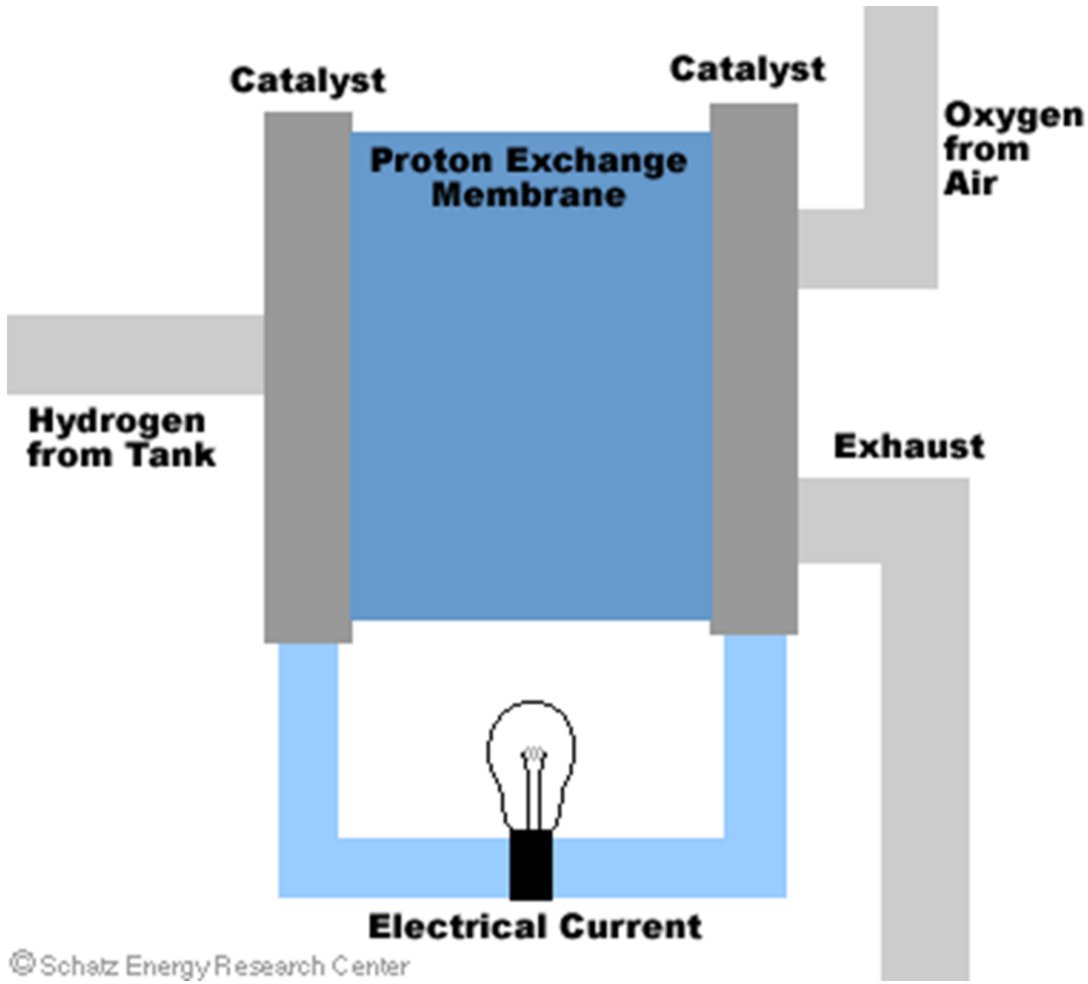


Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

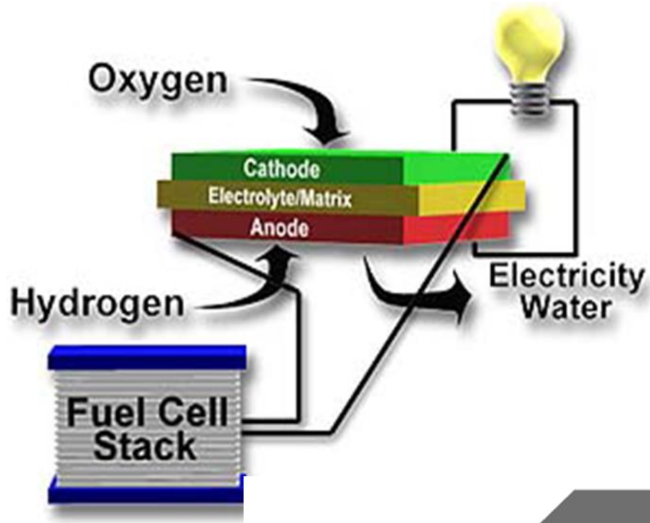
Principle of Operation ...

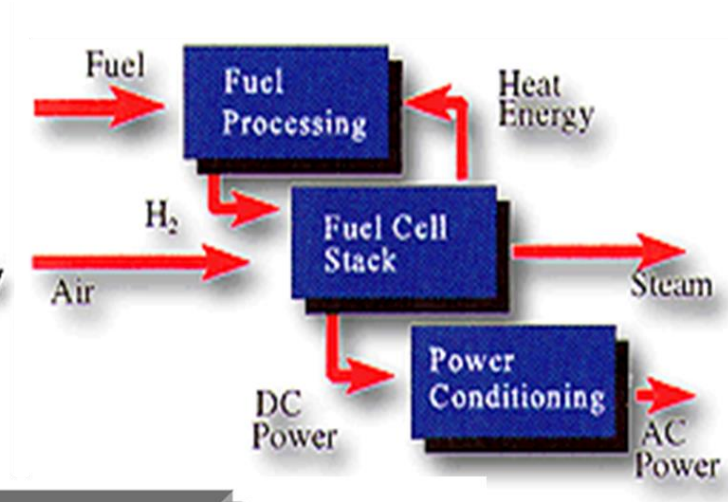


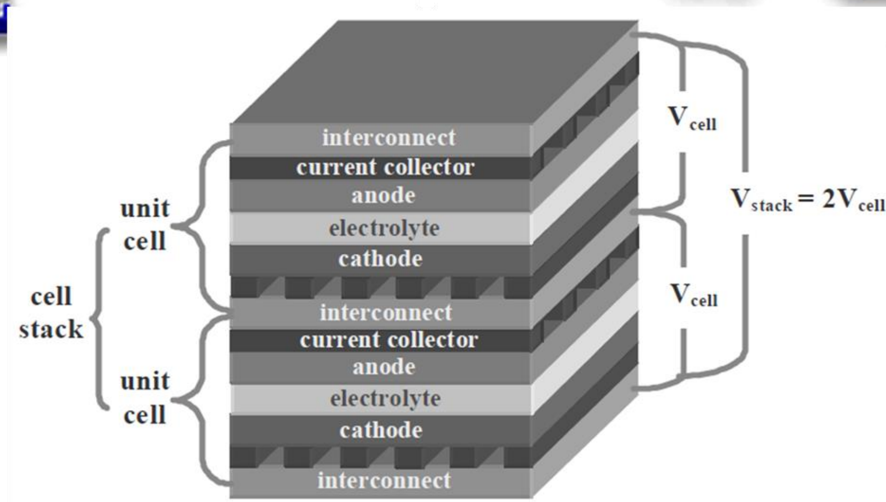
Animation of PEMFC



What are the main components of a Fuel Cell ...

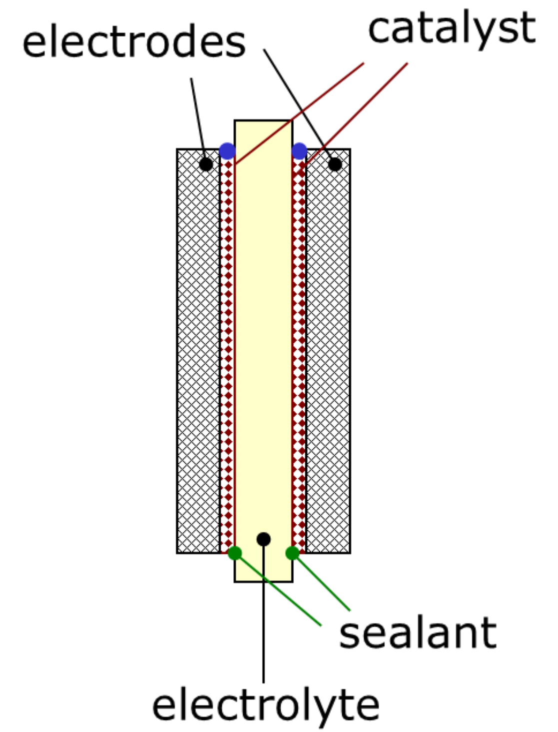






Fuel Cell Components

- Components:
  - Electrolyte (Membrane):
    - Transport ions.
    - Block electrons, gases.
  - Electrodes:
    - Catalyze reactions.
    - Transport:
      - Ions, electrons, gases.
    - May be a composite:
      - (electro)Catalyst + .
      - Conductors +.
      - Pore former.



Membrane-Electrode Assembly (MEA)

Fuel Cell Types (1/2)

Types differentiated by **electrolyte**, temperature of operation

Low T ⇒ H_2 or MeOH; High T ⇒ higher hydrocarbons (HC)

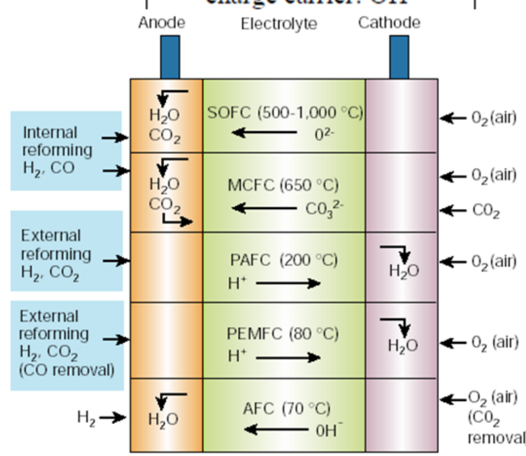
Efficiency tends to ↑ as T ↑, due to faster electrocatalysis

Type **°C** **[°F]**	PEM **90-110** **[200-230]**	AFC **100-250** **[212-500]**	PAFC **150-220** **[300-430]**	MCFC **500-700** **[930-1300]**	SOFC **700-1000** **[1300-1800]**
Fuel	H_2 + H_2O	H_2	H_2	HC + CO	HC + CO
Electrolyte ***Ion***	**Nafion** H_3O^+ ↓	**KOH** OH^- ↑	H_3PO_4 H^+ ↓	Na_2CO_3 CO_3^{2-} ↑	Y-ZrO_2 O^{2-} ↑
Oxidant	O_2	O_2 + H_2O	O_2	O_2 + CO_2	O_2

By-products: H_2O, CO_2

Fuel Cell Types (2/2)

	anodic reaction	electrolyte	cathodic reaction
PEFC	$2H_2 \rightarrow 4H^+ + 4e^-$	polymer membranes charge carrier: H^+	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
SOFC	$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$	mixed ceramic oxides charge carrier: O^{2-}	$O_2 + 4e^- \rightarrow 2O^{2-}$
MCFC	$2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^-$	immobilised molten carbonate charge carrier: CO_3^{2-}	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$
PAFC	$2H_2 \rightarrow 4H^+ + 4e^-$	immobilised liquid H_3PO_4 charge carrier: H^+	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$
AFC	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	immobilised KOH charge carrier: OH^-	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$



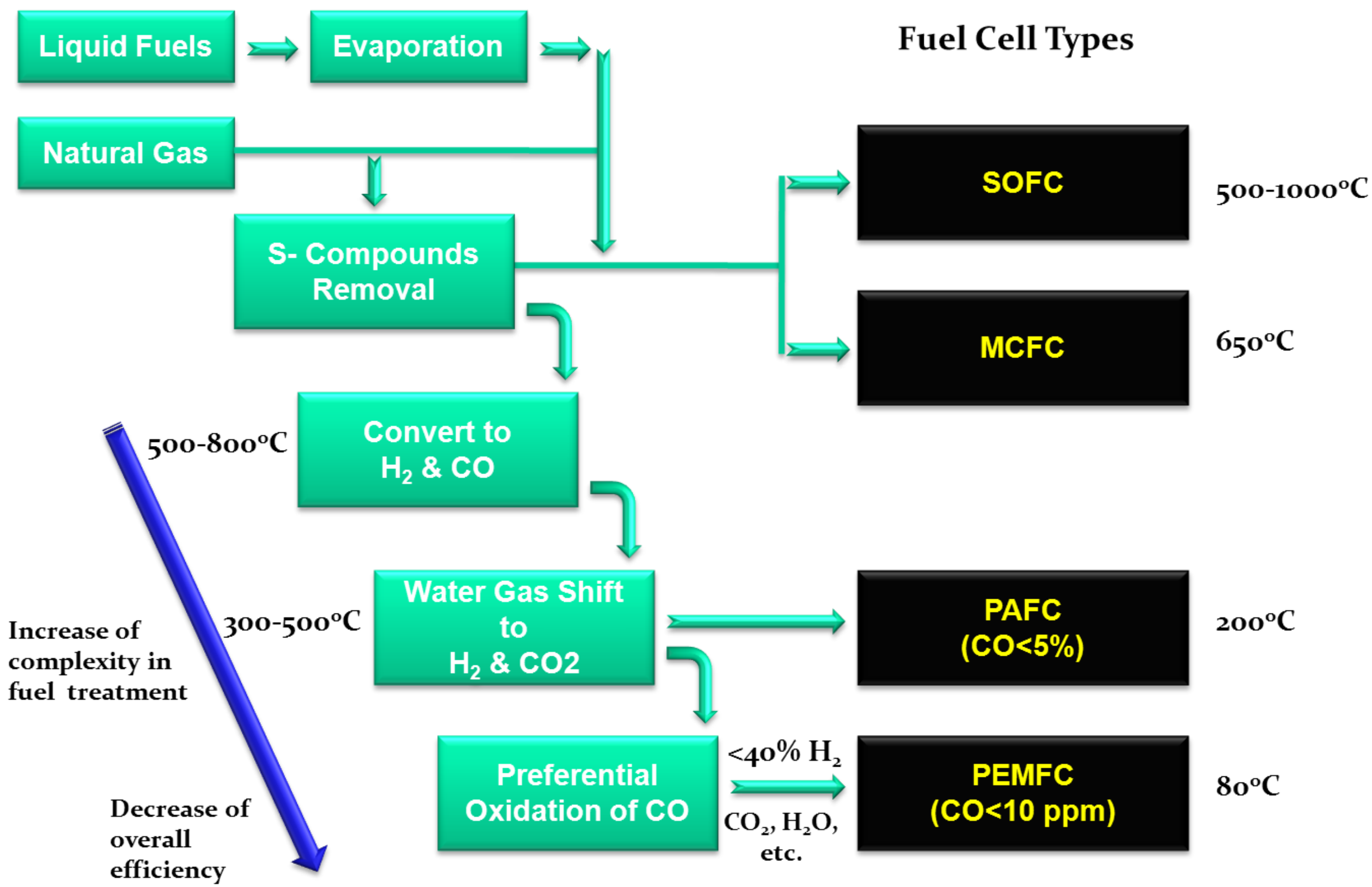
Fuel Cell Choices

Temperature sets operational parameters & fuel choice.

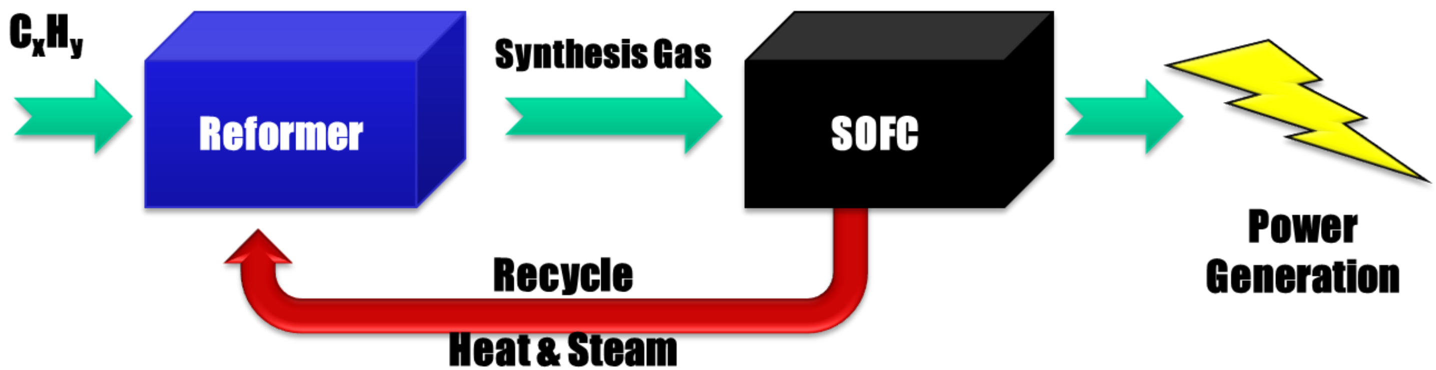
- Ambient Temperature:
  - ✓Rapid start-up.
  - ✗H_2 or CH_3OH as fuels.
  - ✗Catalysts easily poisoned.
- Applications:
  - –Portable power.
  - –Many on/off cycles.
  - –Small size.

- High Temperature:
  - ✓Fuel flexible.
  - ✓Very high efficiencies.
  - ✗Long start-up.
- Applications:
  - –Stationary power.
  - –Auxiliary power in portable systems.

Types of Fuel cells & Process Complexity



Conventional Method



- ✘ Additional cost for fuel treatment.
- ✘ Complexity.
- ✓ Thermal Integration.

Direct use of fuels

$$C_xH_y + \begin{Bmatrix} O_2 \\ CO_2 \\ H_2O \end{Bmatrix} \rightarrow CO + H_2 \qquad \Delta H > 0$$

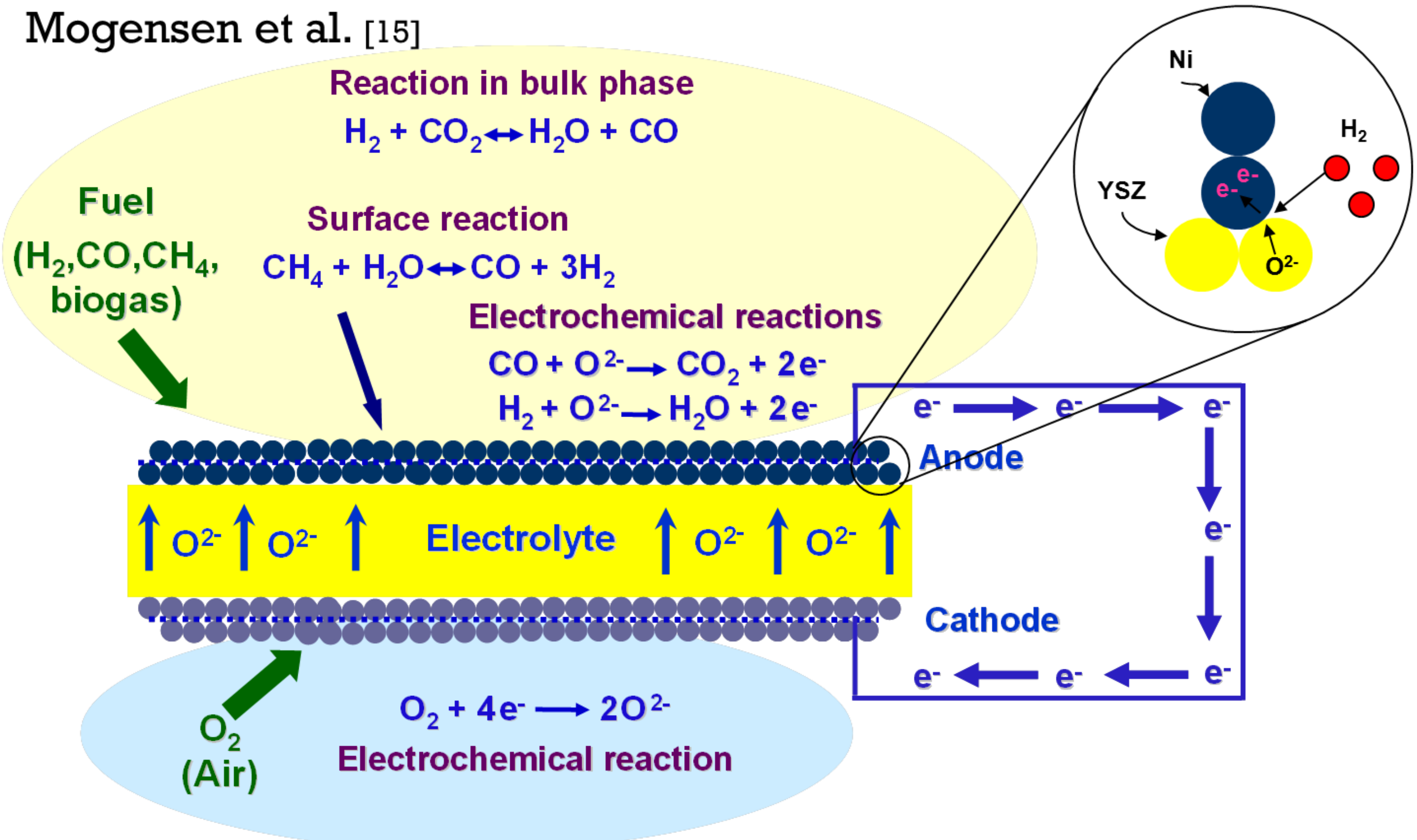
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H \approx 0$$

$$\left.\begin{aligned} C + 2O^{2-} &\rightarrow CO_2 + 4e^- \\ CO + O^{2-} &\rightarrow CO_2 + 2e^- \\ H_2 + O^{2-} &\rightarrow H_2O + 2e^- \end{aligned}\right\} \qquad \Delta H < 0$$

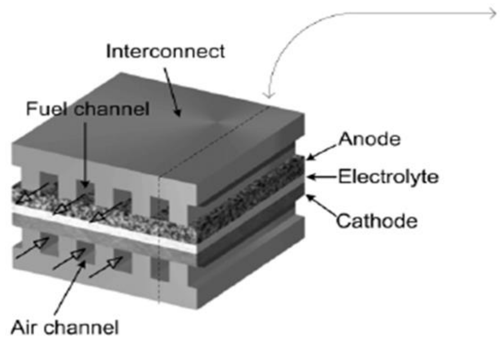
- ✓ Simple and auto-thermal process
- ✓ Lower cost

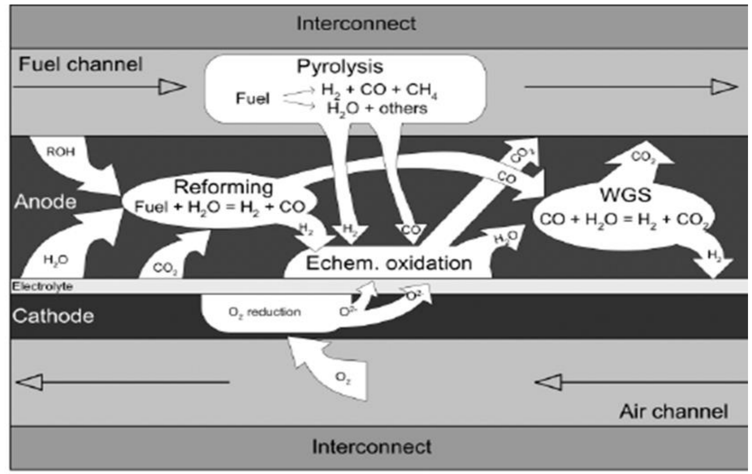
Direct Utilization of Hydrocarbons

Mogensen et al. [15]



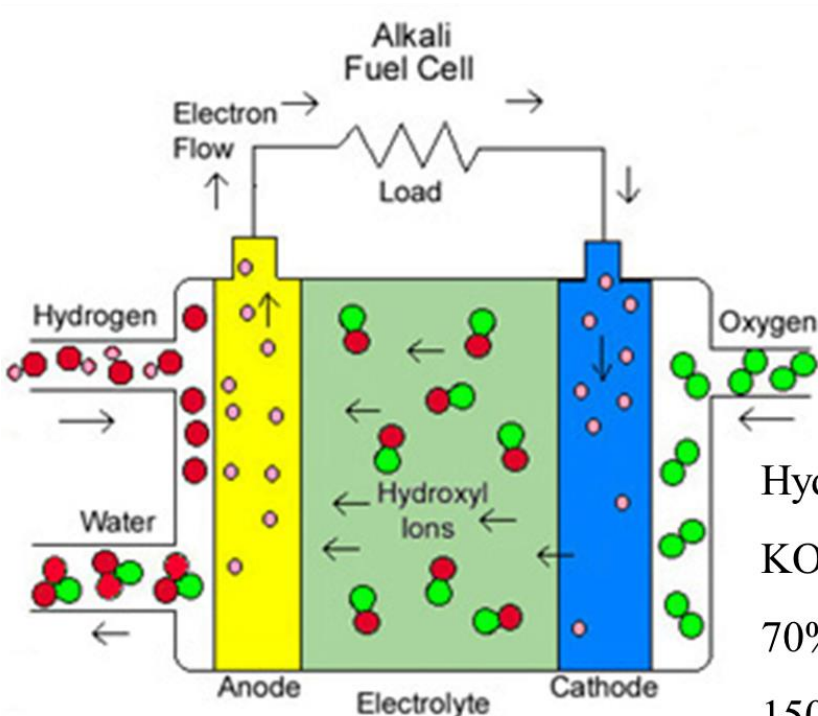
Overview of Anodic Processes





- The fuel can react in the gas-phase (flow channels & anode pores).
- Pyrolysis fragments and the fuel can catalytically decomposed.
- Thermal and catalytic decomposition fragments can be oxidized by O^{2-}
- The CO_2 and H_2O products allow dry/steam reforming of fuel species.
- Water-gas shift reaction.
- Carbon formation due to pyrolysis and Boudouard reactions.

Alkaline Fuel Cells



Hydrogen as a fuel

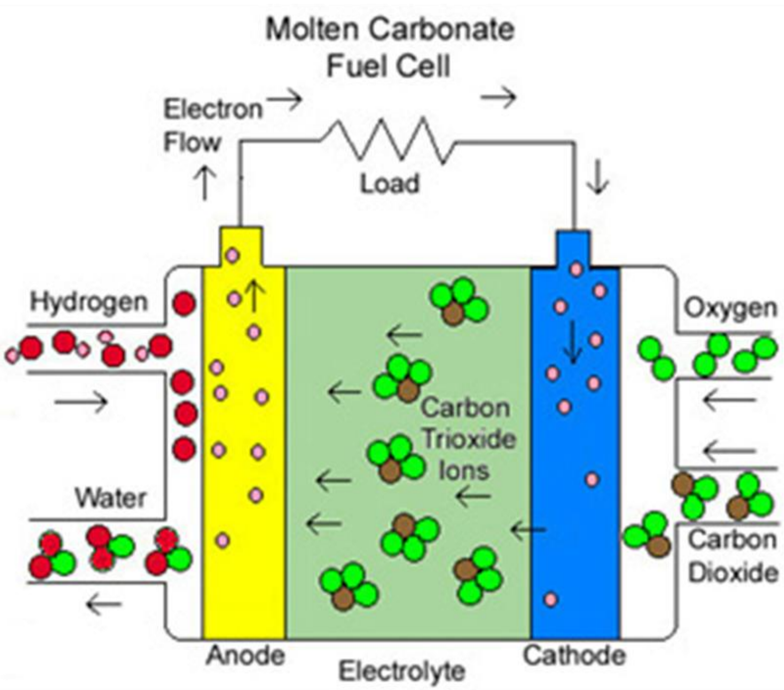
KOH as an electrolyte

70% efficiency

150˚C - 200˚C (operation temperature)

Needs pure hydrogen and Pt electrodes → ($$)

Molten Carbonate Fuel Cells (MCFC)



Carbonate salt (electrolyte)

60 – 80% efficiency

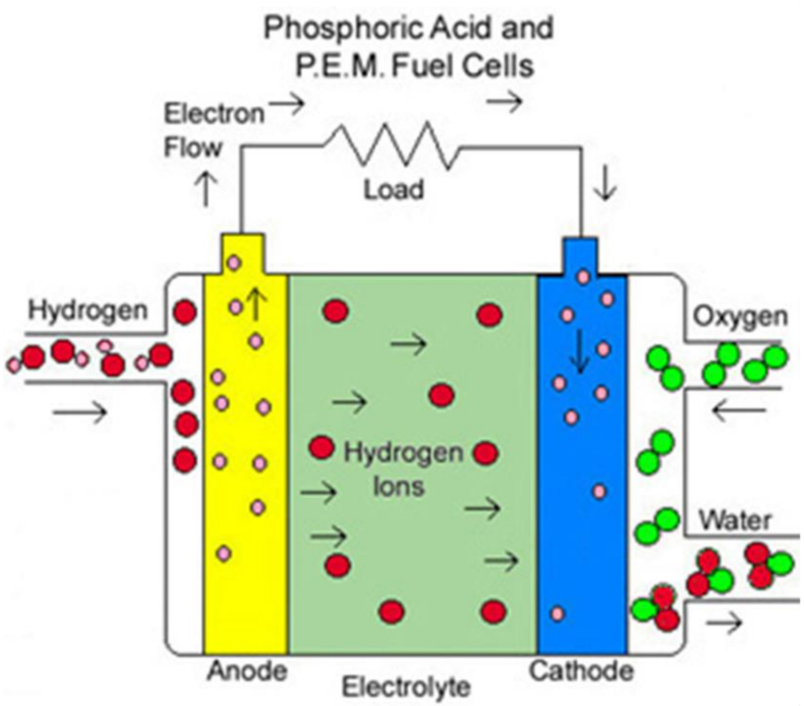
~650˚C (operation temperature)

Nickel (electrode)

The operating temperature is high and can be used for CHP.

Carbonate ions are consumed → production of CO_2

Phosphoric Acid Fuel Cell (PAFC)



Phosphoric acid (electrolyte)

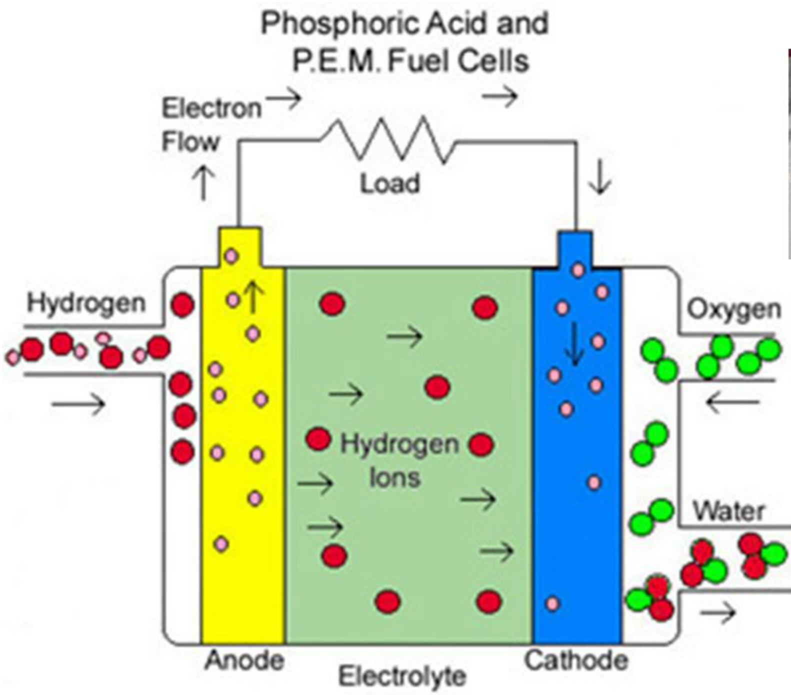
40 – 80% efficiency

150˚C - 200˚C

Corrosive electrolyte

Pt is too expensive

Proton Exchange Membrane Fuel Cell (PEMFC) (1/2)



Polymer Membrane

40 – 50% efficiency

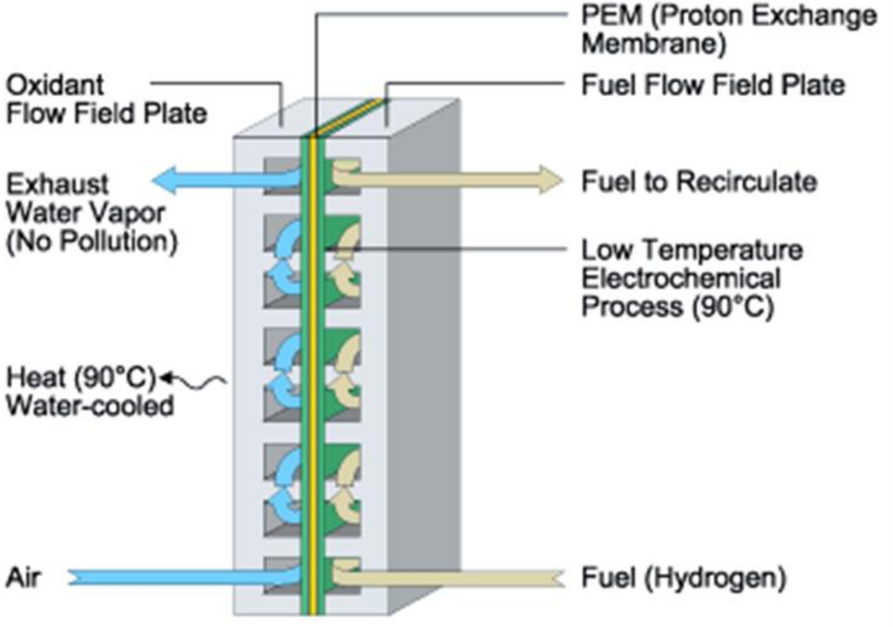
80˚C

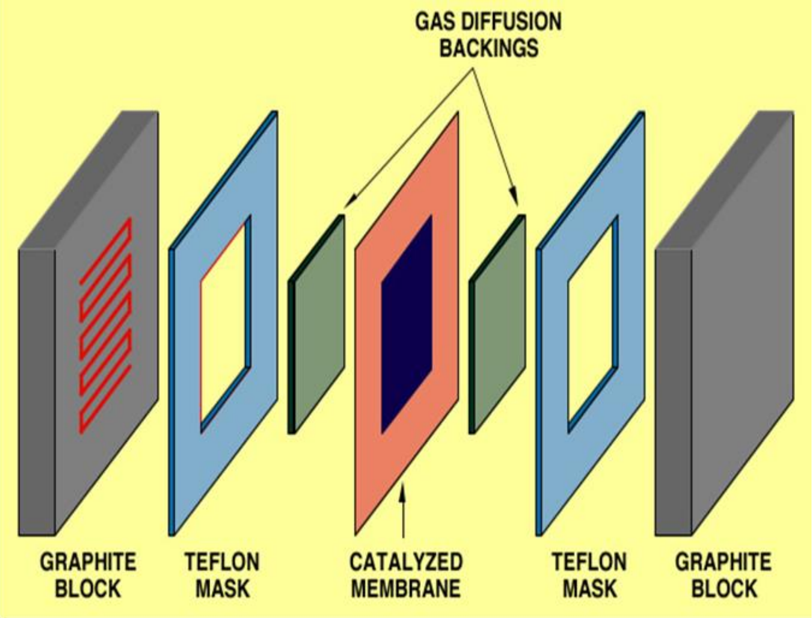
Cross over

Operation temperature appropriate for residential and automotive applications

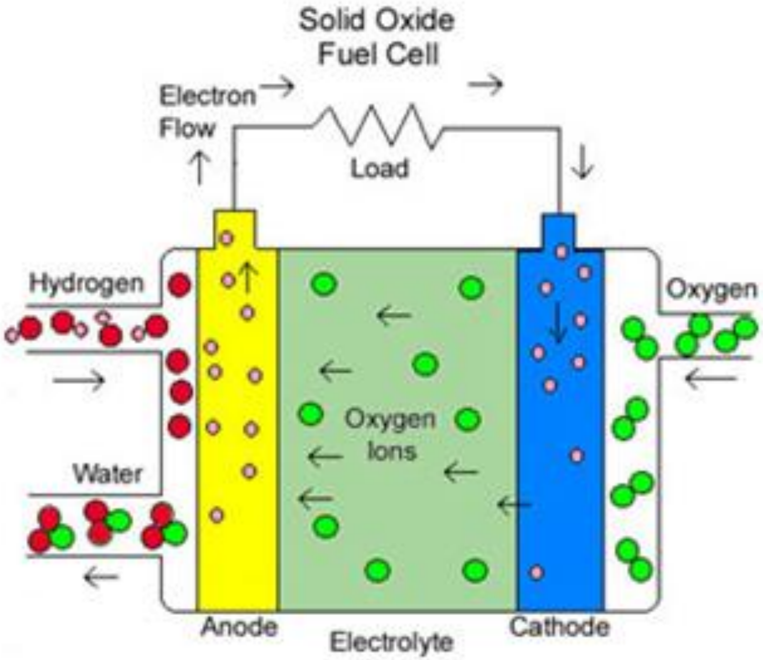
Pt electrodes → $$

Proton Exchange Membrane Fuel Cell (PEMFC) (2/2)





Solid Oxide Fuel Cell (SOFC) (1/2)



Solid electrolyte (ceramic)

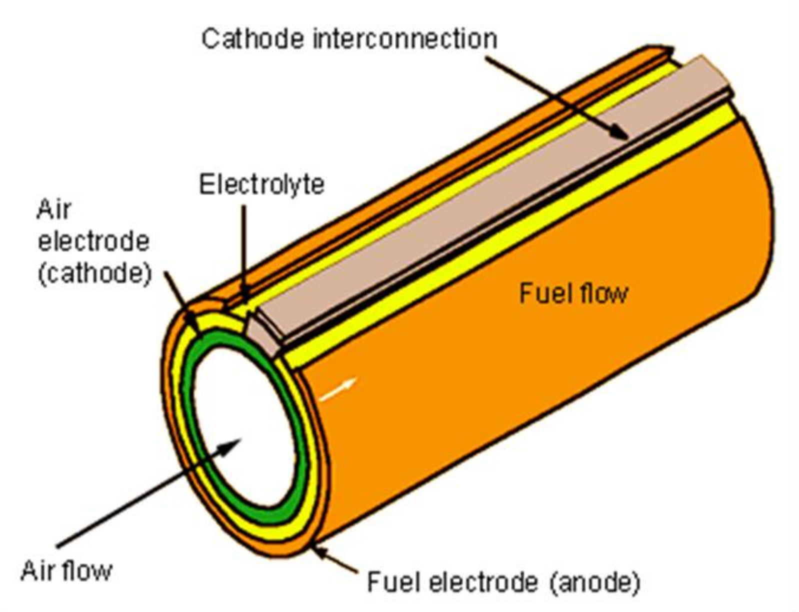
~60% efficiency

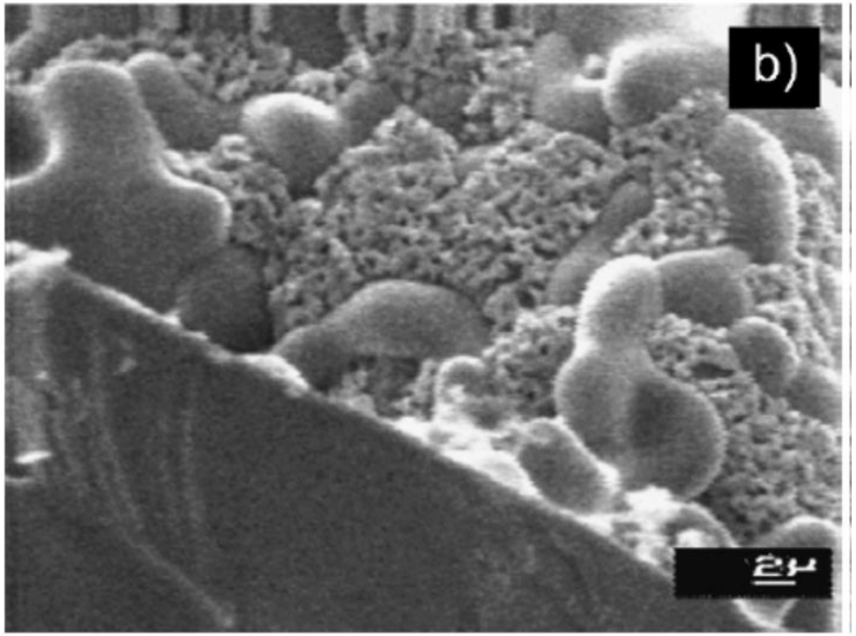
~1000°C

Fuel flexibility

CHP

Solid Oxide Fuel Cell (SOFC) (2/2)





Cathode	$(La,Sr)MnO_3$	porous electrode (2.2 mm)
Electrolyte	$8\%Y_2O_3$-ZrO_2	mixed oxide (30–40 μm)
Anode	$Ni/8\%Y_2O_3$-ZrO_2	porous electrode (100 μm)

Applications

Estimated Costs (1/3)

Table 3.7. Estimates of current PEM costs (Tsuchiya, 2004)

	€/m^2	€/kW$_e$	share, %
Membrane	357	179	14
Electrodes	1016	509	39
Bipolar plates	1179	589	45
Platinum	34	17	1
Peripherals	11	6	0
Assembly		6	0
Total		**1304**	**100**

Table 3.9. Estimates of future PEM stack costs at a cumulative production of 250,000 MW$_e$/a (Tsuchiya, 2004)

	€/m^2	€/kW	share, %
Membrane	36	9–12	16–25
Electrodes	69–107	17–36	48–49
Bipolar plates	25–65	6–21	17–29
Platinum (catalyst)	6	1–2	3–4
Peripherals	3	1	1–2
Assembly		1	2–4
Total		**36–74**	**100**

Estimated Costs (2/3)

Table 3.8. Estimates of SOFC and MCFC distributed power generation system cost (Blesl *et al.*, 2004)

	SOFC		MCFC	
	€/kW$_e$	**Share, %**	**€/ kW$_e$**	**share, %**
Fuel-cell stack	4714	42	4661	50
Boiler	4672	41	2146	23
Operating system	1231	11	820	9
Reformer	52	0	544	6
Heat exchanger	274	2	286	3
Burner	109	1	258	3
Air supply	118	1	31	
Inverter	151	1	88	
Frame	0	0	500	
Total	**11,319**		**9334**	

Table 3.10. Estimated SOFC and MCFC system cost (Blesl *et al.*, 2004)

	SOFC (200 kW)		MCFC (300 kW)	
	€/kW$_e$	**share, %**	**€ /kW$_e$**	**share, %**
Fuel-cell stack	396	33	418	35
Boiler	382	32	311	26
Operating system	104	9	119	10
Reformer	52	4	44	4
Heat exchanger	66	6	60	5
Burner	38	3	47	4
Air supply	38	3	9	1
Inverter	66	6	69	6
Frame	42	4	101	9
Total	**1184**		**1179**	

Estimated Costs (3/3)

Table 3.12. Performance and costs of PEM, SOFC, PAFC and AFC, up to 5 kW_e (Staffell *et al.*, 2007)

	PEMFC	SOFC	PAFC	AFC
Operating voltage, V	0.59–0.73	0.63–0.75	0.64–0.72	0.64–0.82
Operating current density, A/cm^2	0.40–0.90	0.32–0.67	0.16–0.31	0.09–0.24
Power density, W/cm^2	0.27–0.56	0.22–0.46	0.11–0.21	0.06–0.18
Stack efficiency, % HHV	36.5–50.0	42.0–64.5	40.5–54.5	42.5–49.5
System efficiency, % HHV	23.0–31.5	27.0–41.5	26.0–35.0	27.0–32.0
total efficiency, % HHV	63.5–81.5	67.0–71.0	74.0–87.0	~ 87.0
Lifetime, kh	7–21	15–59	30–53	4–8
Lifetime, years	0.7–2.4	1.7–6.7	3.5–6.1	0.5–0.9
Degradation, mV/year	13.1–74.5	28.0–73.6	14.9–39.4	78.8–254
Degradation, %/year	2–11	4–10	2–6	11–35
Stack cost, €/kW_e	300–900	200–600		150–600
System cost, €/kW_e	530–1130	680–1080	2500–5000	375–825
Target retail price, €/kW	220–440	510–970	660–1100	120–230

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