Fuel Cells

(A) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta G^\circ = -237\ kJ\ mol^{-1}$

* Hydrogen combustion is exothermic and spontaneous at standard state.

(B) $CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2$ $\Delta G = -698.2\ \frac{kJ}{mol}$

* burning methanol in O_2 is also exothermic.

Q: How do you get electricity from "burning" H_2 or MeOH (instead of heat)?

Q: what reaction gives you a higher voltage?

$\Delta G^\circ = -nFE^\circ$

$E^\circ = \frac{\Delta G^\circ}{-nF}$

(A) $n = 2\ e^-$

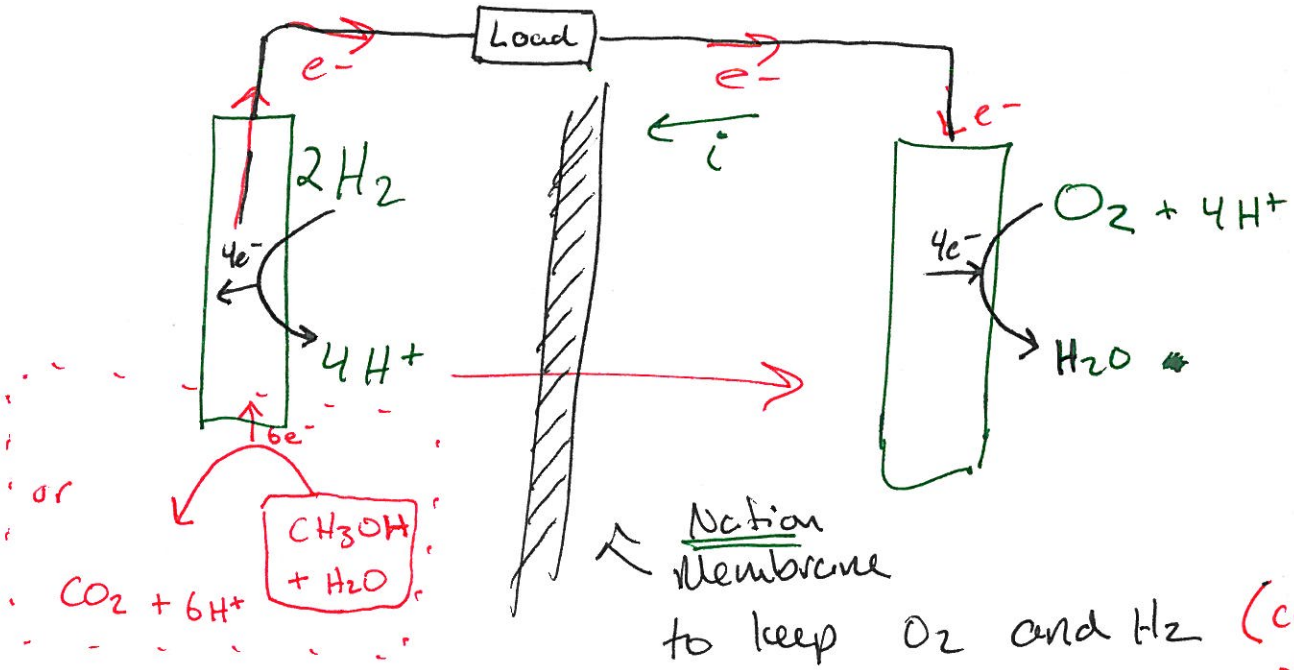
so $E^\circ = \frac{-237{,}000}{-2 \cdot 96485} = \boxed{1.23V}$

(B) $n = 6e^-$

$E^\circ = \frac{-698200}{-6 \cdot 96485} = \boxed{1.21\ V}$

Q So, how do we get the energy out?

A → make electrons travel <u>through</u> a <u>wire</u> for reaction to proceed.

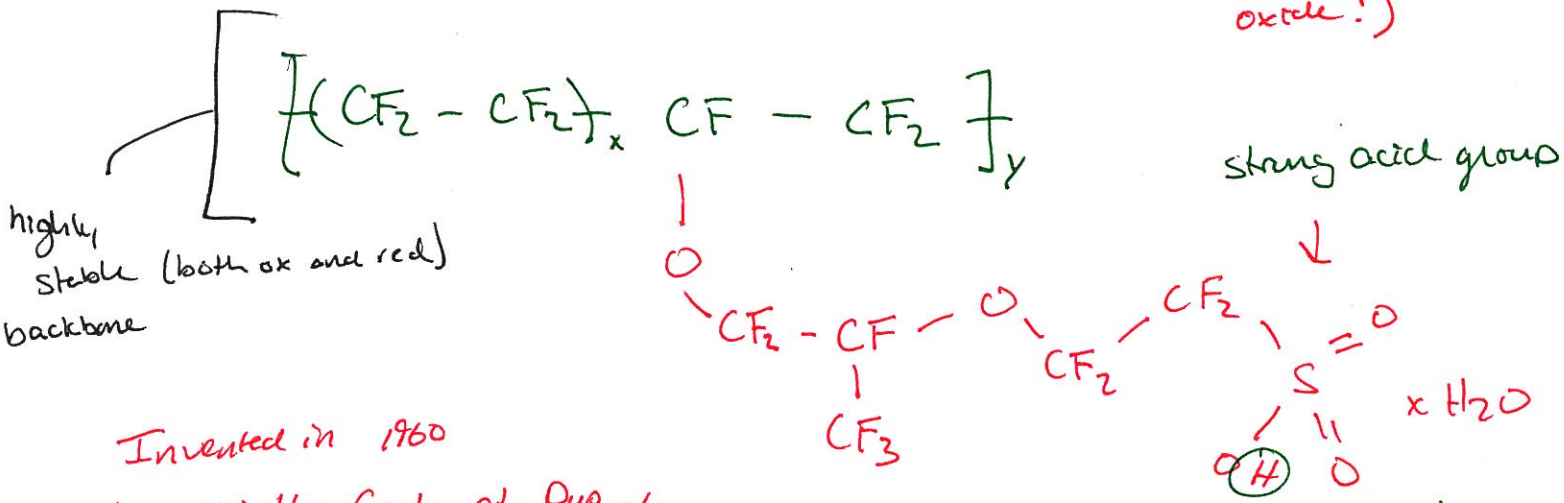


(similiar design for methanol fuel cell)

Nafion Membrane to keep O_2 and H_2 Separated!
(but conduct protons)!

(critical - other fuel cells use other membranes. e.g. SOFC Solid Oxide Fuel cell ... use high T oxygen conducting oxide!)

<u>Nafion</u> - hydrated fluorosulfonic acid ionomer

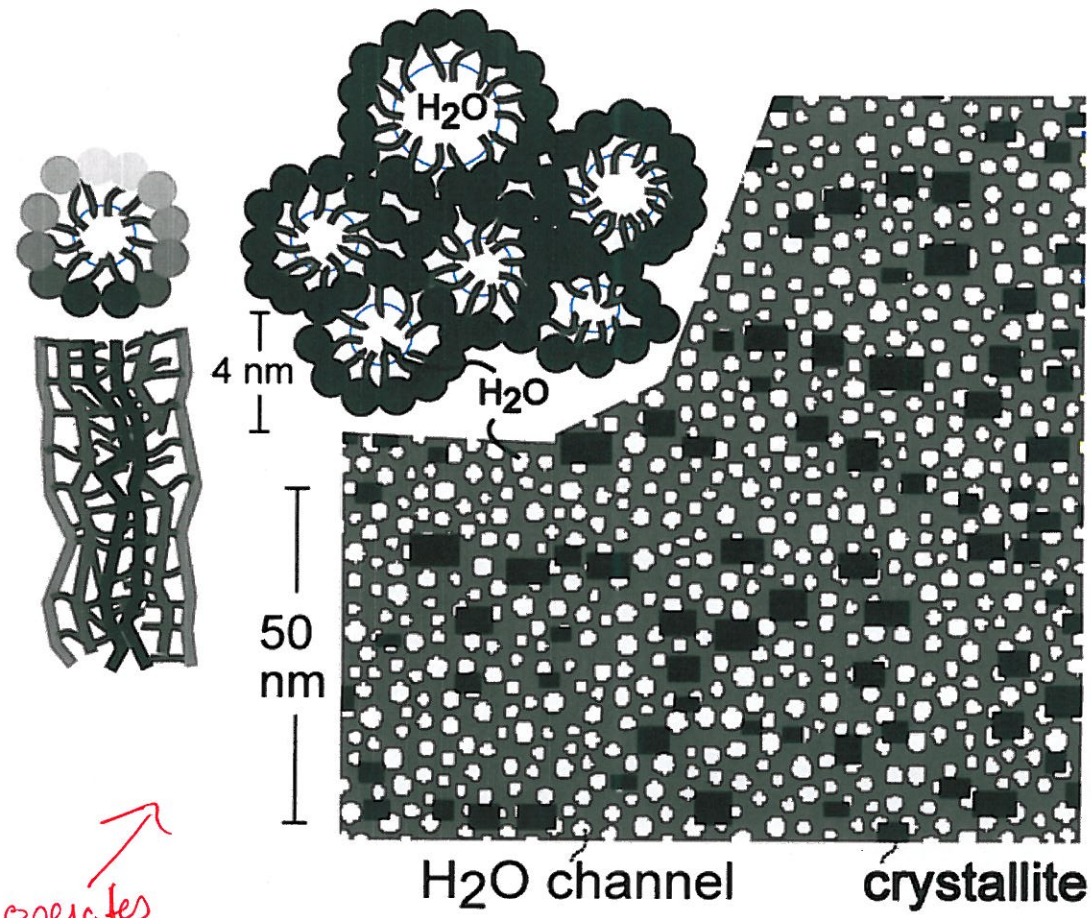


(labile proton can jump from site-out to site

Invented in 1960 by Walter Grot at Dupont.

Nafion Nanostructure Model

Water Channel Model



Model based on simulations of small-angle X-ray scattering data and solid state nuclear magnetic resonance studies.

Sulfonic acid functional groups self-organize into arrays of hydrophilic water channels, each ~ 2.5 nm in diameter, through which small ions can be easily transported.

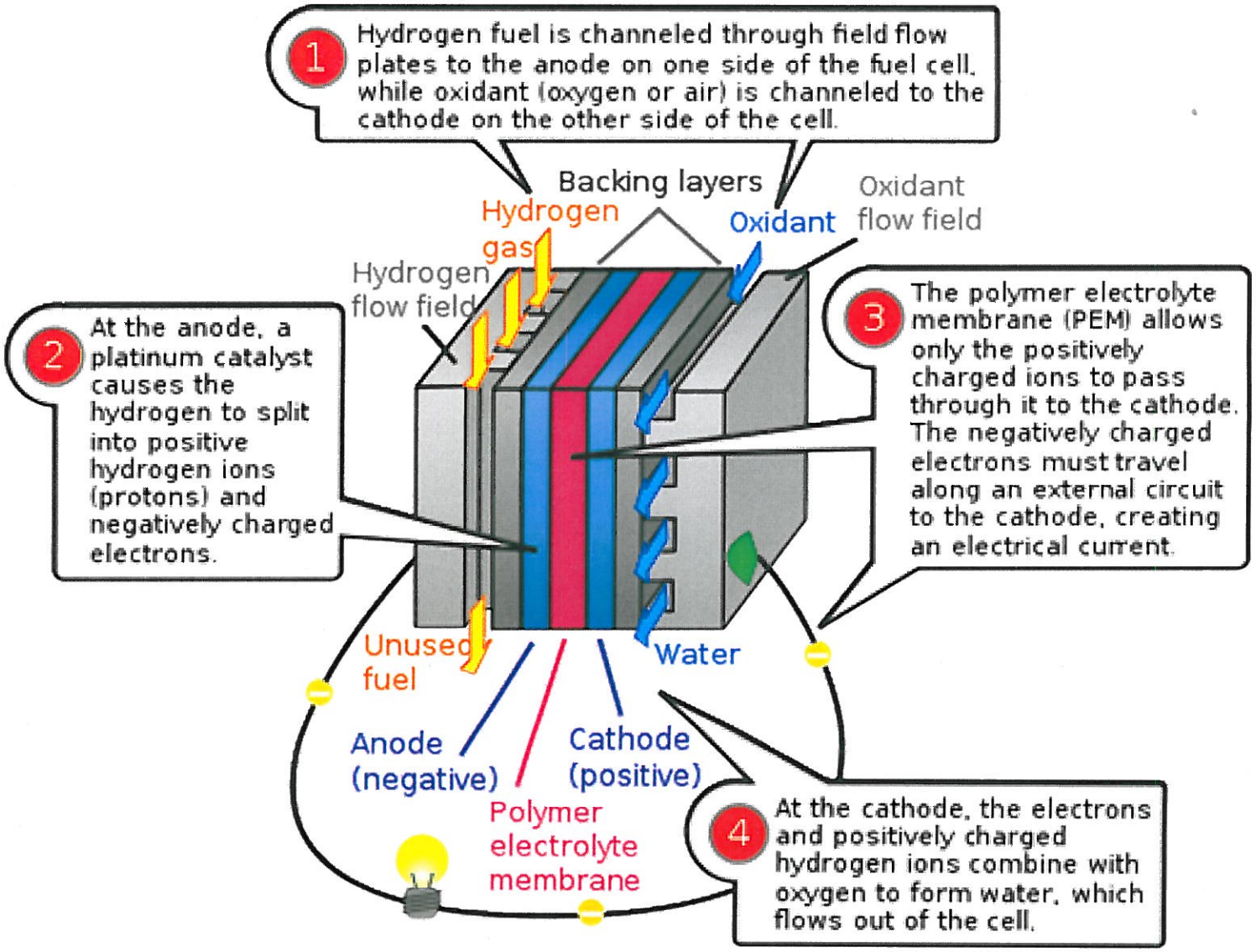
Interspersed between the hydrophilic channels are hydrophobic polymer backbones which provide the observed mechanical stability.

operates near room Temperature to ensure polymer stability

K. Schmidt-Rohr & Q. Chen (2008). "Parallel cylindrical water nanochannels in Nafion fuel-cell membranes". *Nature Materials* **7** (1): 75–83. doi:10.1038/nmat2074

19.2B

Proton exchange membrane fuel cell



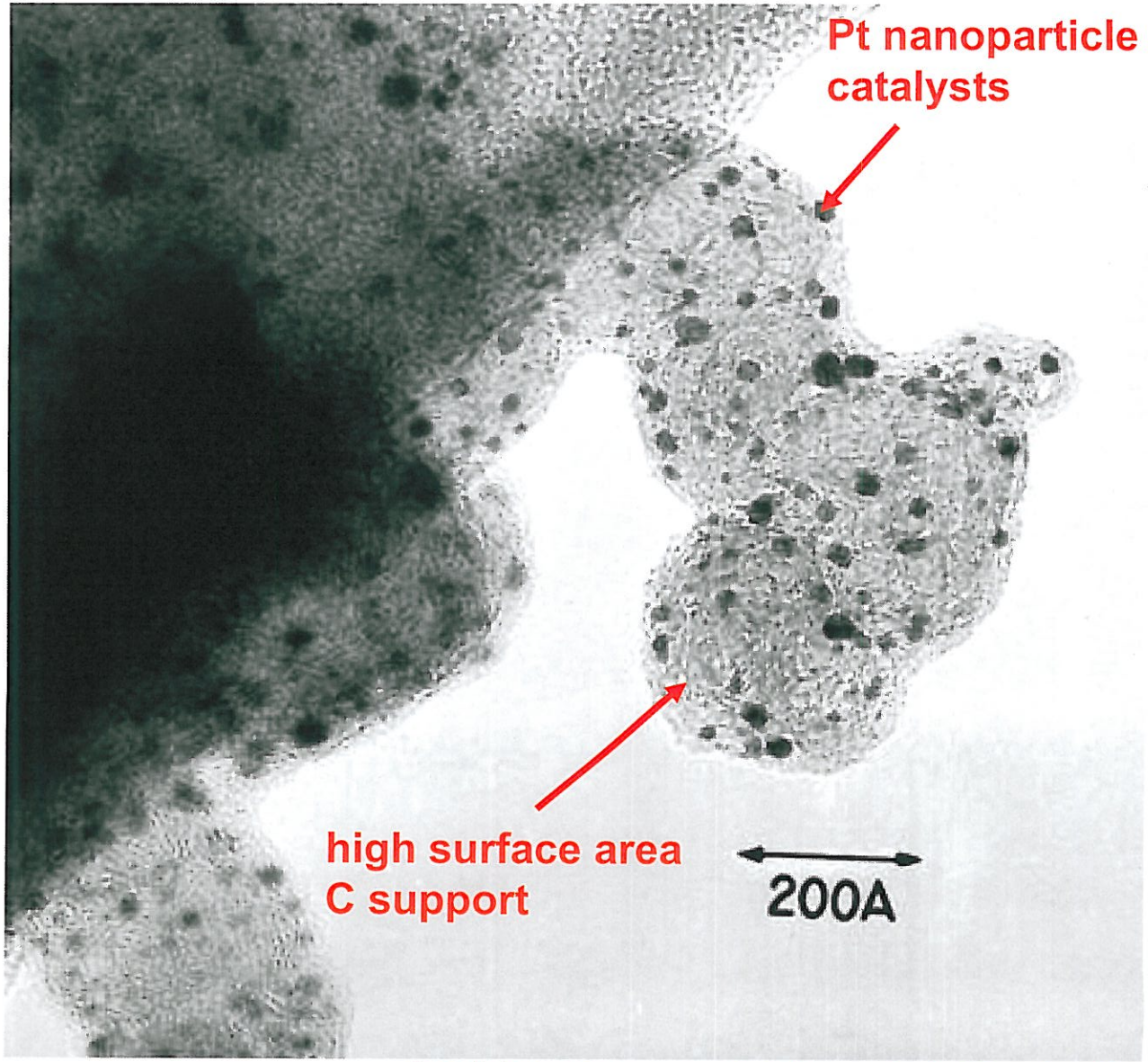
"low temperature" fuel cell. (http://en.wikipedia.org/wiki/File:PEM_fuelcell.svg)

19.22

Anode and cathode materials for LT FCs

Need:

- Delivery of electrons
- Delivery of reactant gas
- Delivery/removal of H^+
- Catalytic for H^+/H_2 or H_2O/O_2



http://electrochem.cwru.edu/ed/encycl/art-c01-carbon.htm

Challenge: good non-Pt catalyst materials!!

Will run out of Pt if everyone has fuel cell…

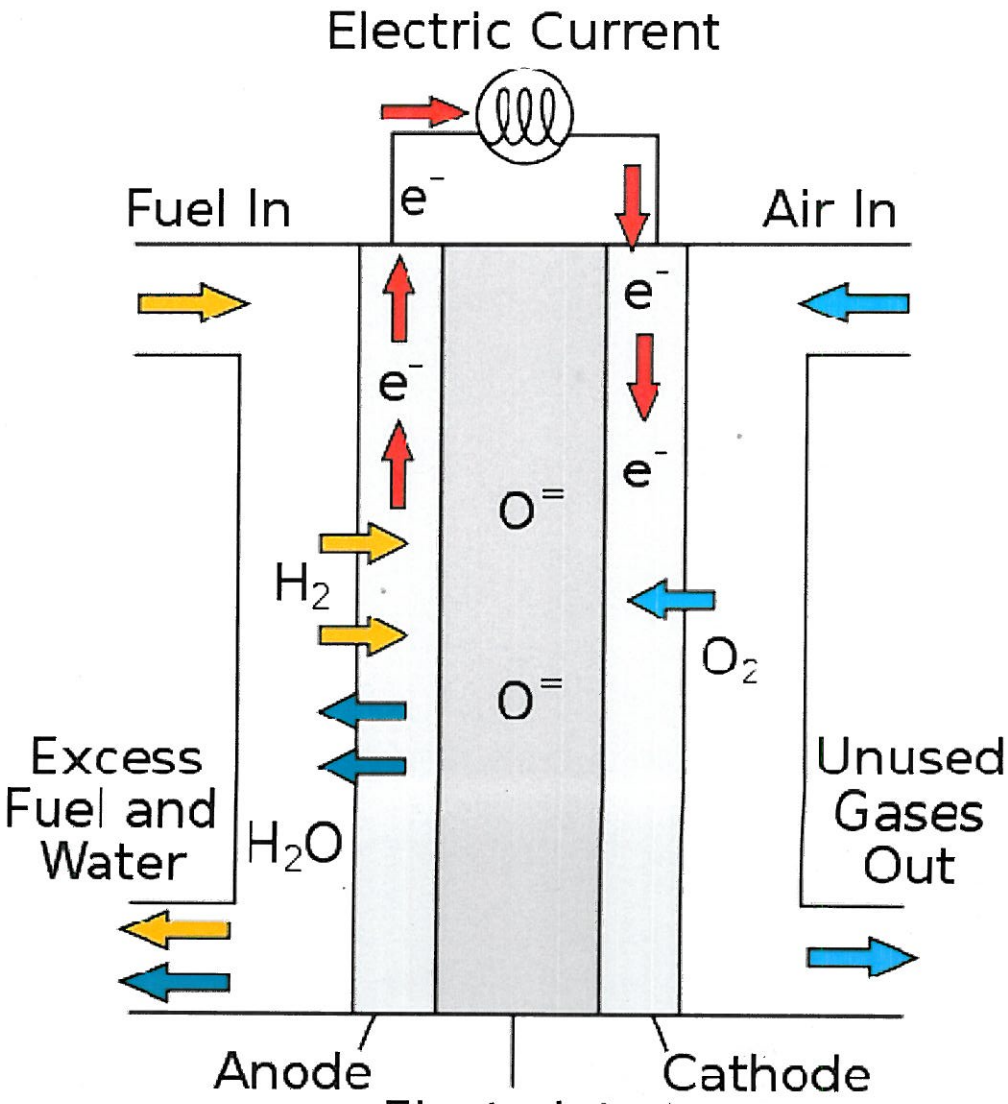
Solid Oxide Fuel Cell

Advantages:

a. **Higher real efficiency due to lower activation overpotential**
b. **Works with variety of hydrocarbon fuels.**

Disadvantages:

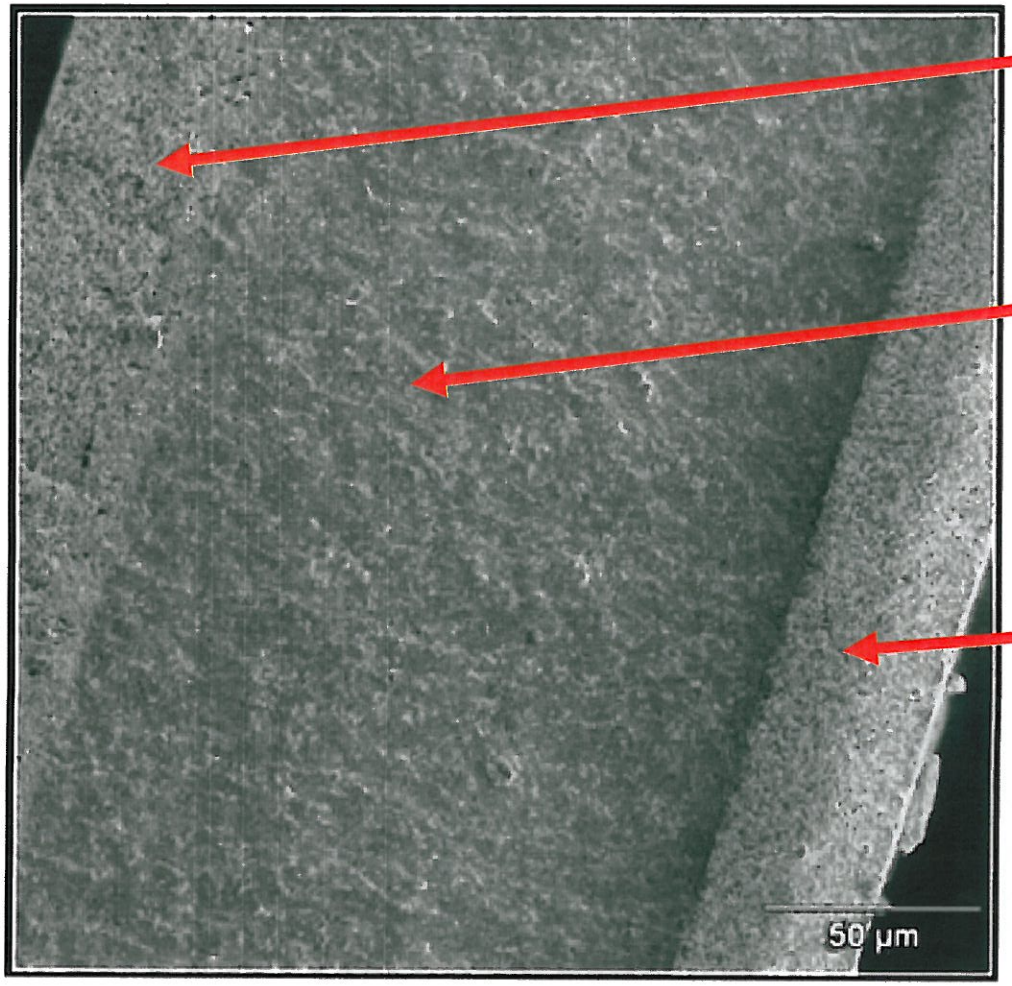
a. **High T (800 °C). Ongoing research to develop O conductors that operate at 500 °C.**
b. **Lower theoretical efficiency (compensated for by using waste heat)**



$$\frac{1}{2}O_2(g) + 2e' + V_o^{\bullet\bullet} \longrightarrow O_o^x$$

19.2E

Solid Oxide Fuel Cell Device Cross-Section



porous cathode
(lanthanum strontium maganite)

electrolyte (YSZ)
Yttria Stabilized Zirconia

porous anode
Ni-YSZ Cermet
(metal ceramic composite)

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

19.2F

Q What is the Maximum Energy you can extract from a fuel cell?

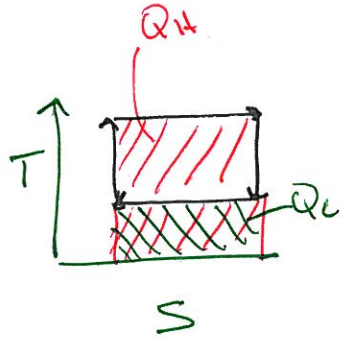
Q. How does that compare to combustion?

$$\Delta G = \Delta H - T\Delta S$$

maximum electrical energy output

maximum extractable heat if burned

always an "entropy energy loss"



$W = Q_H - Q_C$

Combustion : Carnot limit determines maximum efficiency

$$\text{Carnot Limit on } \eta = \frac{T_1 - T_2}{T_1}$$

hot and cold reservoir temperature

if $T_1 = 625\,K$ (~400 °C) $T_2 = 325\,K$ (~50 °C)

then the cycle would be 52% efficient.

to compare fuel cell efficiency to that of a combustion process:

→ total heat produced is ΔH

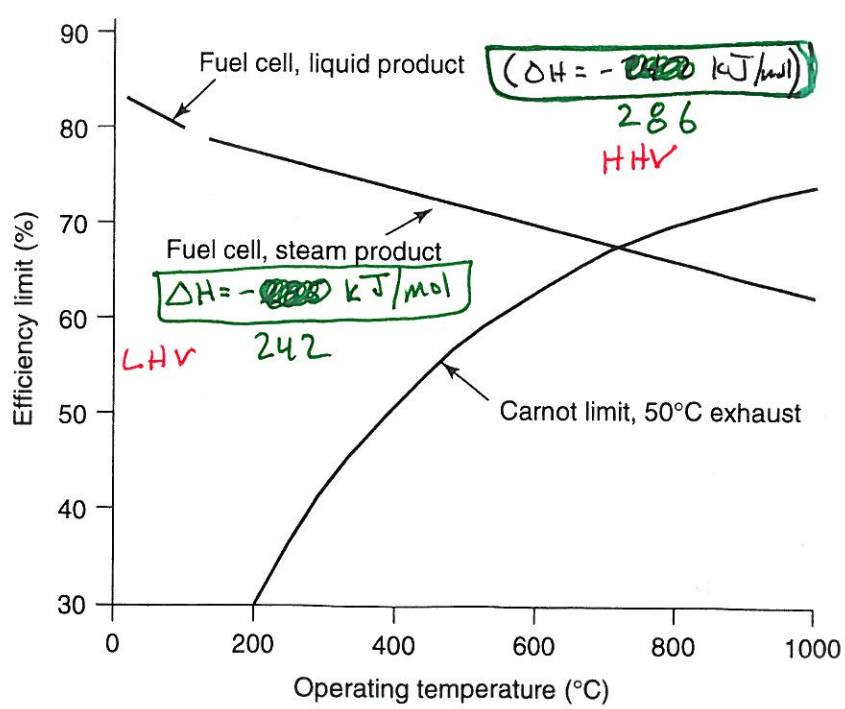
→ total free energy available is ΔG

$$\text{Maximum efficiency} = \frac{\Delta G}{\Delta H}$$ → which is a function of temperature.

$$\underset{\text{negative}}{\Delta G} = \underset{\text{negative}}{\Delta H} - \underset{\text{negative}}{T\Delta S}$$

positive

free energy is less negative than enthalpy due to entropy.



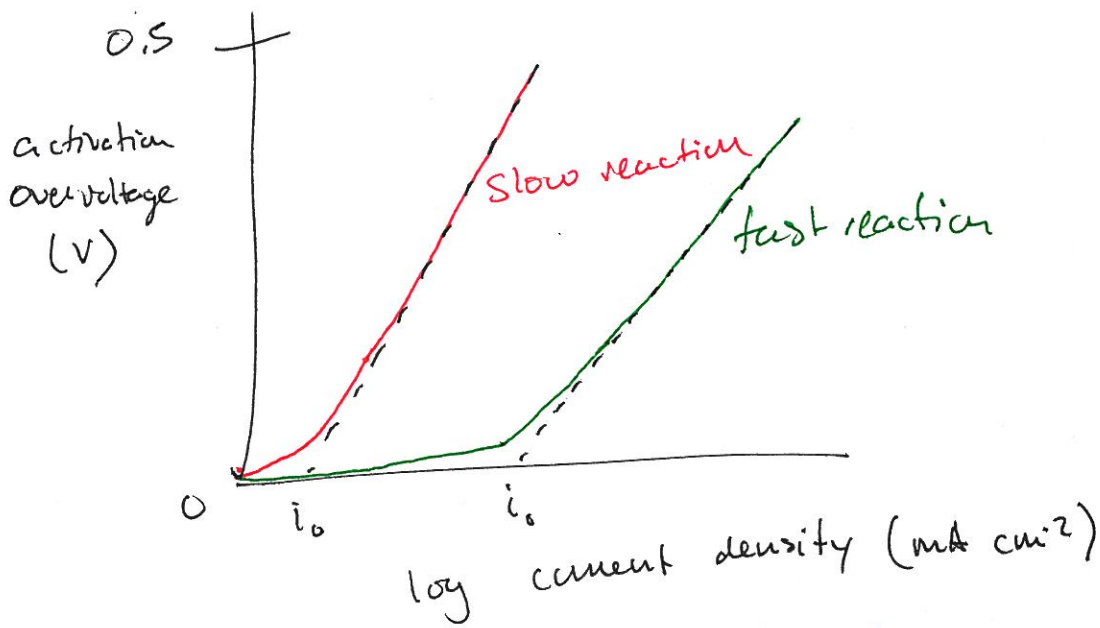
What about realistic efficiencies?

Q What are the losses in a fuel cell?

A. Activation Losses (kinetics)

- catalysts used to do ox/red reactions not infinitely fast

$$-\Delta V_{act} = \eta_{act} = a \log\left(\frac{i}{i_0}\right)$$ — Tafel AGAIN!



Note exponential relationship.

i_0 for H^+/H_2

Pt 5×10^{-4} A/cm^3 ← very fast

Ni 6×10^{-6} A/cm^3

Ag 4×10^{-7} A/cm^3 ← slow

B. Fuel Crossover / internal currents

(i) ideal electrolyte → blocks H_2 / O_2 crossover
→ blocks electronic conductivity

leakage of (current or fuel) leads to parasitic losses in current and open circuit voltage.

⇒ Must apply a voltage in opposite direction as OCV to stop leakage.

↳ part of free energy difference is "wasted" in driving the reverse reaction.

C. Ohmic Losses

– Resistance due to flow of ions through electrolyte and due to e^- through wires and electrodes

$$V = I R_{tot}$$

$$R_{tot} = R_{leads} + R_{electrolyte} + R_{cathode} + R_{anode} \ldots$$

D. Concentration Overpotential

→ if delivery of O_2 or H_2 or H^+ (or removal of species) is not sufficiently fast, ~~diffusion~~ concentration gradients will occur → from Nernst Equation: concentration gradient means potential gradient.

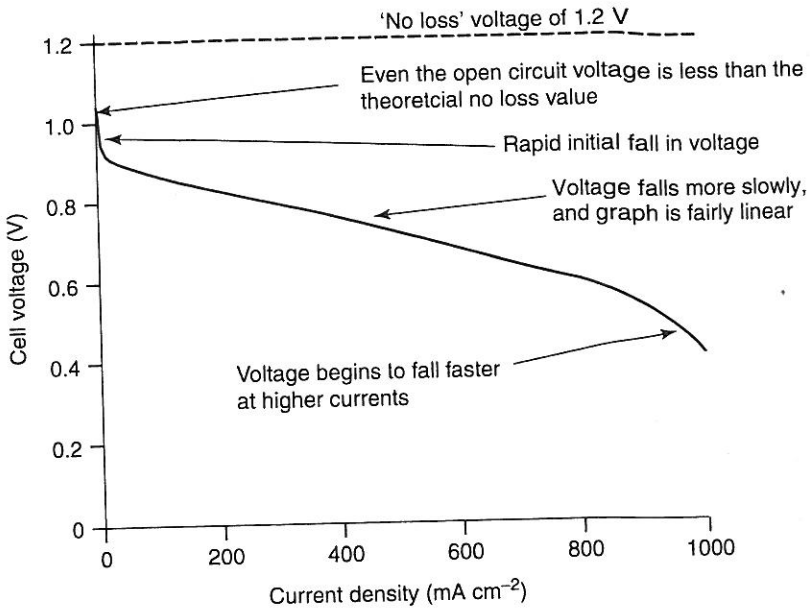


Figure 3.1 Graph showing the voltage for a typical low temperature, air pressure, fuel cell.

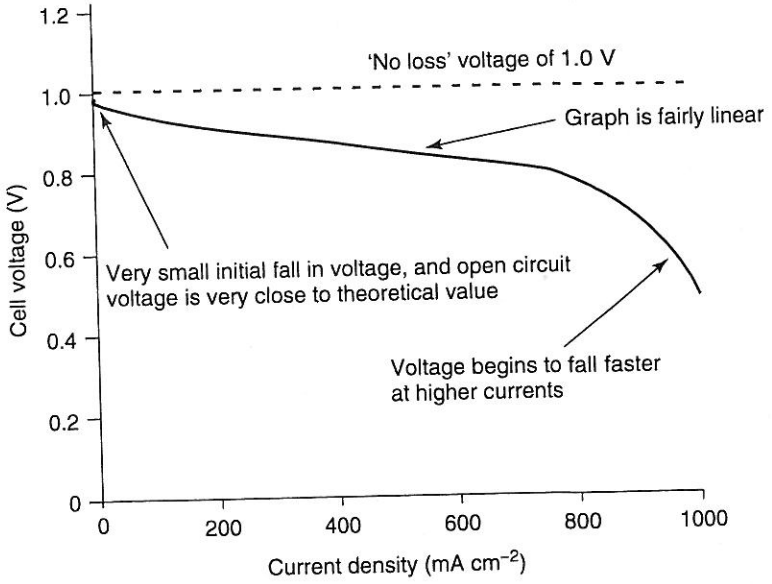


Figure 3.2 Graph showing the voltage of a typical air pressure fuel cell operating at about 800°C.

19.6B

Water Electrolysis

* $H_2O \rightarrow H_2 + O_2$ $E_{rev} = 1.23V$

Common Technologies

I. Alkaline

- mature technology
- Typically two nickel plate electrodes seperated by an hydroxide conducting separator
- conc. KOH
- typically 80 - 150°C, increase kinetics
- run at ~ 0.4 A cm^{-2} current density decrease series resistance

II. PEM Electrolyzers

- Nafion membrane
- operates in high acidic conditions (~ 1M H_2SO_4).

Disadvantage - need catalysts that are stable in acid conditions

→ Pt H^+/H_2

→ IrO_2 O_2/H_2O

(can't use many inexpensive transition metals, e.g., Ni which are soluble in acid)

Advantage

→ membrane separates H_2/O_2 well

- can use to directly pressurize generated hydrogen

→ H_2 w/ high purity → can be used to generate H_2 in-situ. (used in semi processing)

→ anode/cathode separated by very thin membrane → ohmic losses small → Run at high J (~ 1.5 A cm^{-2})