

# Lecture # 8

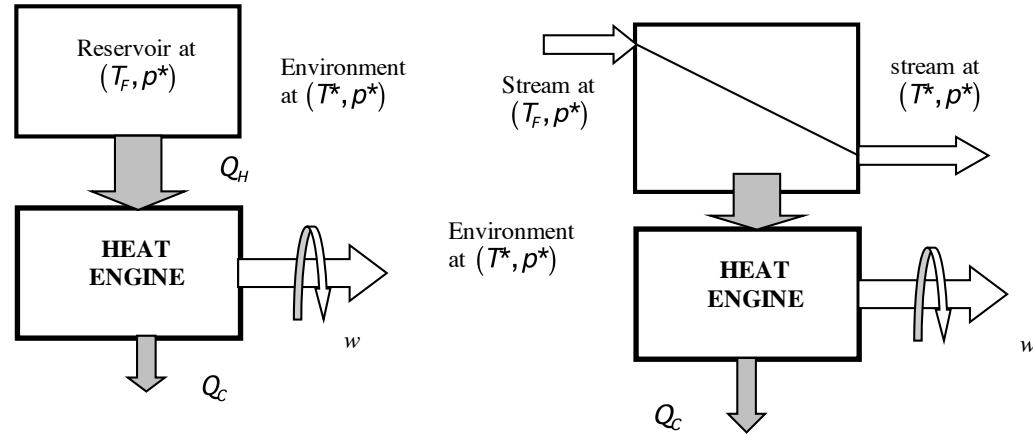
## Electrochemical Thermodynamics 1

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February 26, 2020

- Electrochemical reactions
- Electrodes and electrolytes
- Fuel cell components
- Work generated by a fuel cell
- Voltage and Ideal Efficiency

# Heat engine (heat to work) efficiency



$$\eta_{car} = 1 - \frac{T_L}{T_H}$$

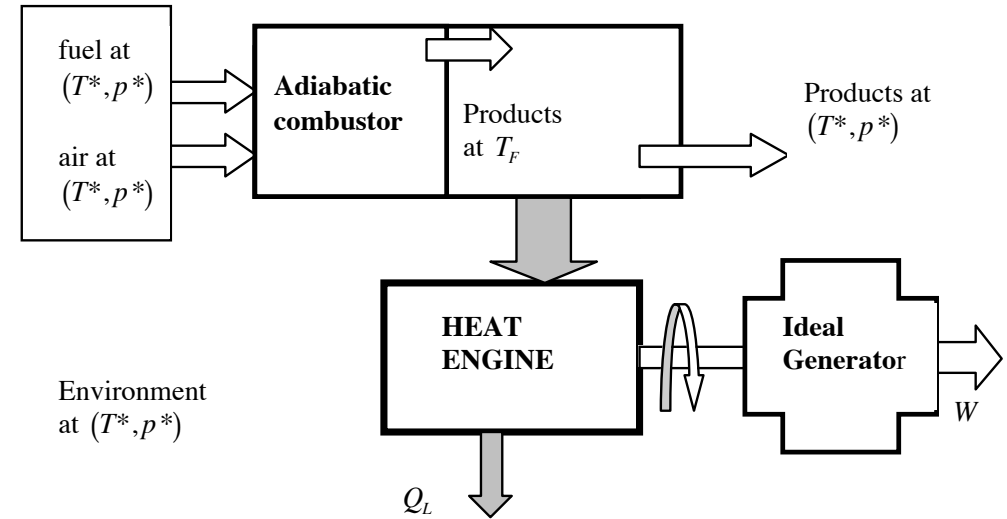
$$= 87.5\% \text{ for } T_H / T_L = 8$$

$$\eta_{car} = 1 - \ln \frac{T_F}{T^*} / \left( \frac{T_F}{T^*} - 1 \right)$$

$$= 70\% \text{ for } T_F / T^* = 8$$

Ideal thermo-mechanical efficiency using practically achievable/manageable temperatures is 70-85%!

# Engines running on adiabatic combustion



$$w_{\max \text{ adiab. comb. eng.}} = w_{\max \text{ chem. eng.}} - T^* \Delta S_{ad \text{ comb}}$$

$$\left( \eta_{\text{best adiabatic comb}} \right) \approx \frac{w_{\max \text{ comb. eng.}}}{\Delta G_R}$$

$$\approx \frac{w_{\max \text{ chem. eng.}}}{\Delta G_R} - \left| \frac{T^* \Delta S_{ad \text{ comb}}}{\Delta G_R} \right|$$

$$= 75\%$$

Keeping **the reaction isothermal and in equilibrium** with the environment produces maximum work

$$Q - W = H_{out} - H_{in} = \Delta H_R$$

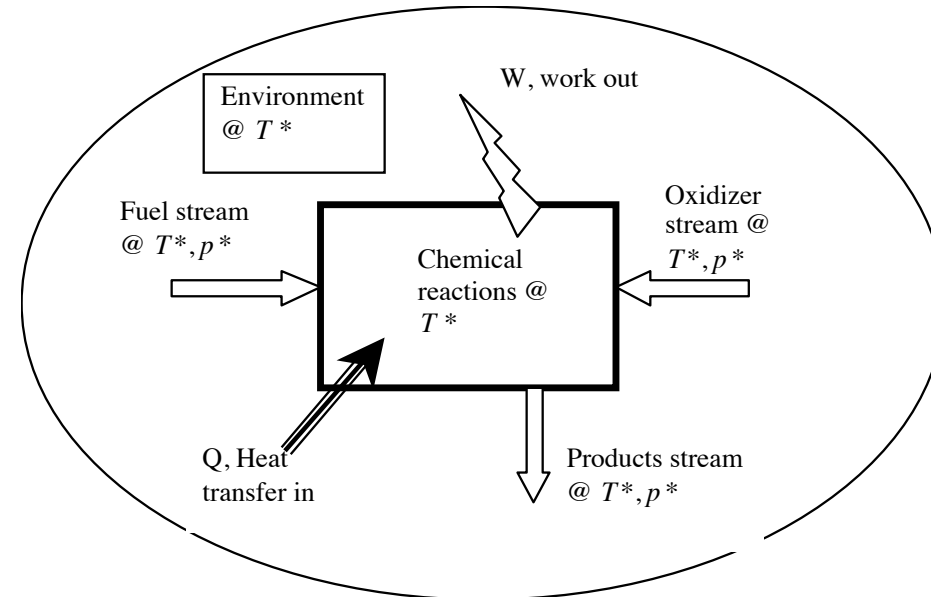
$$\frac{Q}{T^*} = S_{out} - S_{in} = \Delta S_R$$

$$Q = T\Delta S_R \quad \text{heat added}$$

$$\begin{aligned} -W &= (H - TS)_{out} - (H - TS)_{in} \\ &= \Delta H_R - T\Delta S_R \end{aligned}$$

$$W = -\Delta G_R \quad \text{work produced.}$$

The isothermal reaction produces work = Gibbs free energy of reaction, and rejects heat =  $T \cdot$  entropy of reaction



$$T\Delta S_R = \Delta H_R - \Delta G_R = Q$$

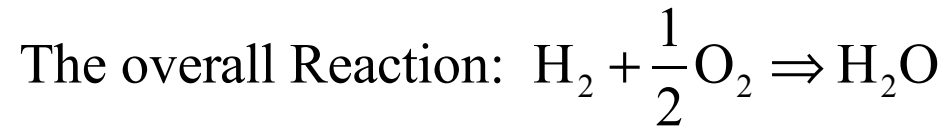
for typical exothermic reactions,

both  $\Delta H_R$  and  $\Delta G_R < 0$

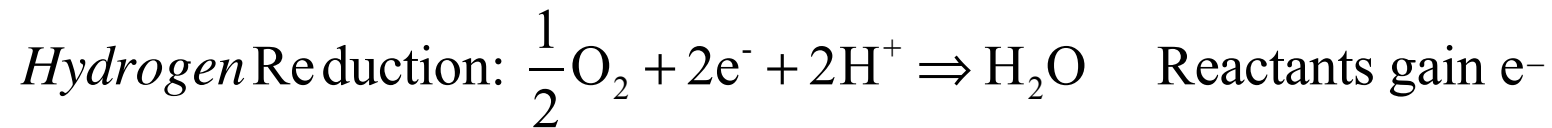
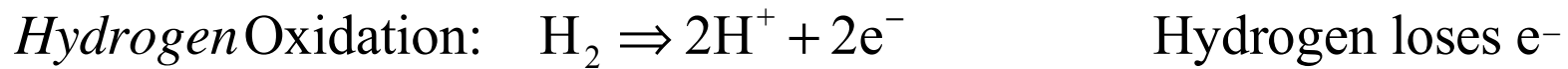
and heat is mostly rejected

(but can also be added) depending on T

How can we perform such an isothermal reaction with work transfer?



can be performed in a Redox Pair (reduction-oxidation), or two electrochemical "half reactions", across an electronically non-conducting material, leading to the formation of charged species;



$\text{H}^+$  ions diffuse through the electrolyte (acidic, +ve ion (proton) transport medium (PEMFC))

$\text{e}^-$  moves through an external resistance

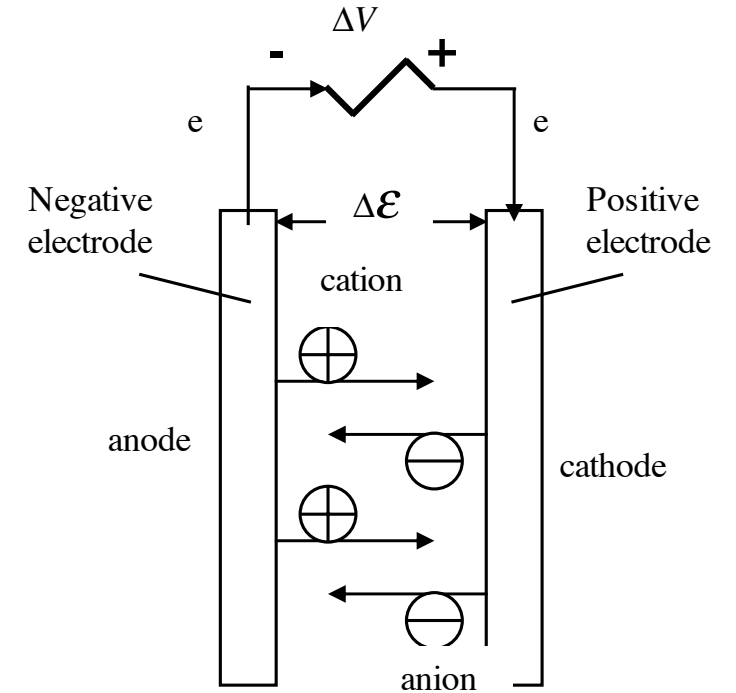
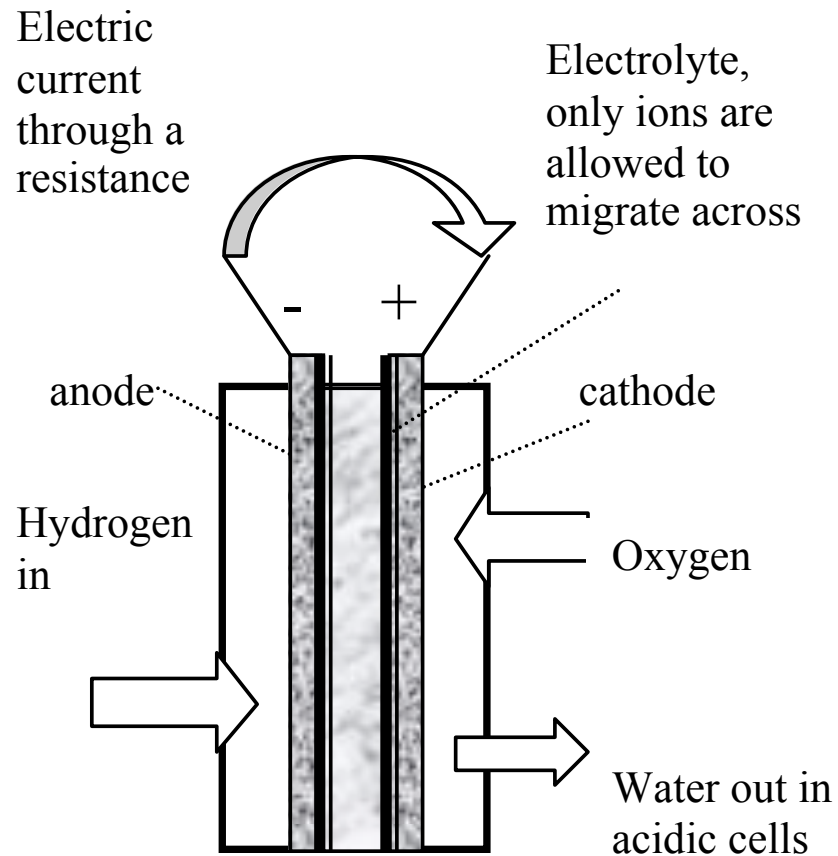
A useful note: the general definition of oxidation and reductions:

Oxidation is Loss of electron (loss of -ve charge or becoming positive)

Reduction is Gain of electron (gain of -ve charge or becoming negative)

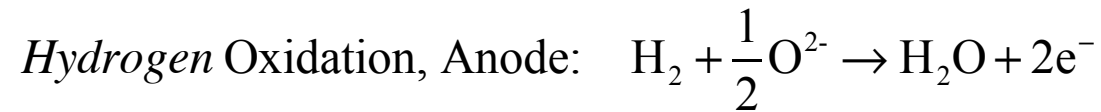
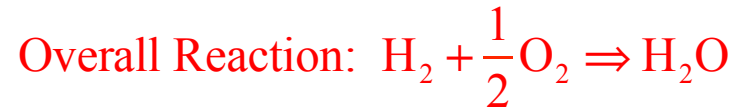
Hydrogen Oxidation:  $\text{H}_2 \Rightarrow 2\text{H}^+ + 2\text{e}^-$       Hydrogen loses  $\text{e}^-$

Hydrogen Reduction:  $\frac{1}{2}\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \Rightarrow \text{H}_2\text{O}$       Reactants gain  $\text{e}^-$

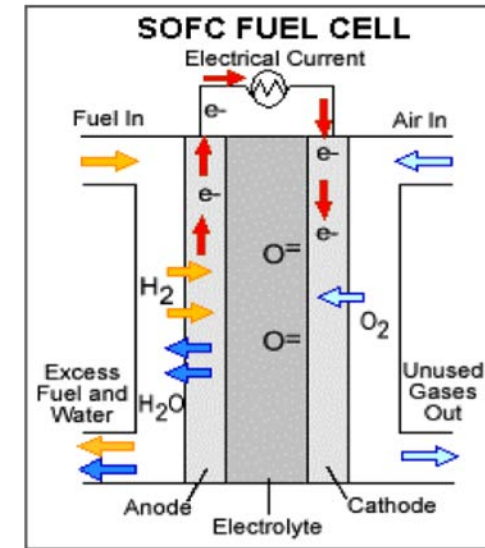


Galvanic or voltaic cell.  
 At finite current,  $\Delta V < \Delta \mathcal{E}$ .  
 In galvanic cells the anode is the -ve electrode and the cathode is the +ve electrode.

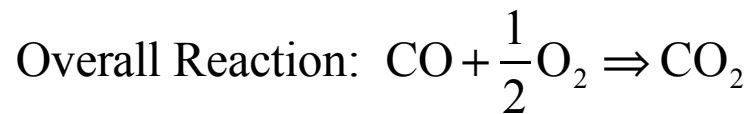
Another redox pair uses an alkaline electrolyte (transports -ve ions):



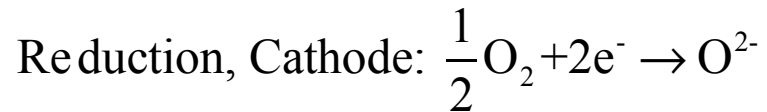
$\text{O}^{2-}$  ions move through the electrolyte from the cathode to the anode



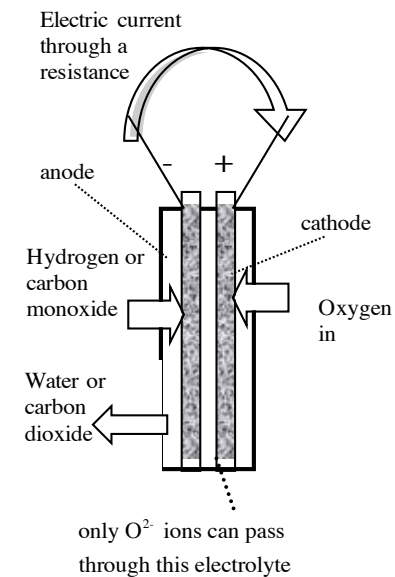
### CO Electrochemical Oxidation



The Redox Pair (two half reaction)



Can combine H<sub>2</sub> and CO in a single cell



Open circuit Work:

$$\begin{aligned}
 (-\Delta G_R(T^*, p^*)) &= \sum_{react} \nu_i' (\hat{h}_i(T^*) - T^* \hat{s}_i(T^*, p^*)) - \sum_{prod} \nu_i'' (\hat{h}_i(T^*) - T^* \hat{s}_i(T^*, p^*)) \\
 &= (-\Delta G_R^o(T^*)) - \sigma \mathfrak{R} T^* \ln \left( \frac{p^*}{p^o} \right) - \mathfrak{R} T^* \ln \left( \frac{\prod_{prod} X_i^{\nu_i''}}{\prod_{react} X_i^{\nu_i'}} \right)
 \end{aligned}$$

$$\Delta G_R^o(T^*) = \sum_{react} \nu_i' (\hat{h}_i(T^*) - T^* \hat{s}_i^o(T^*)) - \sum_{prod} \nu_i'' (\hat{h}_i(T^*) - T^* \hat{s}_i^o(T^*))$$

Important remarks:

1. Reactants are introduced separately.
2. Products mix with one of the reactant stream
3. Or products leave separately through the electrolyte.

Fuel (phase)	LHV (kJ/mol)	$-\Delta G_R^o(T^o, p^o)$ (kJ/mol)
Hydrogen (g), H <sub>2</sub>	241.8	228.6
Carbon (s), C	393.5	394.4
Methane (g), CH <sub>4</sub>	802.3	818
Ethane (g), C <sub>2</sub> H <sub>6</sub>	1427.9	1467.5
Propane (g), C <sub>3</sub> H <sub>8</sub>	2044	2108.4
Butane (g), C <sub>4</sub> H <sub>10</sub>	2658.5	2747.8

Equilibrium or Open-circuit Efficiency:

$$\eta_{OC} = \frac{W_{max}}{\Delta H_{R,H_2O}^*} = \frac{\Delta G_{R,H_2O}^*}{\Delta H_{R,H_2O}^*}$$

For separate streams for hydrogen, oxygen and water: All at 1 atm

$$\Delta G_R^o(T) = \left( \hat{h}(T) - T\hat{s}^o(T) \right)_{\text{H}_2\text{O}} - \left[ \left( \hat{h}(T) - T\hat{s}^o(T) \right)_{\text{H}_2} + \frac{1}{2} \left( \hat{h}(T) - T\hat{s}^o(T) \right)_{\text{O}_2} \right]$$

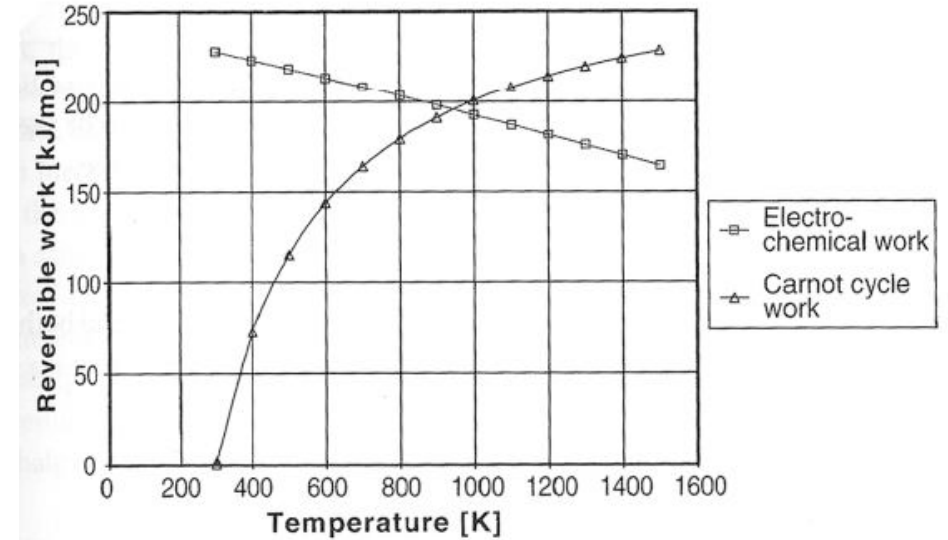
$$\hat{s}^o(T) = \hat{s}(T, p = 1 \text{ atm})$$

$$\eta_{OC} = \frac{\Delta G_{R, \text{H}_2\text{O}}^*}{\text{HHV}_{\text{H}_2\text{O}}}$$

@ T = 300 K: water leaving as liquid:  $\eta_{OC} = 237/286 = 83\%$   
 (water leaving as vapor:  $\eta_{OC} = 228/242 = 94\%$ )

@ T = 500 K: water leaving as vapor:  $\eta_{OC} = 219 / 242 = 76.5\%$

@ T = 1000 K: water leaving as vapor:  $\eta_{OC} = 193 / 245 = 67.3\%$



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- Reversible work produced by H<sub>2</sub>/O<sub>2</sub> cell and a simple Carnot engine.
- Based on the HHV (284 kmol H<sub>2</sub>). Cross over point is 950 K.
- Comparison is not necessarily meaningful.



## Open Circuit Cell Potential:

$$\hat{w}_{\max} = \Delta\hat{g}_R = \Delta\mathcal{E} \zeta \text{ (work of moving charge } \zeta \text{ across a potential difference } \Delta\mathcal{E}\text{)}$$

$$\zeta = n_e \zeta_{e^-} N_a = n_e \mathfrak{F}_a$$

$n_e$ : number of electrons produced when oxidizing one fuel molecule

$$N_a = 6.023 \times 10^{23} \text{ mole}^{-1} \text{ (Avogadro's number)}$$

$$\zeta_{e^-} = -1.602 \times 10^{-19} \text{ Coulombs/electron}$$

$$\mathfrak{F}_a = \zeta_{e^-} N_a = 9.6485 \times 10^4 \text{ Coulombs/mole (Faraday's number)}$$

for the hydrogen-oxygen,  $n_e = 2$ , and  $\zeta = 2\zeta_{e^-} N_a = 2\mathfrak{F}_a$ ,

@ 300K,  $\Delta\mathcal{E} = 1.18$  volts with water leaving in vapor form

$\Delta\mathcal{E} = 1.23$  volts with water leaving in liquid form.

For the methanol-oxygen reaction,  $\Delta\mathcal{E}_o = 1.21$  V.

# The Nernst Equation: effect of pressure and fuel concentration

$$\Delta\mathcal{E}(p^*, T^*) = \Delta\mathcal{E}^0(T^*) - \frac{\mathcal{R}T^*}{n_e \mathcal{S}} \ln \left( \frac{\prod_{prod} (p_i^*)^{v_i''}}{\prod_{react} (p_i^*)^{v_i'}} \right) = \Delta\mathcal{E}^0(T^*) - \frac{\sigma \mathcal{R}T^*}{n_e \mathcal{S}_a} \ln \left( \frac{p^*}{p_o} \right) - \frac{\mathcal{R}T^*}{n_e \mathcal{S}_a} \ln \left( \frac{\prod_{prod} X_i^{v_i''}}{\prod_{react} X_i^{v_i'}} \right)$$

$$= \Delta\mathcal{E}^0(T^*) + \Delta\mathcal{E}_p(p^*, T^*) + \Delta\mathcal{E}_{conc}(X_i, T^*) \quad \text{where } \sigma = \sum_{prod} v_i'' - \sum_{react} v_i'$$

for a hydrogen-oxygen cell:  $\Delta\mathcal{E}_{conc} = \frac{\mathcal{R}T^*}{2\mathcal{S}_a} \left( \ln(X_{H_2})_{fuel} + \frac{1}{2} \ln(X_{O_2})_{oxy} - \ln(X_{H_2O})_{sep/fuel/oxy} \right)$

Equation applied at one point (under equilibrium, things are subtle).

Lower reactants concentrations decrease the OC potential, especially at higher T.

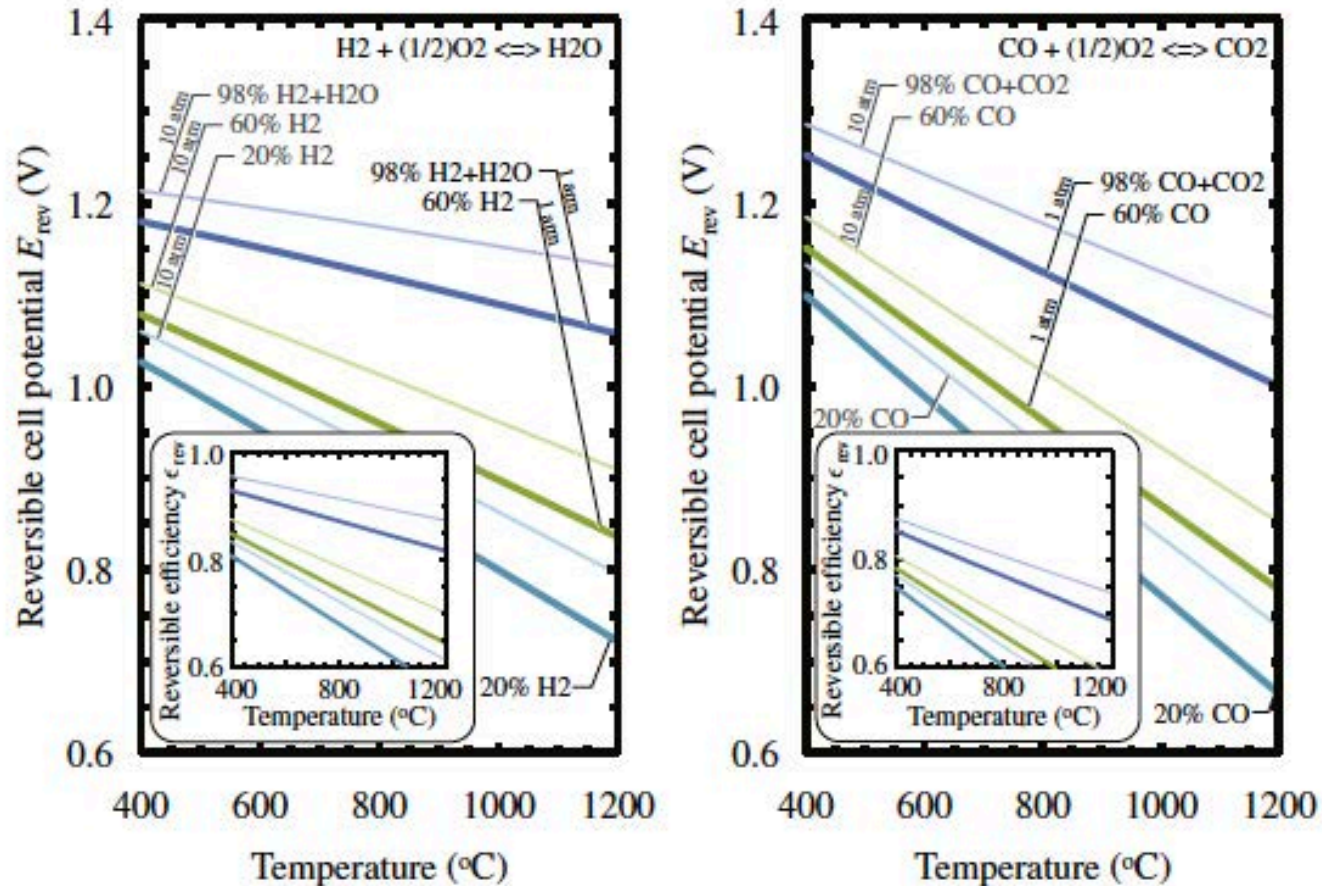
Using air instead of oxygen also penalizes the potential,  $\Delta\mathcal{E}_{conc, O_2} = 2.15 \times 10^{-5} T^* \ln(0.21) = -0.012 @ 350K$

Using products of methane reforming as fuel:  $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

$$X_{H_2} = 0.8, \quad \Delta\mathcal{E}_{conc} = 2.15 \times 10^{-5} T^* \ln(0.8)$$

this reduces the OC by  $\Delta\mathcal{E}_{conc, H_2} = 0.00168V (@350K)$

# Impact of fuel, concentration, temperature and pressure



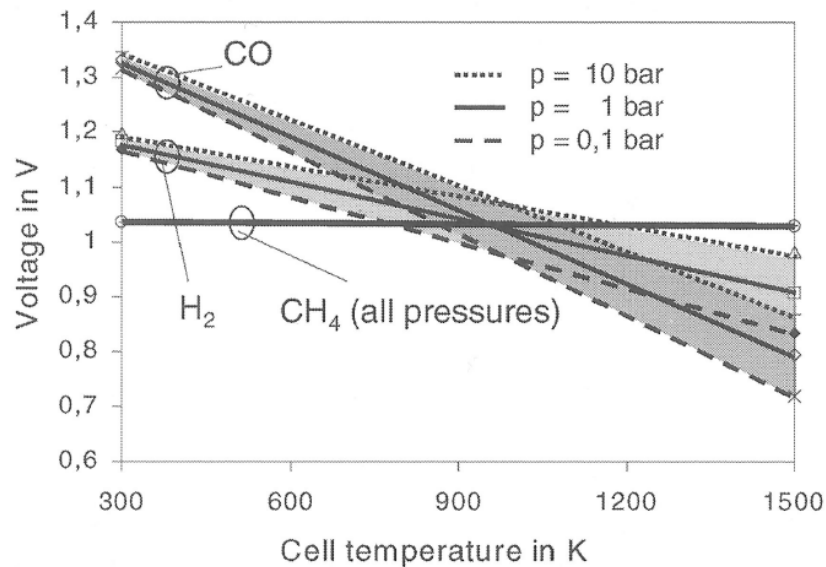
$P=1$ , thick lines  
 $P=10$  thin line

Colors for different  
fuel concentrations

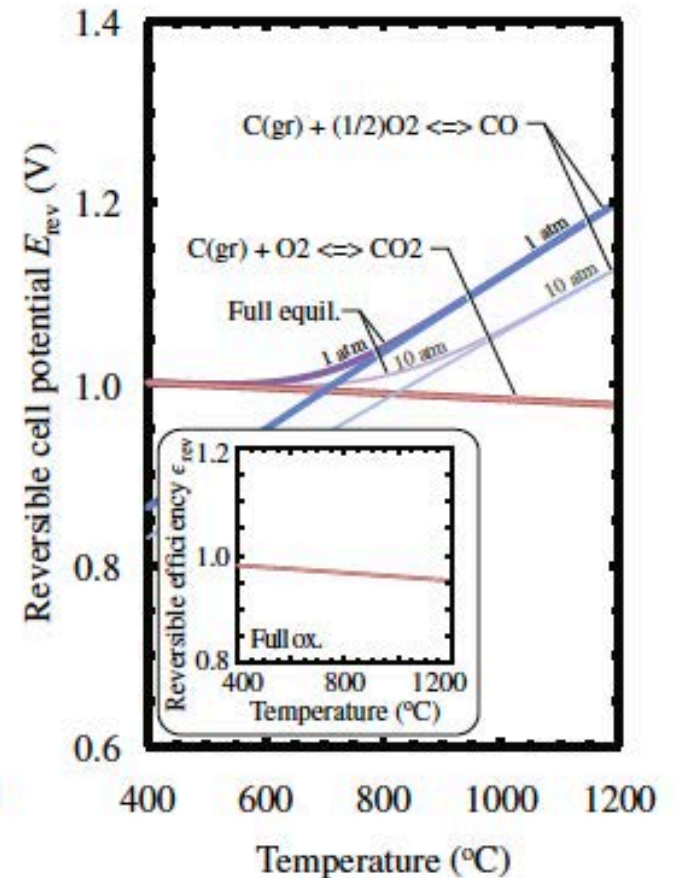
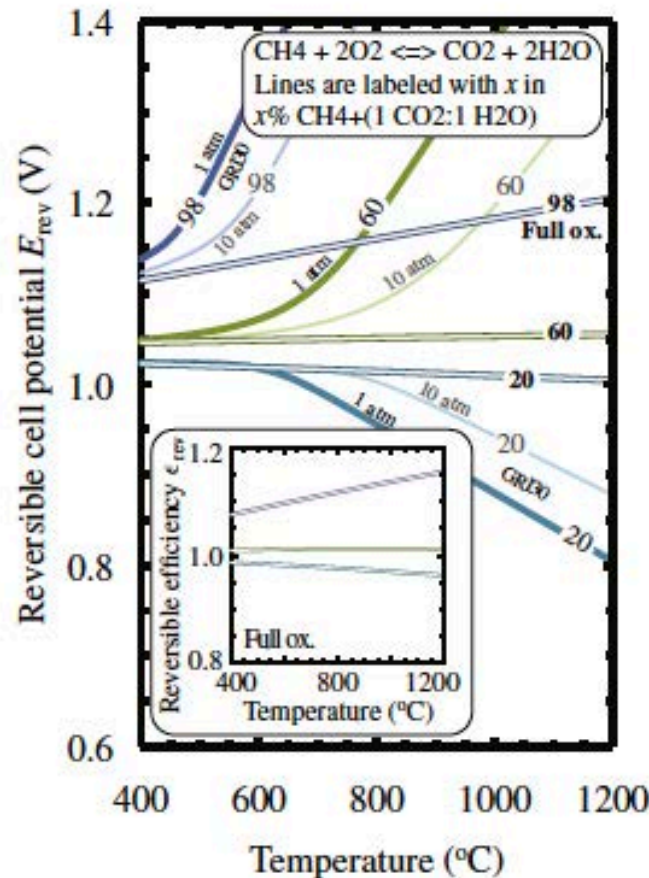
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# Impact of fuel, concentration, temperature and pressure



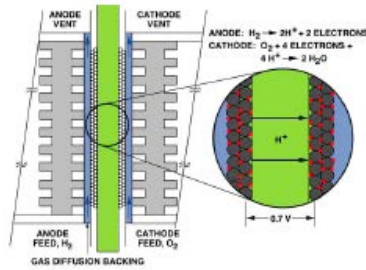
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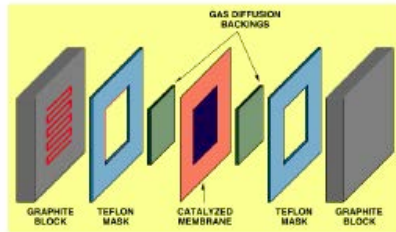
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# Fuel Cell Components



(a)

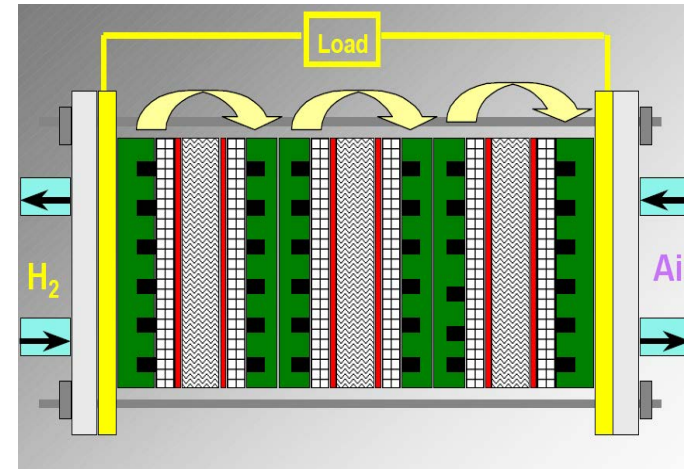
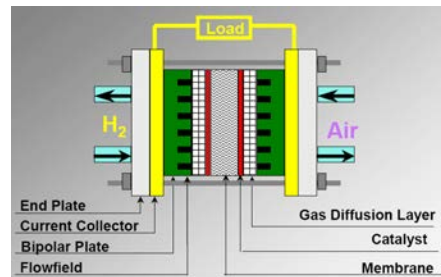


(b)

Figure 3-1 (a) Schematic of Representative PEFC (b) Single Cell Structure of Representative PEFC(1)

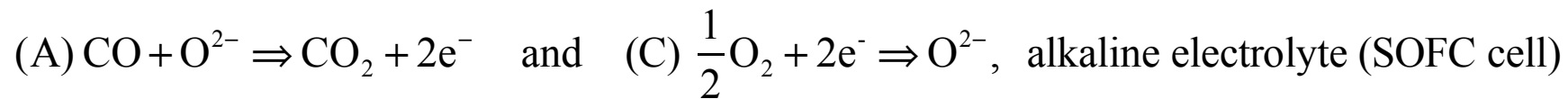
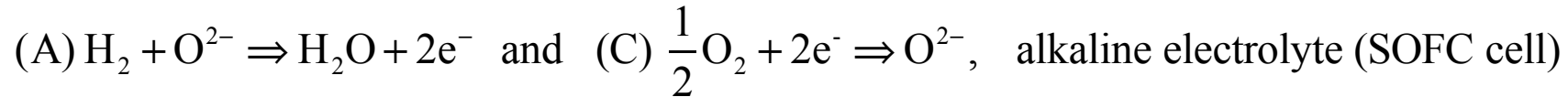
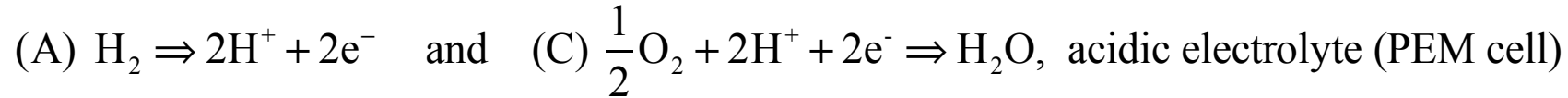
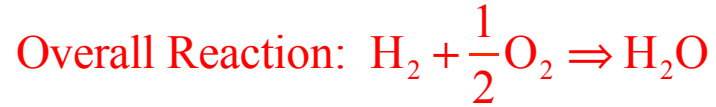
Also known as membrane-electrode-assembly (MEA), and made of one “physical” plate with anode and electrode material deposited on both side.

The membrane is a polymer (nafion) for low T cells and a ceramic plate for high T cells.



Images courtesy of DOE.

# Electrochemical Reactions and Types of Fuel Cells

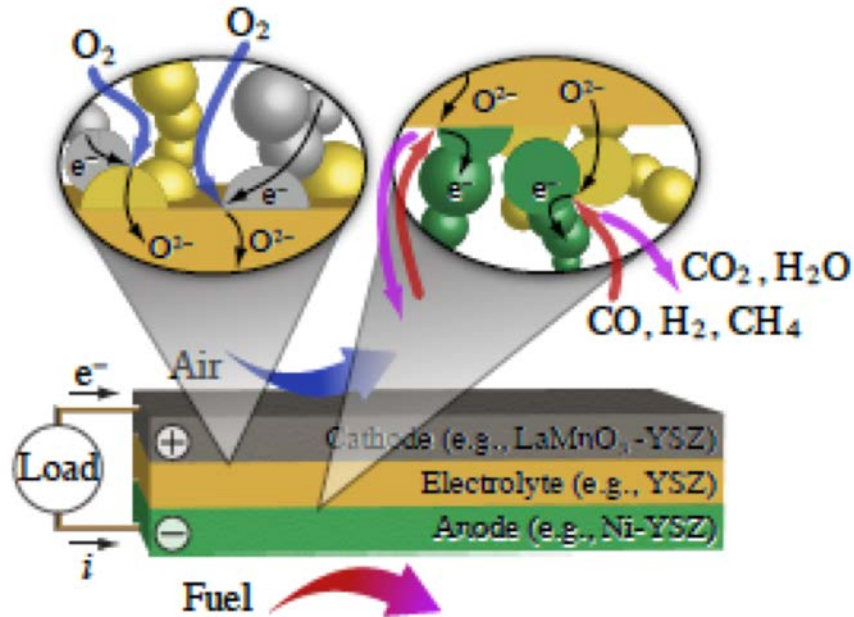


in all, two electrons are produced per oxygen atom.

## Fuel Cell Types

<b>Fuel cell</b>	<b>Proton Exchange</b>	<b>Alkaline</b>	<b>Phosphoric Acid</b>	<b>Molten Carbonate</b>	<b>Solid Oxide</b>
<b>Electrolyte</b>	Polymer ion exchange membrane	potassium hydroxide in asbestos	liquid phosphoric acid in SiC	liquid molten carbonate in LiAlO <sub>2</sub>	Perovskites
<b>Electrode</b>	Carbon	Transition metals	Carbon	Nickels and nickel oxides	perovskites/ metal cermet
<b>Catalyst</b>	Platinum	Platinum	Platinum	Electrode material	Electrode material
<b>Interconnect</b>	Carbon or metal	Metal	Graphite	Stainless steel of nickel	Nickel, ceramics
<b>Temperature</b>	40 - 80 °C	65 - 220 °C	205 °C	650 °C	600 -1000 °C
<b>Charge Carrier</b>	H <sup>+</sup>	OH <sup>-</sup>	H <sup>+</sup>	CO <sub>3</sub> <sup>=</sup>	O <sup>=</sup>
<b>fuel</b>	Hydrogen	Hydrogen	Hydrogen	Hydrocarbon	hydrocarbon

## Materials for Solid Oxide Fuel Cells



In the left bubble, oxygen is reduced at the cathode and oxygen ions are conducted through the electrolyte. Oxygen ions move into the anode (right bubble), where they are used to oxidize the fuel at the three-phase boundary TPB). Electrons released in the charge-transfer reactions are conducted through the anode (metal), to the external circuit.

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LaMnO<sub>3</sub> (lanthanum manganese oxide) is used to catalyze the oxygen reduction reaction on the cathode side  
YSZ (Yittria stabilized zirconia) is use as an ion transport membrane  
Ni (nickel) is used to catalyze the fuel oxidation reaction on the anode side.

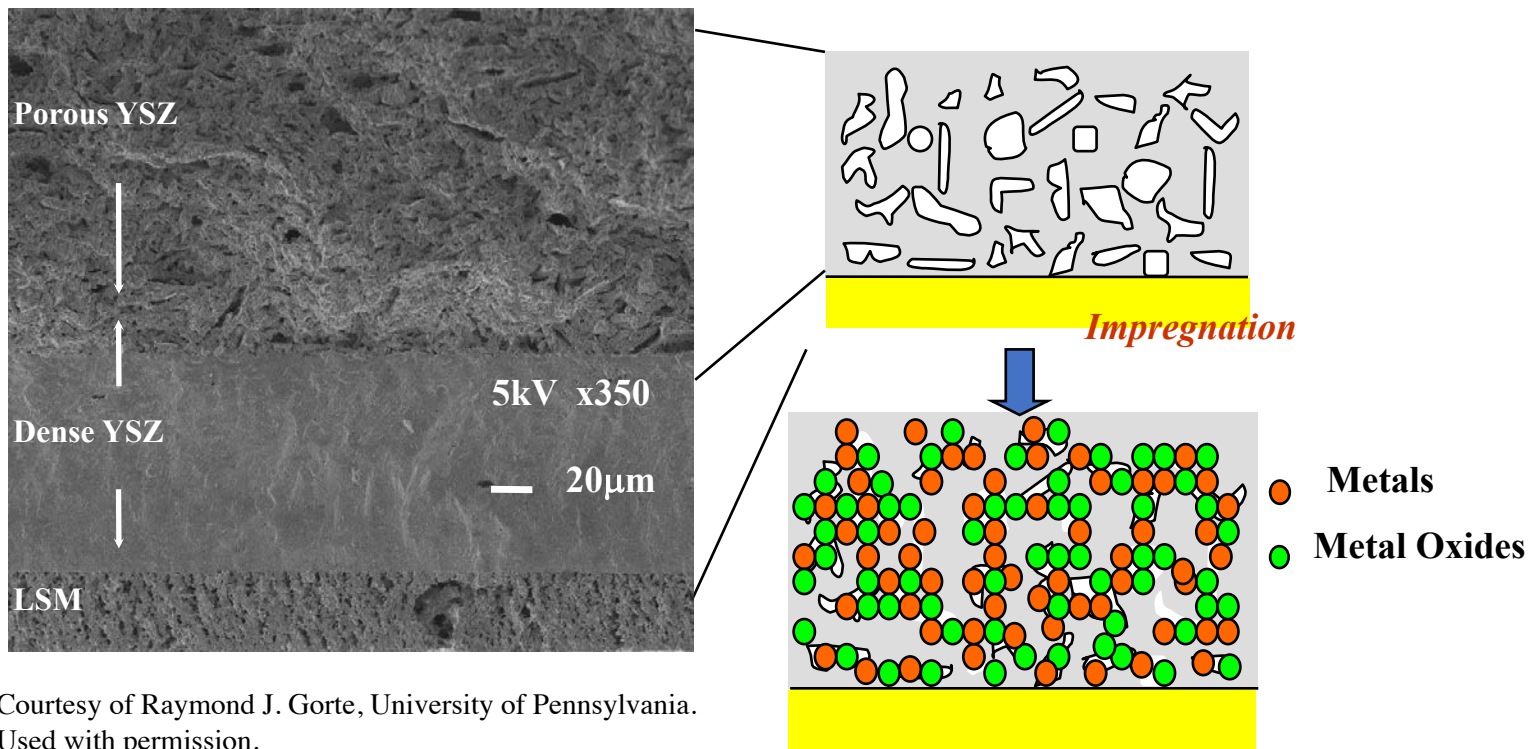


# Solid Oxide Fuel Cells

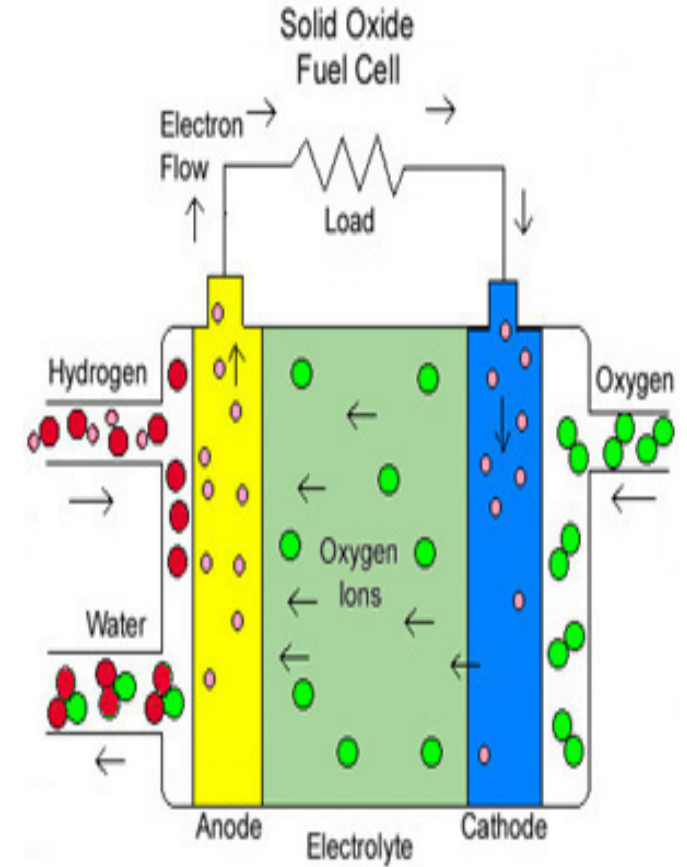
High T cells use regular metals as catalysts

**Electrolyte: YSZ, Anode: Ni-YSZ, Cathode: Sr-doped LaMnO<sub>3</sub>**

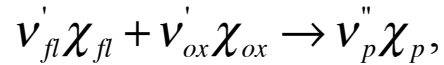
**YSZ = yttria – stabilized zirconia**



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# Fuel Utilization and its impact on the Open Circuit Potential and Cell Efficiency



$$\Delta \mathcal{E} = \Delta \mathcal{E}^{(o)} - \frac{\sigma \mathcal{R}T^*}{n_e \mathcal{F}_a} \ln \left( \frac{p}{p_o} \right) + \frac{\mathcal{R}T}{n_e \mathcal{F}_a} \ln \left( \frac{X_{fl} X_{ox}^{v'_o}}{X_p^{v''_p}} \right)$$

concentrations of fuel and oxidizer decrease between inlet and outlet  
as both are consumed according to their stoichiometric ratio

Partial Fuel utilization:  $\varphi = \frac{n_{fl1} - n_{fl2}}{n_{fl1}}$

@ Inlet:  $X_{fl1} = \frac{1}{1 + n_{d1}}, \quad X_{ox1} = 0.21,$

@ exit:  $X_{fl2} = \frac{1 - \varphi}{1 - \varphi + n_{d1} + v''_p \varphi}, \quad X_{ox2} = \frac{(1 - \varphi) v'_{ox}}{3.76 v'_{ox} + (1 - \varphi) v'_{ox}}$

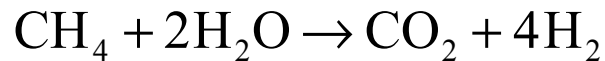
using values at exit gives lower  $\Delta \mathcal{E}$

For a SOFC where products form  
in the fuel channel



Open Circuit potential for different fuel utilization and for 50% oxygen utilization, cell is fueled by hydrogen produced by SMR (Fuel Cell Explained, Laramie et al.)

If products of methane-water reforming are used:



The fuel mixture *has*  $X_{\text{H}_2} = 0.8$

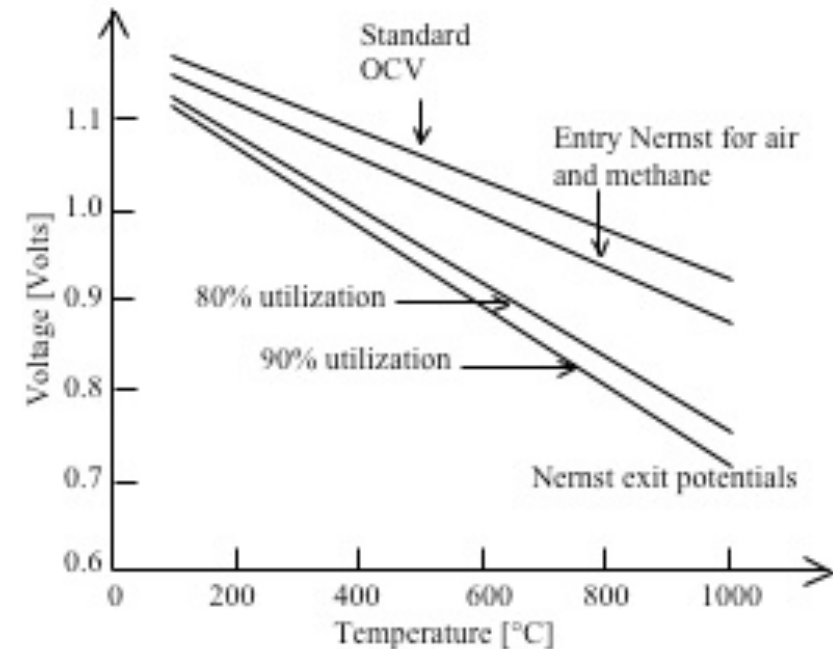
Oxidizer is air,  $X_{\text{O}_2\text{-inlet}} = 0.21$

Much air is flown to ensure that

oxidation is not limited by oxygen

Assume that @ exit, 50% utilized of oxygen,

$$X_{\text{O}_2\text{-exit}} = 0.105$$



There advantages to running the cell at low T, but chemistry is slow and we need a precious metal catalyst, which make it expensive and sensitive to fuel impurities.

- In this example, products are mixed with fuel in the fuel channel, reducing the fuel concentration towards the exit.
- Methane can also be "naturally" reformed internally, hydrogen and CO are more electro-chemically active

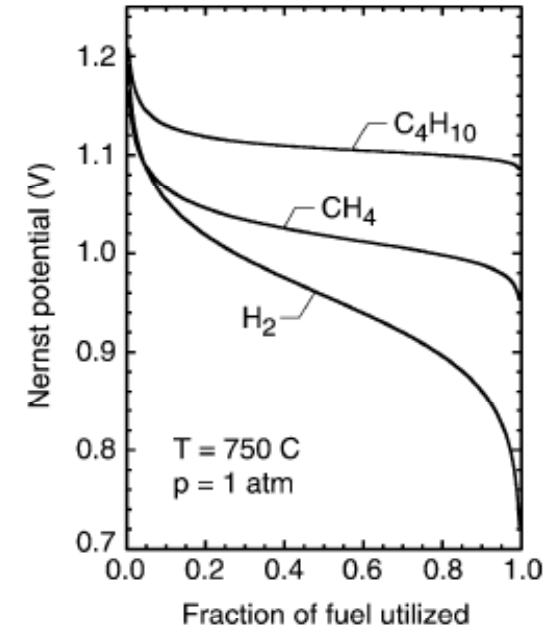
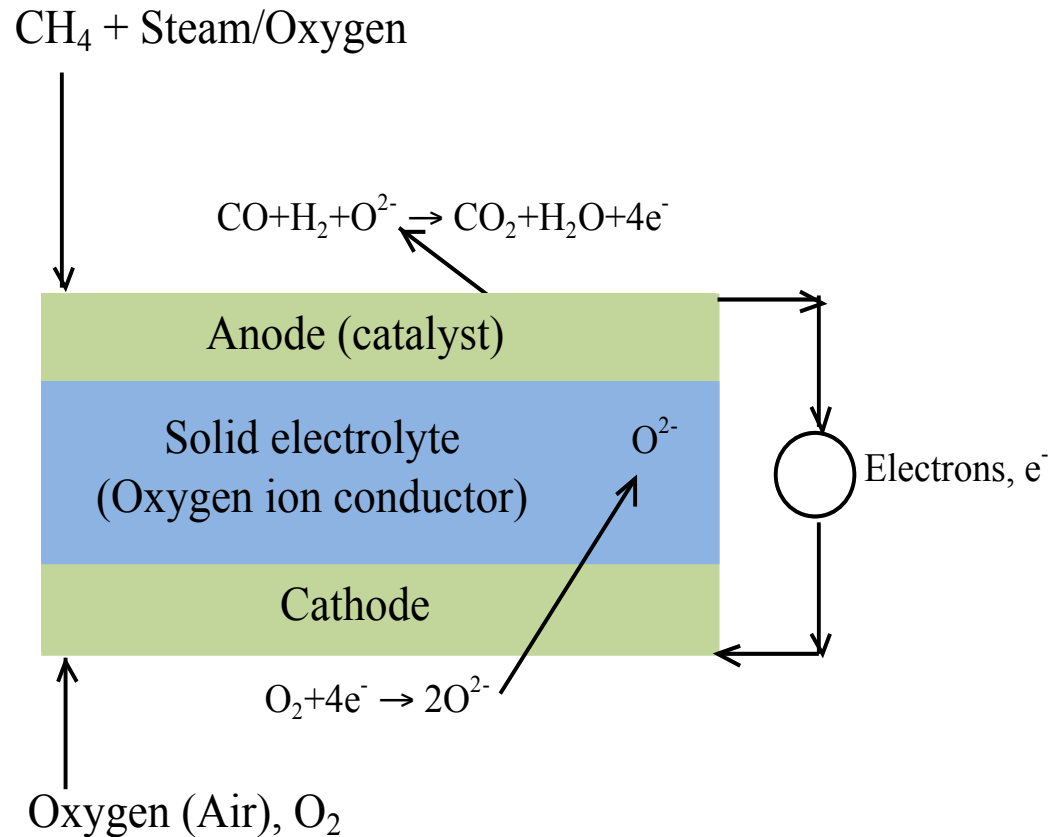
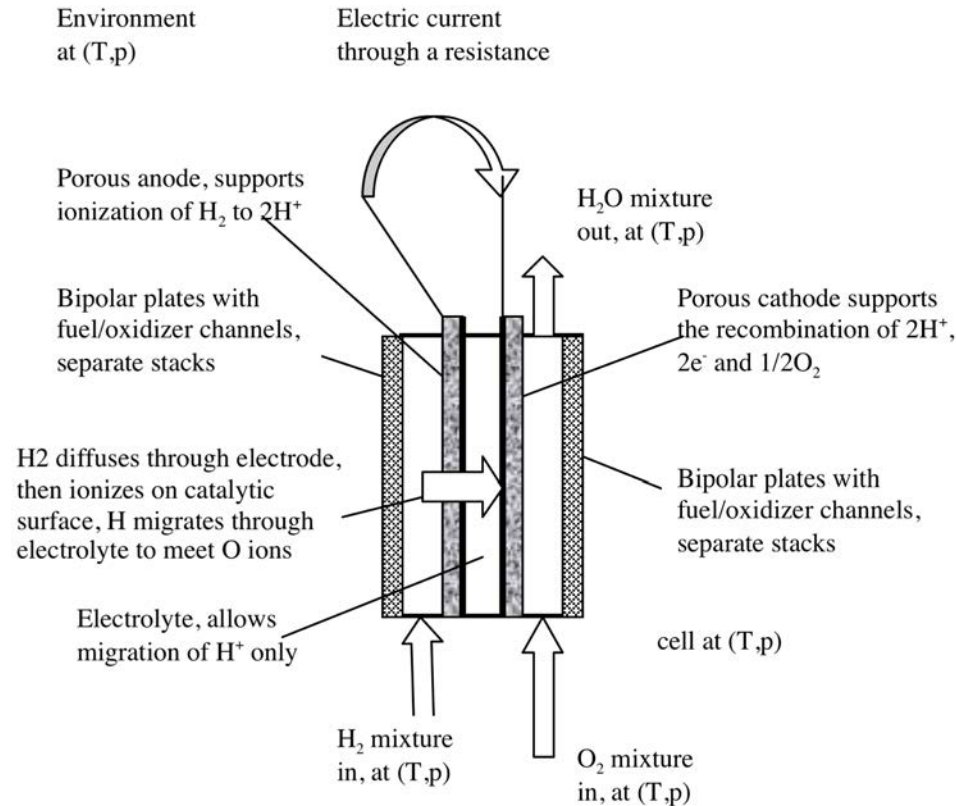


Fig. 3. Nernst potential for three fuels-air systems as a function of percentage of the fuel utilization. As the fuel is "utilized" it is converted to stoichiometric products that dilute the fuel on the anode side. The air is not depleted in this system.

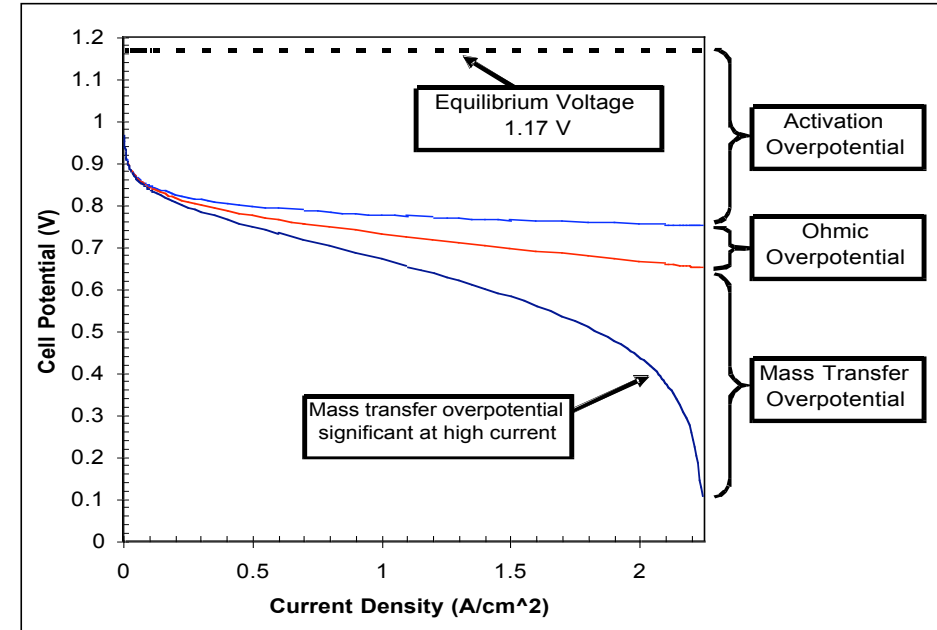
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# Fuel Cell Performance at Finite Current (Power) Conditions

Faraday's Law:  $I = n_e \mathcal{F} \dot{n}_f$  or  $i = n_e \mathcal{F} a j_f$



Components of a PEMFC



Relative contributions depend on design and operating conditions:

- Catalysis, type and density.
- Thickness of electrodes and membrane.
- Water management (in PEM cells).

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2.60J Fundamentals of Advanced Energy Conversion  
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