Losses in Fuel Cells

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

Fuel Cell Thermodynamics

Thermodynamics

Nobel laureate Richard Feynmann said,

"In physics today, we have no knowledge of what energy is."

Self-consisting "laws" from fundamental assumptions based on human experience.

Q: How to "prove" Newton's Law or Schrodinger Equation?

Internal energy (U)

No movement in macroscopic view, but microscopic movement exist.

- Kinetic energy
  - Molecular movement & vibration
- Chemical (potential) energy
  - Bonding between atoms

Laws of Thermodynamics

First law: conservation of energy

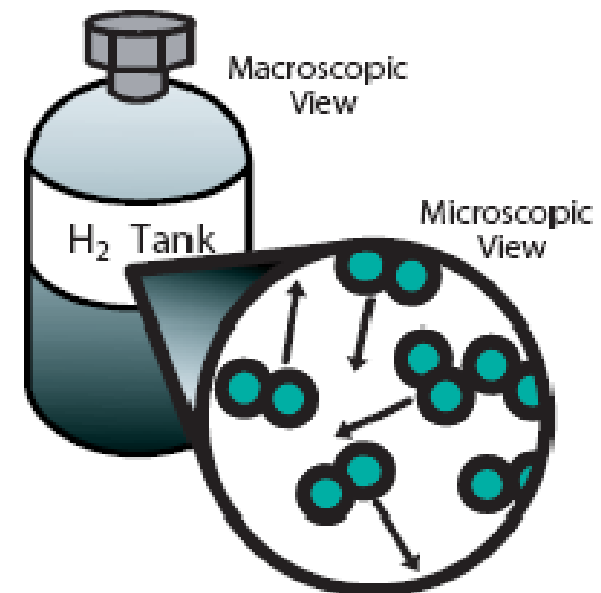$d(Energy)_{univ} = d(Energy)_{system} + d(Energy)_{surroundings} = 0$

$d(Energy)_{system} = -d(Energy)_{surroundings}$

$dU = dQ - dW$

$(dW)_{mech} = pdV$

$dU = dQ - pdV$

Second law: Entropy of a system increases ($dS_{univ} \geq 0$)

Macroscopic: $dS = dQ_{rev}/T$

Microscopic: $S = k \log \Omega$

k: boltzmann's constant

Ω: No. of possible microstates accessible to the system

Entropy Example

a)   b)
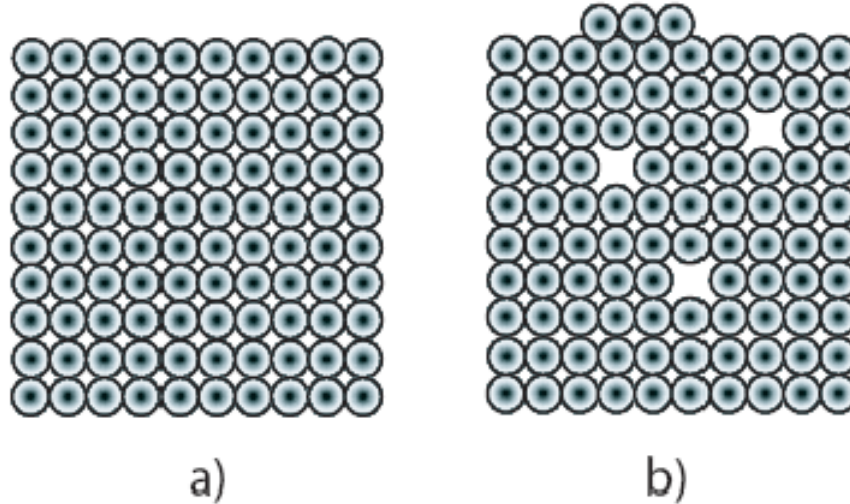
a) A perfect crystal of 100 atoms: only 1 microstate (configuration)

  $S = k \log \Omega = k \log 1 = 0$

b) A crystal of 97 atoms with 100 lattice space:

  $\Omega = {}_{100}C_3 = 1.6 * 10^5$

  $S = 1.66 * 10^{-22}$ J/K

Thermodynamic Potentials

Rules describe energy transfer form one form to another

Let's define four potentials U(S,V), H(S,p), G(T,p),F(T,V) for the variables S, V, T, p

Starting from dU = dQ – pdV = TdS – pdV ⇔ U = U(S, V) or

$$\left(\frac{dU}{dS}\right)_V = T \qquad \left(\frac{dU}{dV}\right)_S = -p$$

(T, p)	(S, p)	(T, V)
$G = U - \left(\frac{dU}{dS}\right)_V S - \left(\frac{dU}{dV}\right)_S V$	$H = U - \left(\frac{dU}{dV}\right)_S V$	
$G = U - TS + pV$	$H = U + pV$	$F = U - TS$
$dG = dU - TdS - SdT + pdV + Vdp$	$dH = dU + pdV + Vdp$	
$dG = -SdT + Vdp$	$dH = TdS + Vdp$	$dF = -SdT - pdV$

Thermodynamics Potential

-TS

+pV

U Internal Energy

U = Energy needed to create a system

F Helmholtz Free Energy

$F° = U° - TS$

F = Energy needed to create a system minus the energy provided by the environment

H Enthalpy

$H° = U° + pV$

H = Energy needed to create a system plus the work needed to make room for it

G Gibbs Free Energy

$G° = U° + pV - TS$

G = Total energy to create a system and make room for it minus the energy provided by the environment

Available Work Under Constant T, P
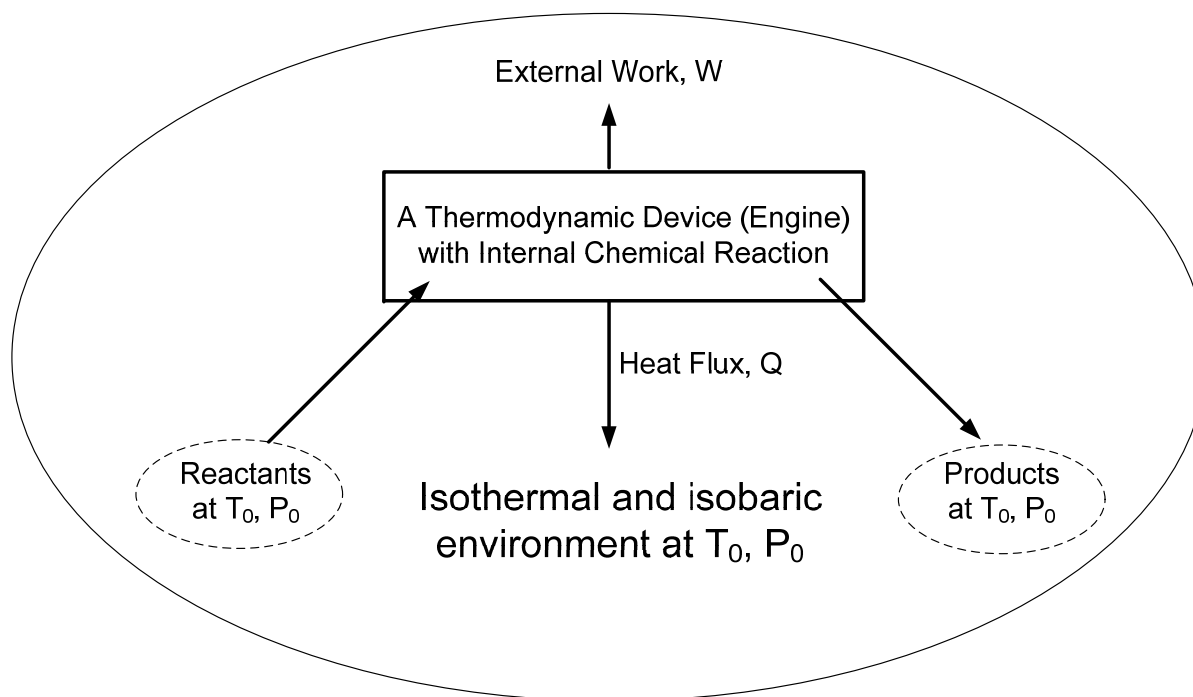
$$H_{Reactants}(T_0, P_0) = H_{Products}(T_0, P_0) + Q_{rev} + W$$

$$W = H_{Reactants}(T_0, P_0) - H_{Products}(T_0, P_0) - Q_{rev}$$
$$= -\Delta H(T_0, P_0) - Q_{rev}$$

$$dS(T_0, P_0) = \frac{dQ_{rev}}{T_0}$$

$$dS(T_0, P_0) = S_{Reactants}(T_0, P_0) - S_{Products}(T_0, P_0) = -\Delta S(T_0, P_0)$$

$$= \int \frac{dQ_{rev}}{T_0} = \frac{Q_{rev}}{T_0}$$

$$Q_{rev} = -T_0 \Delta S(T_0, P_0)$$

$$W = -\Delta H(T_0, P_0) - Q_{rev}$$
$$= -\Delta H(T_0, P_0) + T_0 \Delta S(T_0, P_0)$$
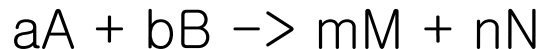$$= -\Delta G(T_0, P_0)$$

Enthalpy of Reaction

Heat of reaction

  dH = TdS + Vdp

  $\Leftrightarrow$ dH = TdS = dQ (heat of reaction)

     = dU + dW for p=const

For general reactions (molar based)

     aA + bB -> mM + nN

Δh_{rxn} = { mΔh(M) + nΔh(N) } − { aΔh(A) + bΔh(B) }

similar for entropy: Δs_{rxn} = {mΔs(M)+nΔs(N)}−{aΔs(A)+bΔs(B)}

Temperature dependency

$$\Delta \hat{h}_f = \Delta \hat{h}_f^0 + \int_{T_0}^{T} c_p(T) dT \qquad \hat{s} = \hat{s}^0 + \int_{T_0}^{T} \frac{c_p(T)}{T} dT$$

Gibbs Free Energy

Lab environment (p=const, T=const)

Among four thermodynamic potentials, Gibbs energy difference drives the spontaneous chemical reaction

$$dG_{T,V} \leq 0$$

$$dG = dH - TdS$$

Reaction:

$$A \Leftrightarrow B$$
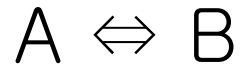
Extent of a reaction ξ: amount of substahce that reacts from A to B and vice versa $d\xi = -dn_A = dn_B$

$\Delta G=0$ reaction is in Equilibrium

$\Delta G<0$ reaction is in Forward direction

$\Delta G>0$ reaction is in Backward direction

Gibbs Free Energy

Gibbs Energy: potential under constant p & T

$G = H - TS$ by definition

$\Leftrightarrow dG = dH - TdS - SdT$

$\Leftrightarrow \Delta g = \Delta h - T\Delta s$ (can be found from tables.)

Electrical work

$dG = d(U+pV) - TdS - SdT$

$= dU - TdS - SdT + pdV + V$에

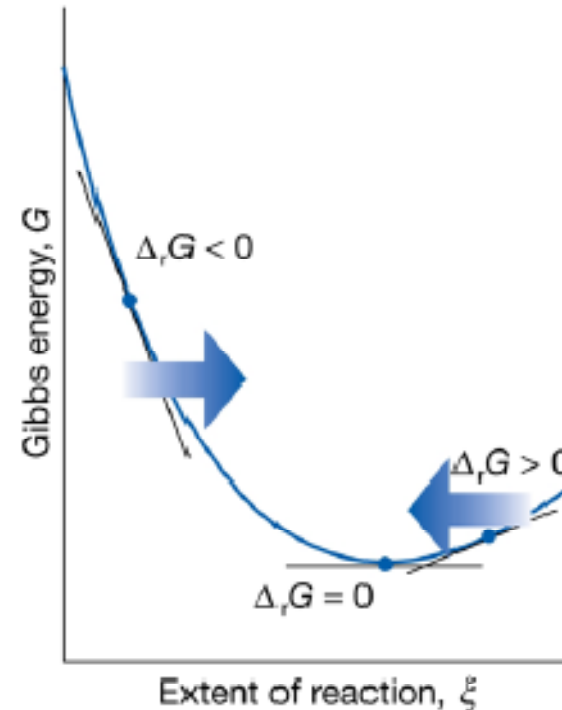$usedU = dQ-dW = d(TS) - dW$

$= SdT + TdS - (pdV + dW_{elec})$

$\Leftrightarrow dG = - dW_{elec}$

$\Leftrightarrow W_{elec} = -\Delta g_{rxn}$

This is valid for any T & p not-changing through reaction

Voltage of electric work

$W_{elec} = EQ = EnF$

F: Faraday number, n: number of electrons involved in reaction

$\Leftrightarrow E = -\Delta g/nF$

Gibbs Free Energy

Dimensional analysis

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

Units:

$$Volt = \frac{J / mol_R}{\dfrac{mol_{e^-}}{mol_R} \dfrac{C}{mol_{e^-}}}$$

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \tag{2.55}$$

has a Gibbs free energy change of -237 kJ/mol under standard state conditions, for liquid water product. The reversible voltage generated by a hydrogen/oxygen fuel cell under standard state conditions is thus:

$$E^0 = -\frac{\Delta \hat{g}^0}{nF}$$
$$= -\frac{(-237,000 \ J/mol)}{(2 \ \frac{mol \ e^-}{mol \ reactant})(96400 \ \frac{C}{mol})}$$
$$= 1.23 \ V \tag{2.56}$$

Standard Electrode Potential

e⁻

Pt   Pt H_2

H^+

Electrolyte (eg. H_2SO_4)

Electrode A

E

electrolyte H_2 on Pt

Cell potentials of most reaction are tabulated from reaction energy.
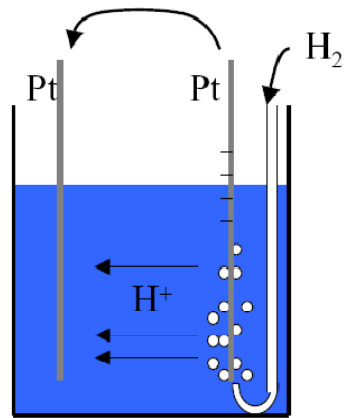
$$E_{cell} = \Sigma E_{half-reactions}$$

The H_2 reaction is defined as the reference, other half cell reactions are measured with respect to the H_2 reaction.
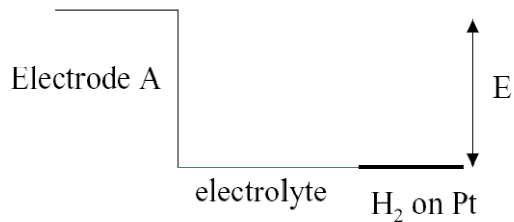
$Li^+ + e^-$	$\rightarrow$	Li	-3.04
$2H_2O + 2e^-$	$\rightarrow$	$H_2 + 2OH^-$	-0.83
$Fe^{2+} + 2e^-$	$\rightarrow$	Fe	-.440
$CO_2 + 2H^+ + 2e^-$	$\rightarrow$	$CHOOH_{(aq)}$	-0.196
$2H^+ + 2e^-$	$\rightarrow$	H_2	+0.00
$CO_2 + 6H^+ + 6e^-$	$\rightarrow$	$CH_3OH + H_2O$	+0.03
$\frac{1}{2}O_2 + H_2O + 2e^-$	$\rightarrow$	$2OH^-$	+0.40
$O_2 + 4H^+ + 4e^-$	$\rightarrow$	$2H_2O$	+1.23
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow$	$2H_2O$	+1.78
$O_3 + 2H^+ + 2e^-$	$\rightarrow$	$O_2 + H_2O$	+2.07
$F_2 + 2e^-$	$\rightarrow$	$2F^-$	+2.87

Standard Electrode Potential

Full cell potentials are obtained by summing half-cell potentials

Electrode A

electrolyte   H$_2$ on Pt   H$_2$ on Pt   electrolyte   Electrode B

Electrode A

Electrode B

E

electrolyte
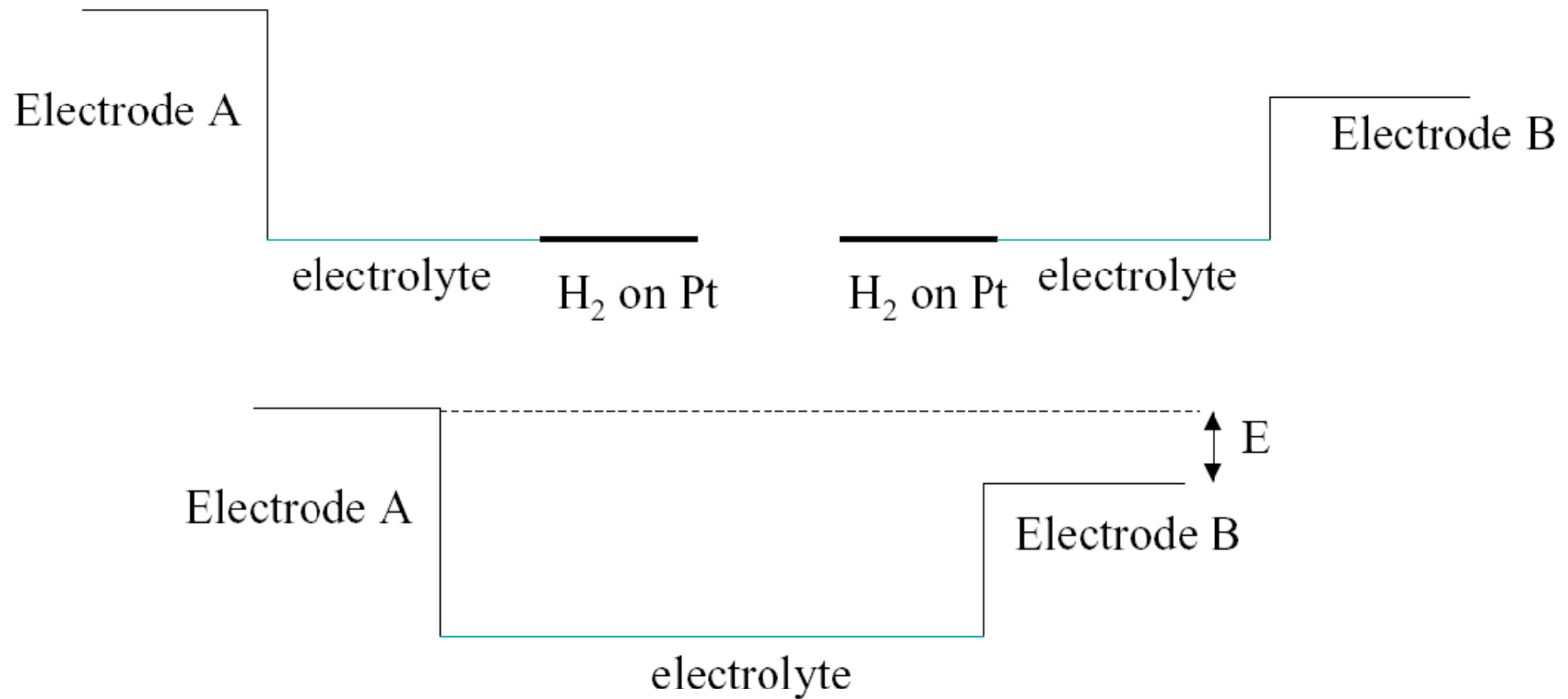
Standard Electrode Potential

Hydrogen fuel cell

$$
\begin{array}{lll}
 & H_2 \rightarrow 2H^+ + 2e^- & E^0 = \text{-}0.000 \\
+ & \frac{1}{2}(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O) & E^0 = +1.229 \\
\hline
= & H_2 + \frac{1}{2}O_2 \rightarrow H_2O & E^0_{cell} = +1.229
\end{array}
$$
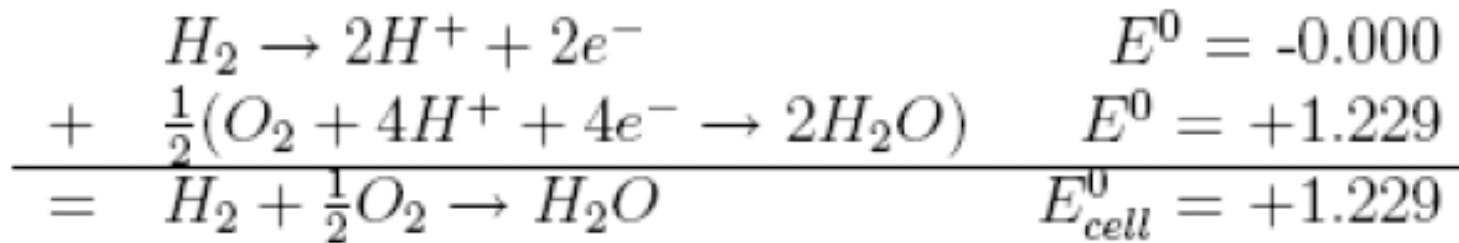
Direct methanol fuel cell

$$
CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O
$$

$$
\begin{array}{ll}
CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- & E^0 = \text{-}0.03 \\
\frac{3}{2}(O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O) & E^0 = +1.229 \\
\hline
CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O & E^0 = +1.199
\end{array}
$$
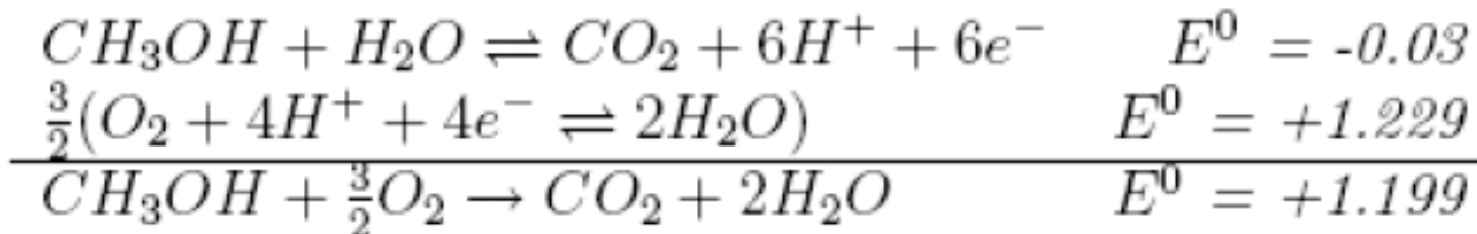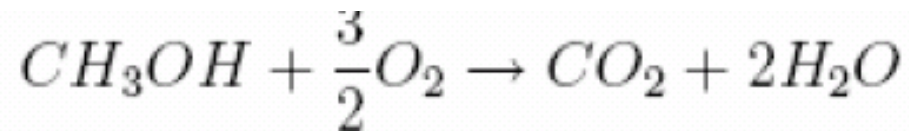
Standard Electrode Potential

Question:

What is the reversible voltage of the same reaction if OH^- is the circulating ion?

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

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad \text{E} = \text{-(-0.83) V}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad \text{E} = \text{+0.40 V}$$
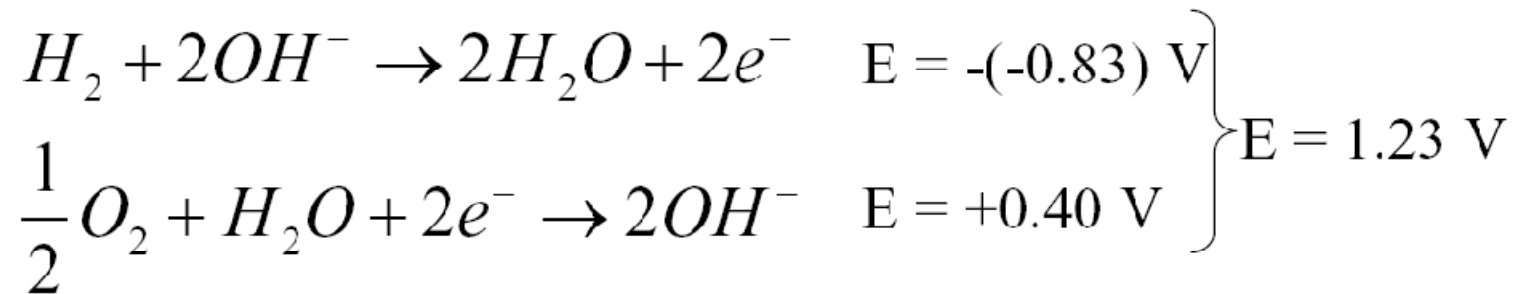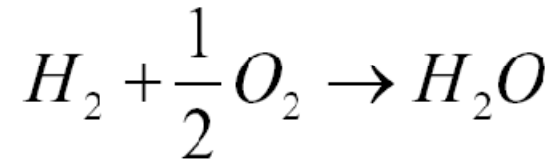
$\left. \right\} \text{E} = 1.23 \text{ V}$

Answer: The circulating ion does not determine the voltage. The overall reaction $\Delta G_{rxn} = -nFE$ sets the reversible voltage. So E = 1.23 V for this reaction as well.

Fuel Cell Efficiency

Fuel Cell

$$\varepsilon = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

$$\varepsilon = 1 - \frac{T_{low}}{T_{high}}$$

Carnot Limit

Efficiency limit / %

Temperature / Celsius
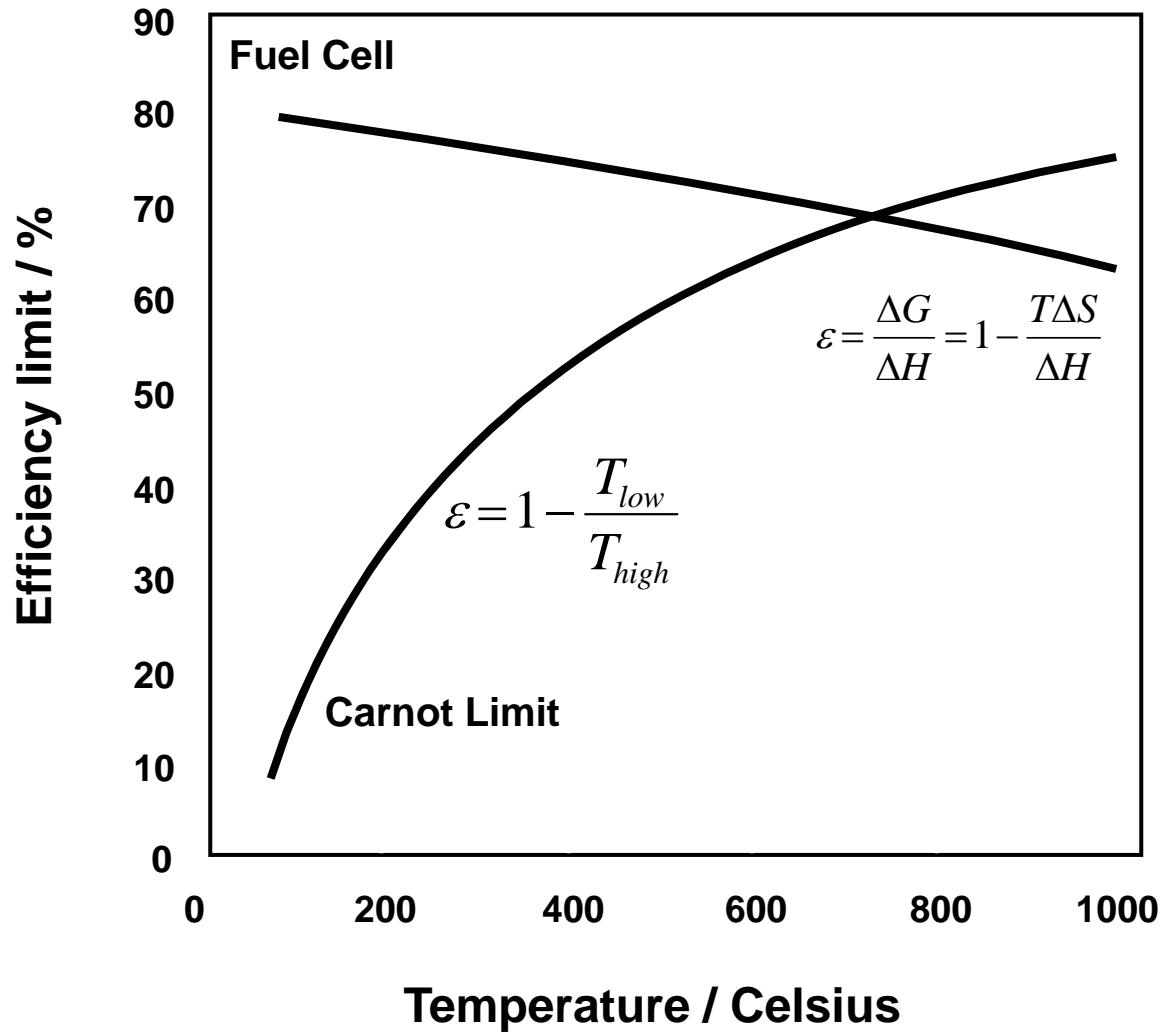
Temperature Effect
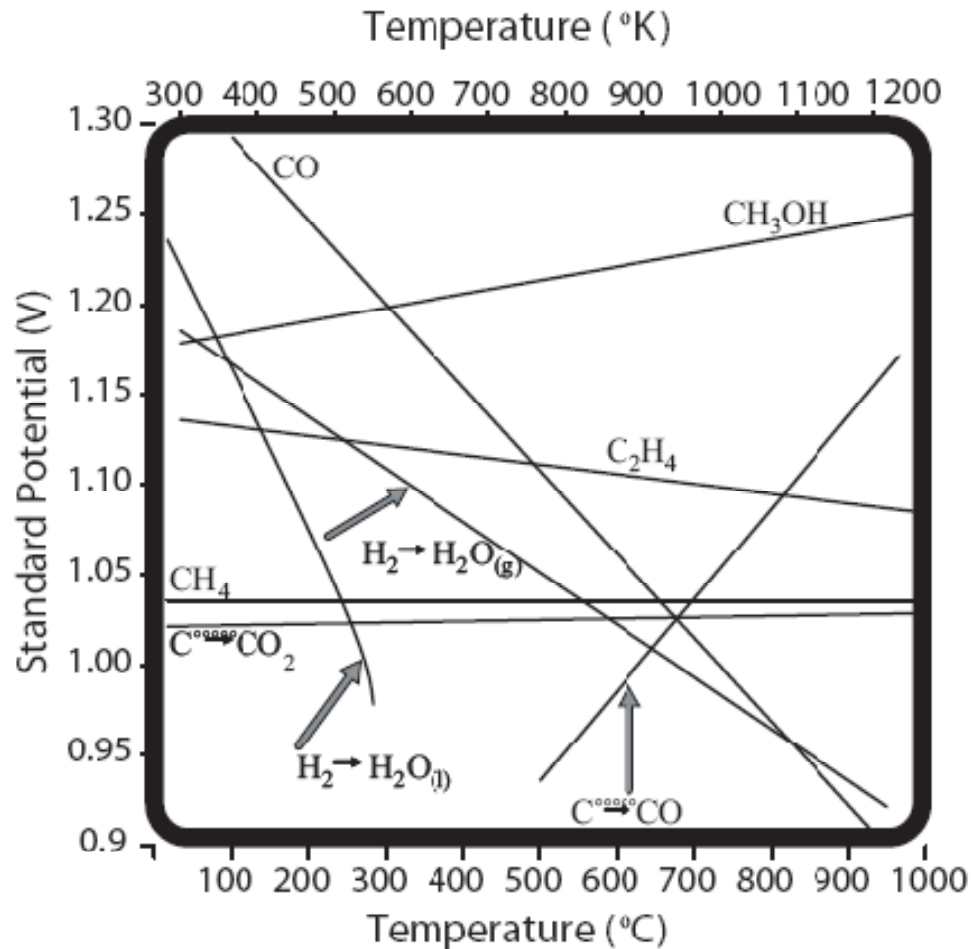
$$dG = -SdT + Vdp$$

$$\left(\frac{dG}{dT}\right)_p = -S \text{ for const p}$$

$$\left(\frac{d(\Delta g)}{dT}\right)_p = -\Delta s \quad (\Delta g = -nFE)$$

$$\left(\frac{dE}{dT}\right)_p = \frac{\Delta s}{nF}$$

$$E_T = E + \frac{\Delta s}{nF}(T - T_0)$$

As **Δs is almost constant vs. temperature,** E decrease with increasing temperature

Pressure Effect

$$dG = -SdT + Vdp$$

$$\left(\frac{dG}{dp}\right)_T = V \text{ for const } T$$

$$\left(\frac{d(\Delta g)}{dT}\right)_T = -\Delta v \quad (\Delta g = -nFE)$$

$$\left(\frac{dE}{dp}\right)_T = \frac{\Delta v}{nF}$$

$$\left(\frac{dE}{dp}\right)_T = \frac{\Delta nRT}{nFp}$$

Pressure also has minimal effect on reversible voltage.

Concentration Effect: Nernst Equation

Chemical Potential μ **is a measure of** how much free energy of a system changes dG **if you** add or remove a amount dn of substance i **while** keeping the other substances, temperature and pressure constant:

$$dG_i = \frac{\partial G}{\partial n_i} dn_i = \mu_i dn_i$$

Combining the first Law with second law for an open system (you can add and remove material to or from the system) – **fundamental equation of chemical thermodynamics:**

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_1 dn_1 + \mu_1 dn_1 + \cdots$$

for const temperature and pressure:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \cdots$$

Concentration Effect: Nernst Equation

Gibbs energy of a ideal gas in a closed container at const temp at different pressures:

$$dG = -SdT + Vdp = Vdp$$

$$dG(p) = G(p_0) + \int_{p0}^{p} Vdp \qquad V = \frac{nRT}{p}$$

$$G(p) = G(p_0) + nRT \ln \frac{p}{p_0}$$

for p_0=1bar as standard state pressure and μ=dG/dn:

$$\mu = \mu^o + RT \ln \frac{p}{p^o} = \mu^o + RT \ln p$$

Example: Available Work at Constant T

$$W = \int_{V_0}^{V_1} p\, dV \qquad pV = nRT_0 = const \quad \text{or} \quad p = \frac{nRT_0}{V}$$

$$= \int_{V_0}^{V_1} \frac{nRT_0}{V} \, dV = nRT_0 \int_{V_0}^{V_1} \frac{dV}{V}$$

$$= nRT_0 \ln \frac{V_1}{V_0} = nRT_0 \ln \frac{p_0}{p_1}$$

$$W = -\Delta g = nRT_0 \ln \frac{p_1}{p_0} = nRT_0 \ln p$$

Nernst Equation

Consider the following electrochemical reaction

$$1A + bB \Longleftrightarrow mM + nN$$
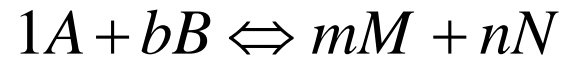
Using the definition of the chemical potential

$$\Delta g = (m\mu_M + m\mu_N) - (\mu_A + b\mu_B) + RT \ln \frac{p_M^m p_N^n}{p_A^1 p_B^b}$$

$$\Delta g = \Delta g^0 + RT \ln \frac{p_M^m p_N^n}{p_A^1 p_B^b}$$
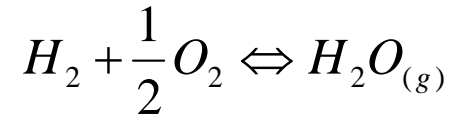
$$(\Delta g = -nFE)$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{p_M^m p_N^n}{p_A^1 p_B^b} : \text{Nernst Equation}$$

In general, Nernst Equation can be expressed as:

$$E = E^0 - \frac{RT}{nF} \ln \frac{\Pi p_{\text{Product}}^{v_i}}{\Pi p_{\text{Reactants}}^{v_i}} \left(or \ E^0 - \frac{RT}{nF} \ln \frac{\Pi a_{\text{Product}}^{v_i}}{\Pi a_{\text{Reactants}}^{v_i}} \right)$$

Nernst Equation: Examples

Consider the hydrogen-oxygen reaction at 120C

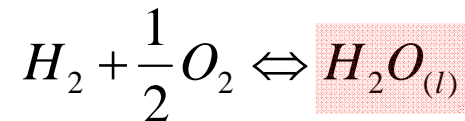$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O_{(g)}$$

Using the Nernst Equation

$$E = E^{120C} - \frac{RT}{nF}\ln\frac{p_{H_2O}}{p_{H_2}\,p_{O_2}^{1/2}}$$

E^{120C} is calculated considering temperature effect

$$E_T = E + \frac{\Delta s}{nF}(T - T_0)$$
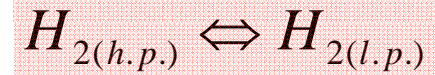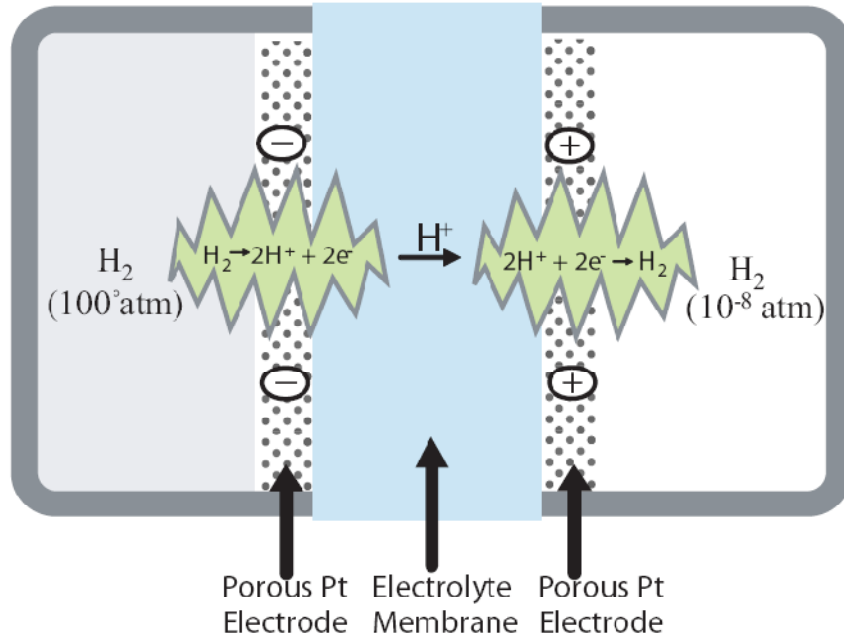
Q: At STP, how to calculate the voltage? (when water is liquid)

$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O_{(l)}$$

A: For pure component, activity = 1 (read the textbook). Thus

$$E = E^0 - \frac{RT}{nF}\ln\frac{1}{p_{H_2}\,p_{O_2}^{1/2}}$$

Concentration Cell

$$H_{2(h.p.)} \Leftrightarrow H_{2(l.p.)}$$

From Nernst Equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{p_{H_2}^y}{p_{H_2}^x}$$

$$= 0 - \frac{8.314 \cdot 298.15}{2 \cdot 96400} \ln \frac{10^{-8}}{100}$$

$$= 0.296V$$

Diagram labels:

H₂ → 2H⁺ + 2e⁻

2H⁺ + 2e⁻ → H₂

H_2 (100 atm)

H_2 (10⁻⁸ atm)

H⁺

Porous Pt Electrode   Electrolyte Membrane   Porous Pt Electrode

Q: How a fuel cell without chemical reaction is possible?

What is the driving force?

A: Electrochemical potential will answer your question.

Electrochemical Potential

In concentration cell, **concentration gradient** will drive the migration (or diffusion) of hydrogen. Previously, we found **chemical potential** is:

$$\mu = \mu^o + RT \ln \frac{p}{p^o} = \mu^o + RT \ln p$$

Porous Pt   Electrolyte   Porous Pt
Electrode   Membrane   Electrode

Thus, high pressure hydrogen has higher chemical potential. The **difference in chemical potentials** generates the **voltage**s in the cell.
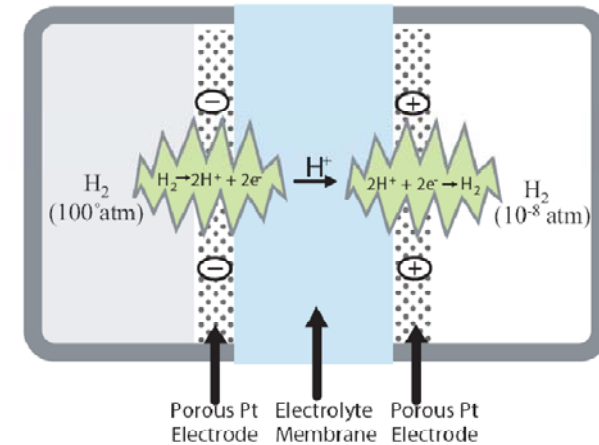
More conveniently, we may use "**electrochemical potential**" defined as

$$\tilde{\mu}_i = \mu_i + z_i F \phi_i = \mu_i^0 + RT \ln p + z_i F \phi_i$$

Electrochemical Potential

At **electrochemical equilibrium,** the net change in the electrochemical potential is 0. (Remember **Δg=0** at chemical equilibrium)

$$\left(\sum_i v_i \tilde{\mu}_i\right)_{products} - \left(\sum_i v_i \tilde{\mu}_i\right)_{reactans} = 0$$

$$\Leftrightarrow \left(\sum_i v_i \mu_i\right)_{products} - \left(\sum_i v_i \mu_i\right)_{reactans} = -z_i F \Delta\phi_i$$

From this fact, you may re-derived the Nernst Equation as:

$$\Delta\phi_{e-} = E = -\frac{\Delta g^0}{nF} - \frac{RT}{nF}\ln\frac{\Pi p_{Product}^{v_i}}{\Pi p_{Reactants}^{v_i}}$$

$$= E^0 - \frac{RT}{nF}\ln\frac{\Pi p_{Product}^{v_i}}{\Pi p_{Reactants}^{v_i}}$$

Heat Dissipation by Fuel Cells

$$P_{in} = \left|\Delta\hat{h}\right| J_{H_2} = P_{Heat} + P_L = P_{Heat} + V \times j$$

$$P_{Heat} = P_{in} - P_L = \left(\frac{\left|\Delta\hat{h}\right|}{nF} - V\right) \times j = \left(E^H - V\right) \times j$$

$$E^H = \frac{\left|\Delta\hat{h}\right|}{nF} = \frac{286,000(J/mol)}{2 \times 96,400(C/mol)} = 1.48V$$

1. Entropy loss

$$P_{Therm} = T\left|\Delta\hat{s}\right| J_{H_2}$$

2. Internal loss in fuel cells: activation, ohmic, concentration losses

3. Heat of condensation

$$P_{cond} = \left|\Delta\hat{h}_{cond}\right| J_{H_2}$$

Heat Dissipation by Fuel Cells

Example

Consider the Ballard fuel cell of Figure 11.7. What is the maximum power that can transferred to a load and what heat is generated? What is the efficiency of the cell? Use the V-I characteristics for 70 C but, to simplify the problem, assume that the operating conditions are at RTP. The product water is removed from the cell in vapor form.

The V-J characteristic of the cells is

$$V_L = 0.913 - 49.3 \times 10^{-6} J, \tag{39}$$

consequently the power output is,

$$P_L = V_L J = 0.913 J - 49.3 \times 10^{-6} J^2 \quad \text{W m}^{-2}. \tag{40}$$

This is the power the cell delivers to a load per square meter of active electrode surface.

The cell delivers maximum power when

$$\frac{dP}{dJ} = 0.913 - 98.6 \times 10^{-6} J = 0, \tag{41}$$

or

$$J = 9260 \quad \text{A/m}^2. \tag{42}$$

At this current, the cell would deliver 4230 W/m^2.

Heat Dissipation by Fuel Cells

If one assumes 100% reactant and current efficiencies (no reactants are lost and all the current generated flows through the load), then the rate of water synthesis is

$$\dot{N} = \frac{J}{qn_eN_0} = \frac{9260}{1.60 \times 10^{-19} \times 2 \times 6.02 \times 10^{-26}}$$

$$= 48 \times 10^{-6} \quad \text{kilomoles } (H_2O)s^{-1}m^{-2}. \quad (43)$$

Hence, the energy input to the cell is

$$P_{in} = \Delta H \dot{N} = 242 \times 10^6 \times 48 \times 10^{-6} = 11,600 \quad W/m^2. \quad (44)$$

Of these, 4200 W/m^2 appear as electric energy in the load, so that $11,600 - 4200 = 7400$ W/m^2 of heat are generated.

Notice that the Joule losses inside the cell amount to

$$P_{Joule} = R_{int}J^2 = 49.3 \times 10^{-6} \times 9260^2 = 4200 \quad W/m^2. \quad (45)$$

Heat Dissipation by Fuel Cells

This is, of course, equal to the power delivered to the load because, for maximum power transfer the load resistance must equal the internal resistance of the generator.

The thermodynamic heat is

$$P_{therm} = T\Delta S \dot{N} = 298 \times 44.4 \times 10^3 \times 48 \times 10^{-6} = 634 \quad \text{W/m}^2. \quad (46)$$

The losses owing to V_{oc} being different from V_{rev} amount to

$$P_{oc} = (V_{rev} - V_{oc})I = (1.185 - 0.913) \times 9260 = 2520 \quad \text{W/m}^2. \quad (47)$$

Necessarily,

$$P_{in} = P_{therm} + P_{oc} + P_{Joule} + P_L \quad (48)$$

The efficiency of this cell is

$$\eta = \frac{P_L}{P_{in}} = \frac{4230}{11,600} = 0.365. \quad (49)$$
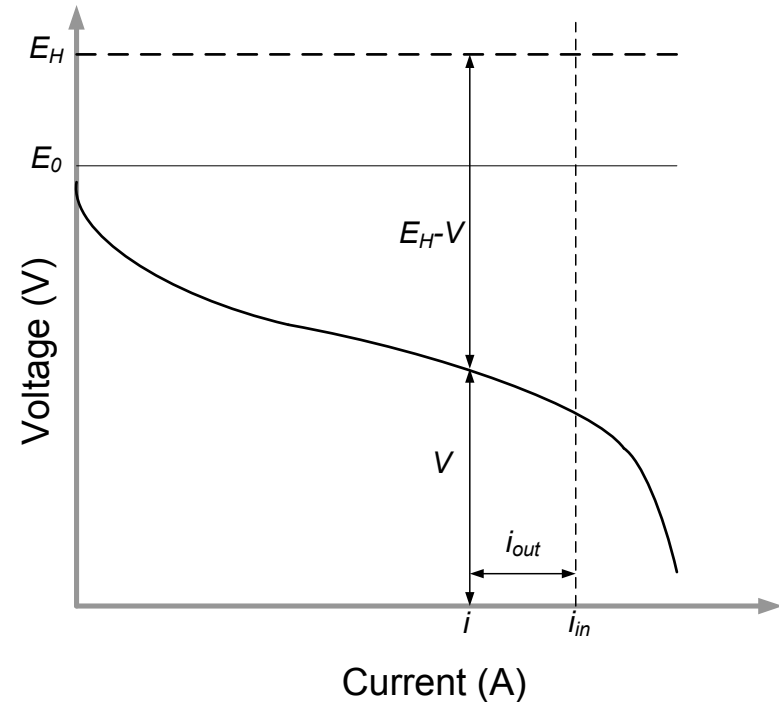
Mass Balance in Fuel Cells

$$j = j_{in} - j_{out} = nF\left(J_{in} - J_{out}\right)$$

$$J_{out} = J_{in} - \frac{j}{nF}$$

If air at 20 mol/s is supplied to a hydrogen−air fuel cell that generates 1000 kA, we can find the oxygen output flux from the fuel cell:

$$J_{O_2,out} = J_{O_2,in} - \frac{j}{nF} = J_{Air,in} \times w_{O_2} - \frac{j}{nF}$$

$$= 20\,mol/s \times 0.21 - \frac{1000000\,A}{4 \times 96400\,C/mol} = 1.6\,mol/s$$
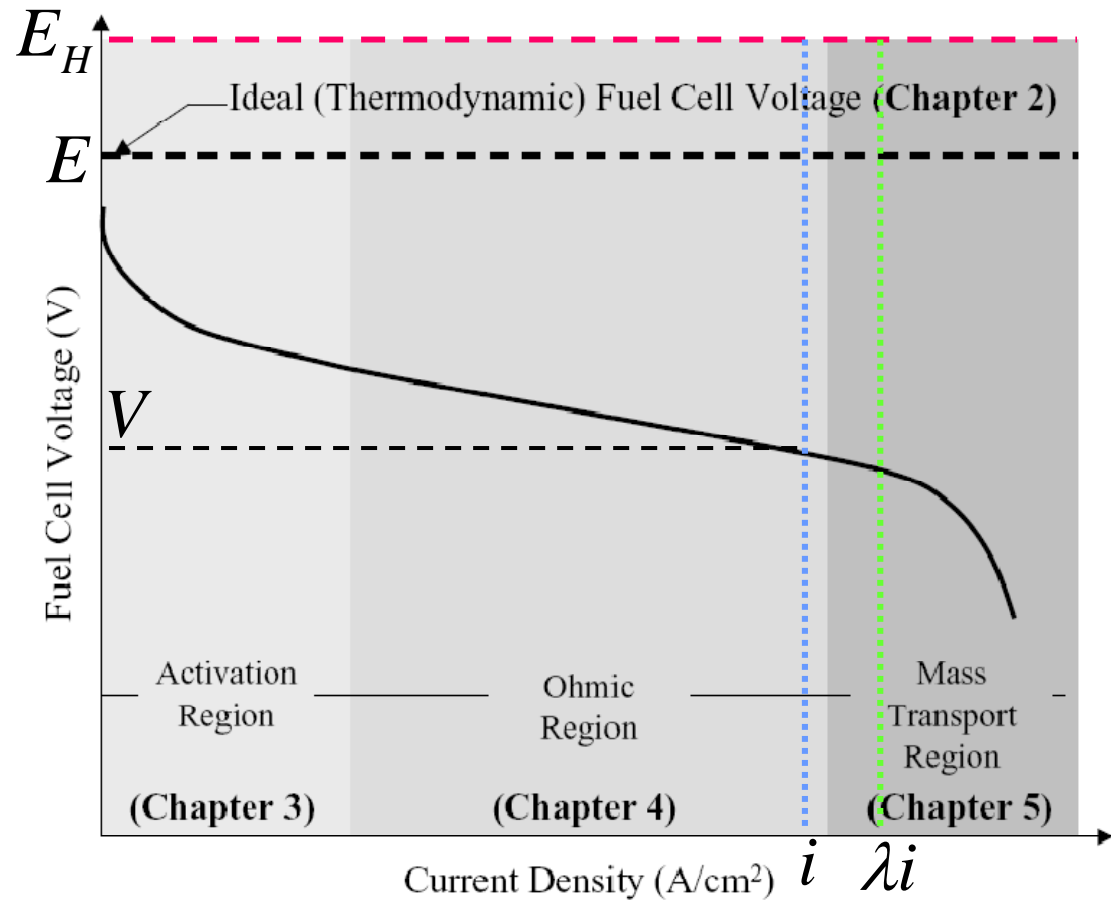
Here, w_{O2} represents the volume ratio of oxygen in air (=0.21)

Real Fuel Cell Efficiency
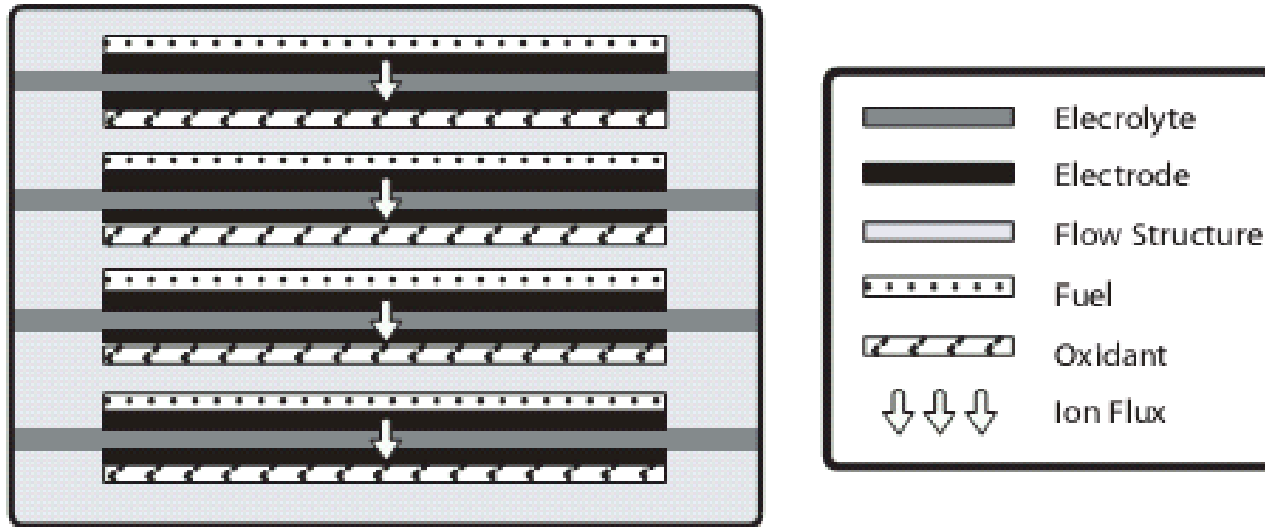
$$\varepsilon_{real} = \varepsilon_{real} \times \varepsilon_{real} \times \varepsilon_{real}$$

$$= \left(\frac{\Delta G}{\Delta H}\right)\left(\frac{V}{E}\right)\left(\frac{i/nF}{v_{fuel}}\right)$$

$$= \left(\frac{E}{E_H}\right)\left(\frac{V}{E}\right)\left(\frac{1}{\lambda}\right)$$

$\lambda = \text{stoichiometric number}$

$$= \frac{\text{supplied fuel rate}}{\text{consumed fuel rate}}$$

Fuel Cells Stacks

Legend:
- Elecrolyte
- Electrode
- Flow Structure
- Fuel
- Oxidant
- Ion Flux

$$V_{total} = V_{cell} \times \text{number of cells}$$

$$I_{total} = I_{cell}$$

$$P_{total} = I_{total} \times P_{total} = I_{cell}V_{cell} \times \text{number of cells}$$

$$= P_{cell} \times \text{number of cells}$$