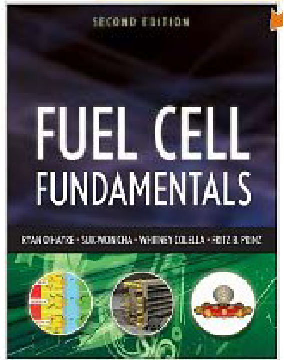
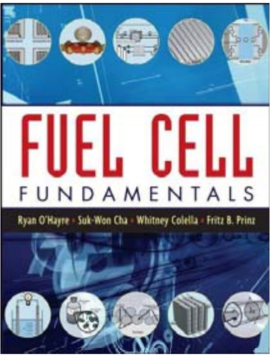
446.671 Fuel Cell Science & Technology

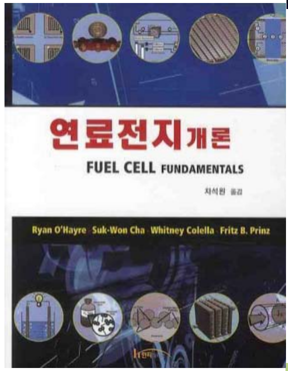
Course Introduction



- **Instructor:** Suk Won Cha
  - Office: 301-1417, Phone: 880-1700, Email: swcha@snu.ac.kr, Office Hours: A/O



- TA: Sanghoon Ji
  - Office: 314-311, Phone: 880-8050
    Email: Office Hours: A/O



- Text:
  - 1. R. O'Hayre, S. W. Cha, W. Collela, F. B. Prinz, *Fuel Cell Fundamentals 2nd Ed*, Wiley, 2009 (Available(?) at the engineering bookstore.)
  - 2. *DOE Fuel Cell Handbook*, 7th Ed. (2004) (Available for free on the web).

Course Introduction

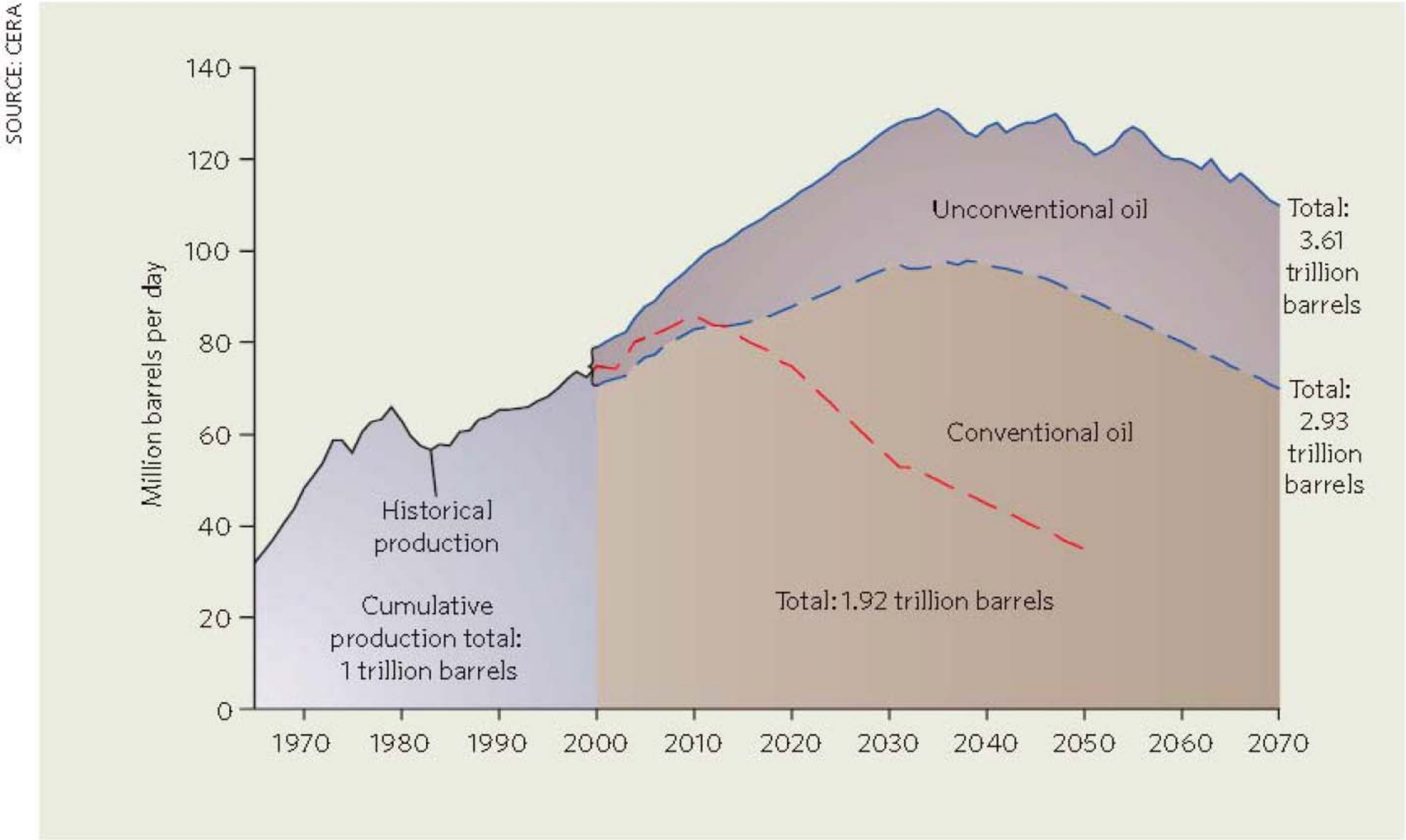
- **Prerequisites:** Engineering Mathematics, Basic Physics or Chemistry, Basic Thermodynamics, or equivalent.
- **Course Homepage:** http://fuelcell.snu.ac.kr
- **Lecture schedule:** Every Tue, Thu 4:00PM–5:15PM, Bld 301, Rm 204
- **Grading:**
  - *Homework (25%)* Problem sets as homework for each lecture topic corresponding to each chapter of the main textbook. Due at the <u>beginning of class</u>. 10% penalty for each day late. No acceptance after solutions are posted – generally a couple of days after the assignment is due.
  - *Midterm (25%)* An 1 hour in-class exam. Open book policy.
  - *Final Exam (40%)* A comprehensive 3 hour in class final exam. Open book policy.
  - *Class Attendance (10%)*

Course Introduction

Weeks	Date	Contents
1	3/3,5	Introduction
2	3/10,12	Fuel Cell Thermodynamics
3	3/17,19	Fuel Cell Kinetics I
4	3/24,26	Fuel Cell Kinetics II
5	3/31,4/2	Fuel Cell Charge Transport I
6	4/7,9	Fuel Cell Charge Transport II
7	4/14,16	Fuel Cell Mass Transport
8	4/21,23	Fuel Cell Modeling I, Midterm Exam
9	4/28,30	Fuel Cell Modeling II
10	5/5,7	Fuel Cell Characterization I
11	5/12,14	Fuel Cell Characterization II
12	5/19,21	Fuel Cell Systems Integration and Subsystem Design
13	5/26,28	Environmental Impact of Fuel Cells
14	6/2,4	Fuel Cell Design
15	6/9,11	Final Exam

Introduction to Fuel Cells

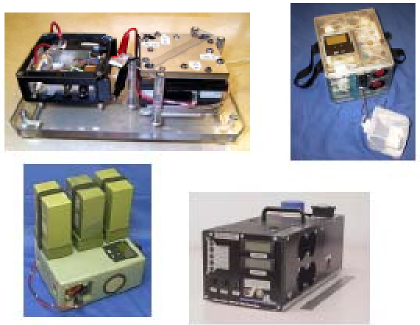
Why Fuel Cell?



Twin peaks: peak-oil supporters think we have already reached or will soon reach a historical maximum of oil production (red line); others argue that oil production will not peak until at least 2030 (blue lines).

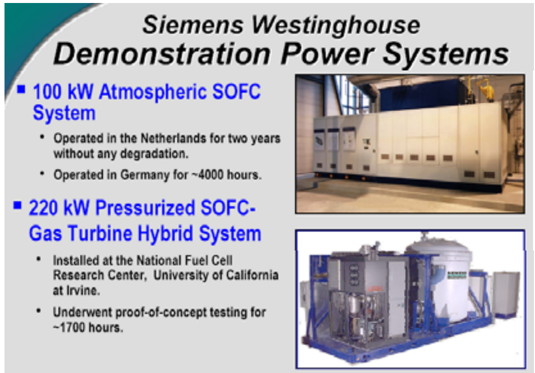
Why Fuel Cell?

Soldier & Sensor Power (10-100W)



Auxiliary Power Units (500-3000W)

Cogeneration Applications (>3000W)



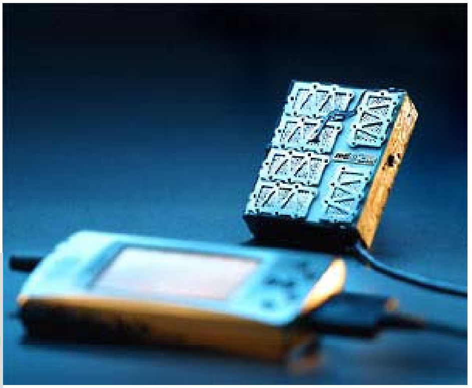
Siemens Westinghouse
Demonstration Power Systems

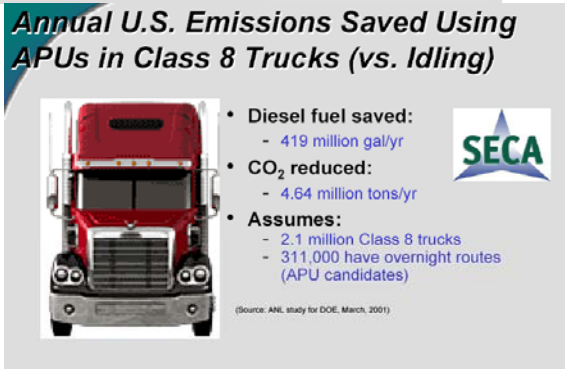
- 100 kW Atmospheric SOFC System
  - Operated in the Netherlands for two years without any degradation.
  - Operated in Germany for ~4000 hours.
- 220 kW Pressurized SOFC-Gas Turbine Hybrid System
  - Installed at the National Fuel Cell Research Center, University of California at Irvine.
  - Underwent proof-of-concept testing for ~1700 hours.

High Efficiency

Clean Energy

Renewable Energy

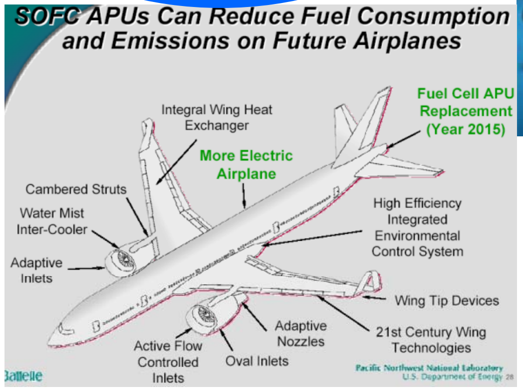




Annual U.S. Emissions Saved Using APUs in Class 8 Trucks (vs. Idling)

- Diesel fuel saved:
  - 419 million gal/yr
- CO_2 reduced:
  - 4.64 million tons/yr
- Assumes:
  - 2.1 million Class 8 trucks
  - 311,000 have overnight routes (APU candidates)

(Source: ANL study for DOE, March, 2001)



SOFC APUs Can Reduce Fuel Consumption and Emissions on Future Airplanes

What Is A Fuel Cell?

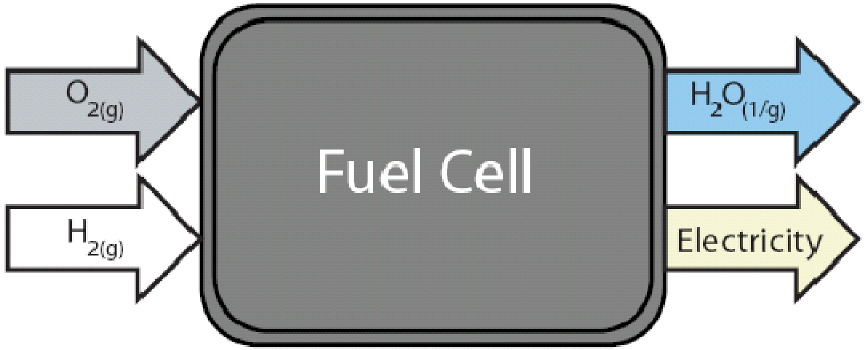
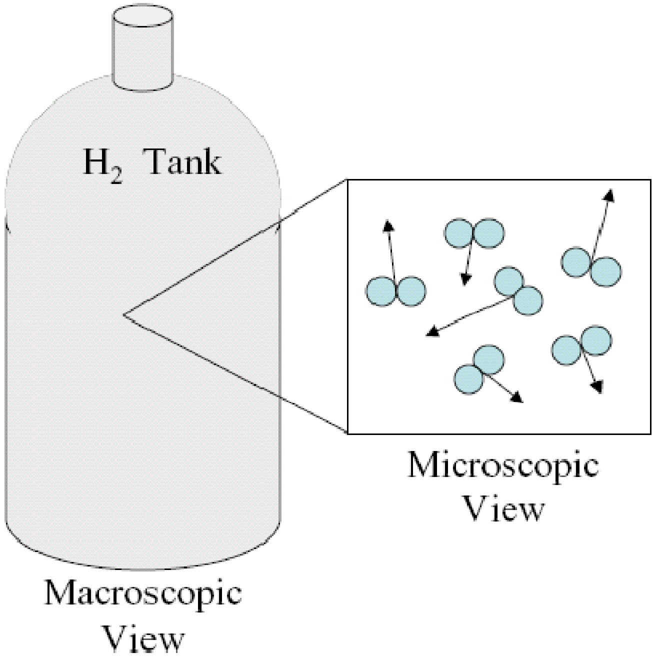
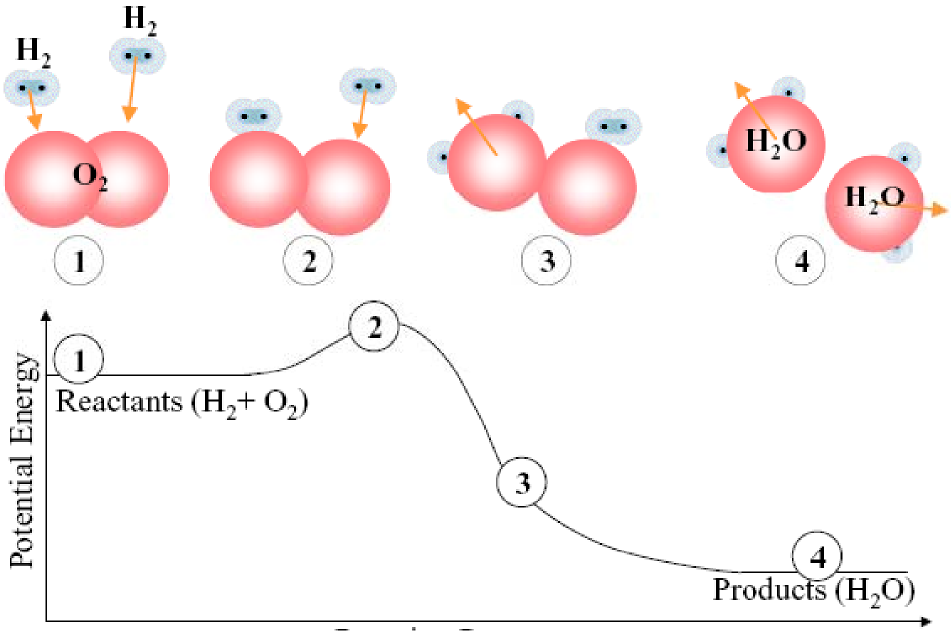


Figure 1.1: General concept of a hydrogen/oxygen (H_2/O_2) fuel cell.

- Electrochemical energy conversion device
  - Directly converts chemical energy to electrical energy
  - Heat engines: chemical -> thermal -> mechanical -> electrical
  - Losses are associated in any conversion step.

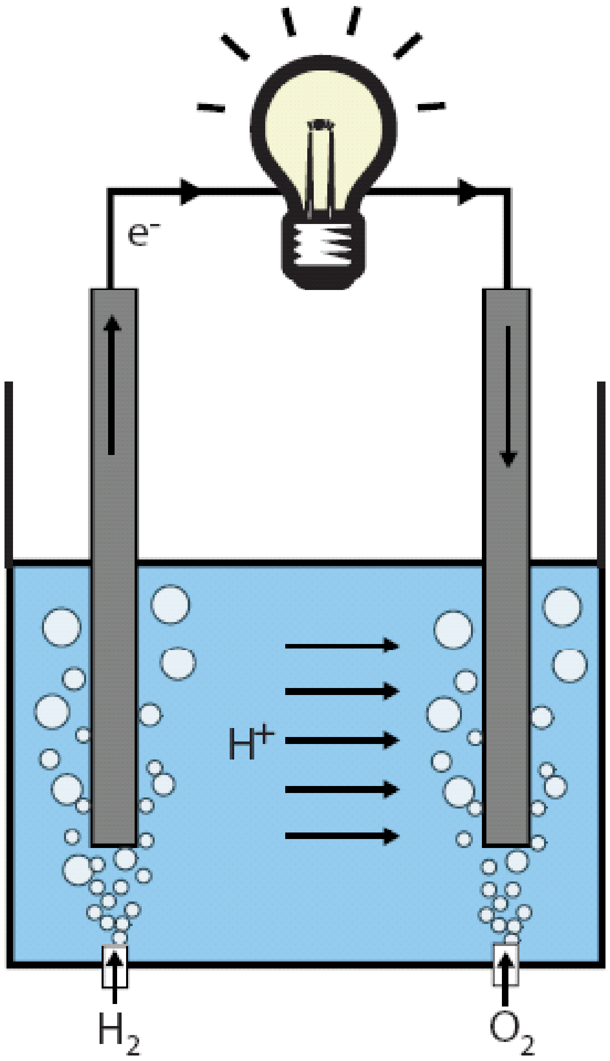
Driving Force





- Chemical reaction
  - Any substance favors more stable states.
  - **Energy** (usually heat) is released during the process

A Simple Fuel Cell



Full cell reaction

$H_2 + 0.5\ O_2 \rightarrow H_2O$

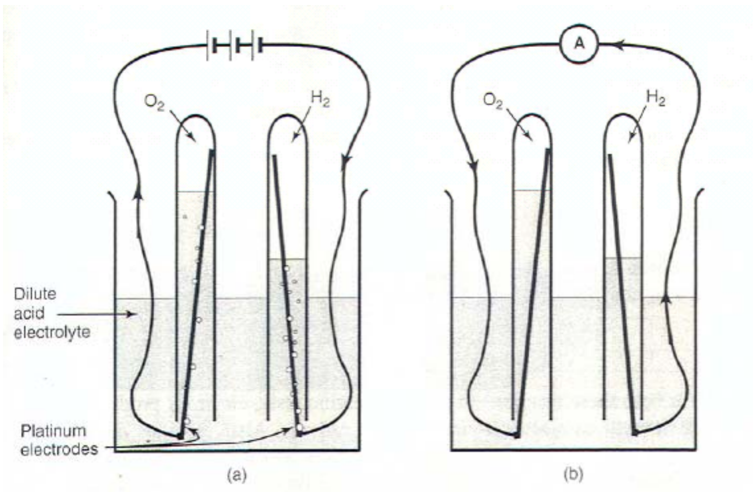
Half cell reaction

Anode: Oxidation (loss electrons)

$H_2 \rightarrow 2H^+ + 2e^-$

Cathode: Reduction (gain electrons)

$0.5\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$



Note that the arrows represent the flow of negative electrons from – to +.

William Grove's drawing

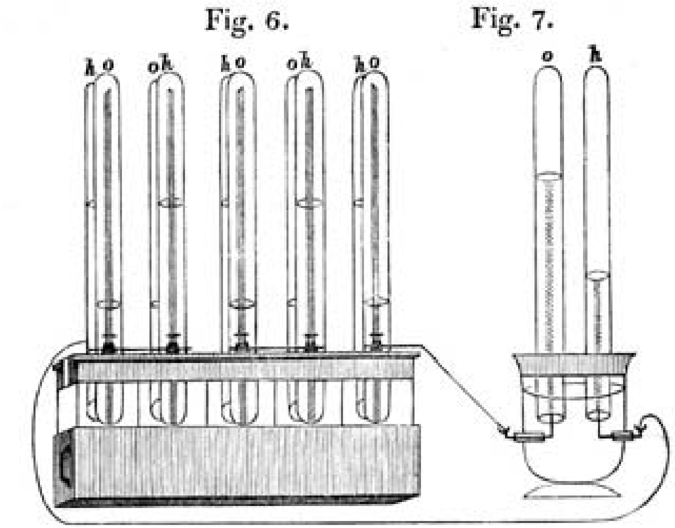
A Brief History*

- **Electrolysis of water** by British scientists William Nicholson and Anthony Carlisle in 1800
- **Sir W. Grove** discovered **hydrogen-oxygen fuel cell** (gas battery what he called) in 1839 using sulfuric acid as electrolyte.

  (Otto invented 4 stroke IC engines in 1867)

William Robert Grove
(1811 -1896)

- **Friedrich Wilhelm Ostwald** (1853 - 1932), experimentally determined the interconnected roles of the various components of the fuel cell: **electrodes**, **electrolyte**, oxidizing and reducing agents, anions, and cations, in 1893.



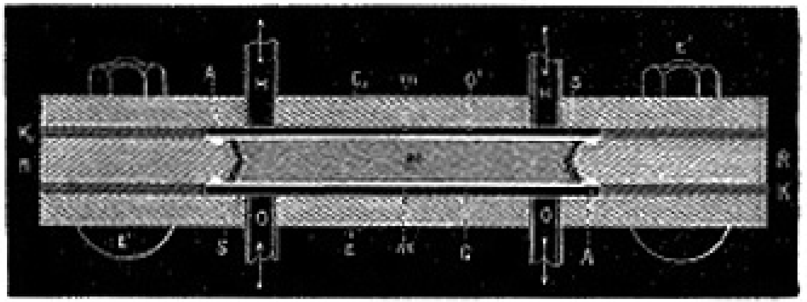
William Grove's drawing of an experimental "gas battery" from an 1843 letter

* from Smithsonian Institution

A Brief History

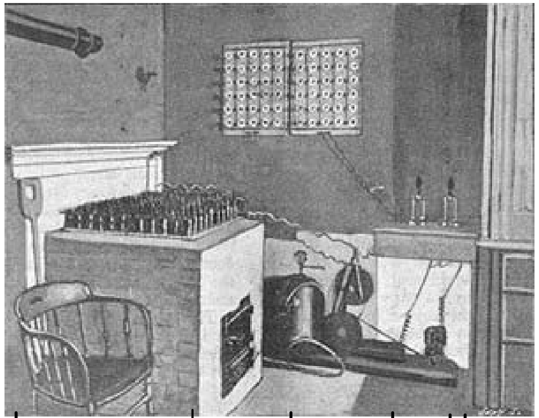
- **L. Mond** (1839 –1909) and **C. Langer** (d. 1935)'s fuel cell
  - Coal-derived "Mond-gas“ as fuel
  - 6 amps per square foot at .73 volts
  - Thin, perforated platinum electrodes
  - Electrolyte in a quasi-solid form; soaked up by a porous non-conducting material

FIG. 1.



Mond and Langer's fuel cell design from 1889

- Conclusion of **L. Cailleteton** (1832–1913) and **L. Colardeau** in 1894 – "only precious metals" would work for fuel cells to make it a impractical device.
- Carbon battery (for home) by **William W. Jacques** (1855 –1932)
  - injected air into an alkali electrolyte, react with a carbon electrode.
  - Actual reaction was thermoelectric of 8% efficiency instead of electrochemical reaction of 82% efficiency

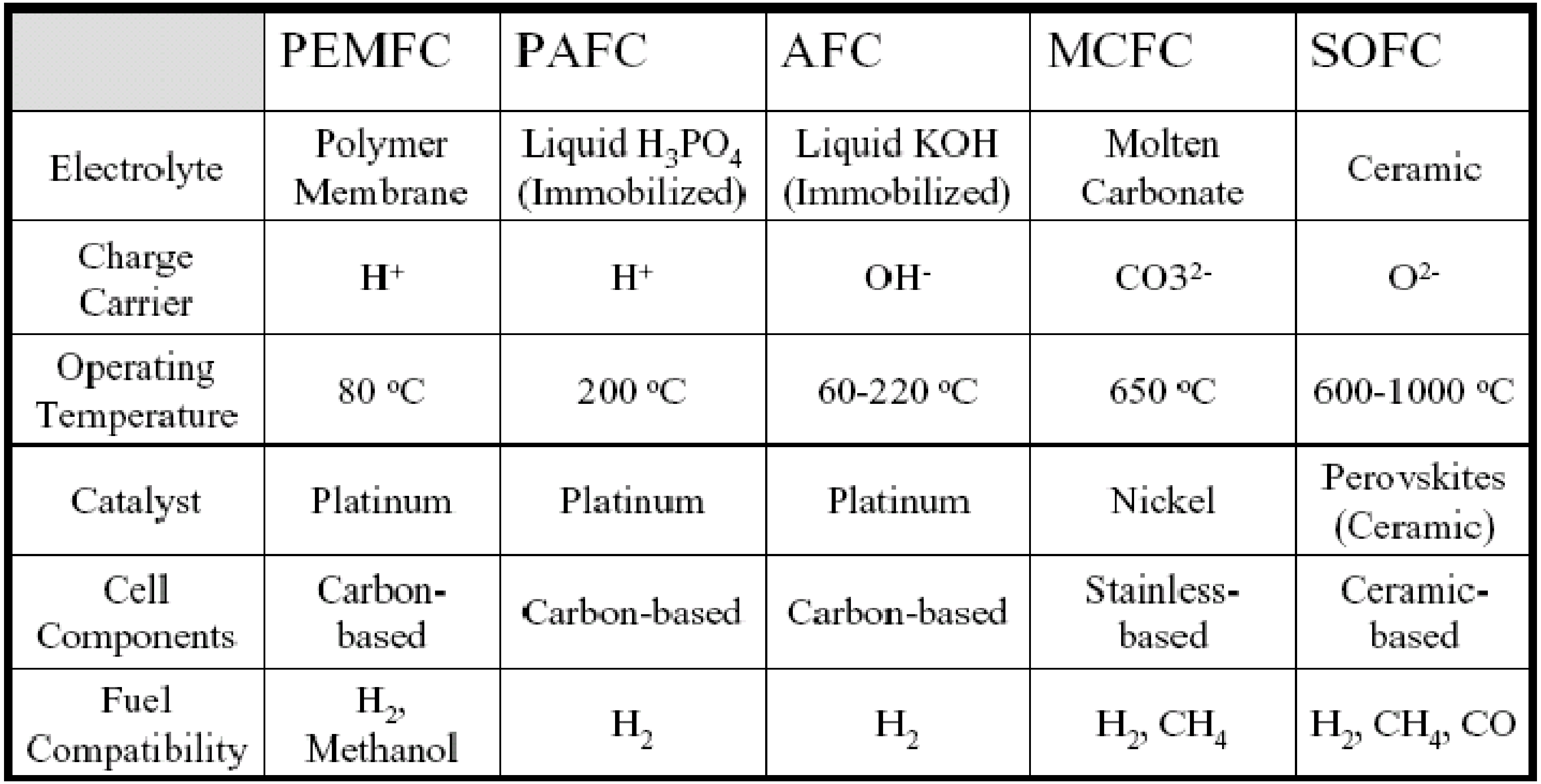


Jacques' carbon battery apparatus, 1896

A Brief History

- In 1900, **Nernst** demonstrated SOFC using YSZ
- **E.Bauer** (1873 –1944), **O. K. Davtyan,** during the first half of the 20th century,
  - Established the fundamentals of high temperature fuel cells such as the *molten carbonate* and solid oxide fuel cell.
- **Francis Thomas Bacon** (1904 –1992)
  - In 1939, he built a cell that used nickel gauze electrodes and operated under pressure as high as 3000 psi.
  - In 1958, he demonstrated an **alkali cell** using a stack of 10-inch diameter electrodes for Britain's National Research Development Corporation. Bacon experimented with **potassium hydroxide (KOH)** instead of using the acid electrolytes. KOH performed as well as acid and was **not** as **corrosive** to the electrodes.
  - Though **expensive**, Pratt & Whitney licensed Bacon's **reliable** cell for the Apollo spacecraft fuel cells.
- **Various fuel cells types** began to follow divergent paths after 1960's, as some types were seen as more suitable for some applications than others.

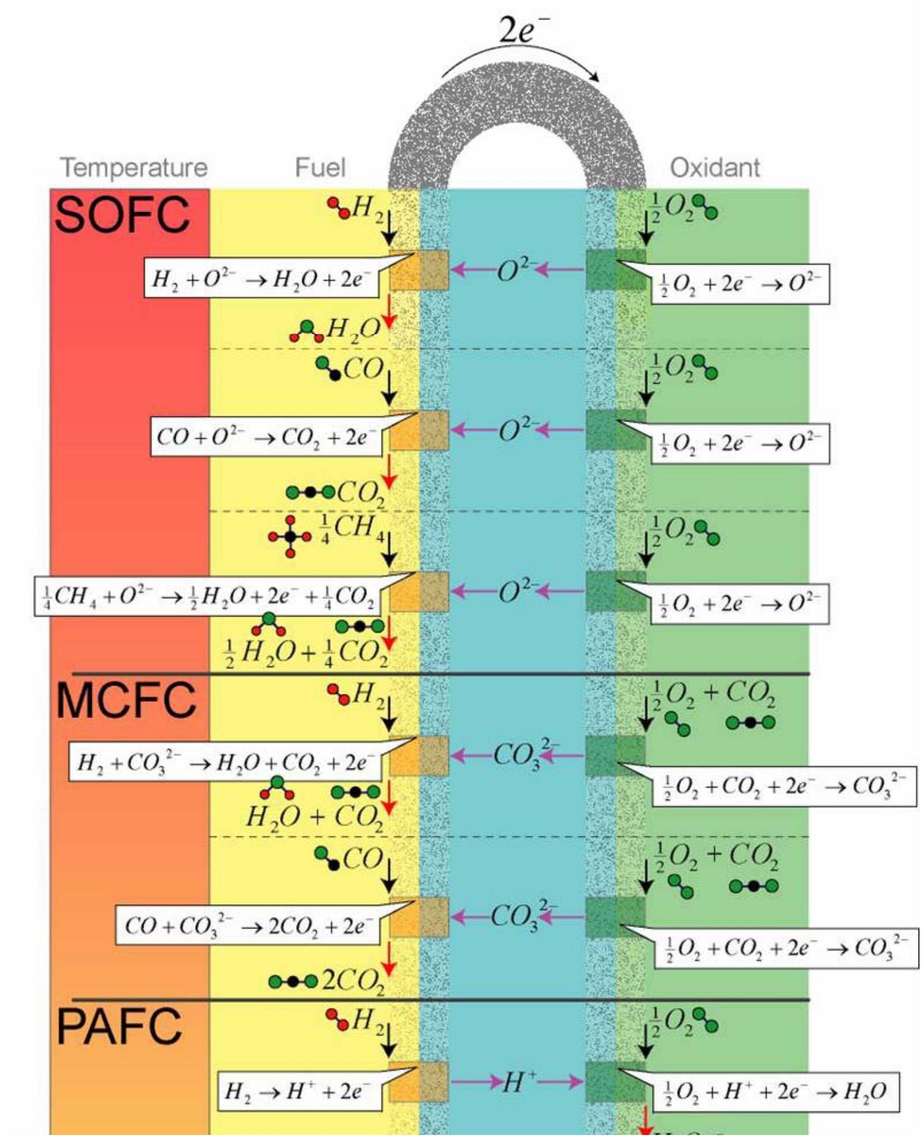
Fuel Cell Types

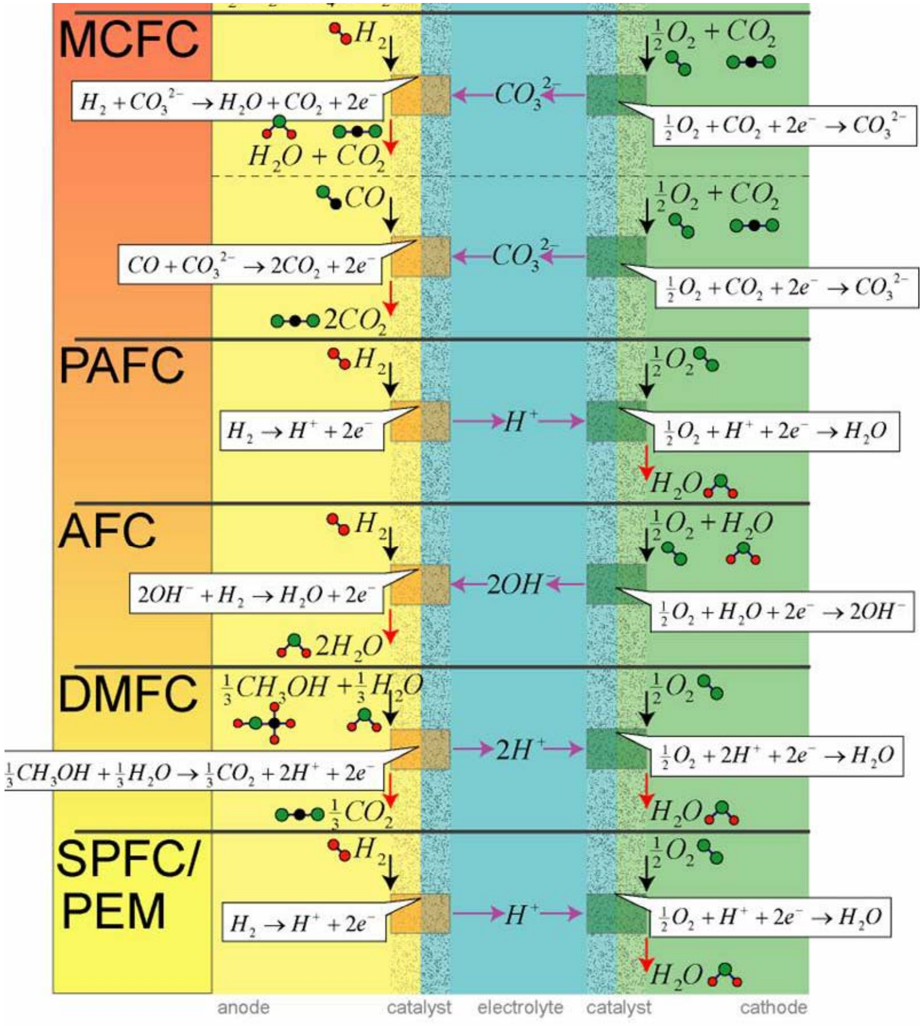


	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Polymer Membrane	Liquid H_3PO_4 (Immobilized)	Liquid KOH (Immobilized)	Molten Carbonate	Ceramic
Charge Carrier	H^+	H^+	OH^-	$CO3^{2-}$	O^{2-}
Operating Temperature	80 °C	200 °C	60-220 °C	650 °C	600-1000 °C
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites (Ceramic)
Cell Components	Carbon-based	Carbon-based	Carbon-based	Stainless-based	Ceramic-based
Fuel Compatibility	H_2, Methanol	H_2	H_2	H_2, CH_4	H_2, CH_4, CO

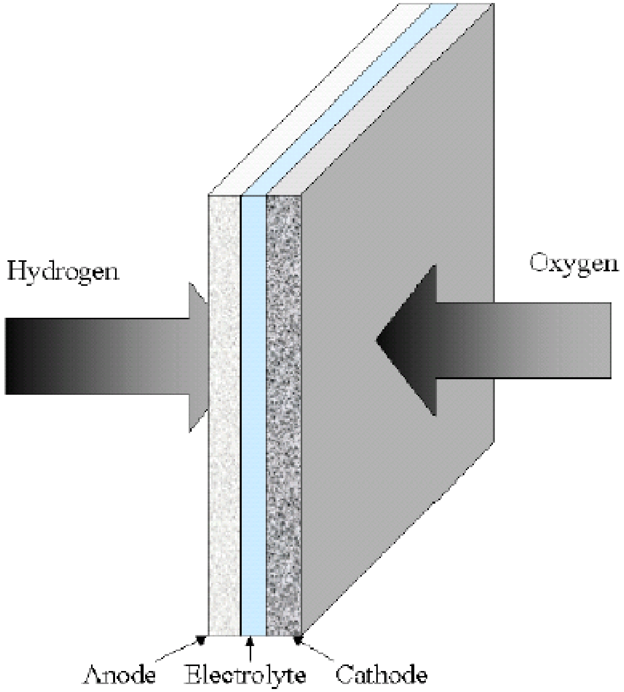
- Electrolyte determines the type of fuel cells and operation temperature.
  - Operation temperature significantly affects the use of other components such as catalyst.

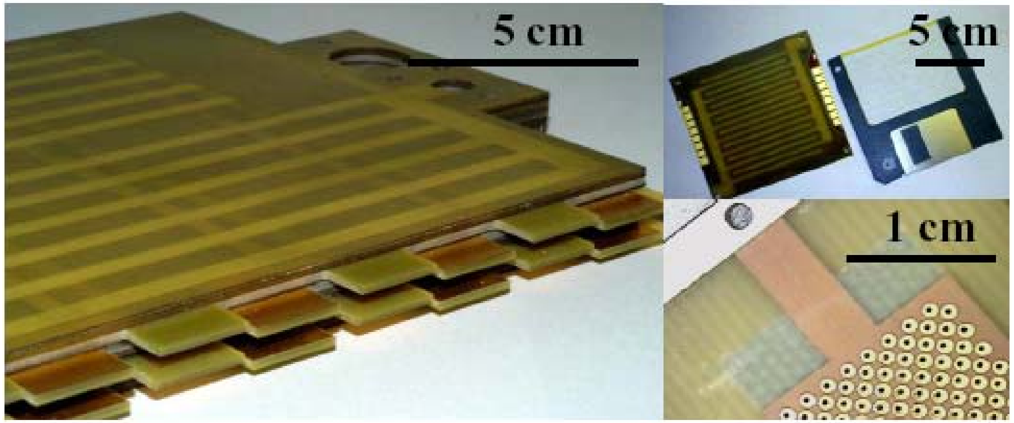
Fuel Cell Types





Compact Fuel Cells



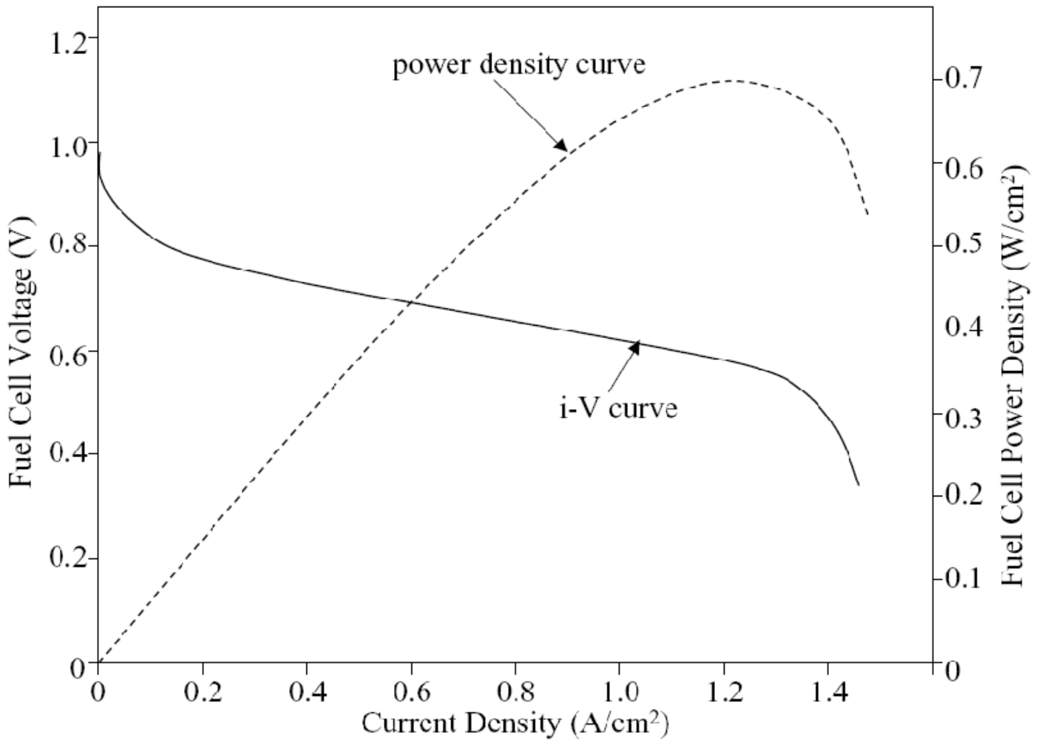


- Membrane-Electrode-Assembly (MEA)
  - Electrolyte: Immobilized liquid (MCFC, AFC, PAFC), Solid electrolyte (PEMFC (DMFC), SOFC)
  - Electrode: mixed conducting, porous solid containing catalyst materials

Fuel Cell: Pros & Cons

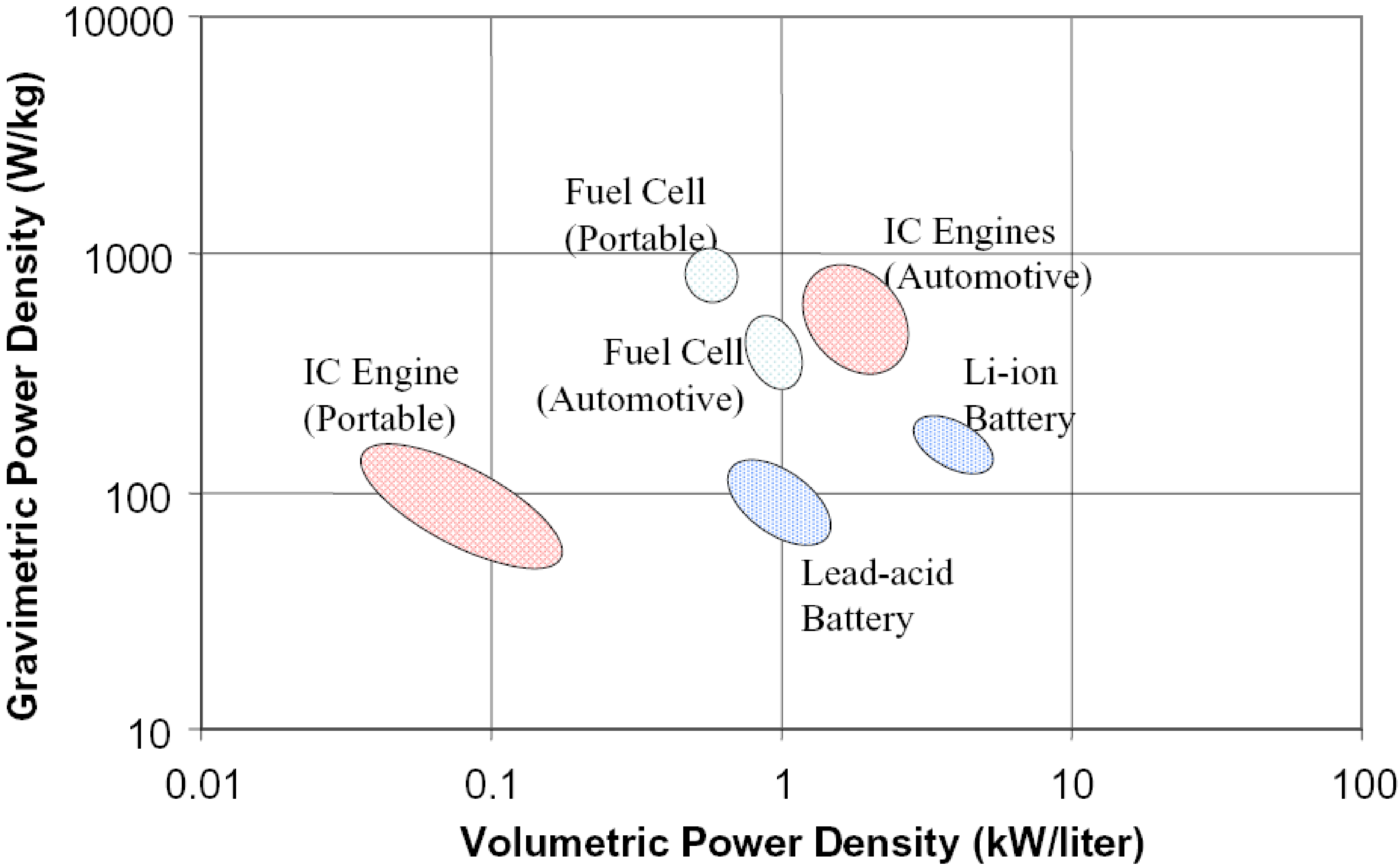
- Pros
  - Avoid carnot cycle limitations
  - High efficiency
  - No undesired reactions (NOx Sox), low particulate emissions
  - Silent mechanically robust
  - Scaleable, dispatchable
- Cons
  - Expensive
  - Fuel availability
  - Power/energy density (especially for portable appplications)
  - Operating temperature
  - Environmental posion
  - Durability during start/stop cycle

Fuel Cell Performance

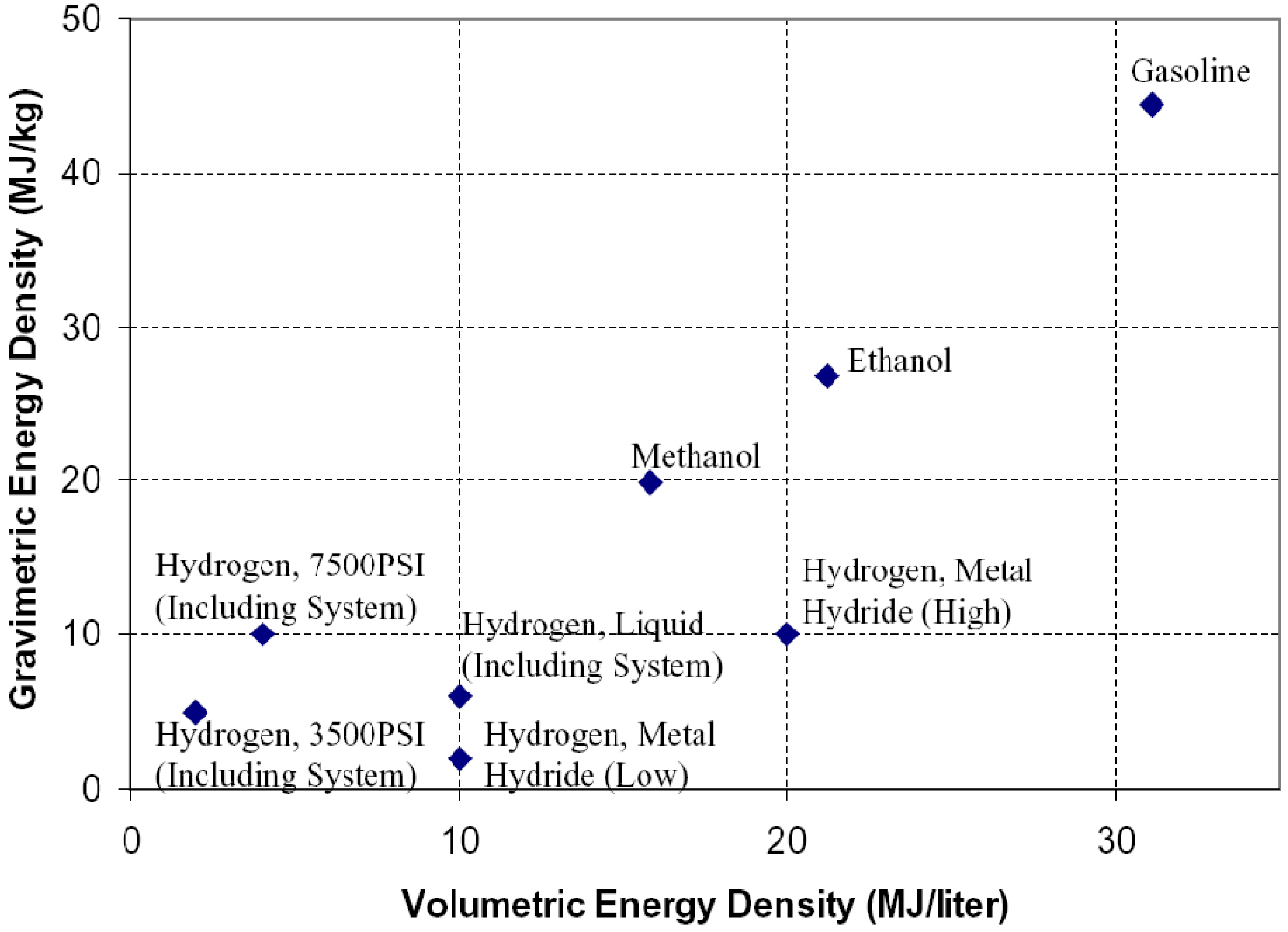


- Energy: U [J]
  - Work stored in a power system
  - Sets the operation time of a power system
- Power: P = U/time [J/s=W] = I [A] * V [V]
  - U [J] = P * time [Wh] (1 Wh = 3600 J)

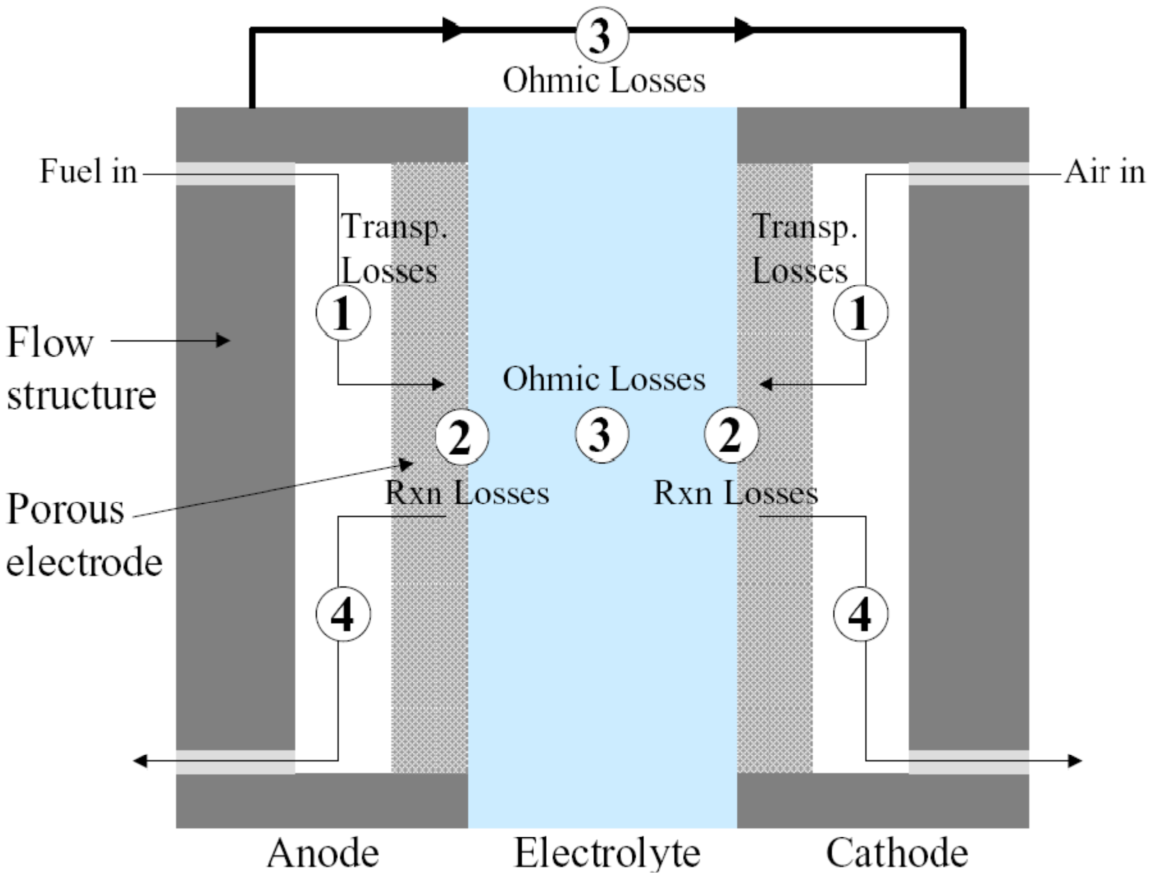
Power Density of Selected Technology



Energy Density of Selected Fuels

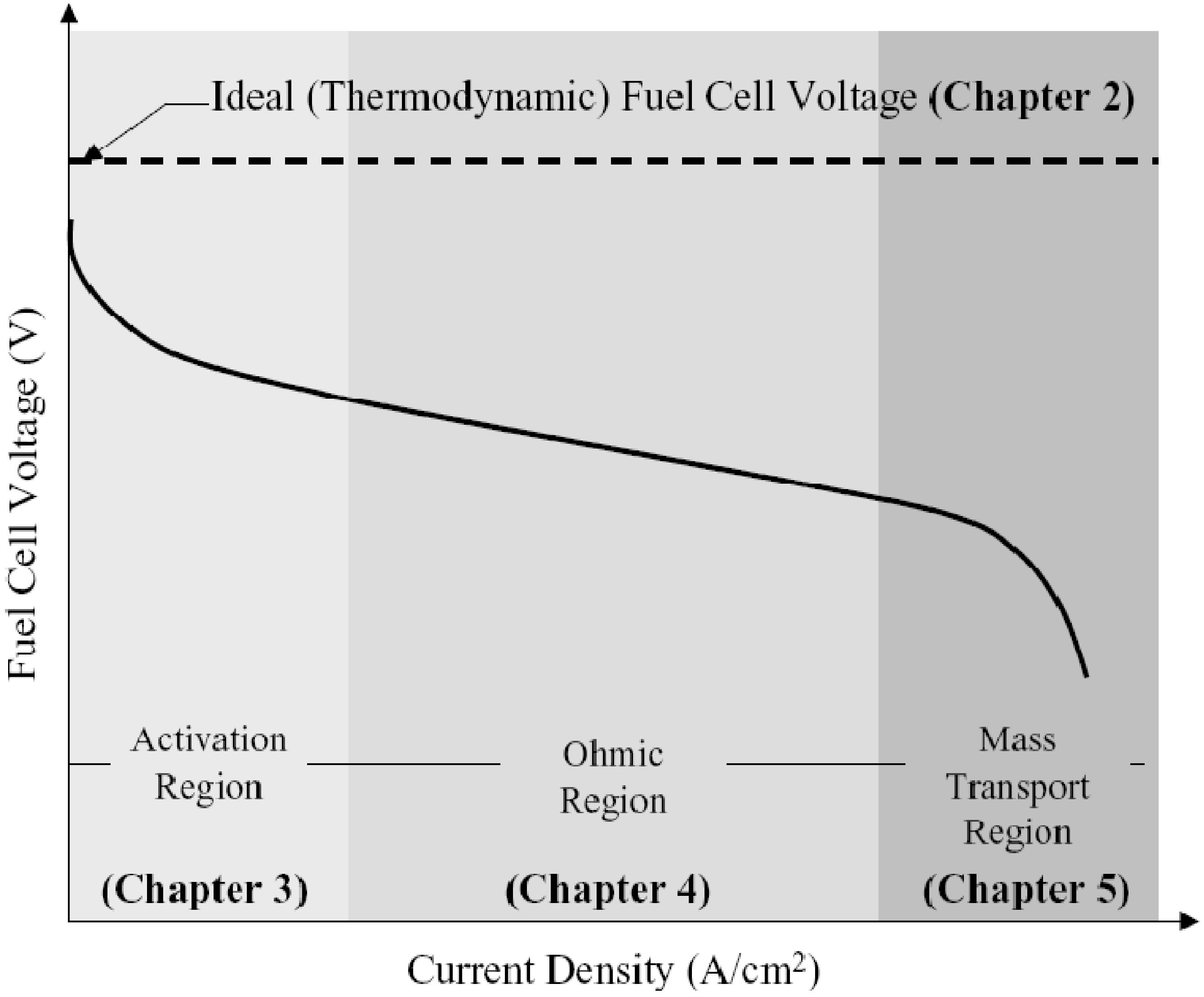


Transport, Losses & Componets

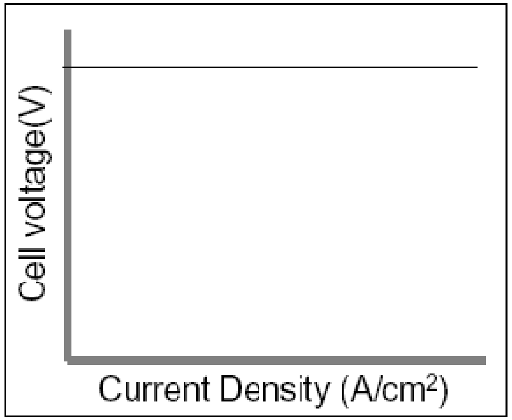


1. Reactant transport @ flow field & electrode: mass transport loss
2. Electrochemical reaction @ electrode (catalyst) : activation (reaction) loss
3. Ionic (electronic) conduction @ electrolyte : ohmic loss
4. Product removal @ flow field & electrode: mass transport loss

Losses in Fuel Cells



Losses in Fuel Cells


Reversible Voltage (Chapter 2)

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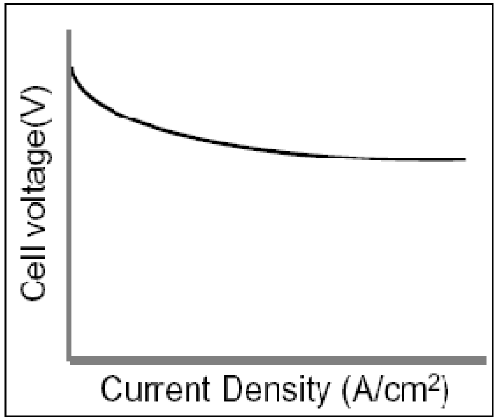
Rxn. Loss (Chapter 3)

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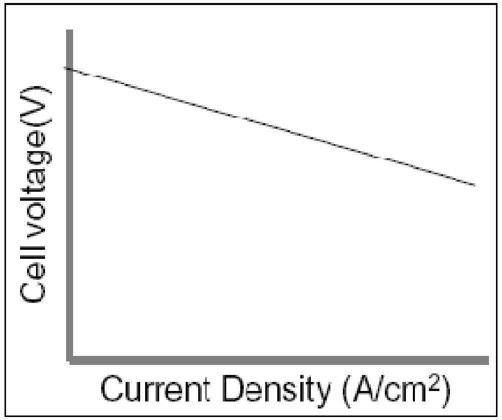
Ohmic Loss (Chapter 4)

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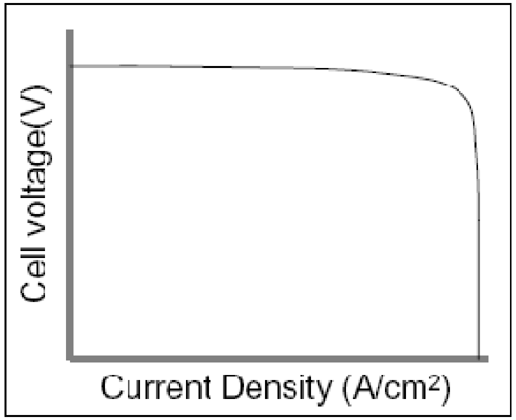
Concentration Loss (Chapter 5)

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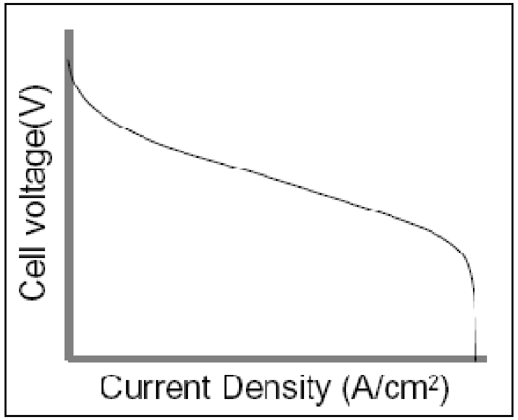
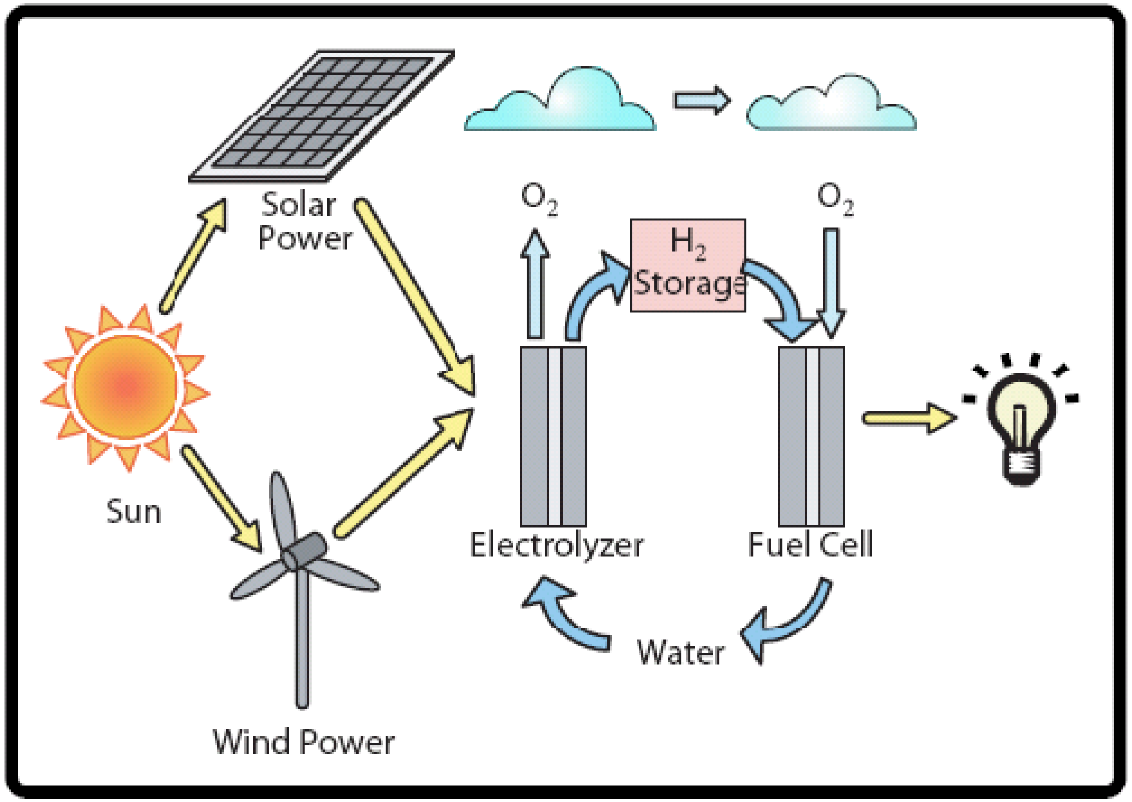

Net Fuel Cell Performance

$$V = E_{thermo} - \eta_{act} - \eta_{ohmic} - \eta_{conc}$$

Fuel Cell Terms May Be Confusing

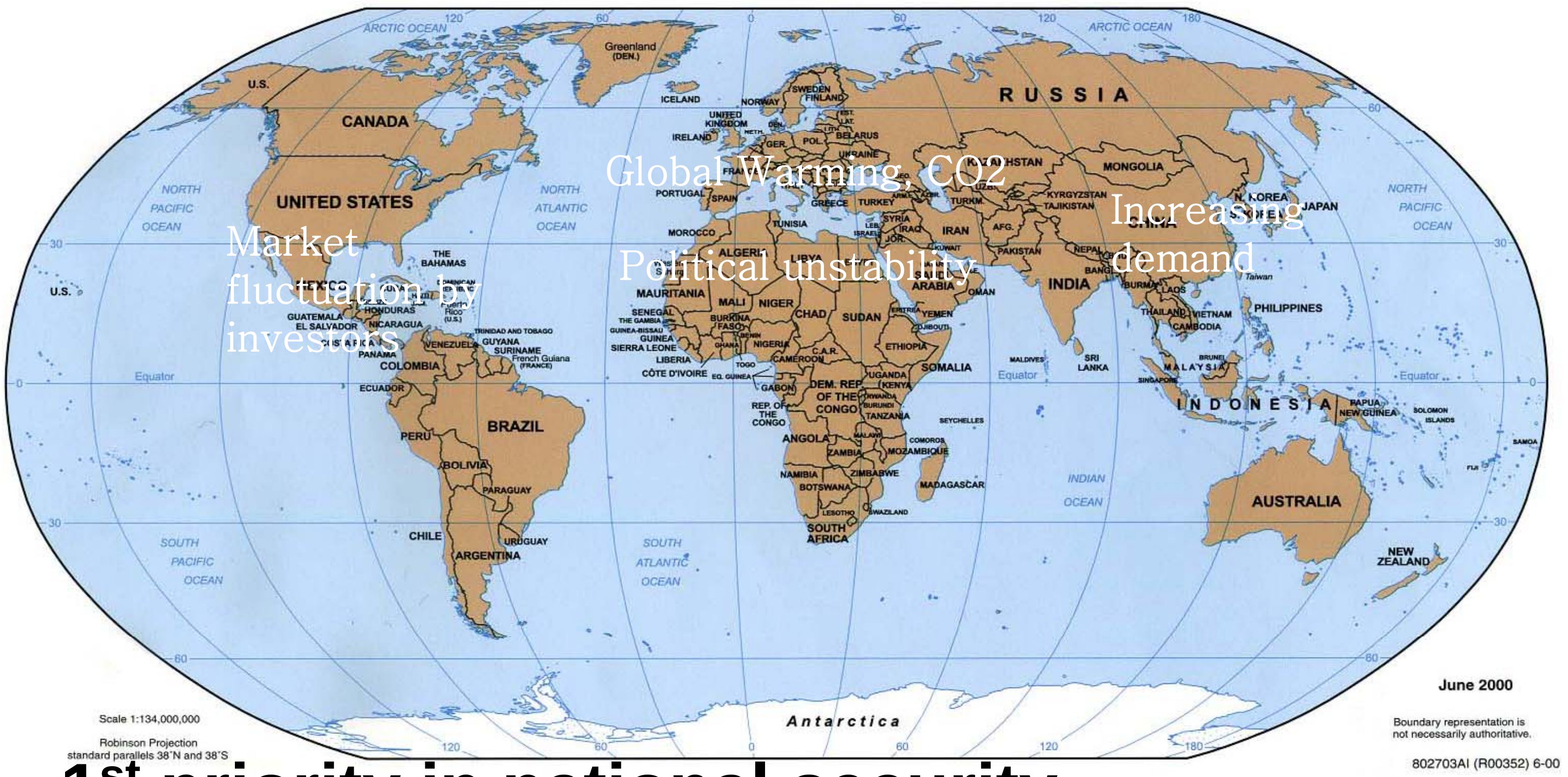
- Electrolyte or membrane
- Electrode or anode or cathode or catalyst layer or diffusion layer or current collection layer
- Flow structure or flow field or flow channels or separator
- Current density (per area), energy density (per volume), power density (both!)
- I-V curve or polarization curve
- losses vs. overpotentials
- Ohmic loss or IR loss
- Reaction loss or activation loss or faradaic loss
- Mass transportation loss or concentration loss
- Voltage or potential
- This not the end of the list!!!

Hydrogen Economy



- How fuel cells fit to each energy sectors?
  - Residence: small distributed power systems
  - Industry: large distributed power systems
  - Transportation: portable power systems

Energy Issue



Global Warming, CO2

Increasing demand

Market fluctuation by investors

Political unstability

Scale 1:134,000,000

Robinson Projection
standard parallels 38°N and 38°S

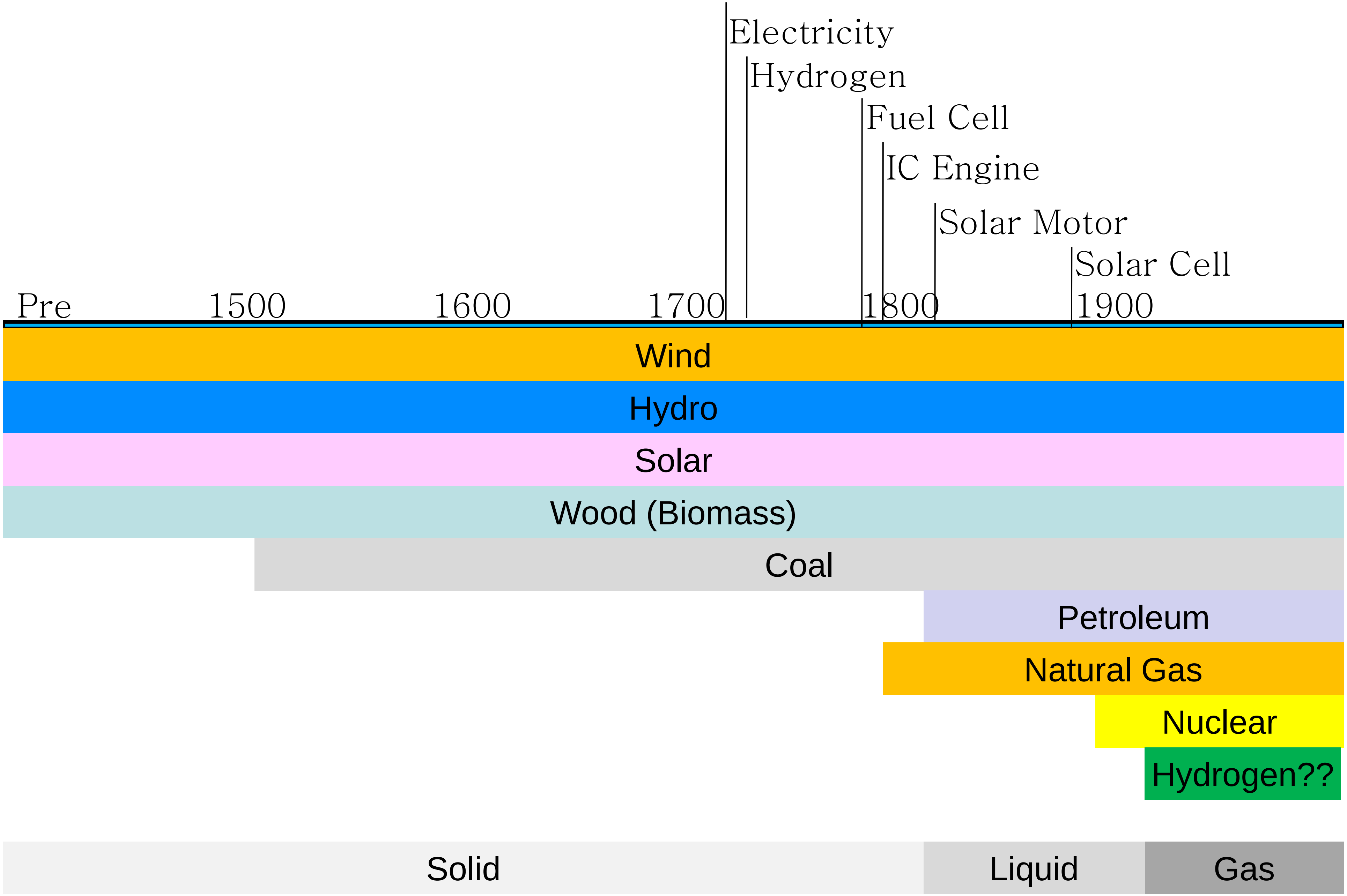
June 2000

Boundary representation is not necessarily authoritative.

802703AI (R00352) 6-00

- **1st priority in national security**
- **Technical, social, economical and political**
- **No one can solve the problem currently**
  - Continuous R&D is a must

History of Energy



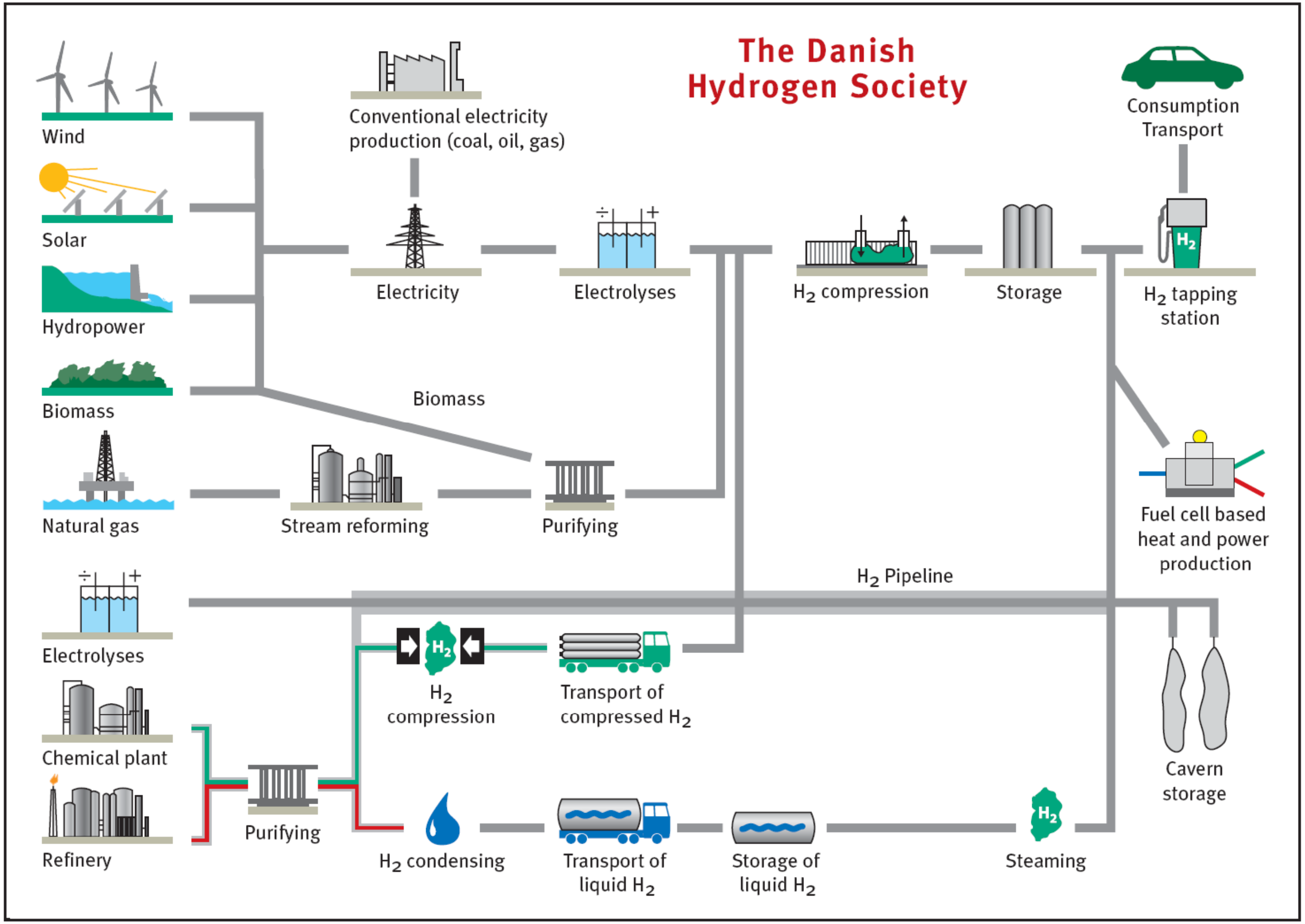
Electricity
Hydrogen
Fuel Cell
IC Engine
Solar Motor
Solar Cell

Pre
1500
1600
1700
1800
1900

Wind
Hydro
Solar
Wood (Biomass)
Coal
Petroleum
Natural Gas
Nuclear
Hydrogen??

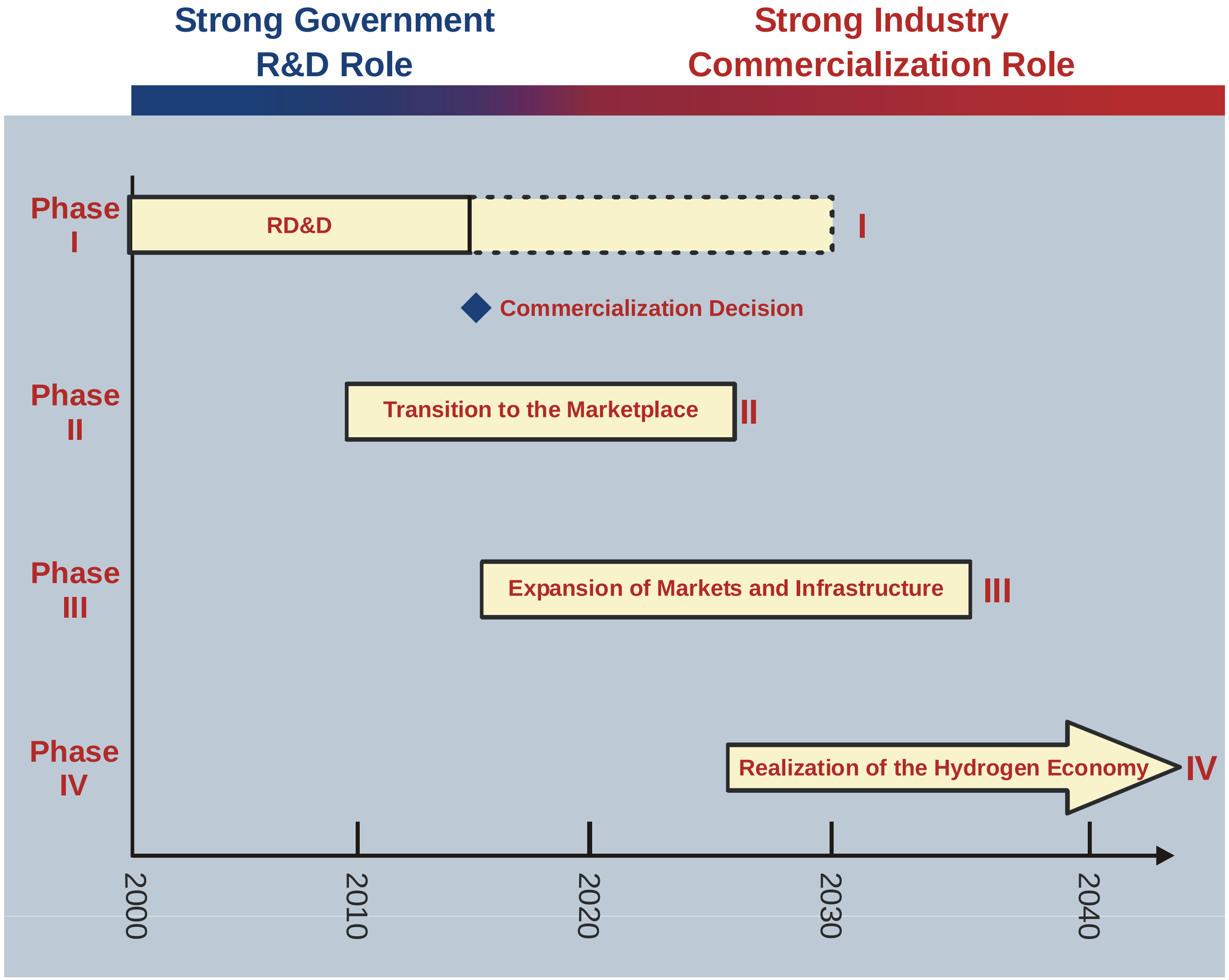
Solid
Liquid
Gas

Hydrogen for Automotive



http://www.investindk.com/db/filarkiv/631/Brint_aug2005.pdf

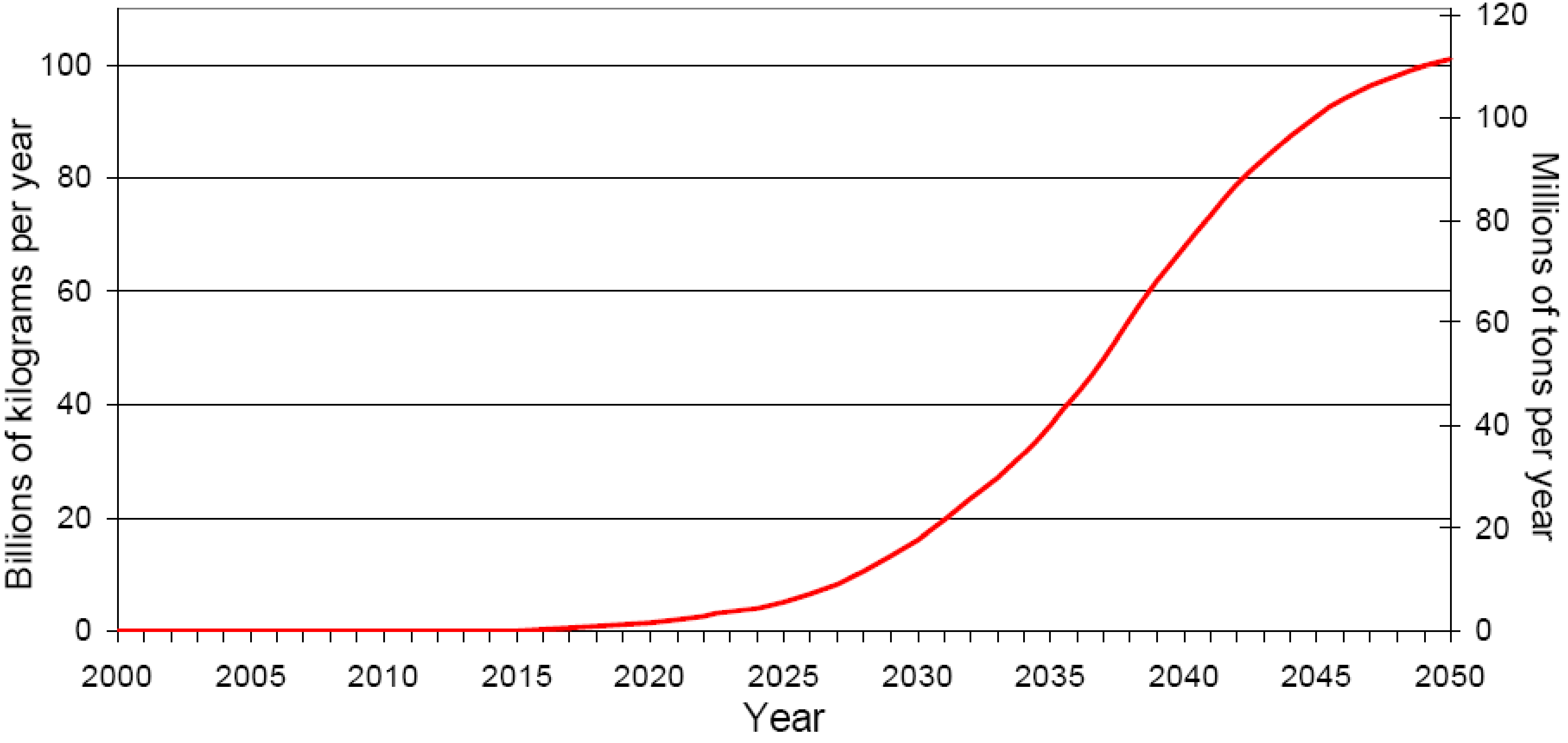
DOE Hydrogen Economy Timeline



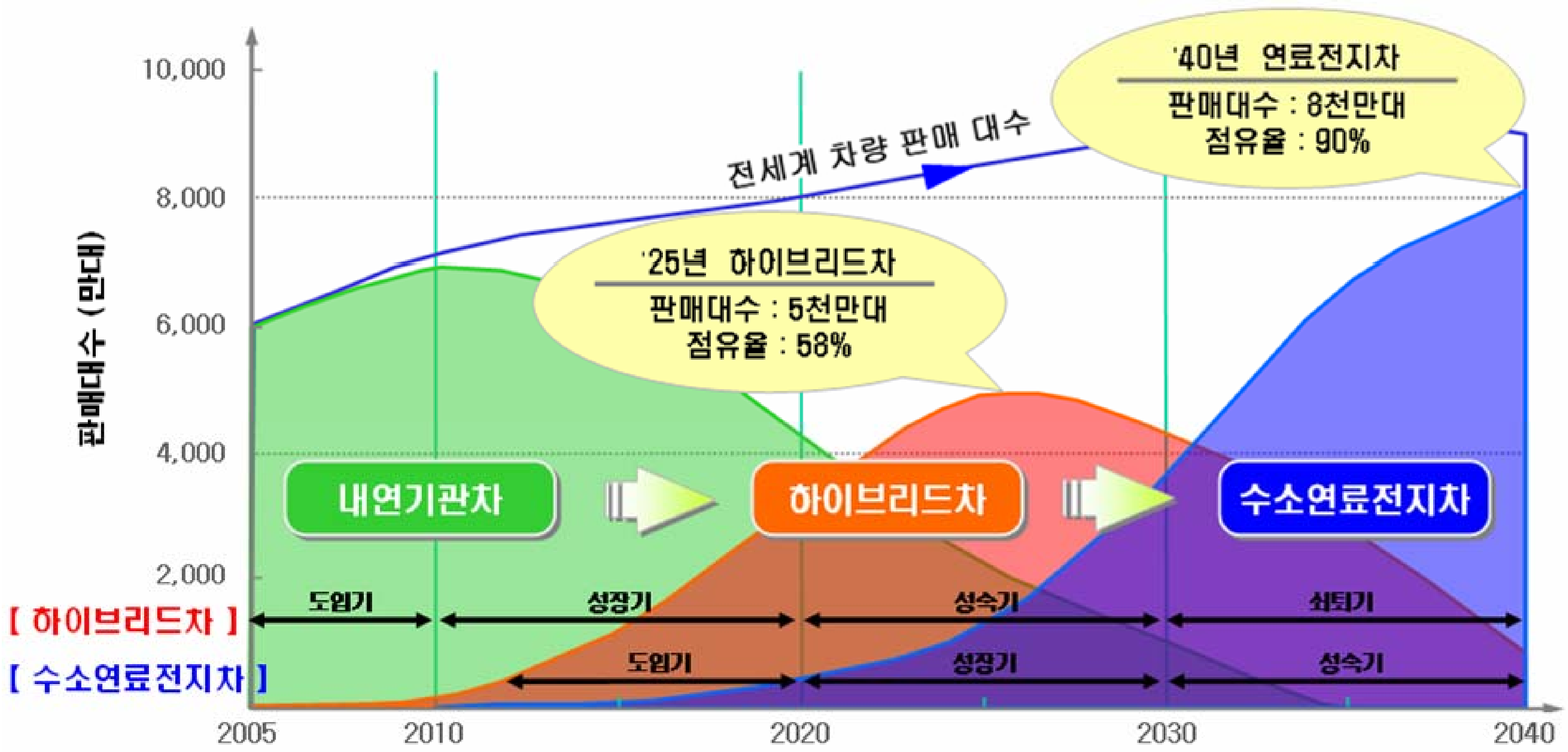
Transitional Phases

- I. Technology Development Phase
- II. Initial Market Penetration Phase
- III. Infrastructure Investment Phase
- IV. Fully Developed Market and Infrastructure Phase

Hydrogen Penetration Scenario(US)



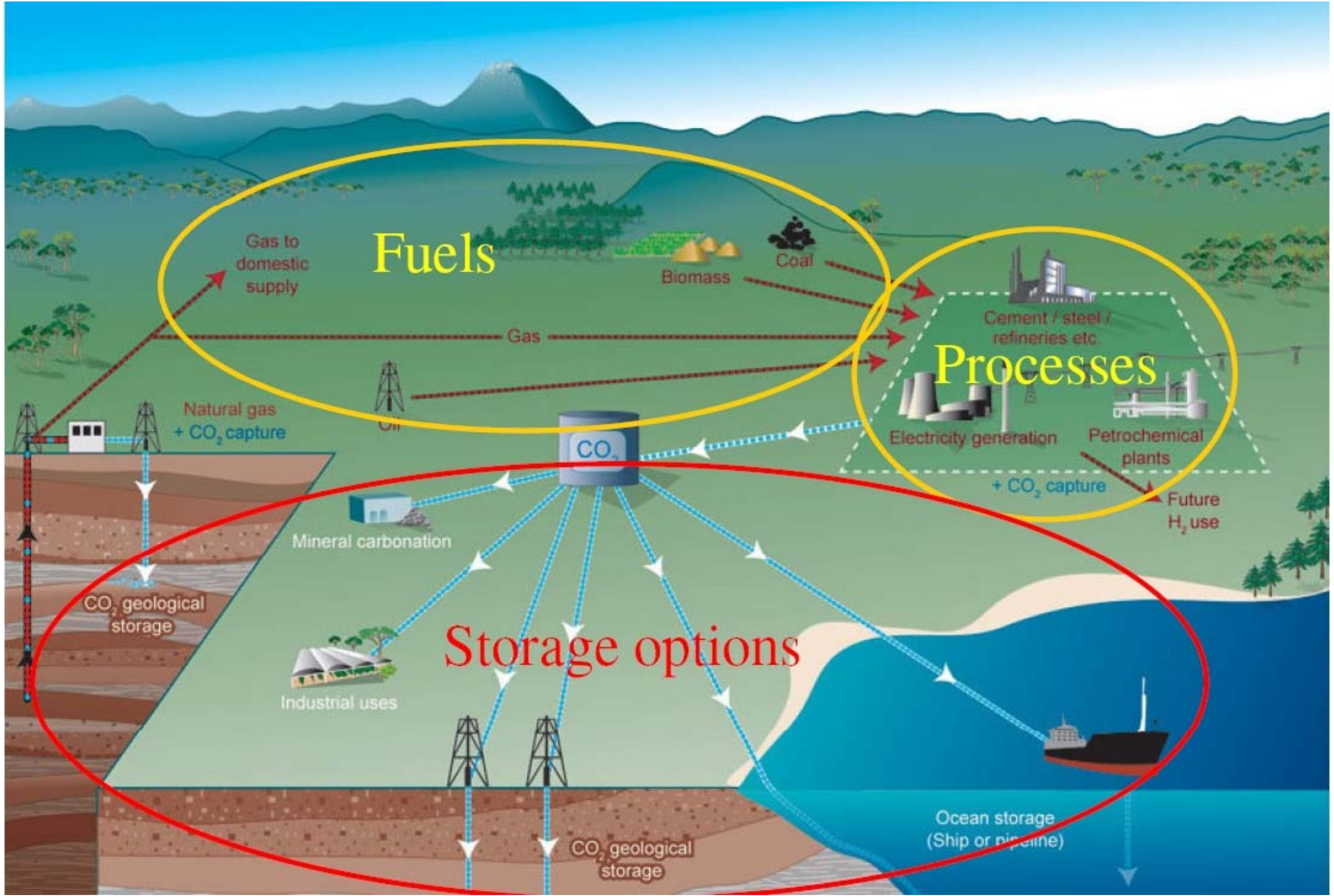
Market for Fuel Cell Automotive



Source : Automotive World Car Industry Forecast Report, Global Insight, 2004
The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs, The National Academies, 2004

- Market penetration takes long time even from a optimistic scenario.

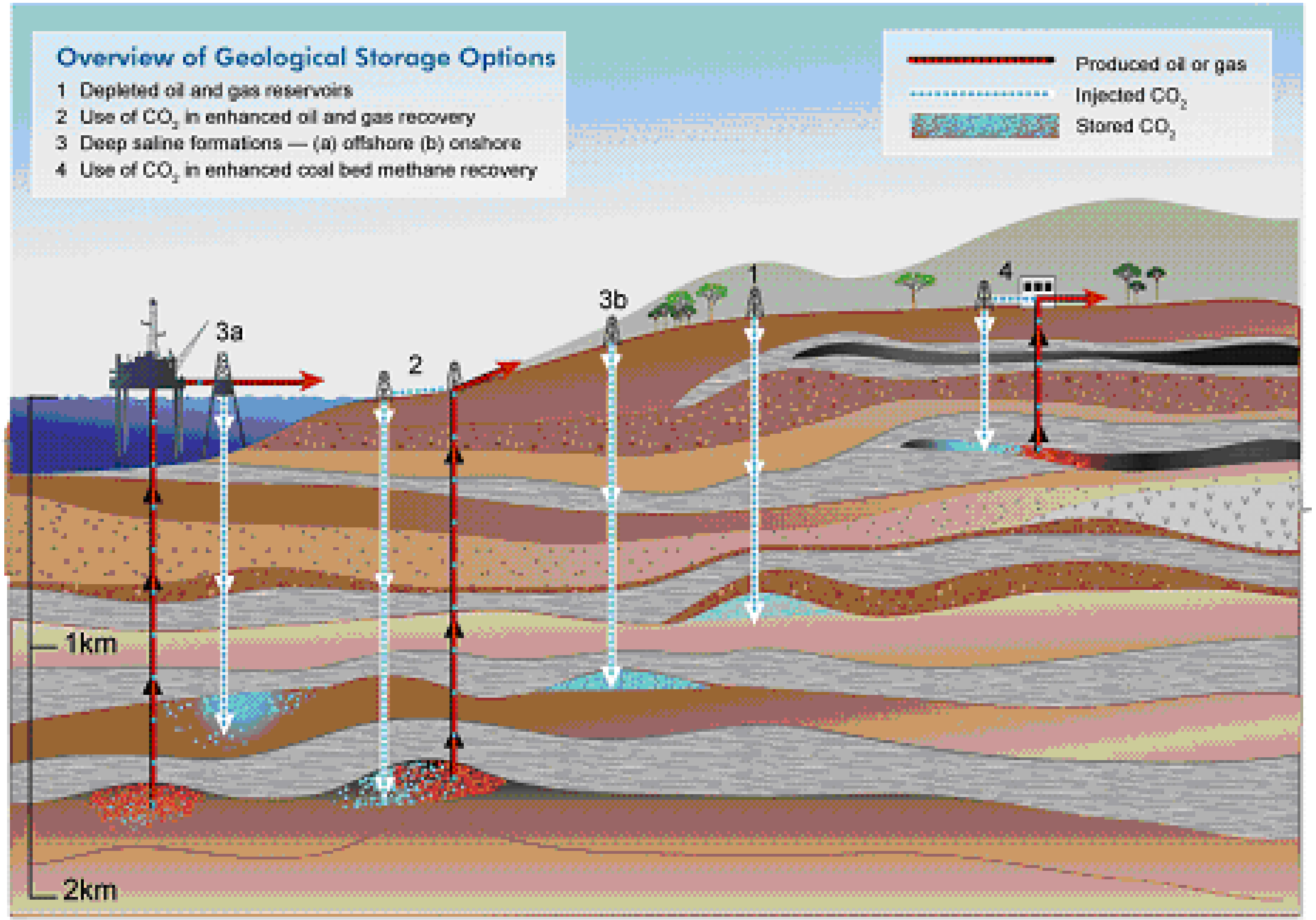
Carbon Capture & Storage



	Natural gas combined cycle	Pulverized coal	Integrated gasification combined cycle
Without capture (reference plant)	0.03 - 0.05	0.04 - 0.05	0.04 - 0.06
With capture and geological storage	0.04 - 0.08	0.06 - 0.10	0.06 - 0.09
With capture and Enhanced oil recovery	0.04 - 0.07	0.05 - 0.08	0.04 - 0.08

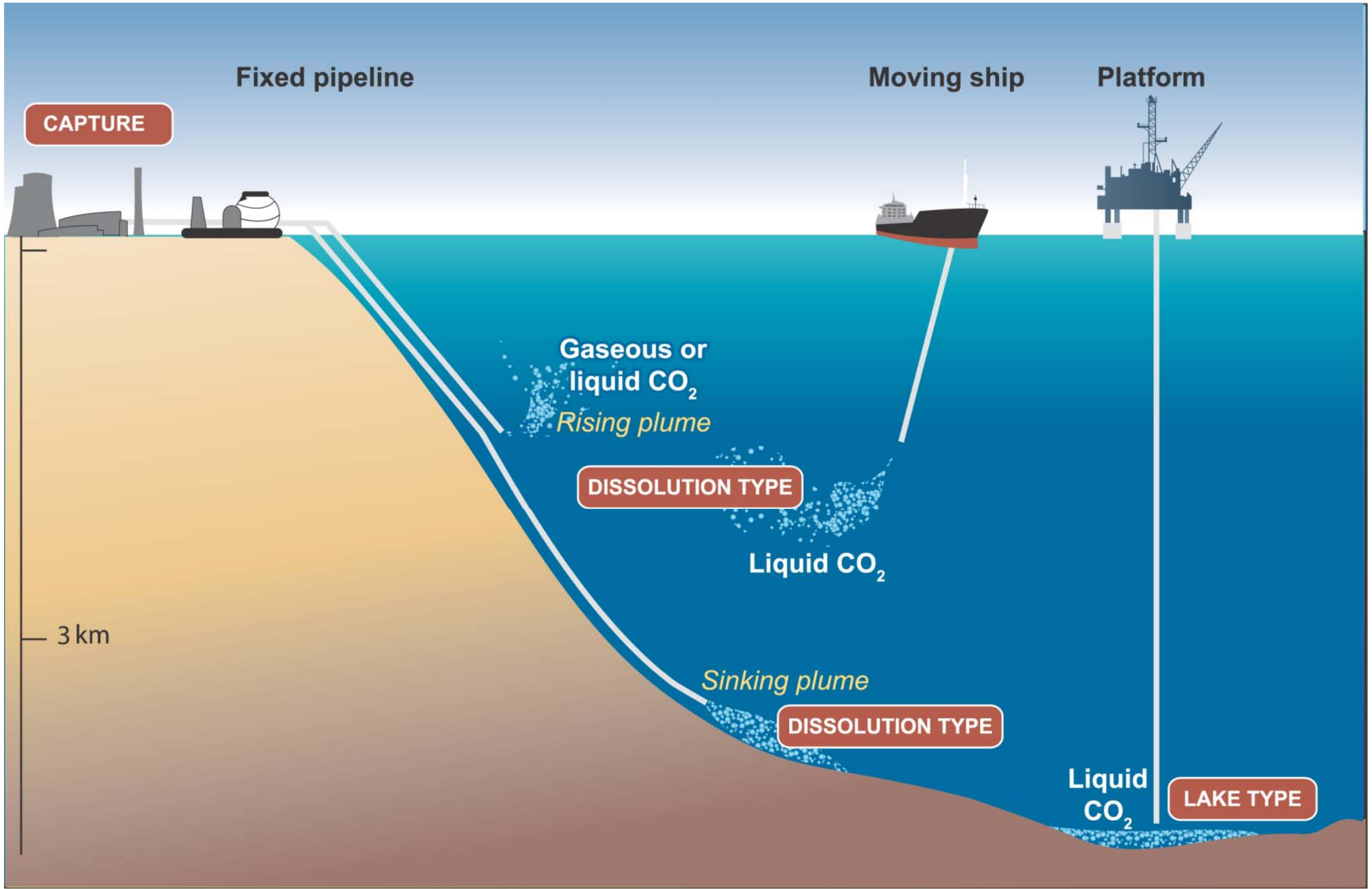
All costs refer to costs for energy from newly built, large-scale plants. Natural gas combined cycle costs are based on natural gas prices of US$2.80–4.40 per GJ (LHV based). Energy costs for PC and IGCC are based on bituminous coal costs of US$1.00–1.50 per GJ (LHV. Note that the costs are very dependent on fuel prices (which change continuously), in addition to other factors such as capital costs. Also note that for EOR, the savings are greater for higher oil prices. Current gas and oil prices are substantially higher than the figures used here. All figures in the table are from Table 8.3a in [IPCC, 2005][1].

Carbon Capture & Storage



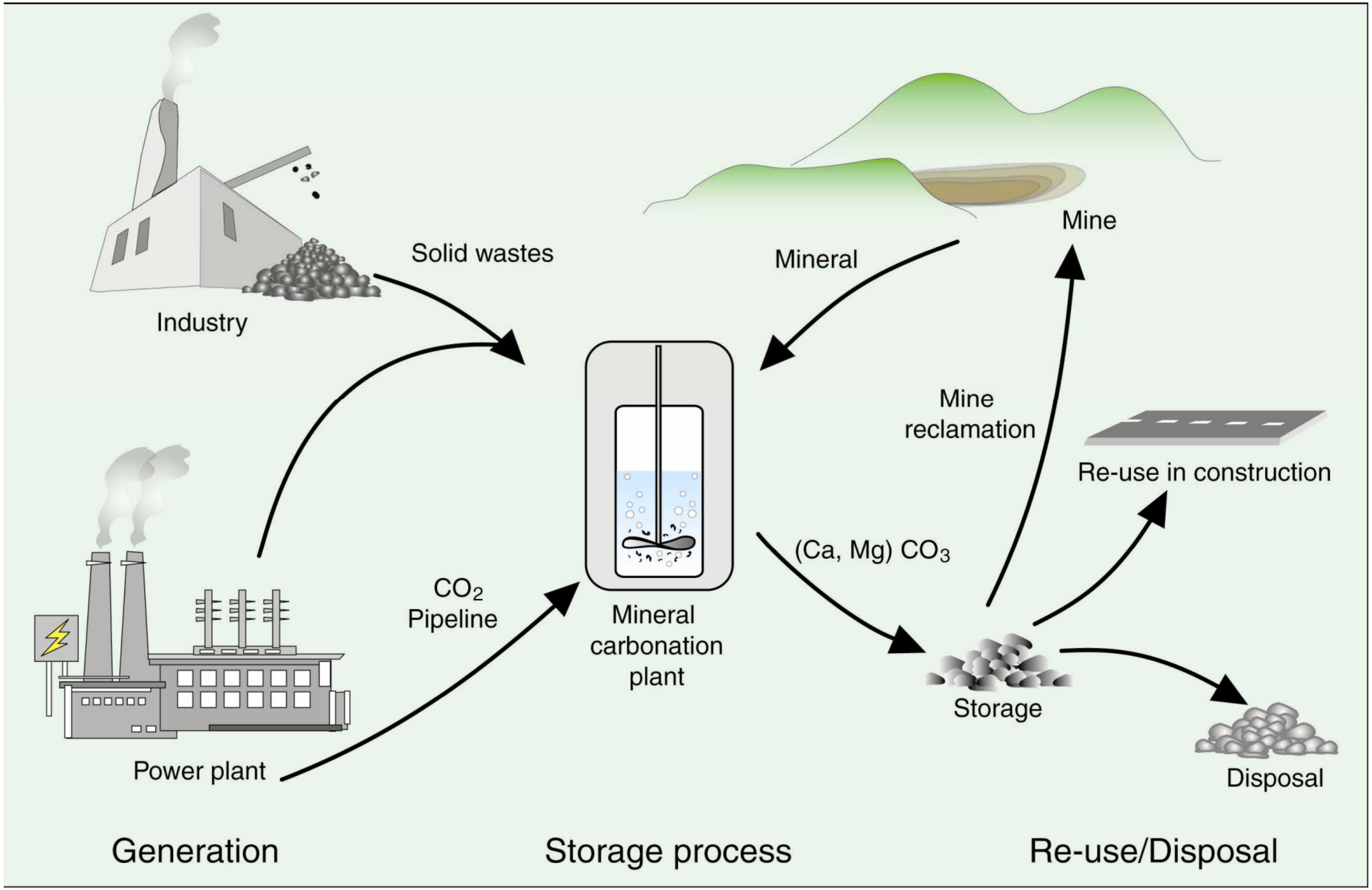
- Leakage issue

Ocean Storage

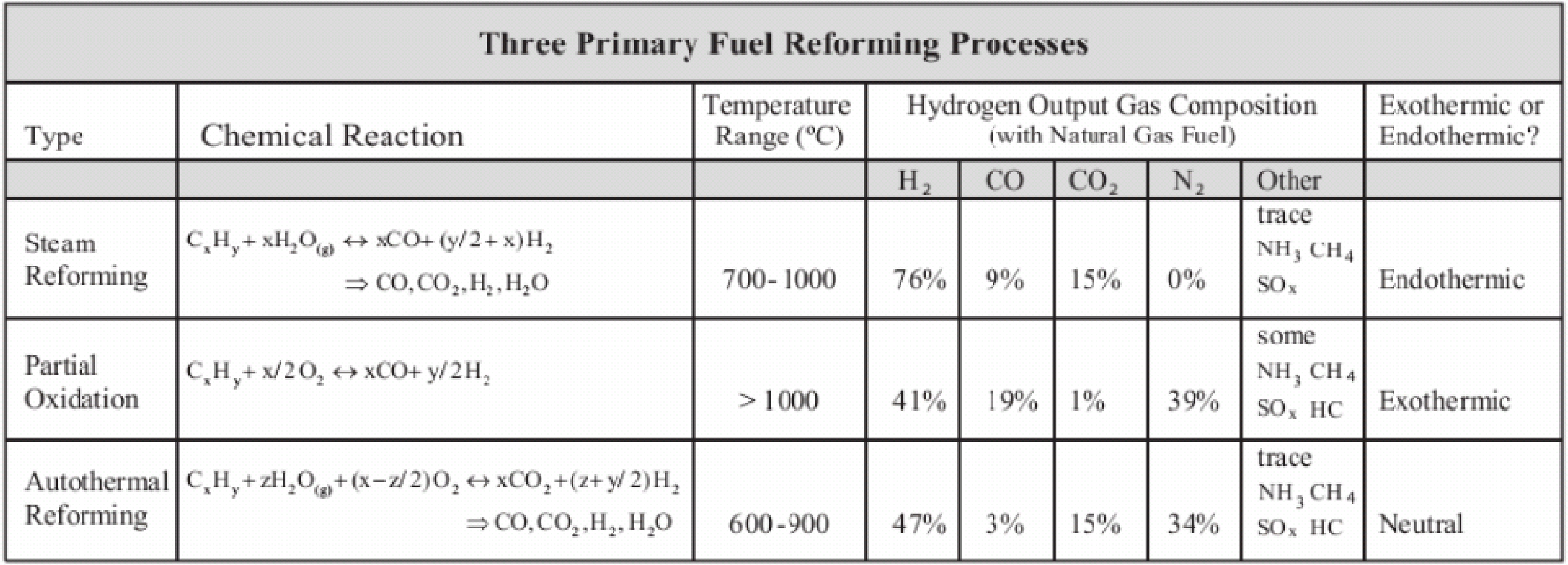


- pH change
- Mortality of ocean organisms
- Ecosystem consequences
- Chronic effects unknown

Mineral carbonation



Hydrogen from Natural Gas(Reforming)

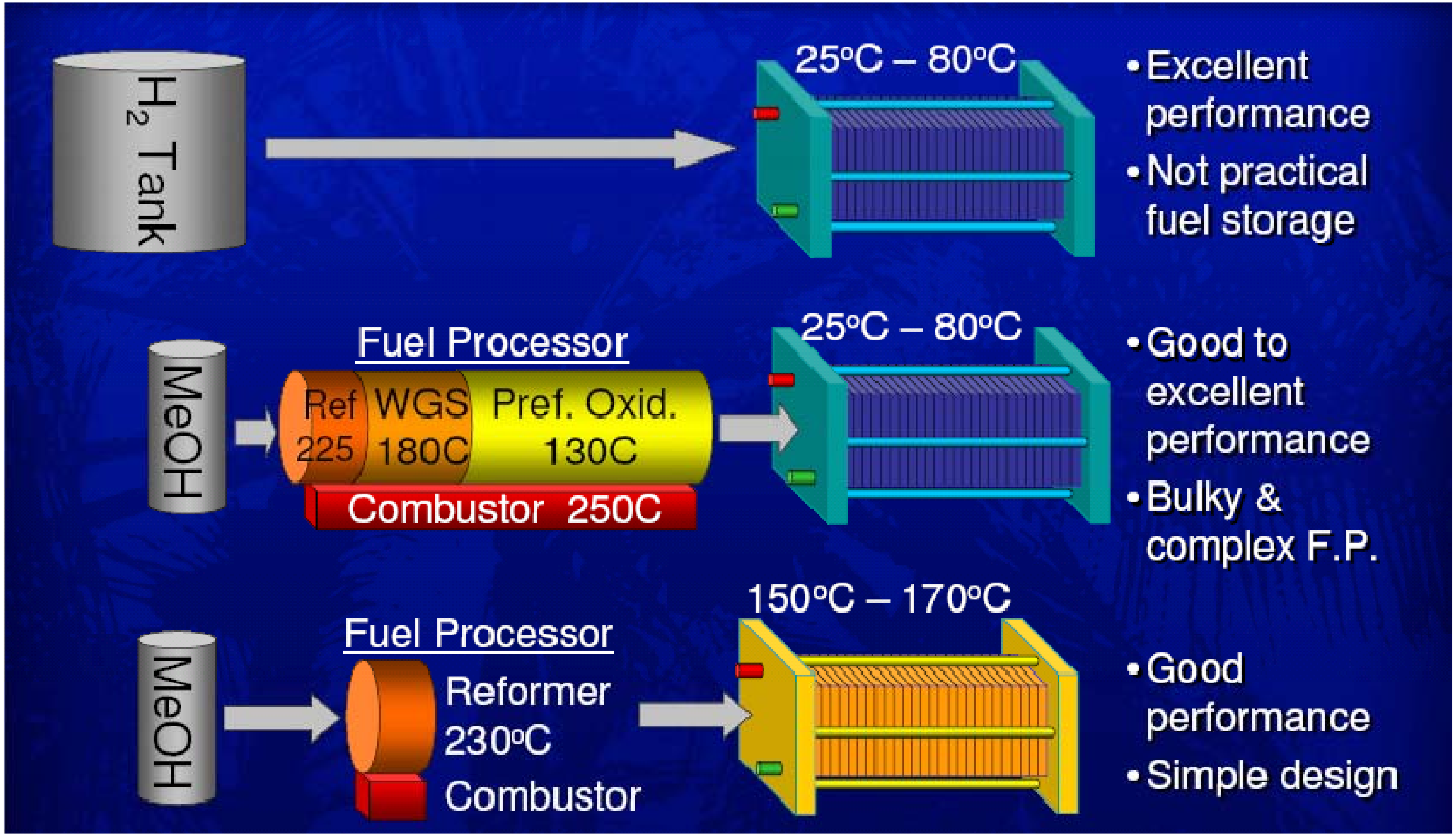


Three Primary Fuel Reforming Processes

Type	Chemical Reaction	Temperature Range (°C)	Hydrogen Output Gas Composition (with Natural Gas Fuel)					Exothermic or Endothermic?
			H_2	CO	CO_2	N_2	Other	
Steam Reforming	$C_xH_y + xH_2O_{(g)} \leftrightarrow xCO + (y/2 + x)H_2$ $\Rightarrow CO, CO_2, H_2, H_2O$	700-1000	76%	9%	15%	0%	trace NH_3 CH_4 SO_x	Endothermic
Partial Oxidation	$C_xH_y + x/2\,O_2 \leftrightarrow xCO + y/2\,H_2$	> 1000	41%	19%	1%	39%	some NH_3 CH_4 SO_x HC	Exothermic
Autothermal Reforming	$C_xH_y + zH_2O_{(g)} + (x - z/2)O_2 \leftrightarrow xCO_2 + (z + y/2)H_2$ $\Rightarrow CO, CO_2, H_2, H_2O$	600-900	47%	3%	15%	34%	trace NH_3 CH_4 SO_x HC	Neutral

- **Most common hydrogen production technology today (95% from SMR)**
- **Transition and long term solution with cost competitiveness**

Hydrogen by Reforming

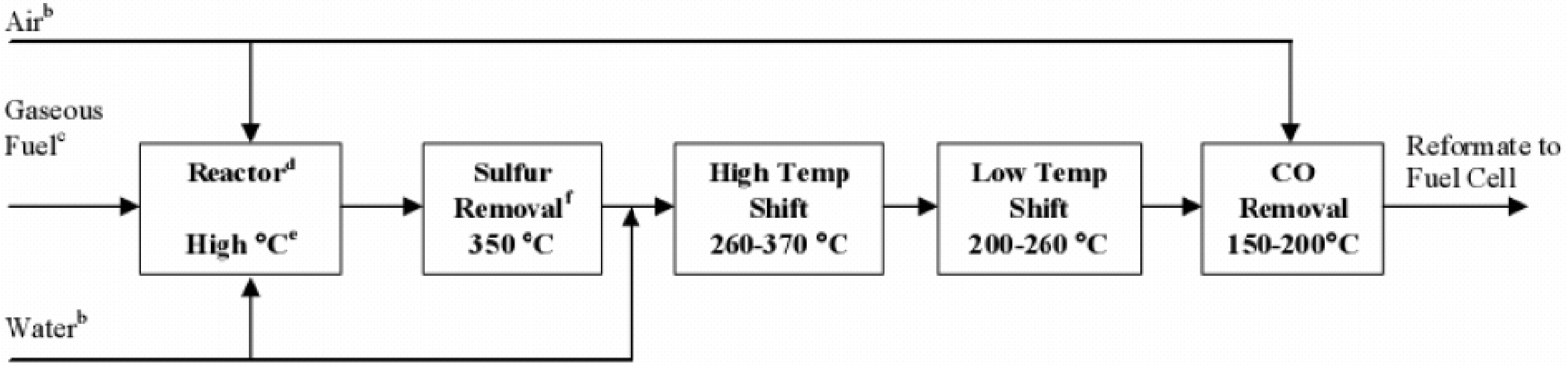


- Excellent performance
- Not practical fuel storage

- Good to excellent performance
- Bulky & complex F.P.

- Good performance
- Simple design

Steam Reforming



a) - For MCFC & SOFC, no high temperature shift, low temperature shift, or CO removal required.
- For PAFC and circulating AFC, no CO removal required after low temperature shift.
- For PEFC, all components required except that for high temperature CO removal eliminated or reduced in complexity.

b) Possible to use residual air, water, and heat of fuel effluent from fuel cell and other downstream components.

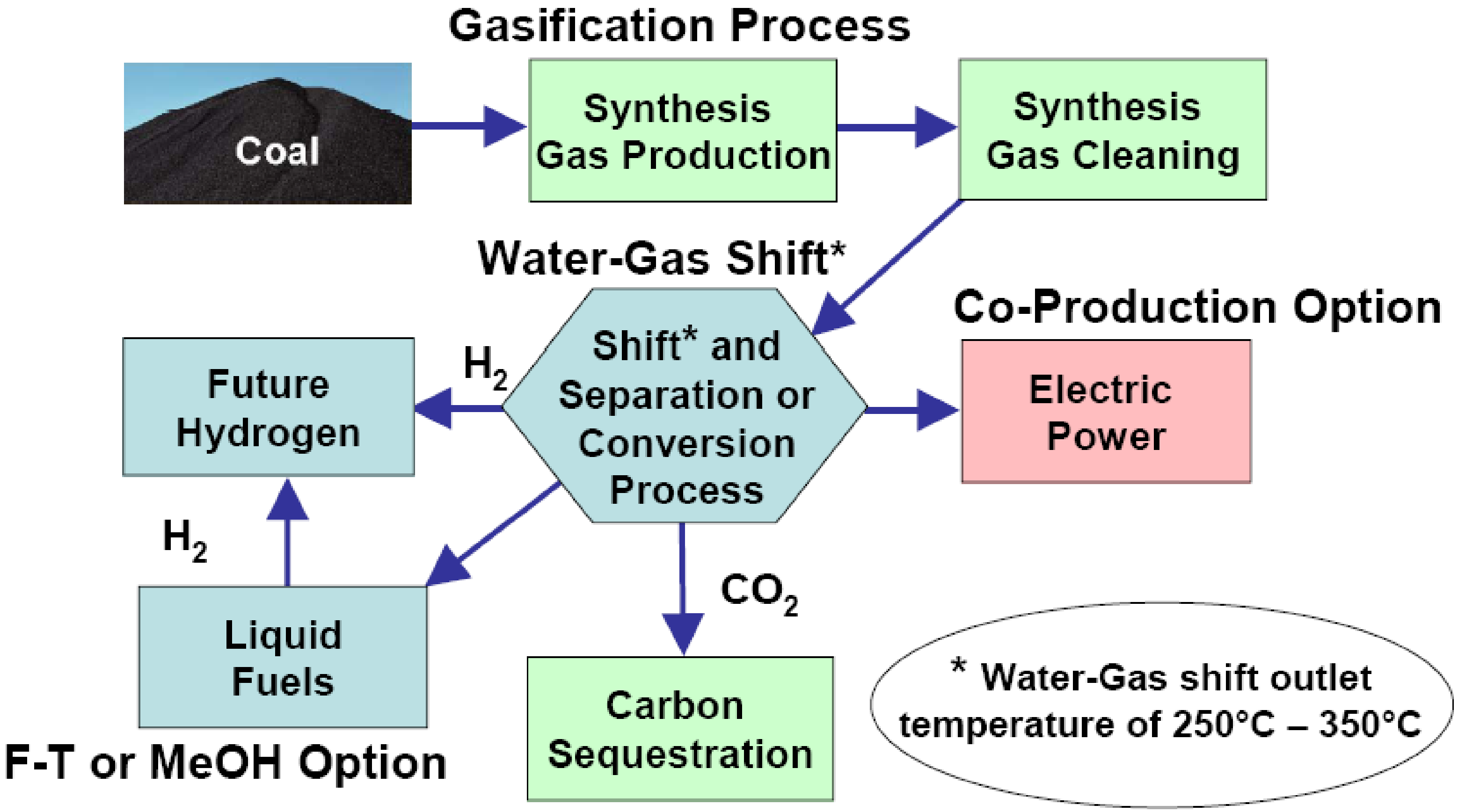
c) Vaporizer required for liquid fuels.

d) Non-catalytic POX fuel processor does not require water.

e) Temperature dependent on fuel, sulfur content of fuel, and type of reactor.

f) Can be located prior to, within, or after the reactor; liquid desulfurizer located prior to the vaporizer.

Hydrogen From Coal



Gasification Process

Coal

Synthesis Gas Production

Synthesis Gas Cleaning

Water-Gas Shift*

Shift* and Separation or Conversion Process

Co-Production Option

Electric Power

Future Hydrogen

H_2

H_2

Liquid Fuels

CO_2

Carbon Sequestration

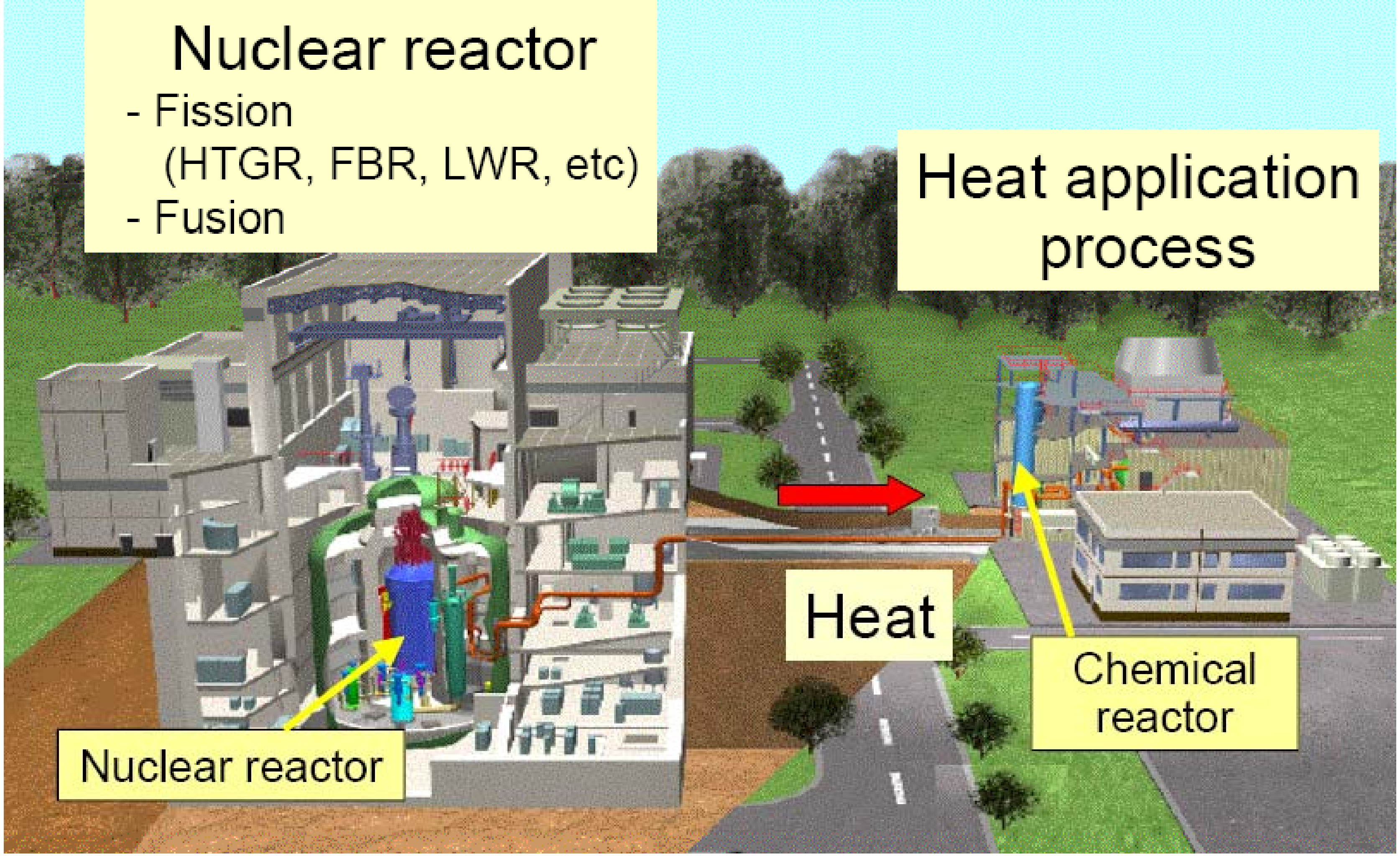
F-T or MeOH Option

* Water-Gas shift outlet temperature of 250°C – 350°C

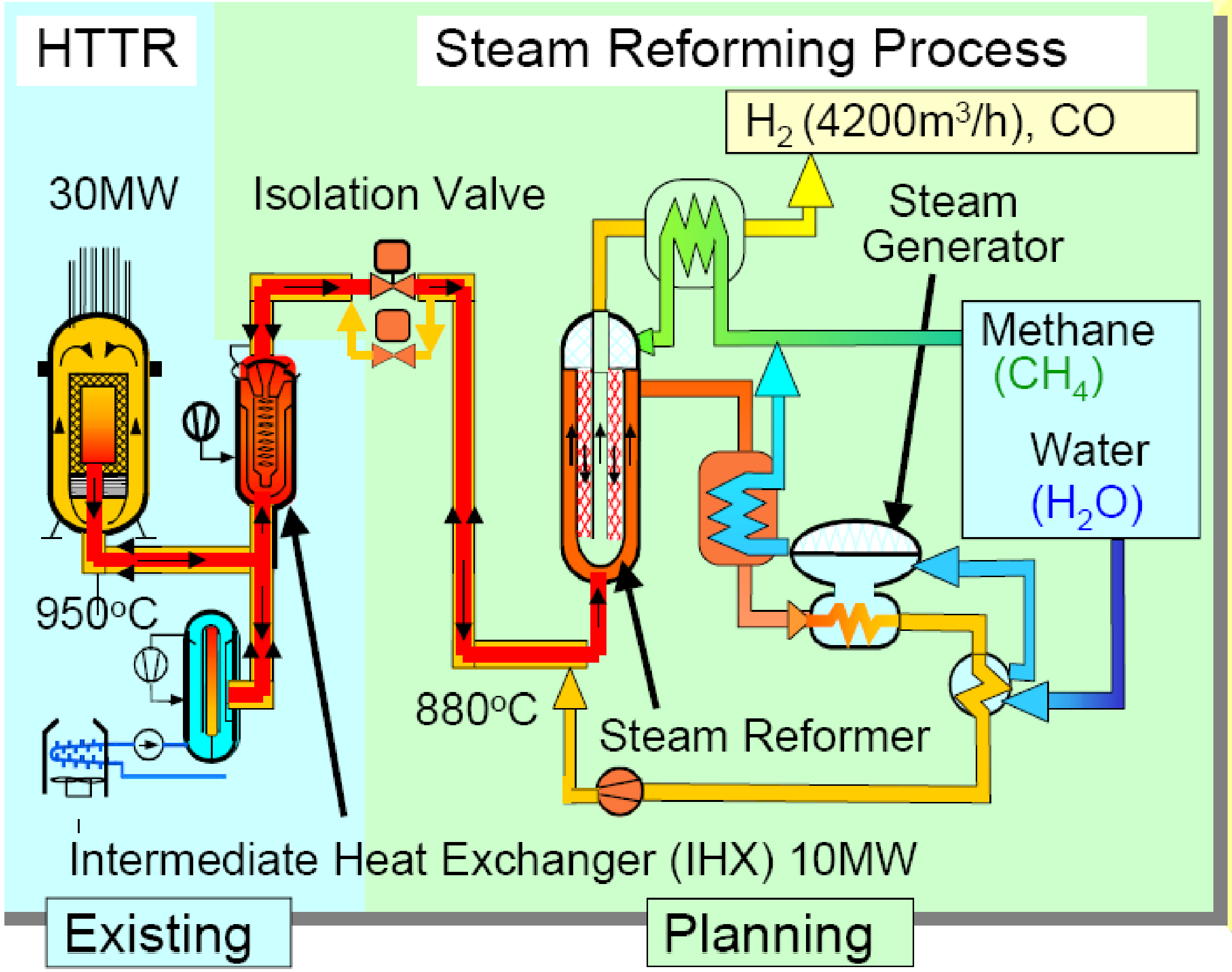
$$CH_{0.8} + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species}$$

- **Cheap but dirty (pollutant, CO2, dust etc)**
- **Long term solution by large gasification plant**
- **Needs further development such as IGCC**

Nuclear Production of Hydrogen



Nuclear Assisted SMR



1st candidate of H_2 Production Process connected with HTTR

⬇

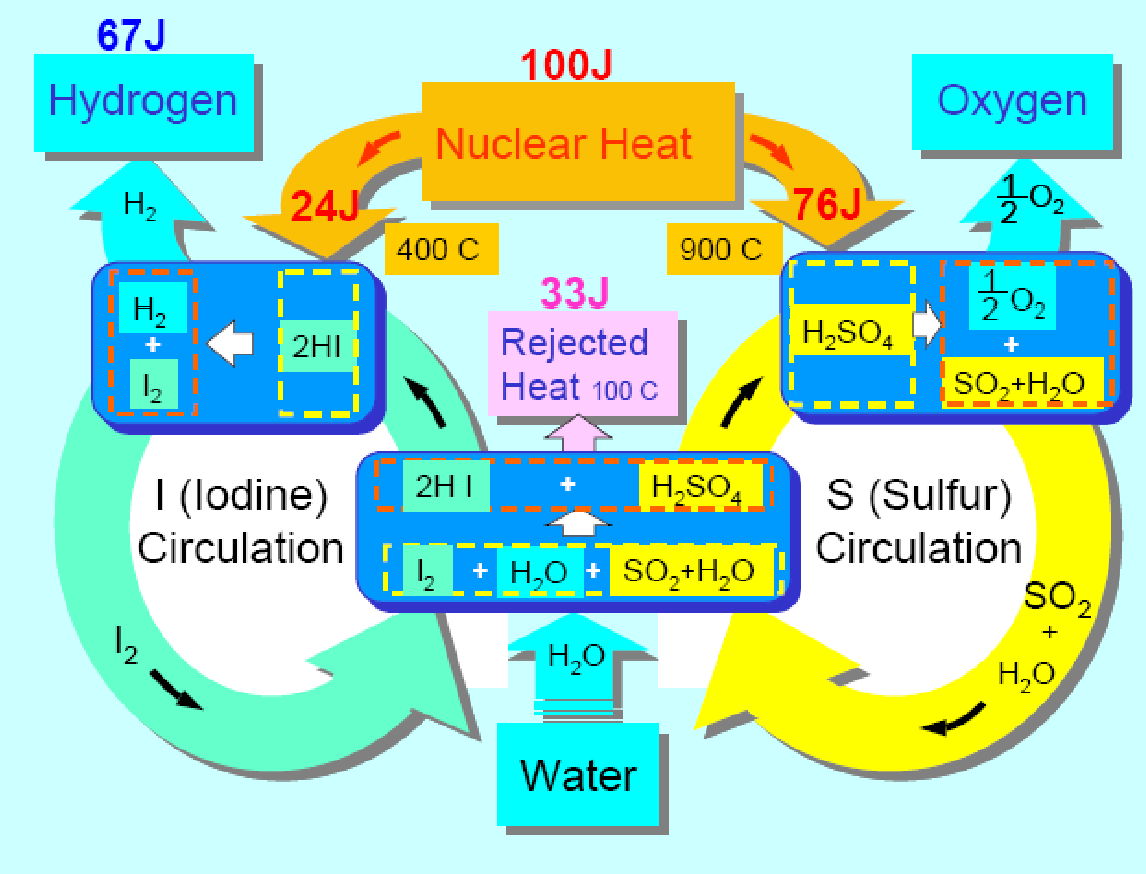
Safety Evaluation And Components Development

⬇

Establish technologies for connecting heat application process with HTGR

Thermochemical IS Process

- More than 4000°C necessary for pyrolysis of water
- Pyrolysis with water and heat of 900°C by three chemical reactions



Subjects

- ✧ Close cycle test
- ✧ High-efficiency test
- ✧ R&D on material with anti-corrosion

$$2HI \rightarrow H_2+I_2$$

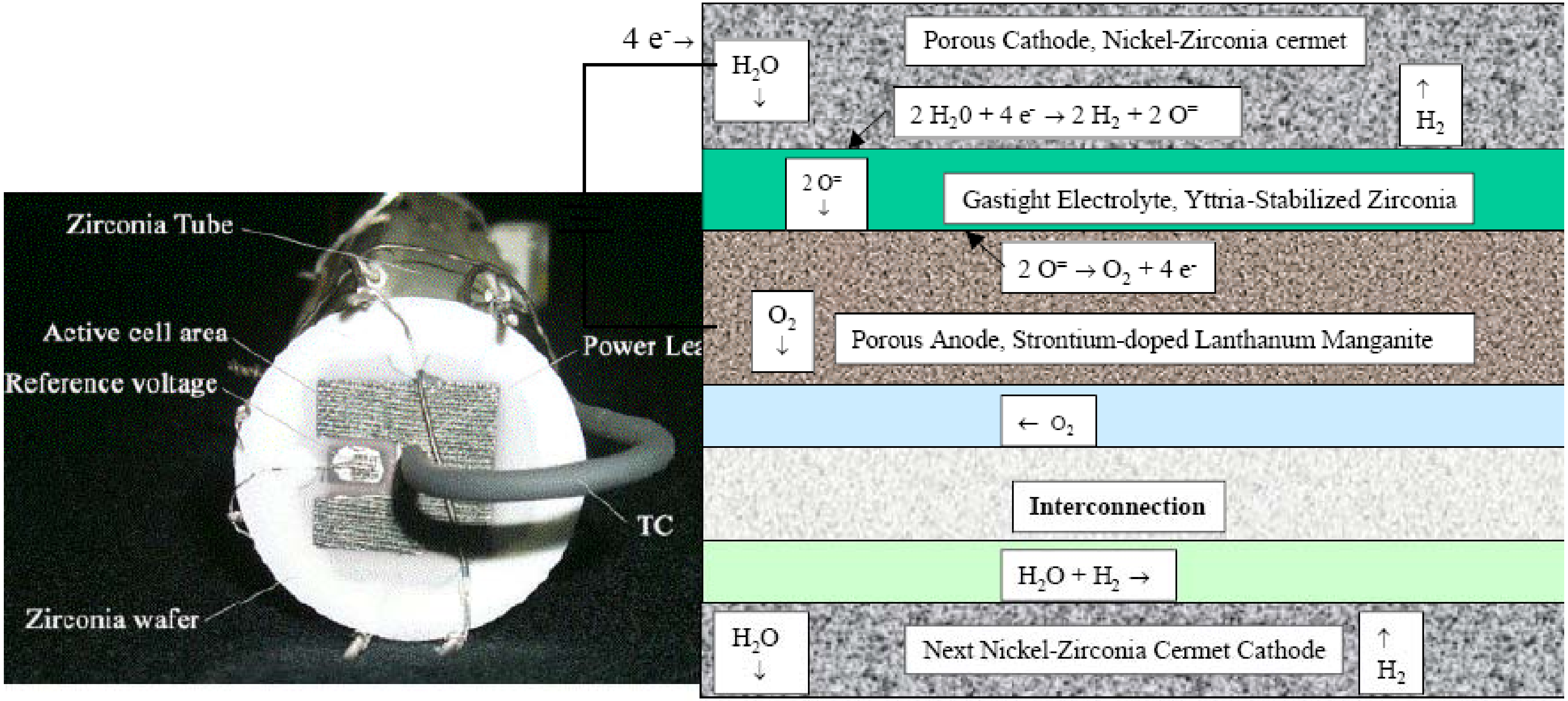
$$H_2SO_4 \rightarrow 1/2O_2 +SO_2+H_2O$$

$$I_2+SO_2+2H_2O \rightarrow 2HI+H_2SO_4$$

$$+$$

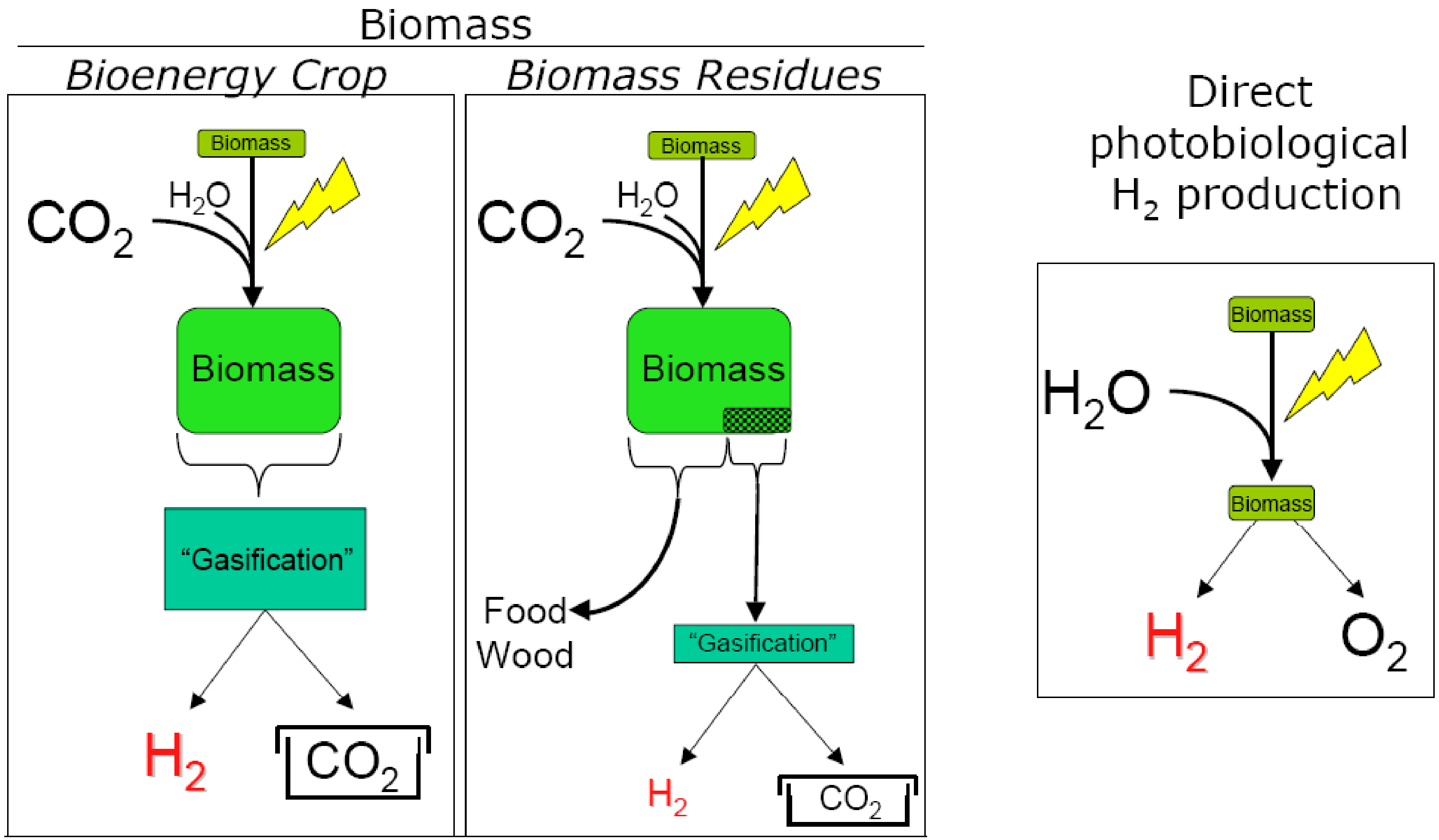
$$H_2O \rightarrow H_2+1/2O_2$$

Steam Electrolysis



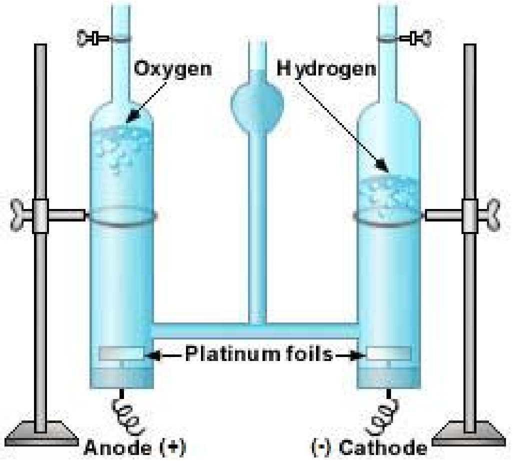
- **Reverse operation of solid oxide fuel cell with heat from nuclear power plant (~800C)**
- **Highly efficienct**
- **Stability issue of materials in high T**

Hydrogen from Biomass



- **Low efficiency**
- **Possible danger on the price of crops**
- **Stability issue of materials in high T**
- **Phtobio-production is attractive, but requires significant amount of research**

Hydrogen from Electrolysis



- **PEM or liquid electrolyte**
- **High T electrolyzer is efficient but less developed**
- **PEM electrolyzer cost ~ PEMFC cost**
- **Suitable for distributed renewable energy system**

Hydrogen from Electrolysis

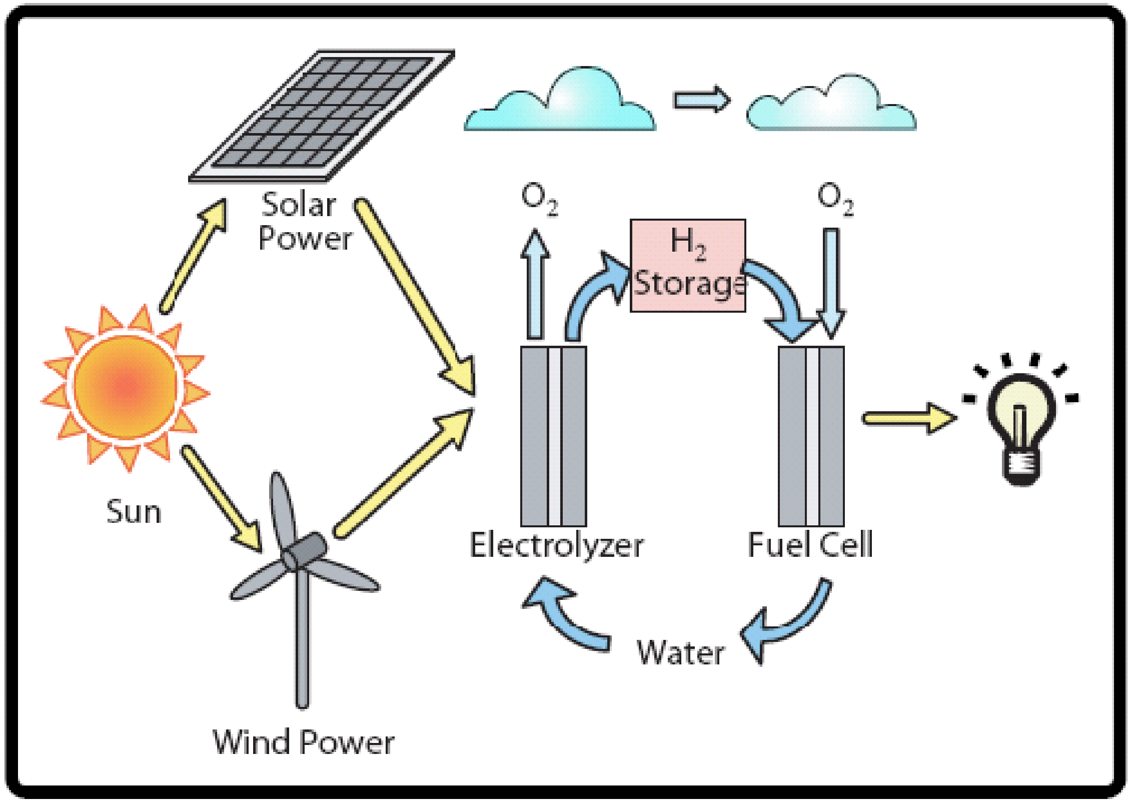
Hydrogen cost from wind energy

	Current Technology		Future Technology	
	(w/grid back up)	(no grid back up)	(w/grid back up)	(no grid back up)
Average Cost of Electricity (cents/kWh)	6	6	4	4
Wind turbine capacity Factor (%)	30	30	40	40
Hydrogen ($/kg)	6.64	10.69	3.38	2.86
Carbon emissions (kg of C/kg of H_2)	3.35	0	2.48	0

- **Most competitive**
- **Transition and long term solution**
- **Cost and system integration issue**

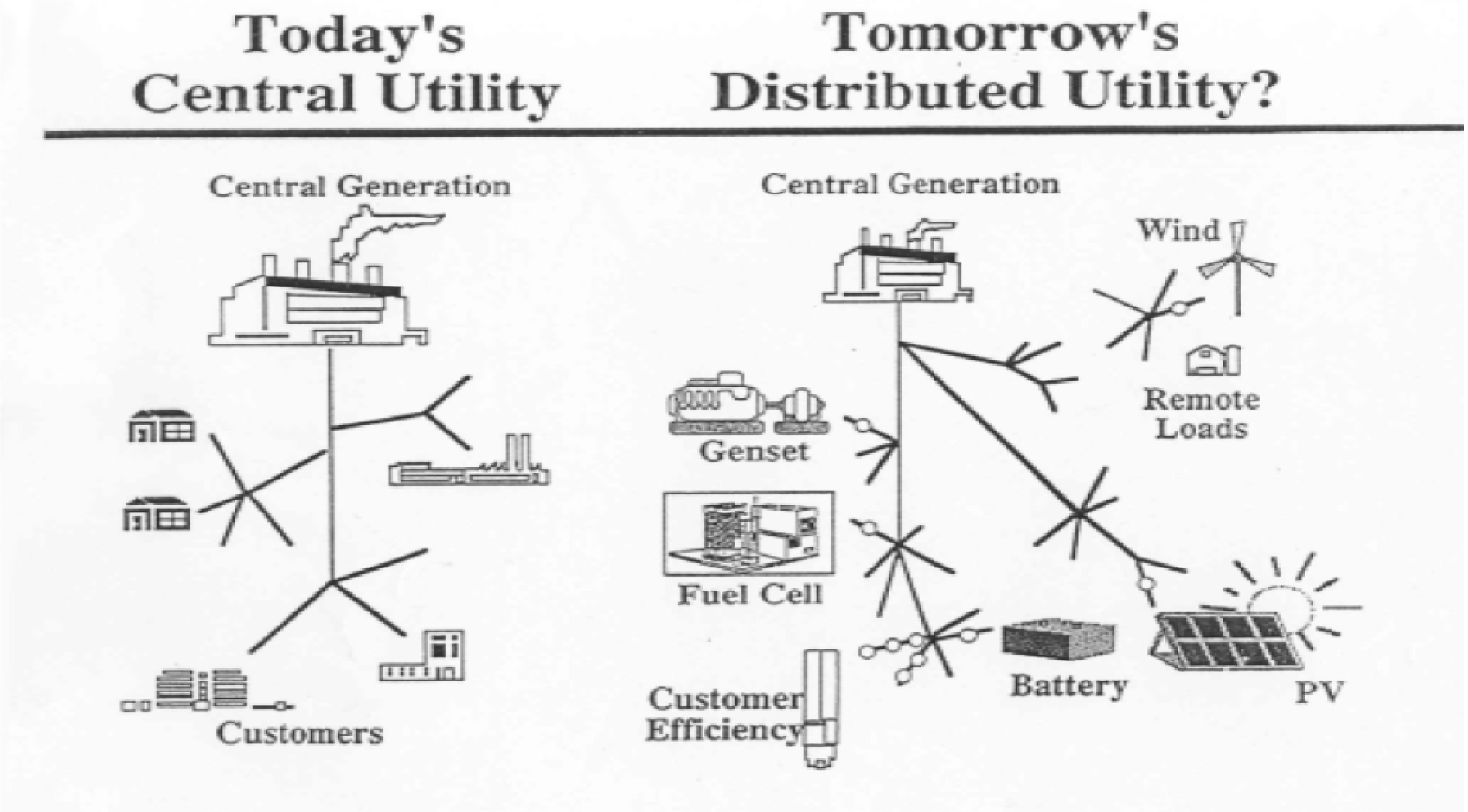
Hydrogen from Electrolysis

Hydrogen from solar energy



- **Potential long term solution**
- **Too expensive (~$28/kg H2)**
- **Needs more investigation**

Distributed Power in Future?



Hydrogen Production Cost

방법	원료 (가격)	가격($/GJ)
대규모 증기개질	메탄가스 ($5-6/GJ)	8-10
현지 증기개질 (수소생산+소비지)	메탄가스 ($5/GJ)	20-40
석탄가스화	석탄 ($1.70/GJ)	10-15
전기분해	전기 ($30-110/MWh)	11-42

*Korea Energy Economy Institute

Hydrogen Production Cost by Source

원료	원료	가격($/GJ)
천연가스 + 탄소처리 및 저장	천연가스	8-10
석탄가스화 + 탄소처리 및 저장	석탄	10-13
육상 풍력단지	물	15-25
해상 풍력단지	물	20-30
태양광발전	물	25-50
원자력발전	물	15-20
HTGR 열병합발전	물	10-25

- Huge Fresh Water Demand

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Hydrogen Production Cost by Method

수소제조방법	원 료	규모(10^6Nm^3/d)	가격($/GJ)
메탄가스 증기개질법	메탄가스	25.4	5.97
석탄가스화	석탄	6.78	9.87
탄화수소가스화(부분산화법)	코크스 배가스	2.14	6.94
바이오매스 가스화	바이오매스		9.69
바이오매스 열분해	바이오매스		8.86
전기분해(대규모, 일반)	물	2.8	20.60
전기분해 (PV)	물	0.209(2010)	24.80
전기분해(풍력)	물	0.279(2020)	11.00
전기분해(태양열, 접시형)	물	0.15(2020)	60.48
전기분해(태양열, 타워형)	물	0.829(2020)	34.14
전기분해(태양열, 고온열분해)	물		48.94

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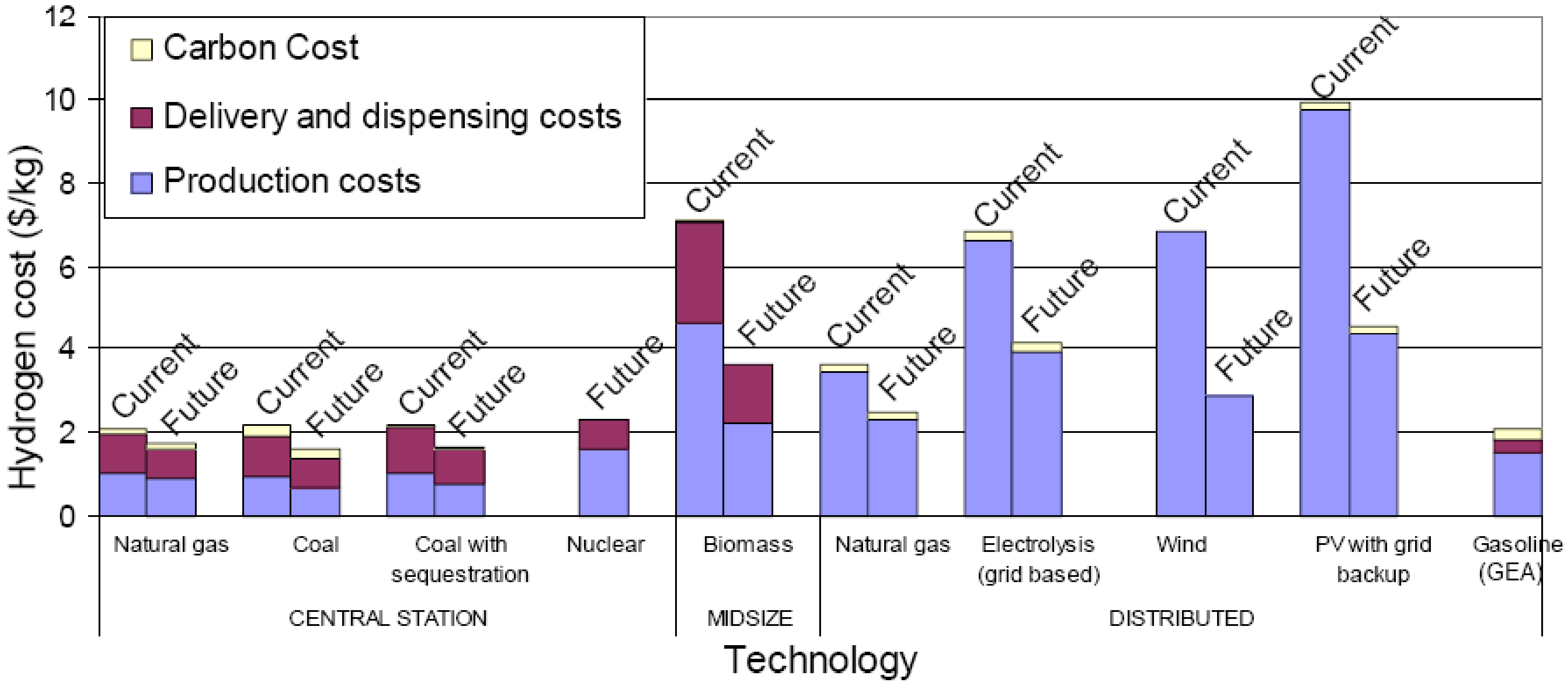
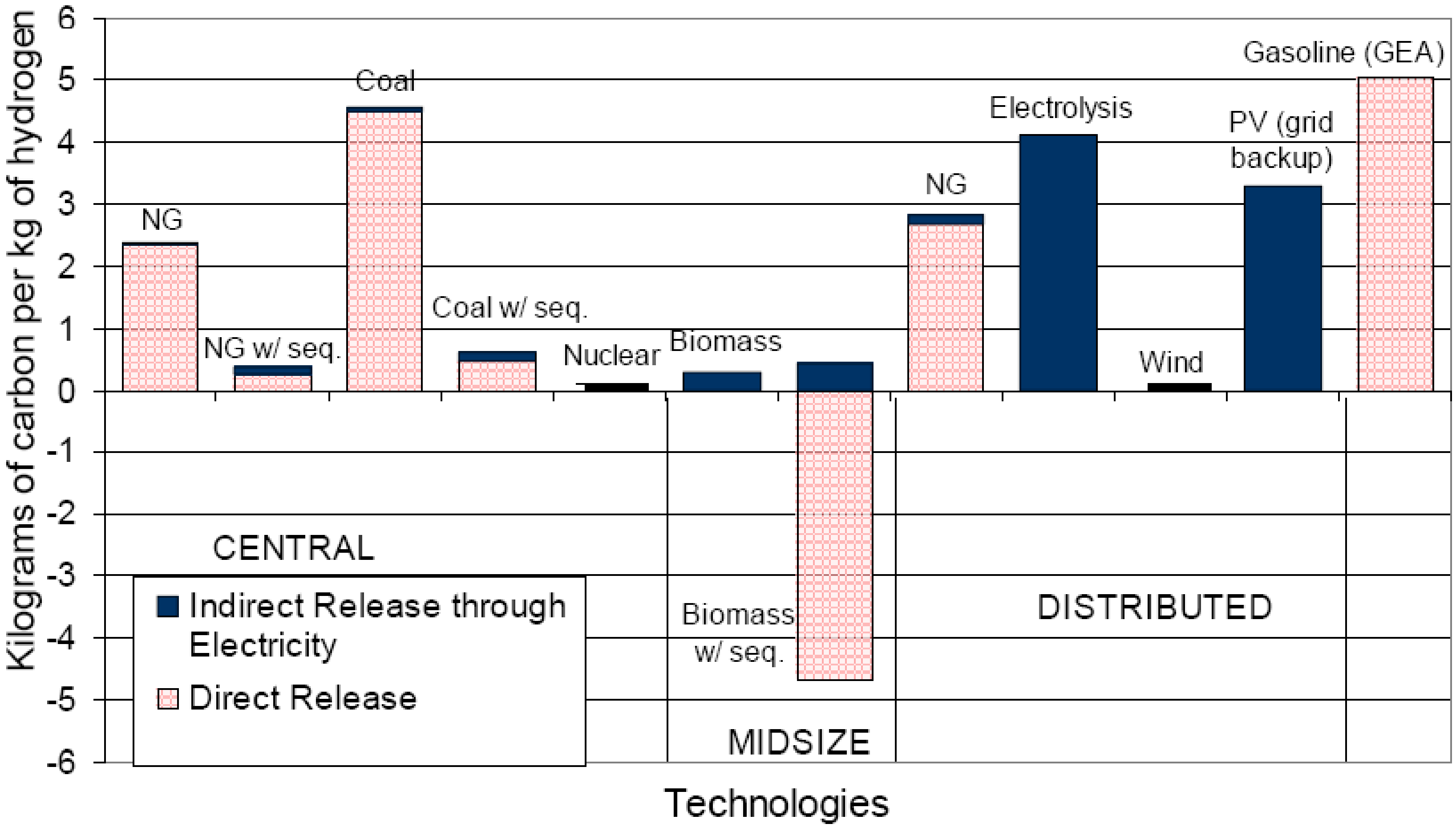
Consumer Hydrogen Price



- *GEA = Gasoline Efficiency Adjusted – scaled to hybrid vehicle efficiency*

Estimation of CO2 Production



Issues on Hydrogen Economy

- **Hydrogen is energy carrier not source**
  - Must consider costs for hydrogen production, processing, delivery, storage, and consumption
  - Demands enormous R&D cost
  - Consume too much energy to produce hydrogen compared to oil production

- **Hydrogen economy vs Hybrid economy**
  - Hydrogen may not be the BEST energy carrier (e.g. methanol economy by G. A. Olah)
  - On-site hydrogen production from renewable energy