

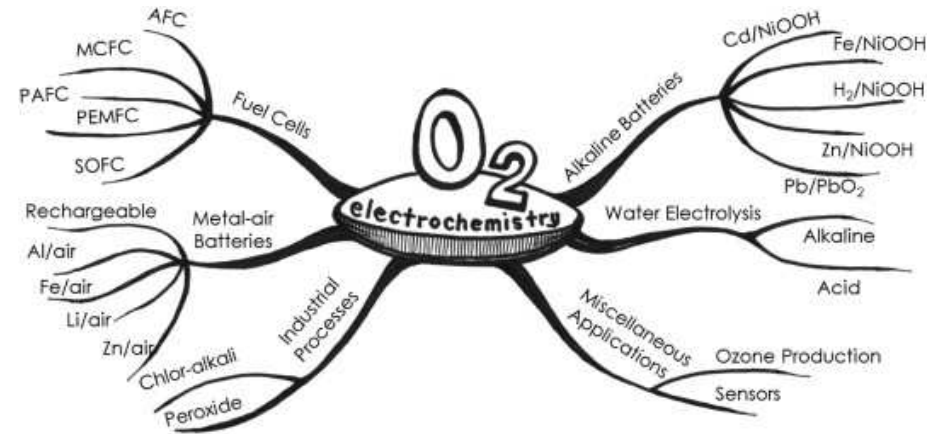
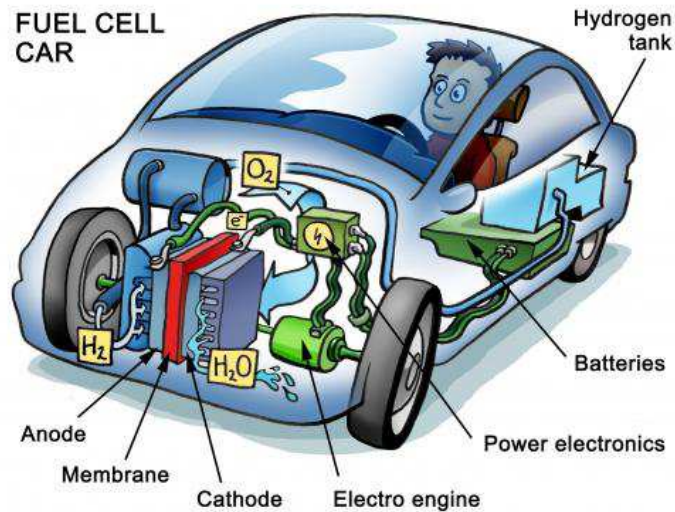


Semester 2. 2013.  
SS CHEM.CH4008/SS PCAM.CH4061.

# Electroactive Chemically Modified Electrodes : Fundamentals, Characterization and Applications.

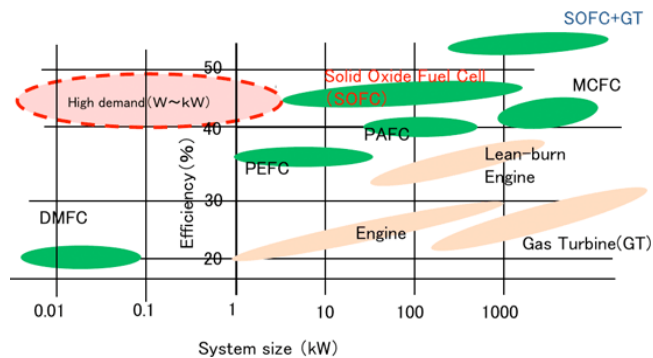


Professor Mike Lyons  
School of Chemistry TCD.  
Room 3.2 Chemistry Building.  
Email: [melyons@tcd.ie](mailto:melyons@tcd.ie)



# Lecture 1

## Sustainable Electrochemical Energy Conversion: Challenges and opportunities.



# Energy: 'the moon shot (Apollo 11, 1969) of our generation'

- "Energy is the single most important challenge facing humanity today." Nobel Laureate Rick Smalley, April 2004, Testimony to U.S. Senate.
- "...energy is the single most important scientific and technological challenge facing humanity in the 21st century..": Chemical and Engineering News, August 22, 2005.
- "What should be the centerpiece of a policy of American renewal is blindingly obvious: making a quest for energy independence the moon shot of our generation", Thomas L. Friedman, New York Times, Sept. 23, 2005.







Wave



Solar



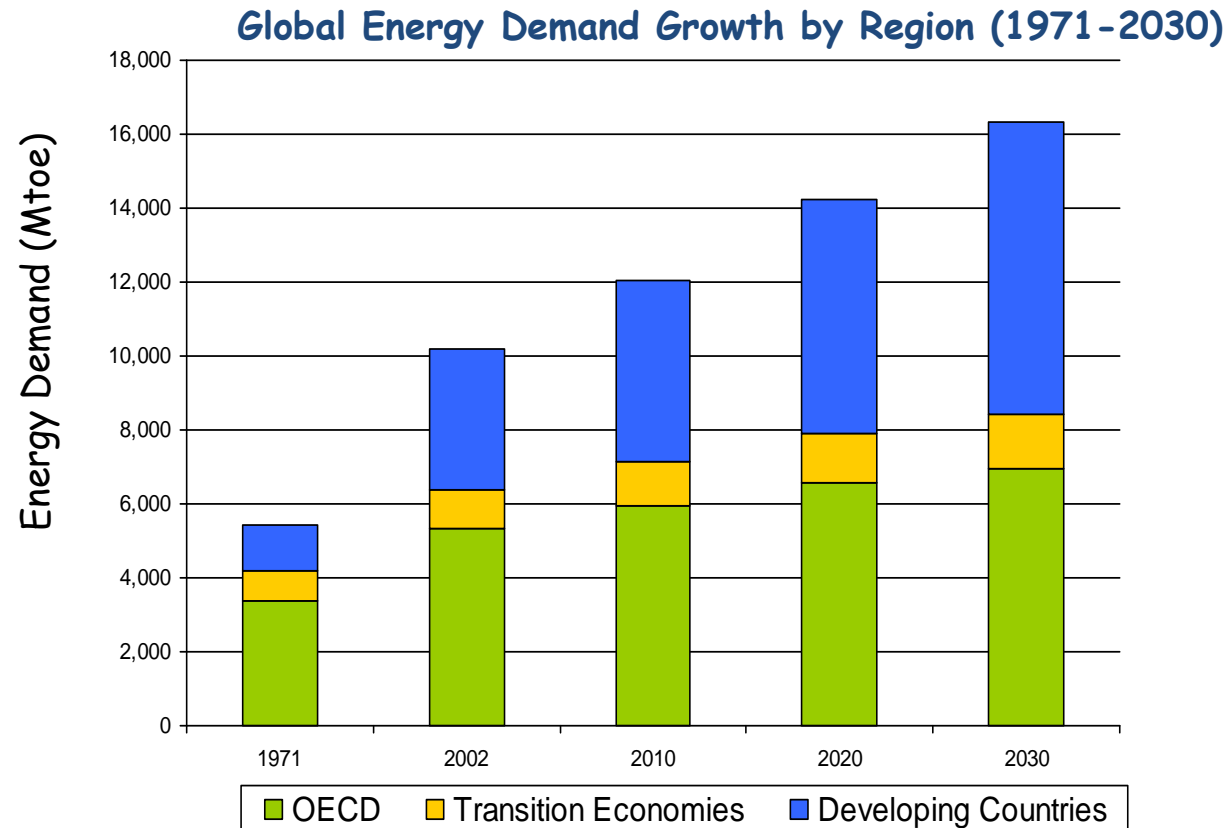
Wind



Electrochemical Fuel Cell

# energy demand - growth projections

Global energy demand is set to grow by over 60% over the next 30 years -  
74% of the growth is anticipated to be from non-OECD countries



- Notes:
1. OECD refers to North America, W. Europe, Japan, Korea, Australia and NZ
  2. Transition Economies refers to FSU and Eastern European nations
  3. Developing Countries is all other nations including China, India etc.

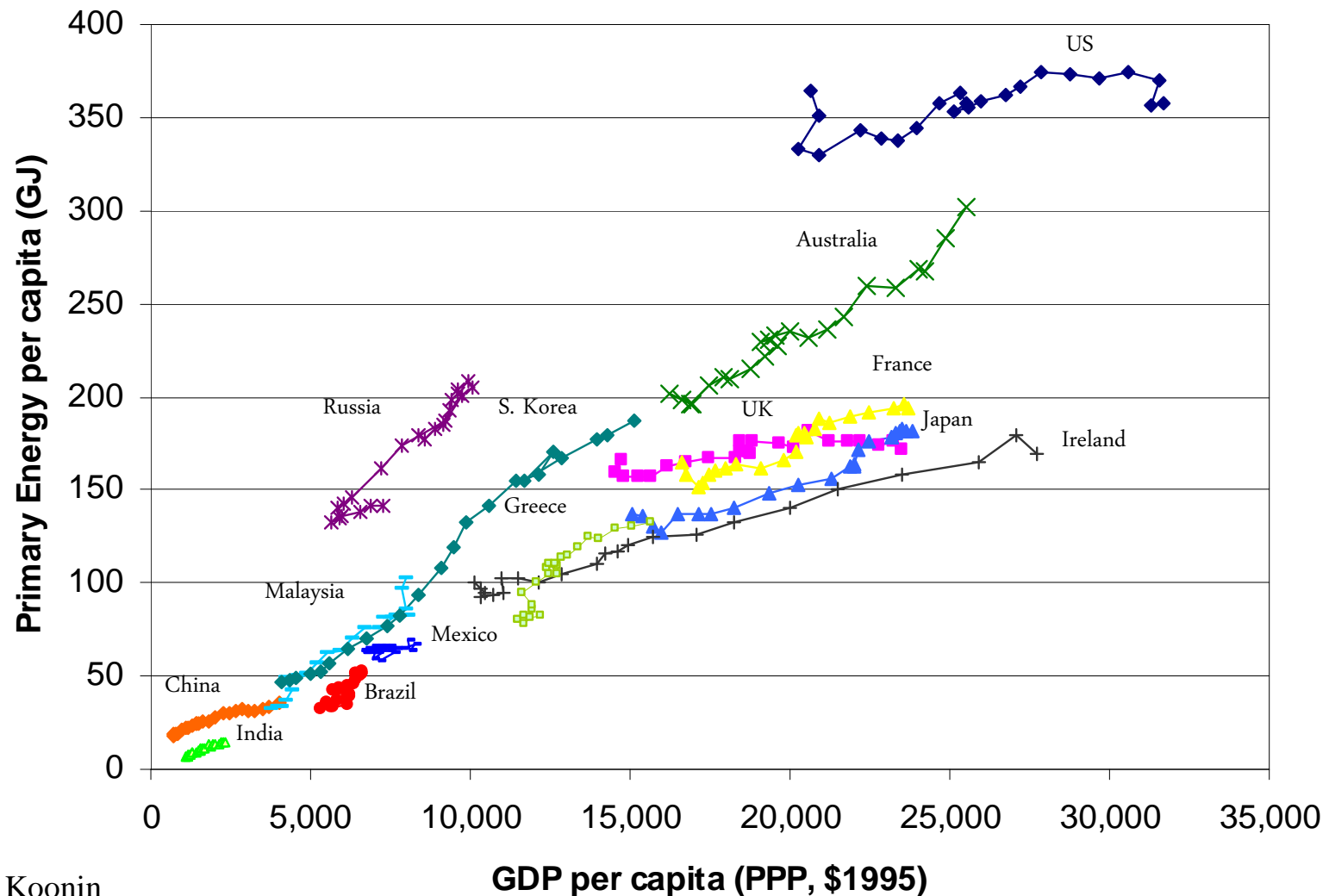
Source: IEA World  
Energy Outlook 2004

# growing dislocation of supply & demand

- N. America, Europe and Asia Pacific are the three largest demand centres
- But, have a small share of the remaining oil and gas reserves; coal is the exception
- Their collective shares are:
- Oil - 80% of demand; 15% of conventional reserves (28% incl. unconventional reserves)
- Gas - 61% of demand; 32% of reserves
- Coal - 89% of demand; 69% of reserves

# Energy use grows with economic development

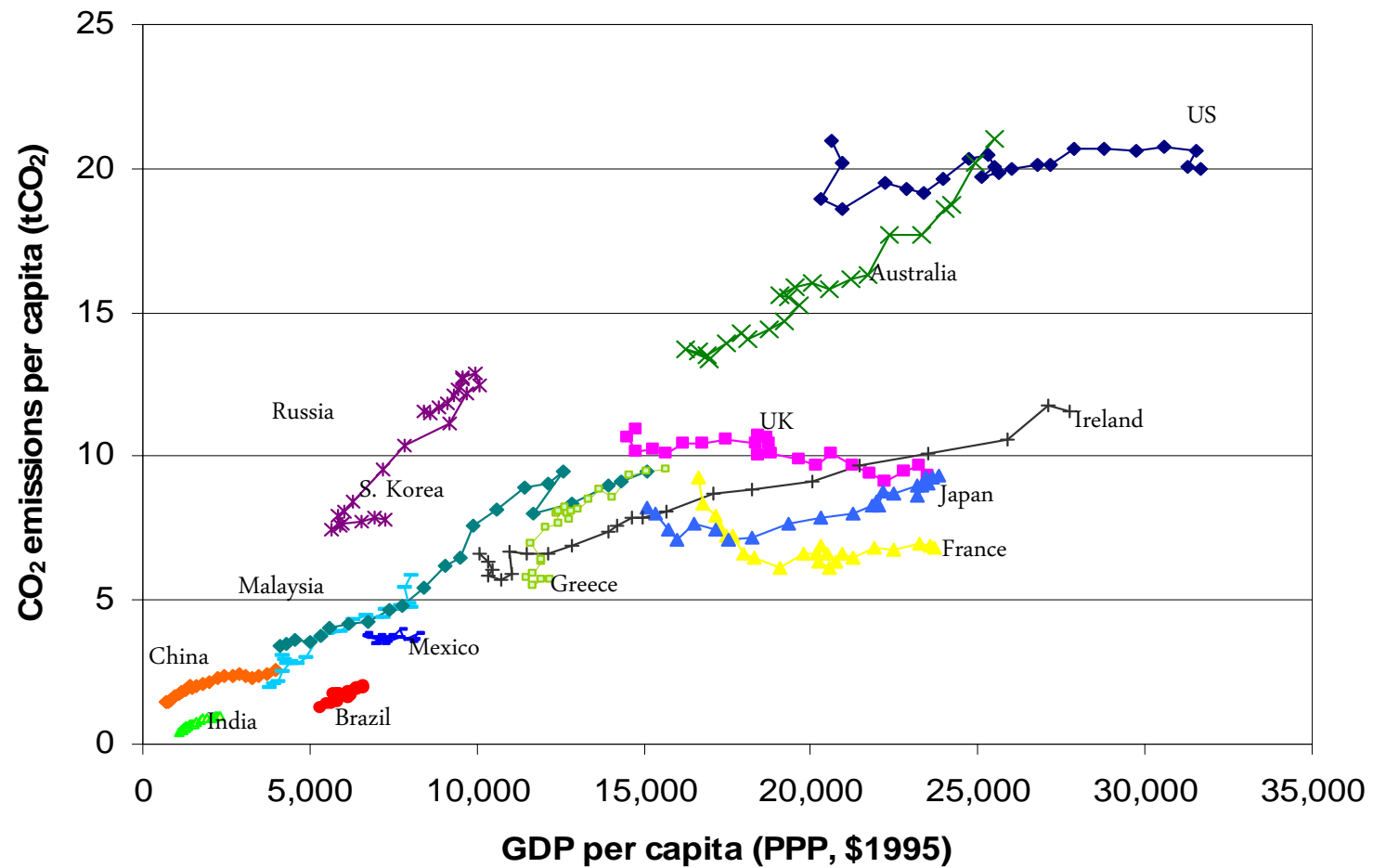
energy demand and GDP per capita (1980-2002)



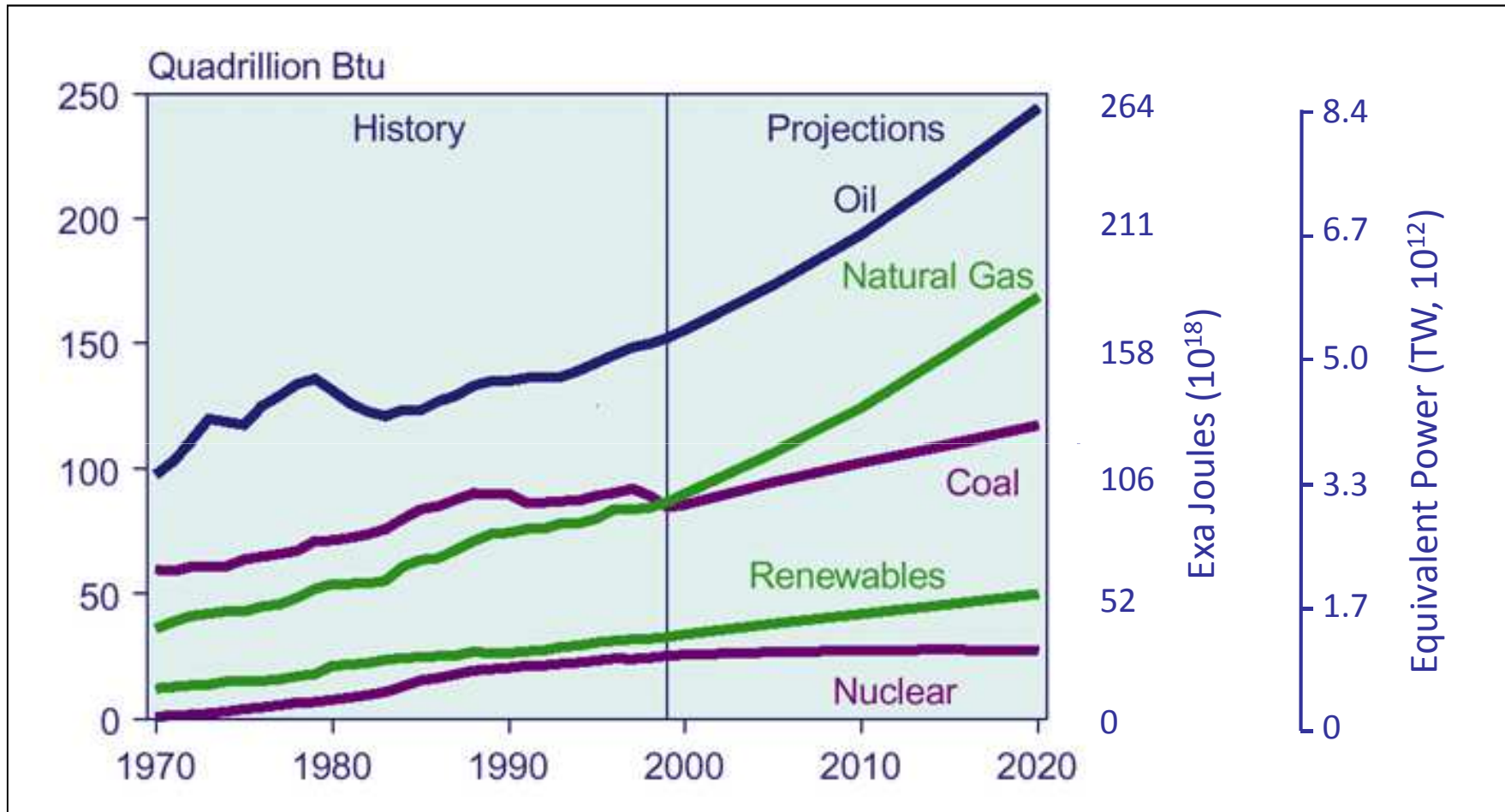
Steven Koonin

Source: UN and DOE EIA

# CO<sub>2</sub> emissions and GDP per capita (1980-2002)







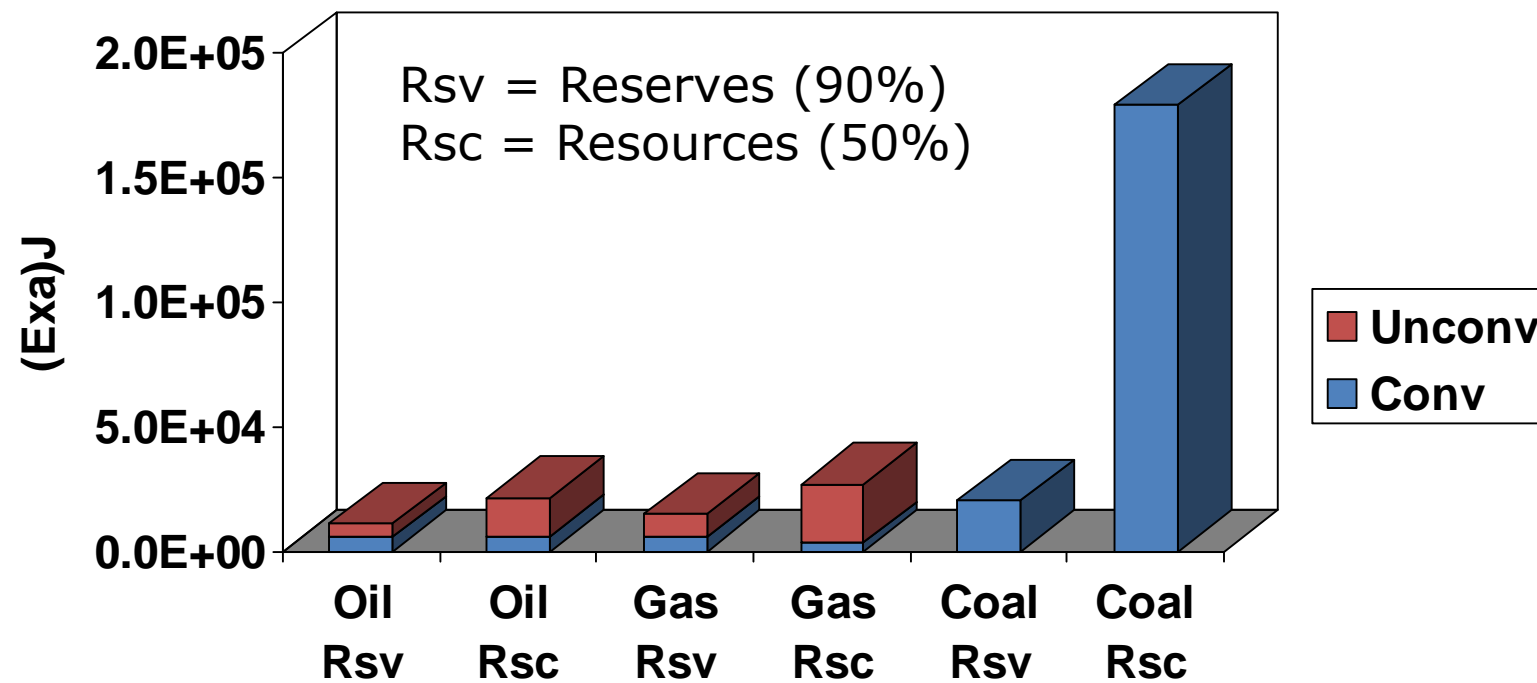
1999 totals:

400 Q-Btu, 422 EJ, 13TW

2020 projections:

630 Q-Btu, 665 EJ, 21TW

} 90% fossil

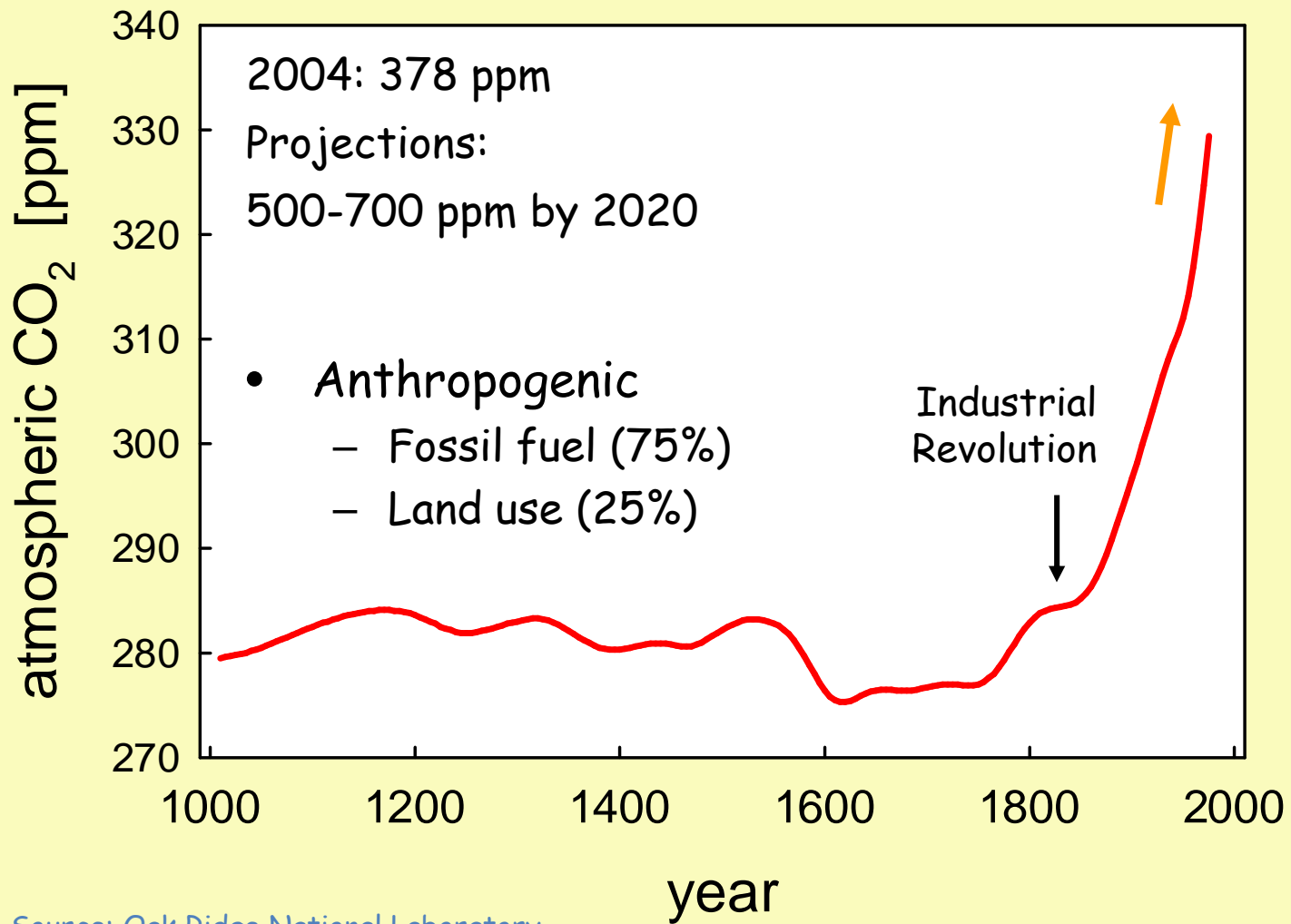


Source	Reserves, yrs	Resources, yrs	Total, yrs
Oil	13 - 20	10 - 35	23 - 55
Gas	11 - 25	7 - 40	18 - 65
Coal	32	270	300
	56-77	287-345	

} > 400 yrs

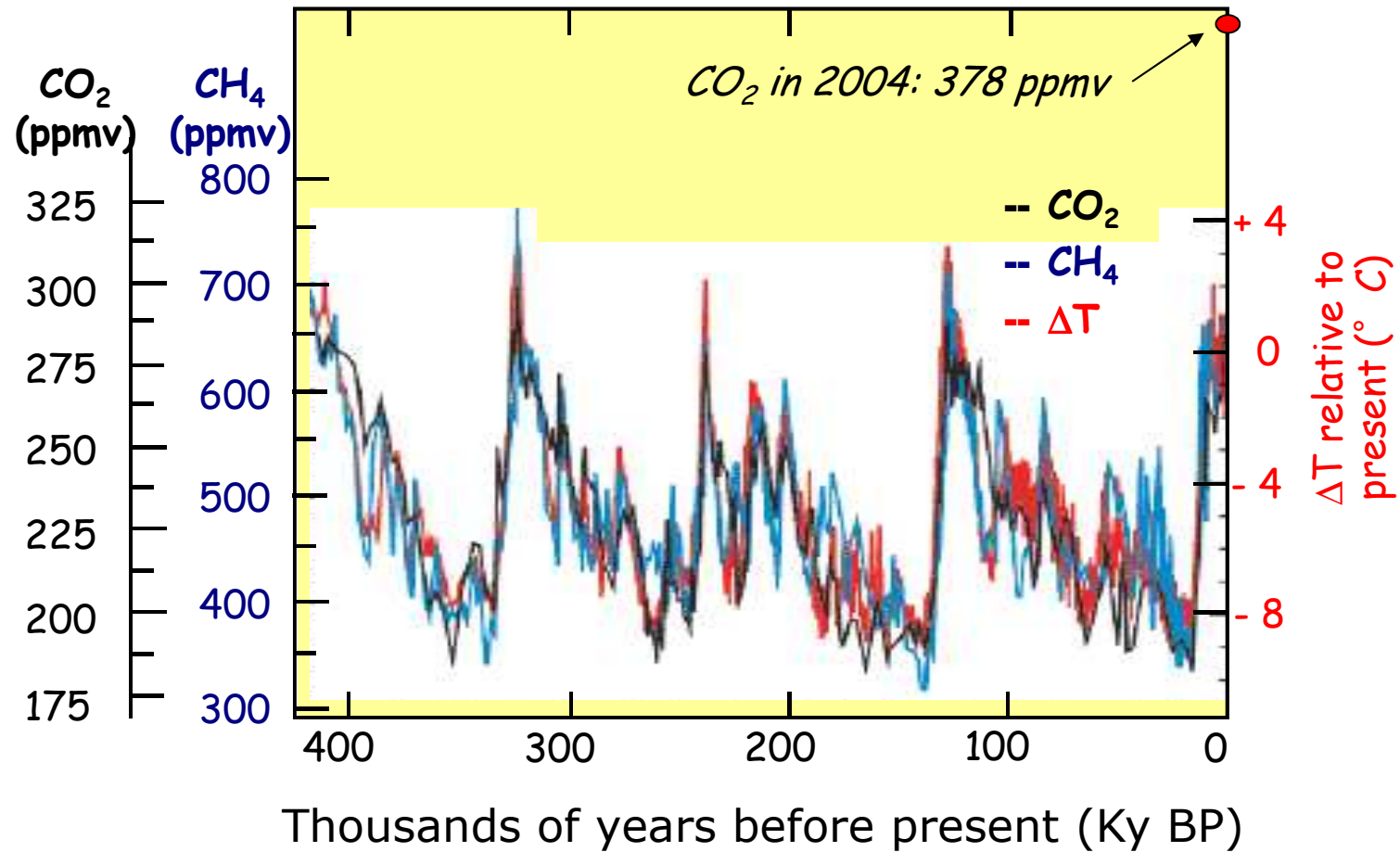
# Environmental Outlook

## Global CO<sub>2</sub> levels



Source: Oak Ridge National Laboratory

# Environmental Outlook



Intergovernmental Panel on Climate Change, 2001; <http://www.ipcc.ch>  
N. Oreskes, *Science* **306**, 1686, 2004; D. A. Stainforth et al, *Nature* **433**, 403, 2005

# Energy Outlook

## Supply

- Fossil energy sufficient for world demand into the foreseeable future
- High geopolitical risk
- Rising costs

## Environmental Impact

- Target
  - Stabilize  $CO_2$  at 550 ppm
  - By 2050
- Requires
  - 20 TW carbon-free power
  - One 1-GW power plant **daily** from now until then

## Urgency

- Transport of  $CO_2$  or heat into deep oceans:
  - *400-1000 years;  $CO_2$  build-up is cumulative*
- Must make dramatic changes within next few years

# The Energy Solution

## Solar

$1.2 \times 10^5$  TW at Earth surface  
600 TW practical

The need:  
~ 20 TW by 2050

## Wind

2-4 TW extractable

## Tide/Ocean Currents

2 TW gross

## Geothermal

12 TW gross over land  
small fraction recoverable

## Nuclear

Waste disposal

## Fossil with sequestration

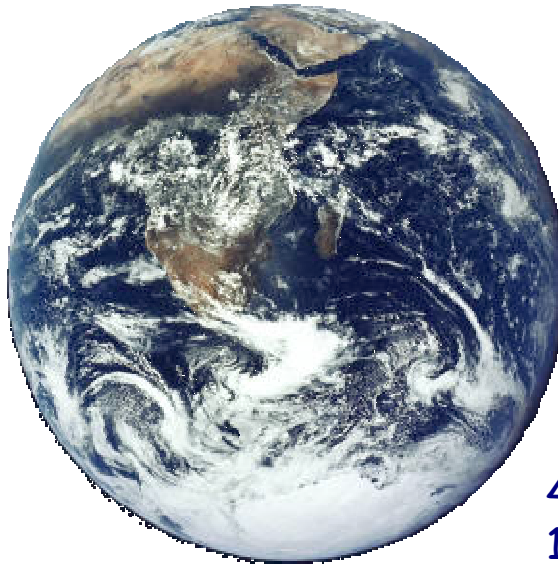
1% / yr leakage -> lost in 100 yrs

## Biomass

5-7 TW gross  
all cultivatable  
land not used  
for food

## Hydroelectric

4.6 TW gross  
1.6 TW technically feasible  
0.9 TW economically feasible  
0.6 TW installed capacity





# The Energy Solution

- Sufficient Domestic Supply
  - Coal, Nuclear, Solar
- Environmentally Sustainable Supply
  - Solar (Nuclear?)
- Suitable Carrier
  - Electricity? Hydrogen? Hydrocarbon?
- Challenges
  - Convert solar (nuclear) to **convenient** chemical form
  - Efficient consumption of chemical fuel

## Current: Hydrocarbon Economy

Based on use of Fossil Fuels

- Pollution
  - Local
  - Global
- Energy Dependent
- Cost
  - Supply

## Future : Hydrogen Economy

Benefits of Hydrogen

- Replace a limited fuel supply
- Security
- Clean.
- Hydrogen : most Abundant Element
- Almost always found in compounds
  - e.g.  $H_2O$
- High specific energy
- An energy carrier, not a form of primary energy.



Data from Science (2004) states that it costs \$5 to produce the amount of hydrogen that releases an amount of energy equivalent to a gallon of gasoline. Costs dropping by 1\$ per gallon gas equivalent each 3 year period. DOE (US) Roadmap aim:  $H_2$  production 1.50 \$ per gallon of gas equivalent or less.

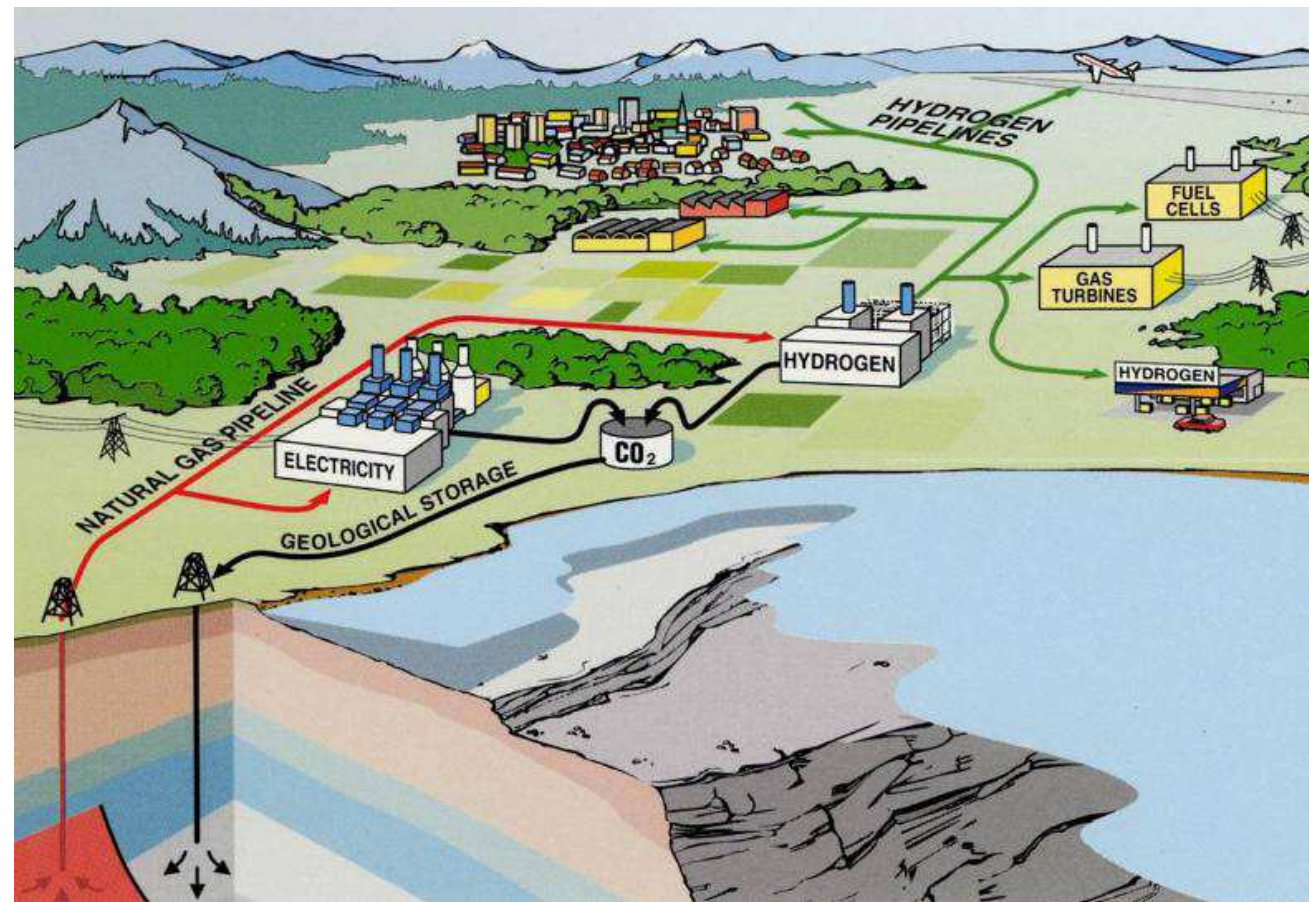
## Problems faced by Hydrogen Economy

Production  
Storage  
Fuel Cells  
Safety  
Infrastructure

*"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."*

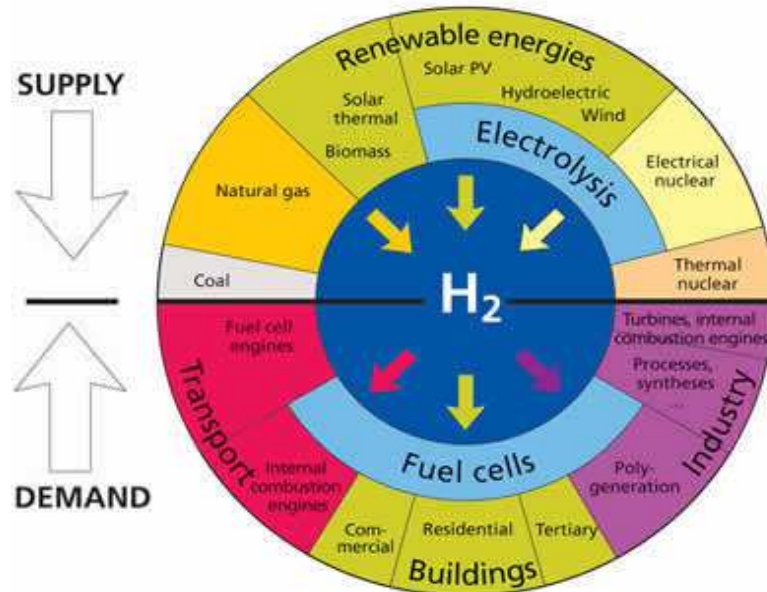
Jules Verne (1870) *L'île mystérieuse*

Unlike oil, gas and coal hydrogen doesn't exist in large quantities in nature in a useful form. Like electricity it is an energy carrier, which must be produced using energy from another source. Hydrogen, however, has the advantage that it can be stored more easily. Today, nearly half the hydrogen produced in the world is derived from natural gas via a steam-reforming process. The natural gas reacts with steam in a catalytic converter. The process strips away the hydrogen atoms, leaving carbon dioxide as the by-product. Therefore, in the future, hydrogen must be produced from renewable energy sources.



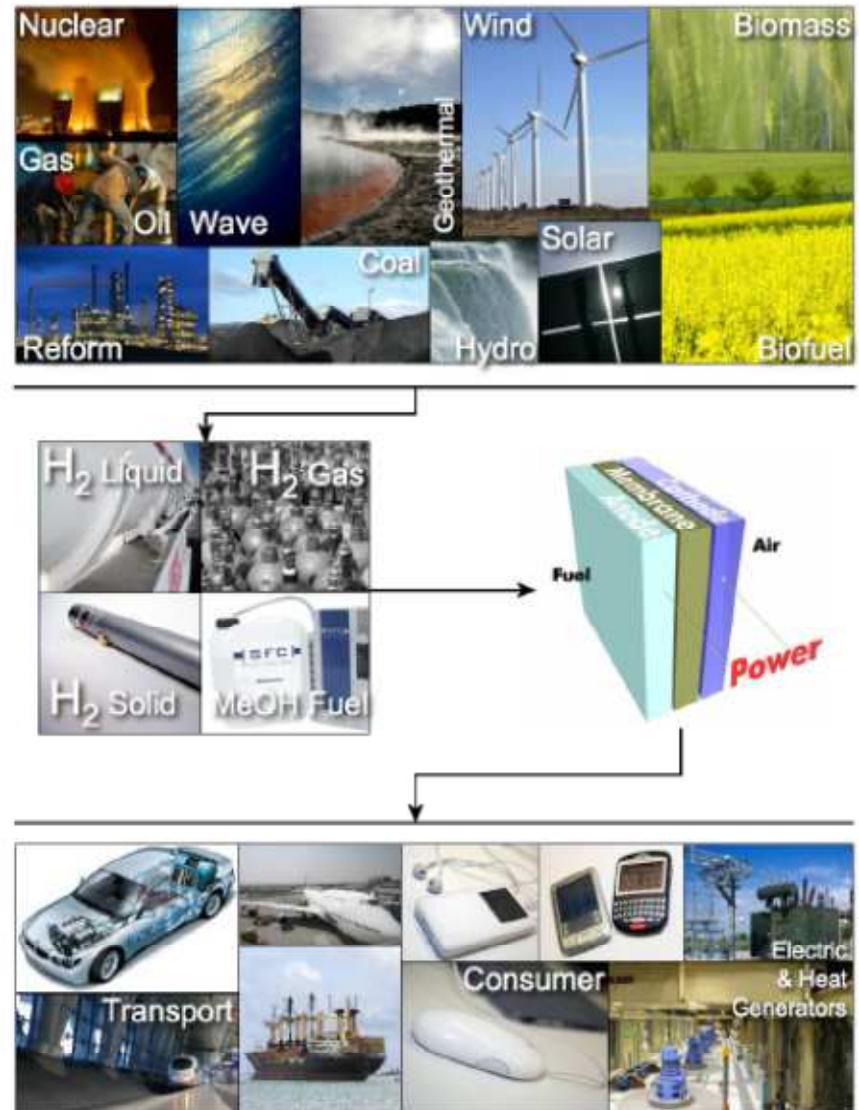


# The Hydrogen Economy: Hydrogen as an energy carrier.

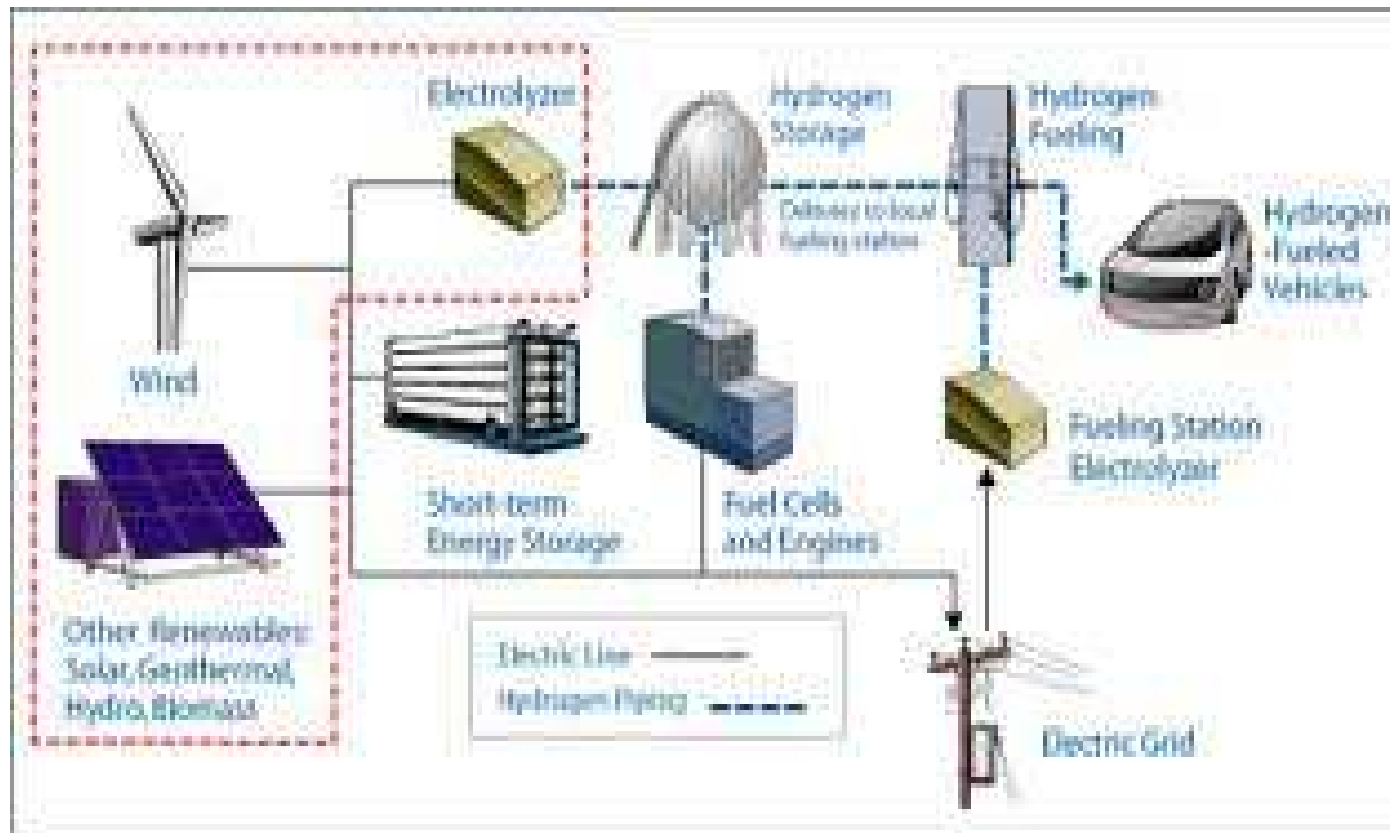


G.W. Crabtree, M.S. Dresselhaus, M.V. Buchanan, 'The hydrogen Economy' Physics Today, Dec.2004, pp.39-45.  
U. Bossel, 'Does a hydrogen economy make sense?' Proc. IEEE, 94 (10)(2006), pp.1826-1836.

P.P. Edwards, V.L. Kuznetsov, W.I.F. David, N. Brandon. Energy Policy 36(2008) 4356-4362.



# Hydrogen Economy



## How do we produce Hydrogen?

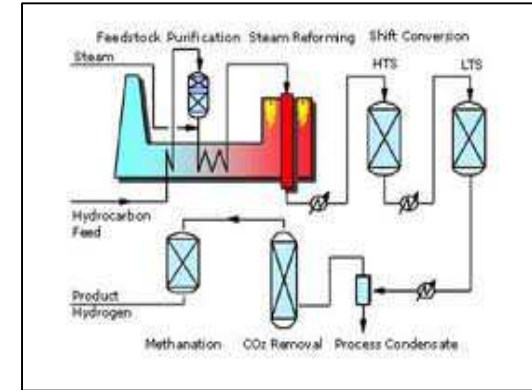
- Breaking down compounds
  - Fossil Fuels
  - Water Electrolysis
- 48% Natural Gas, 30% Oil, 18% Coal
  - Natural Gas Steam Reforming (SR):
    - $\text{CH}_4 + \text{H}_2\text{O} + \text{Energy} \rightarrow \text{CO} + 3 \text{H}_2$
    - $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
  - Kvaerner-process:
    - $\text{C}_n\text{H}_m + \text{Energy} \rightarrow n\text{C} + 1/2m\text{H}_2$

Water Electrolysis (WE): generates pure hydrogen

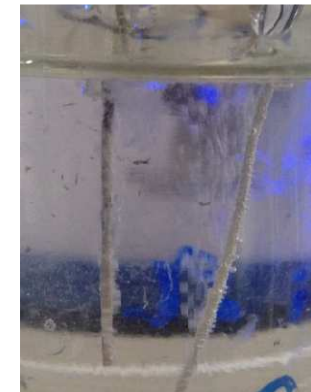
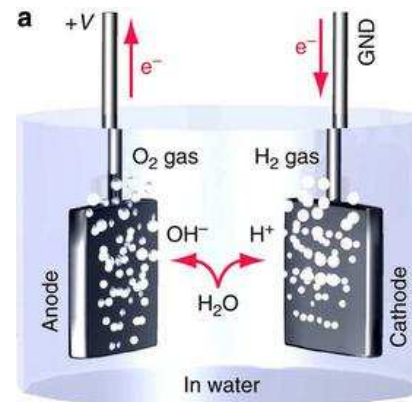
Electrical power sources are connected to two electrodes which are placed in water:

- Anode (oxidation):  $2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4e^-$
- Cathode (reduction):  $2 \text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$

Most of the 4% produced by electrolysis is a side product in the production of industrial chlorine



WE Process consumes about 50kWh of electricity per kg of Hydrogen produced  
Energy efficiency is in the range of 50-80%





# Chlor alkali Process: $\text{Cl}_2$ and $\text{H}_2$ production.



Anode Reaction

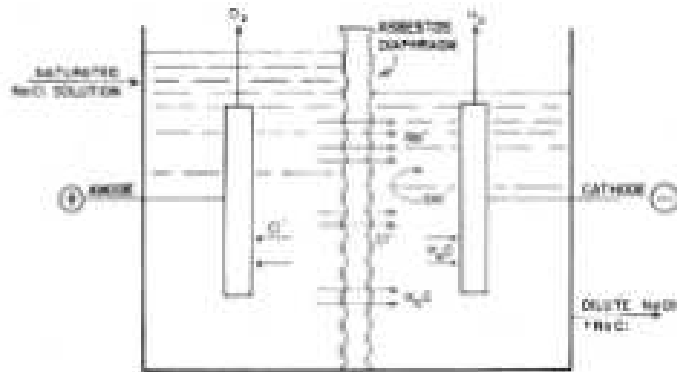
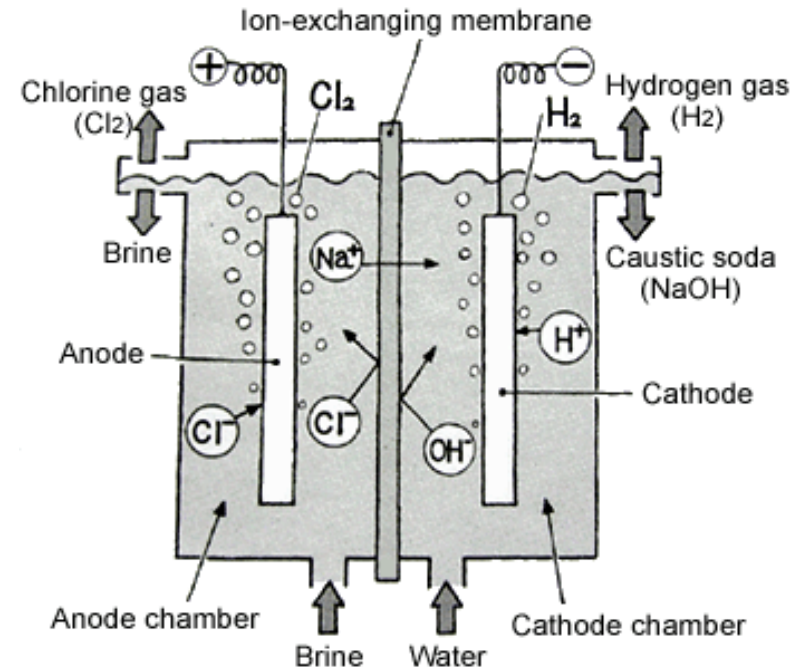
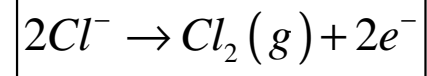
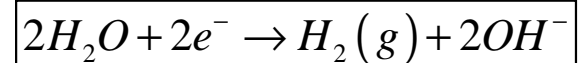
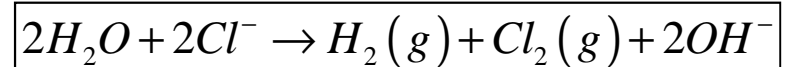


Figure 1. Schematic of a diaphragm type chlor-alkali cell.

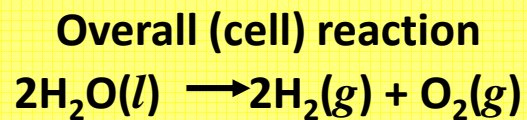
Cathode Reaction



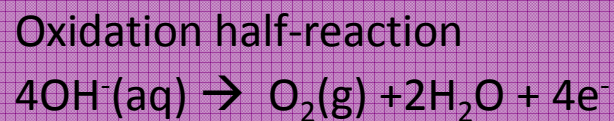
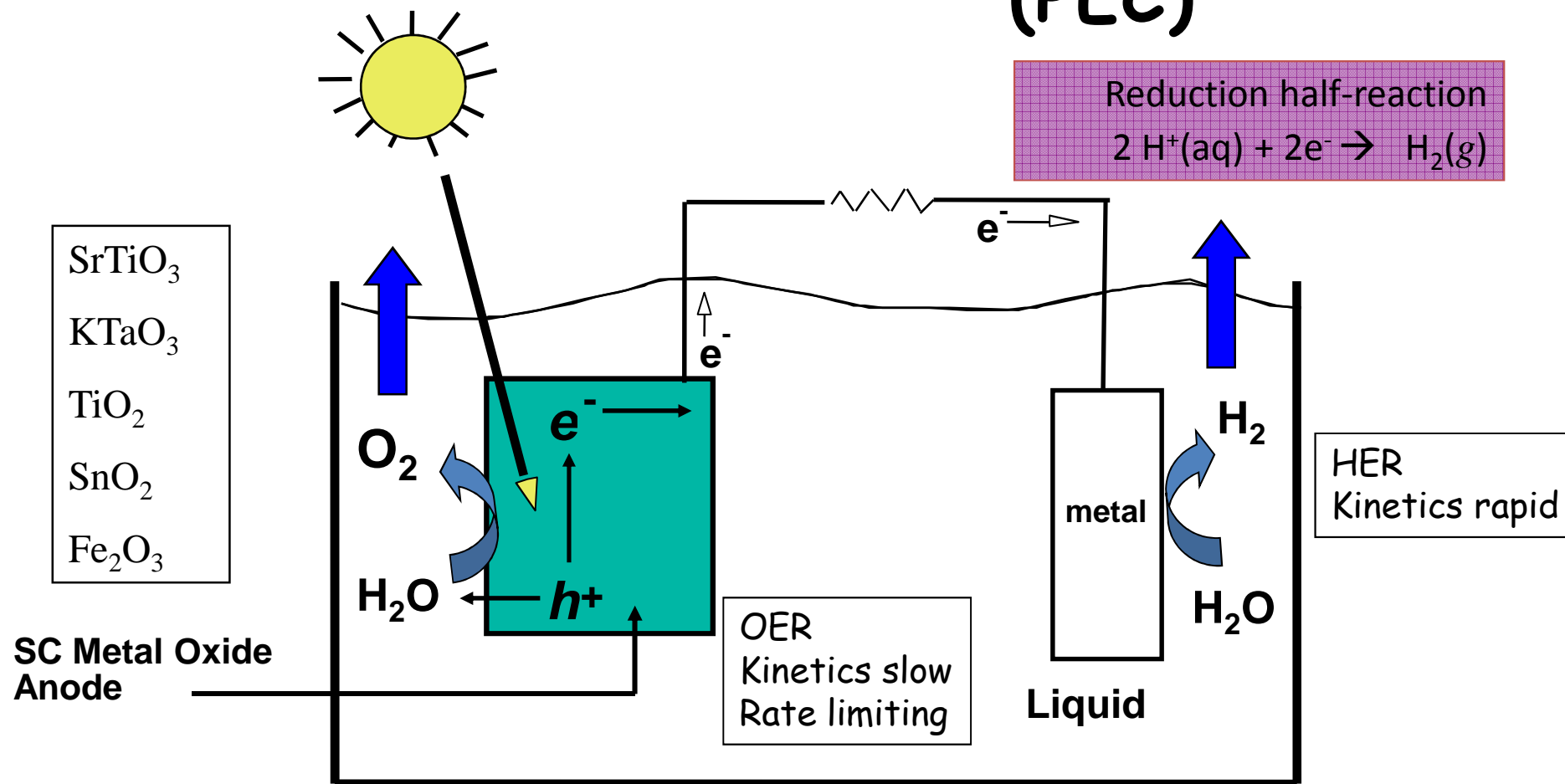
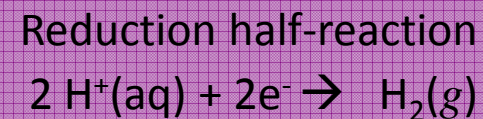
Net cell reaction



$\text{RuO}_2/\text{TiO}_2$  good anode material.



# Photoelectrochemical Cell (PEC)



Light is Converted to Electrical + Chemical Energy

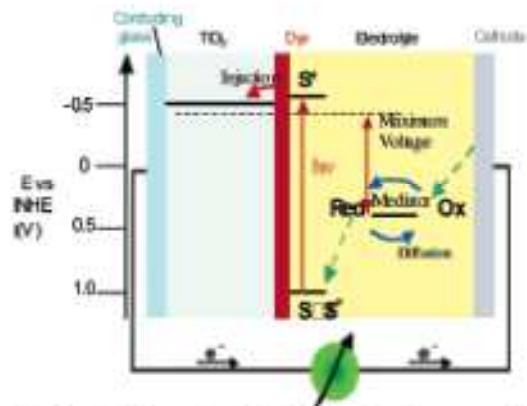


Figure 1. Principle of operation of the dye-sensitized nanocrystalline solar cell. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of a semiconductor oxide film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The energy levels drawn match the redox potentials of the N3 sensitizer ground state and the iodide/triiodide couple shown in Figure 5.

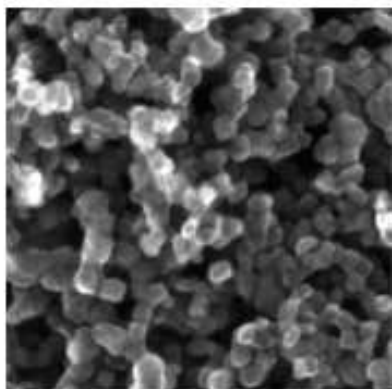
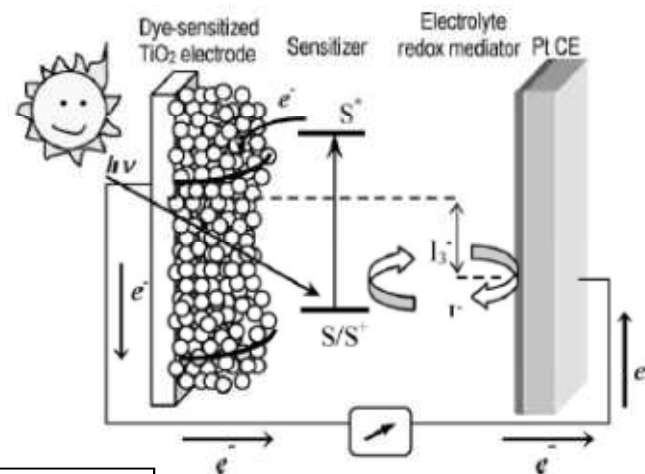


Figure 2. Scanning electron micrograph of a sintered mesoscopic  $\text{TiO}_2$  film supported on an FTO glass. The exposed facets of the anatase nanocrystals are mainly oriented in the (101) direction. The average particle size is 20 nm.



## Photo-electrochemistry in action: DSSC Systems

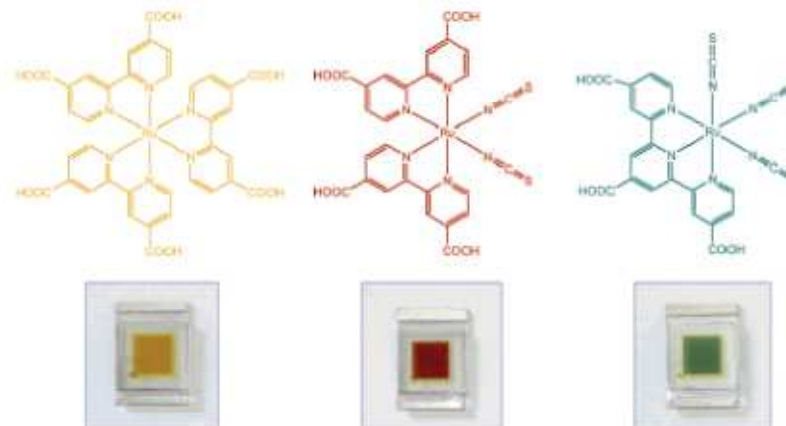
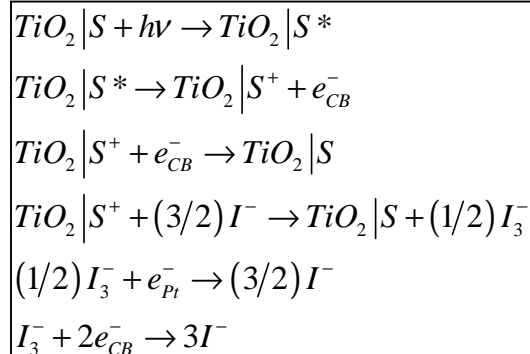
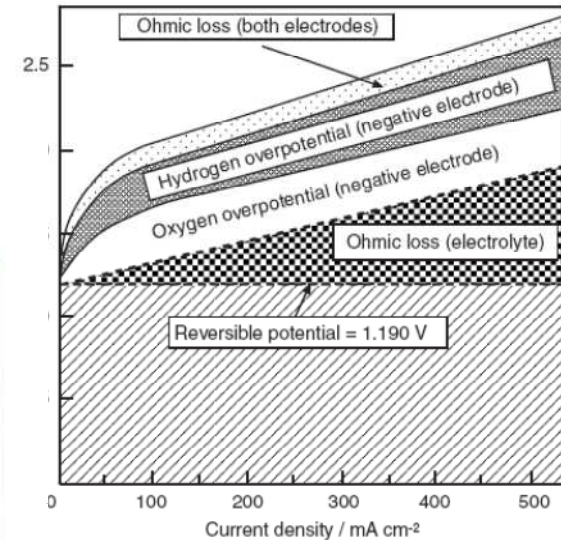
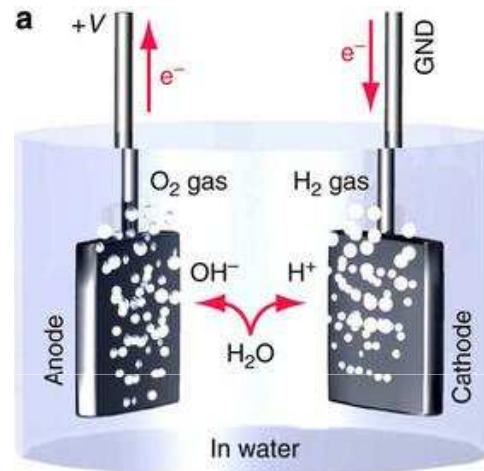
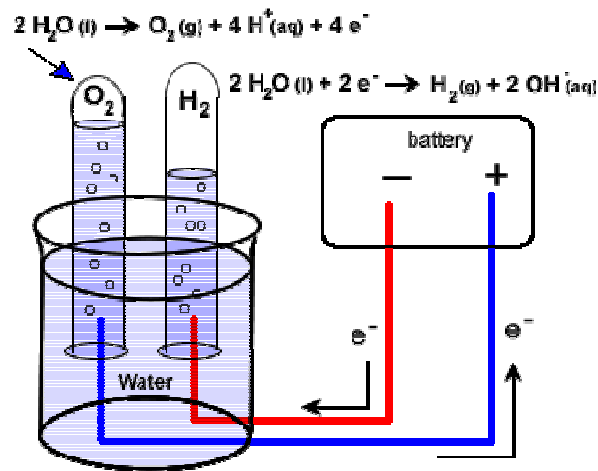


Figure 5. Structure of the ruthenium sensitizers  $\text{RuL}_3$  (yellow)  $\text{cis-RuL}_2(\text{NCS})_2$  (red) and  $\text{RuL}'(\text{NCS})_3$  (green) where  $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid and  $\text{L}' = 2,2',2''$ -terpyridyl-4,4''-tricarboxylic acid. The lower part of the picture shows nanocrystalline  $\text{TiO}_2$  films loaded with a monolayer of the respective sensitizer. The film thickness is 5  $\mu\text{m}$ .

M Gratzel, Inorg. Chem., 44 (2005) 6841-6851.  
P.V. Kumar, J.Phys. Chem.B., 106 (2002) 7729-7744.

# Electrolysis cell: electrochemical substance producer

Electrical energy produces chemicals.



Performance (voltage vs. current density) of a basic (unactivated), unipolar electrolyzer running at 90 °C.

Thermodynamics  
(Nernst Potential)

Kinetics: Cathode reaction  
Overpotential

Ohmic potential:  
Cell design

$$E(i) = E_{e,cell} + |\eta_C| + \eta_A + IR$$

Kinetics: Anodic reaction overpotential

Overpotential losses increase net electrical energy needed as input to drive reactions at electrodes.

Need to minimize all overpotential losses to make applied potential as close to Nernst potential as possible.

# Fuel Cell : Electrochemical Energy Producer

Thermodynamics  
(Nernst Potential)

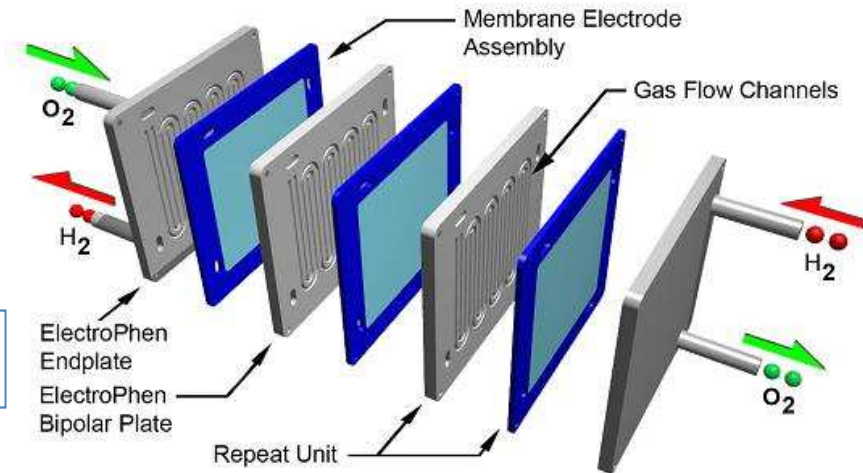
Kinetics: Anodic reaction  
overpotential

$$E(i) = E_{e,cell} - |\eta_C| - \eta_A - IR$$

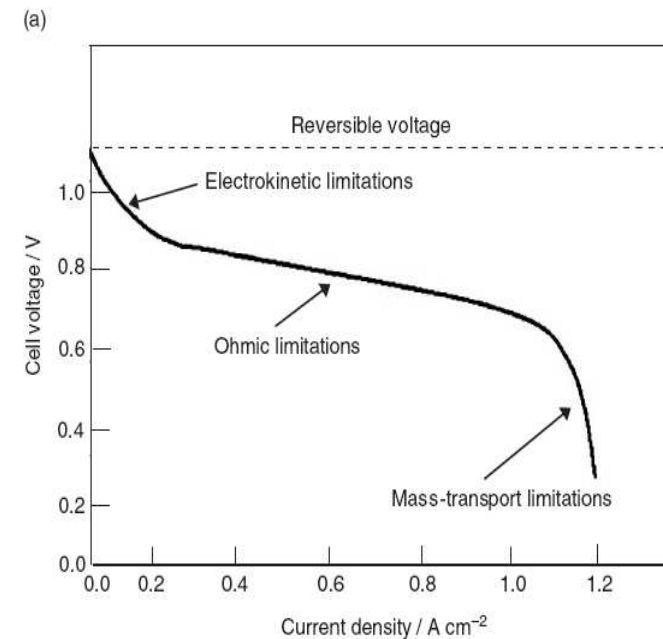
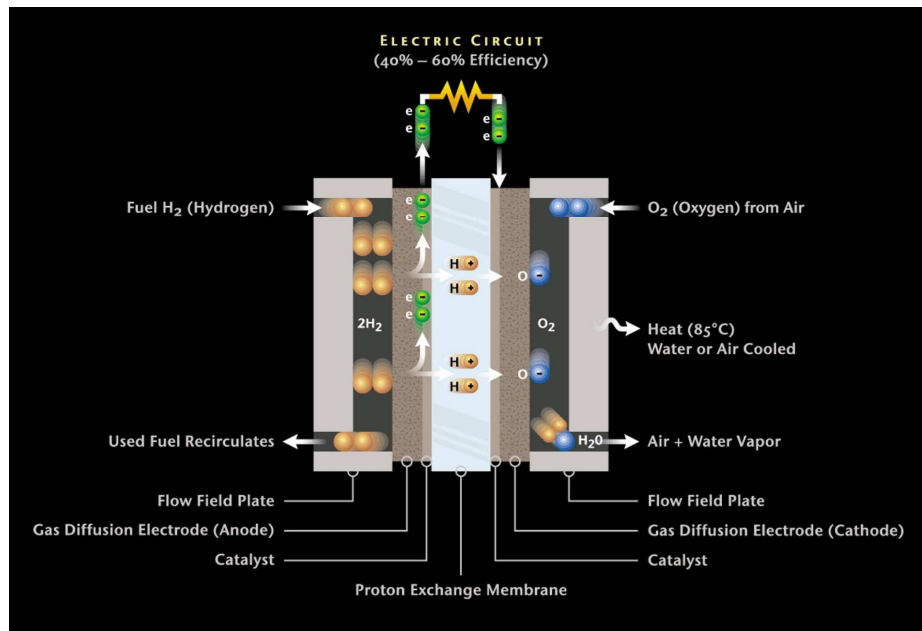
Kinetics: Cathode reaction  
Overpotential

Ohmic potential:  
Cell design

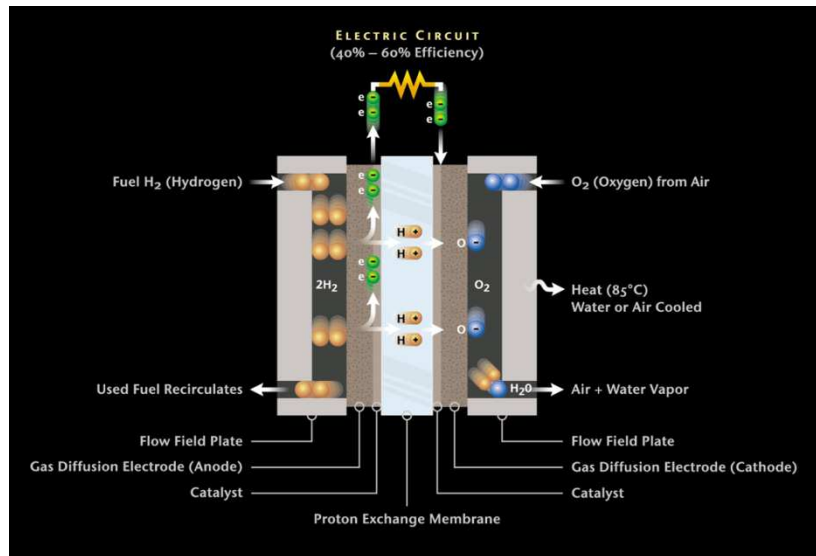
Overpotential losses reduce net  
voltage output.



Ballard PEM Fuel  
Cell

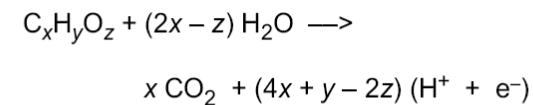
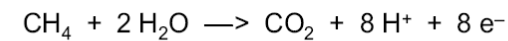
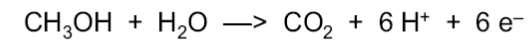
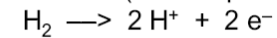




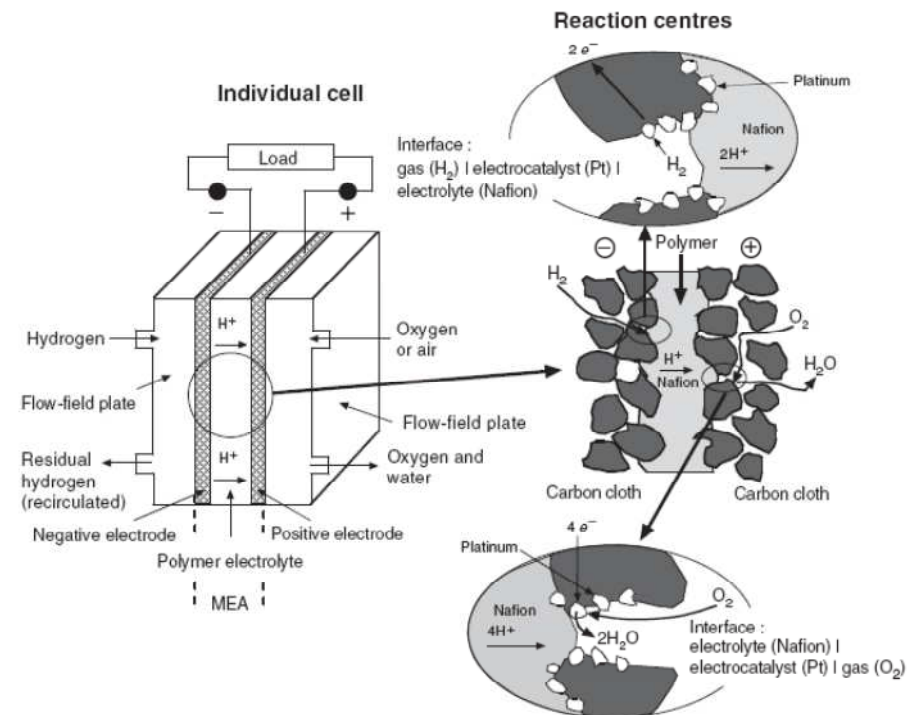
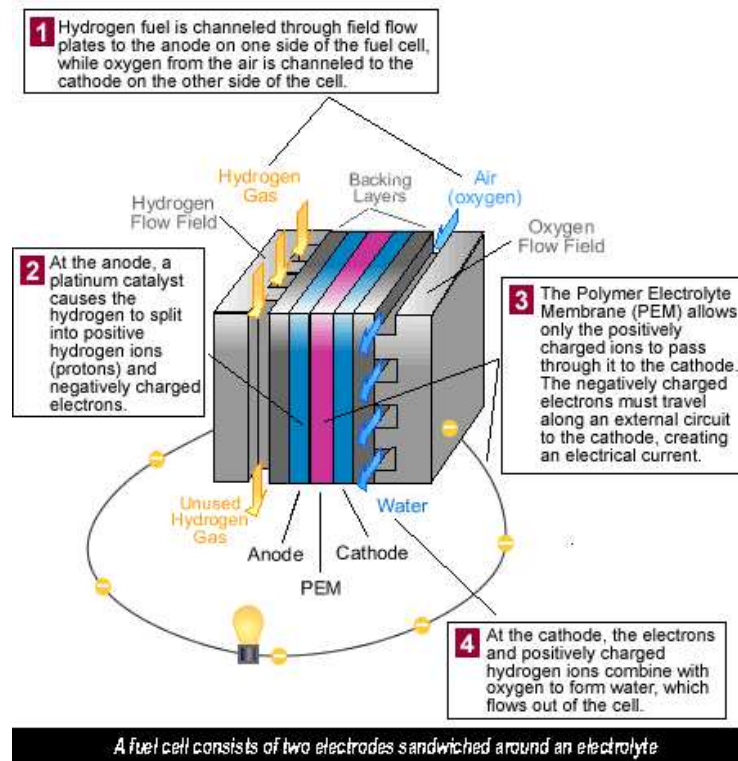
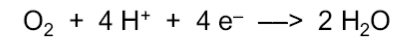


## Electrocatalytic Reactions

- Oxidation (several possible fuels)

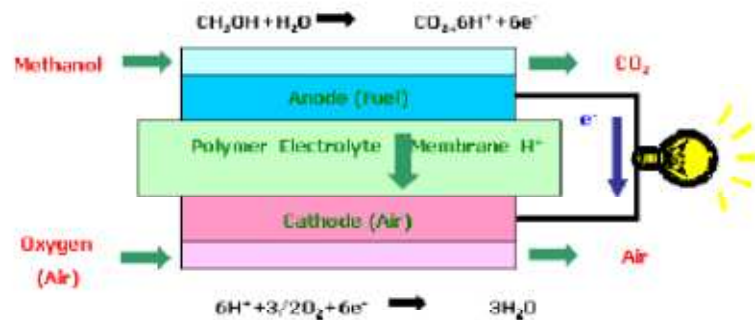
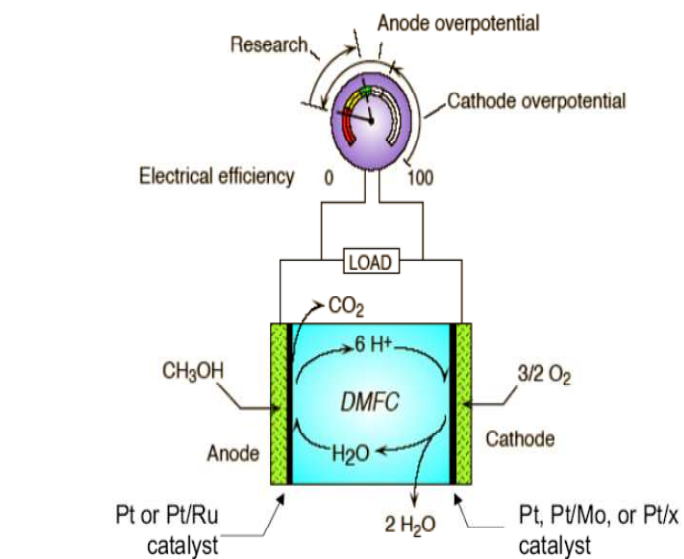


- Reduction





## Example: DMFC



Schematic of a direct methanol fuel cell (Courtesy of Toshiba)

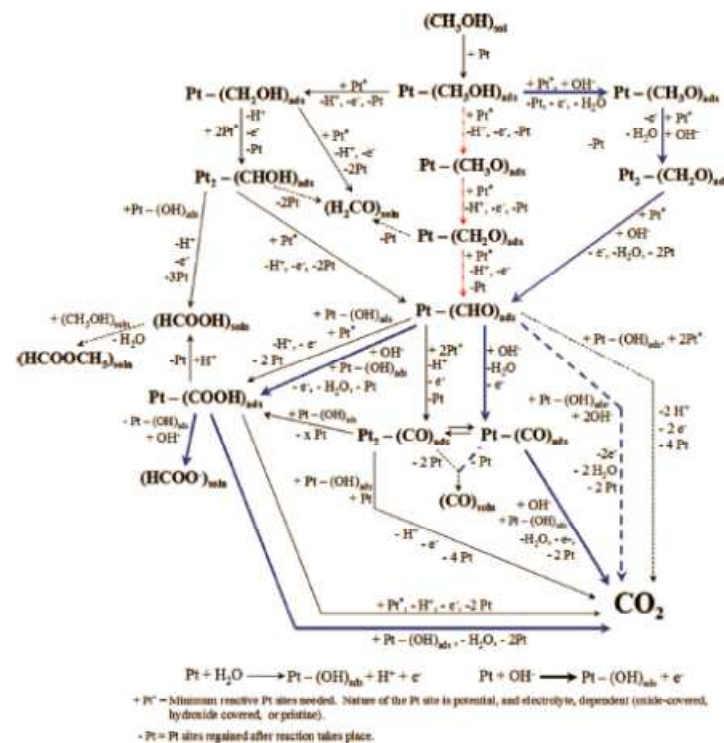
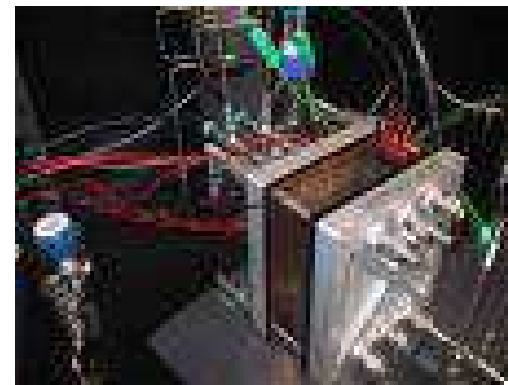


Fig. 1 Detailed pathway for the oxidation of MeOH in acid (—) and alkaline (---) electrolyte. Dashed lines represent pathways that have been suggested in the literature for acidic and alkaline electrolytes respectively, but are unlikely to occur under typical experimental condition. The pathway (red line) corresponds to the initial dehydrogenation pathway as determined by UHV experiments.

# The bottom line

- Water electrolysis device:
  - Very sluggish Oxygen Evolution Reaction (OER) kinetics (v. high overpotential) limit device operational effectiveness (higher electrical energy input required)
- Fuel Cell:
  - Very sluggish Oxygen Reduction Reaction (ORR) kinetics limit voltage output of device
- For both device types the cathodic Hydrogen Evolution Reaction (HER) or the anodic Hydrogen Oxidation Reaction (HOR) are reasonable kinetically facile.

- Optimizing the kinetics of the oxygen electrode and understanding the mechanism of the oxygen electrode reaction presents a grand challenge and has direct implications for photo-electrochemical splitting of water.

Metal oxide materials exhibit useful potential as catalysts for OER and ORR in electrochemical energy conversion devices.

J.Lee, B. Jeong, J.D. Ocon,  
Oxygen electrocatalysis in chemical energy  
conversion & storage Technologies.  
Curr. Appl. Physics, 13 (2013) 309-321.

# Course Outline

- In these lectures (4/CH4008, 6 CH4061) we focus attention on:
  - Electrochemically generated hydrous transition metal oxides (TMO)
  - Electro-precipitated TMO
  - Thermally prepared TMO
  - Nanostructured TMO.
- Major focus will be on current research performed by SFI Trinity Electrochemical Energy Conversion & Electrocatalysis (TEECE) Group.
- We examine aspects of the redox surface chemistry exhibited by oxidized metal and metal oxide modified electrodes in aqueous solution.
  - Specific focus on redox potential/pH response of metal oxide modified electrode (non-traditional pH sensing)
- We discuss techniques used to characterise such materials (both microscopic, electrochemical and spectroscopic).
- We examine mechanism & kinetics of demanding multistep, multielectron transfer reactions such as:
  - Anodic oxygen evolution reaction (OER)
  - Cathodic oxygen reduction reaction (ORR)
  - Glucose oxidation (non-enzymatic glucose sensing)