

# WEEK 2/3: Lecture 1/2

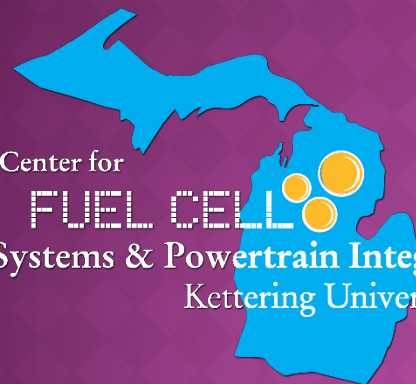
## Fuel Cell Electrochemistry



### *MECH-526*

# FUEL CELL SCIENCE & ENGINEERING

Center for  
**FUEL CELL**  
Systems & Powertrain Integration  
Kettering University



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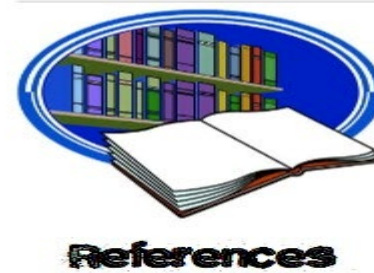
Mechanical Engineering

Kettering University

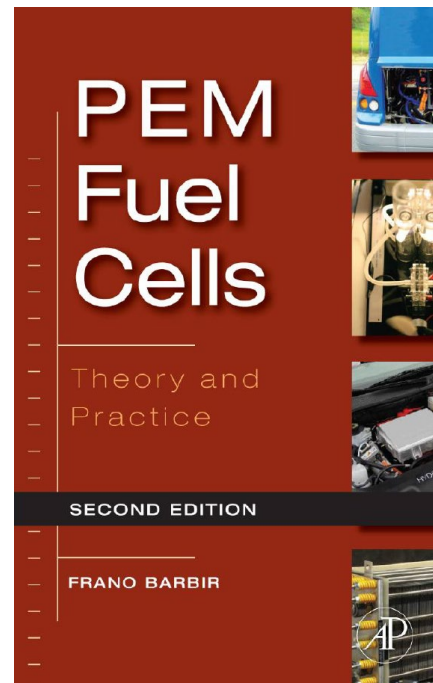
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# REFERENCES:

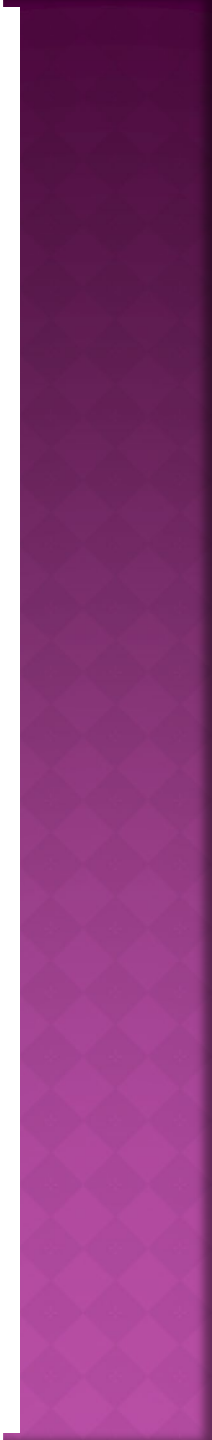


- ◉ PEM Fuel Cells: Frano Barbir, ELSEVIER.
- ◉ Fuel Cell Explained: Larmie & Dicks, WILEY.
- ◉ Fuel Cell Fundamentals: O'hayre, Cha, et al., WILEY.





**REVIEW**



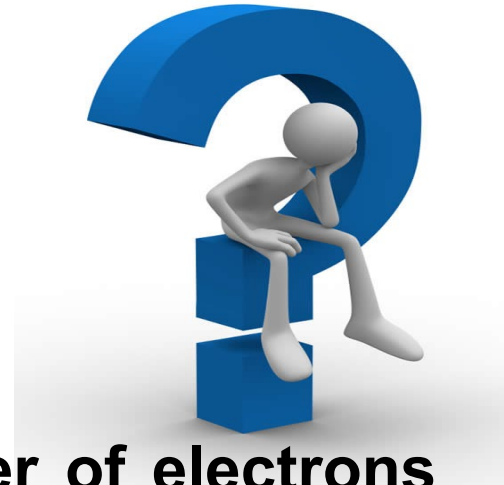
# Engineering Lab Report Elements

- ▶ Typed
- ▶ Scientific Objectives
- ▶ Experimental set-up and process
- ▶ Data Collection
- ▶ Data Reduction & Engineering Calculations
  - ▶ **COMPUTER GENERATED PLOTS**
- ▶ Data Analysis and Reflection
- ▶ Information Learned Personally
- ▶ Professional Work Only
- ▶ **Data W/O Analysis is Meaningless**

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# ***Some Basic Questions***



- How do we determine the number of electrons taking part in a fuel cell reaction such as in hydrogen-oxygen fuel cell or methanol fuel cell?**
- What is the maximum voltage that a fuel cell can produce?**
- How much energy and enthalpy are produced in hydrogen-oxygen fuel cell reaction?**
- How fast the electrode reactions proceed? Do they control any?**

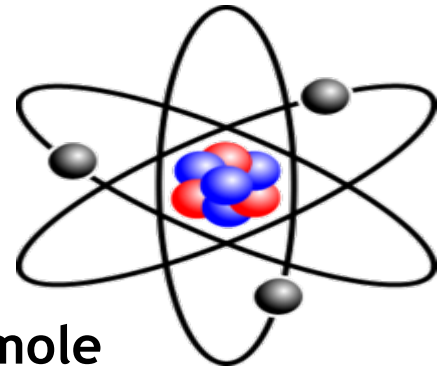
# SOME BASIC TERMINOLOGY

$$\text{Power Density} = \frac{\text{Power}}{\text{Volume}} \quad \text{kW/m}^3 \text{ or kW/L}$$

$$\text{Energy Density} = \frac{\text{Energy}}{\text{Volume}} \quad \text{kWh/m}^3 \text{ or kJ/m}^3$$

$$\text{Specific Power} = \frac{\text{Power}}{\text{Mass}} \quad \text{W/kg}$$

# BASIC DEFINITIONS



- Avogadro Number  $N = 6.022 \times 10^{23}$  electrons/mole
- 1 electron has  $e = 1.602 \times 10^{-19}$  Coulombs/electron.
- Faraday Constant:
  - $F = Ne = 6.022 \times 10^{23} \times 1.602 \times 10^{-19} = 96485$  Coulombs/moles of electrons
- A little chemistry produces a lot of electricity
- Total Charge ( $Q$ =Coulombs) & CURRENT (Amp = C/sec):

$$Q = n \left[ \frac{\text{moles of electrons}}{\text{mole of reactant}} \right] \cdot F \left[ \frac{\text{Coulombs}}{\text{moles of electrons}} \right] = \frac{\text{Coulombs}}{\text{mole of reactant}} \rightarrow \text{CHARGE}$$
$$I = \frac{dQ}{dt} \rightarrow \text{CURRENT}$$

$$1 \text{ Amp} = 1 \text{ C/sec}$$

$$1 \text{ A-sec} = 1 \text{ C}$$

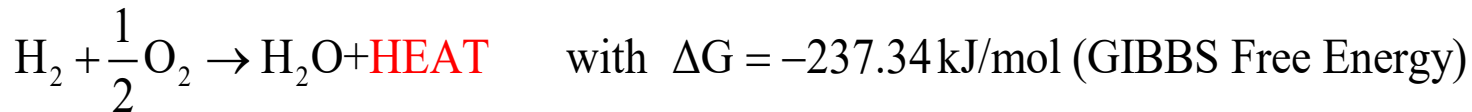
$$1 \text{ Volt} = \text{J/C}$$

$$\text{Watts} = \frac{\text{Joules}}{\text{sec}}$$

$$W = \frac{J}{s}$$

# FUEL CELL OPERATION—GALVANIC CELL

- The **anode reaction** in fuel cells is “**direct oxidation**”. “**OXIDATION**” is a process where electrons are “**removed**” from a species. “i.e. Negative Electrode”.
- The **cathode reaction** is “**oxygen reduction**”. “**REDUCTION**” is a process where electrons are “**added**” to a species. “i.e. Positive Electrode”.
- **Electrons flow from ANODE (-) to CATHODE (+) for fuel cells (opposite for batteries).**
- For H<sub>2</sub>/O<sub>2</sub> fuel cell, overall reaction is (GIBBS=max work possible)



The product of this reaction is “**water released**” at the cathode or anode depending on the type of the fuel cell.

- The open circuit voltage  $E^0$  at standard conditions of **25°C** and 1 atmosphere pressure for the H<sub>2</sub>/O<sub>2</sub> Fuel Cell is:

$$n = \frac{\text{moles of electrons}}{\text{moles of reaction}} = 2(\text{hydrogen moles/reaction})$$

$$F = \text{Faraday's Constant} = 96,485 \frac{\text{coulombs}}{\text{moles of electrons}}$$

$$\begin{aligned} \frac{\Delta G}{nF} &= \frac{\frac{\text{Joules}}{\text{mole of reaction}}}{\frac{\text{moles of electrons}}{\text{moles of reaction}} \times \frac{\text{coulombs}}{\text{moles of electrons}}} = \frac{\text{Joules}}{\text{coulombs}} \\ &= \text{Volts} \end{aligned}$$

$$E_{\text{max}}^0 = \frac{-\Delta G}{nF} = 1.23 \text{ V / cell}$$



# GIBBS FREE ENERGY

- The **Gibbs free energy** of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.  $G = H - TS$ . H is enthalpy, T is temperature, and S is entropy.
- Used to calculate the MAXIMUM of **REVERSIBLE** work that may be performed by a thermodynamic system at a constant temperature and pressure. **BUT NOT THE SPEED OF REACTION.**
- When using Gibbs free energy to determine the spontaneity of a process, we are only concerned with changes in “G”, rather than its absolute value.
- When the process occurs under standard conditions (25C/1Bar/1M), we calculate the GIBBS free energy using the **Standard Free Energy of Formation**,  $\Delta G_f^0$

$$\Delta G = G_{Final} - G_{Initial}; [J / kg] \quad H_2 + 1/2O_2 \rightarrow H_2O + \text{Heat}$$

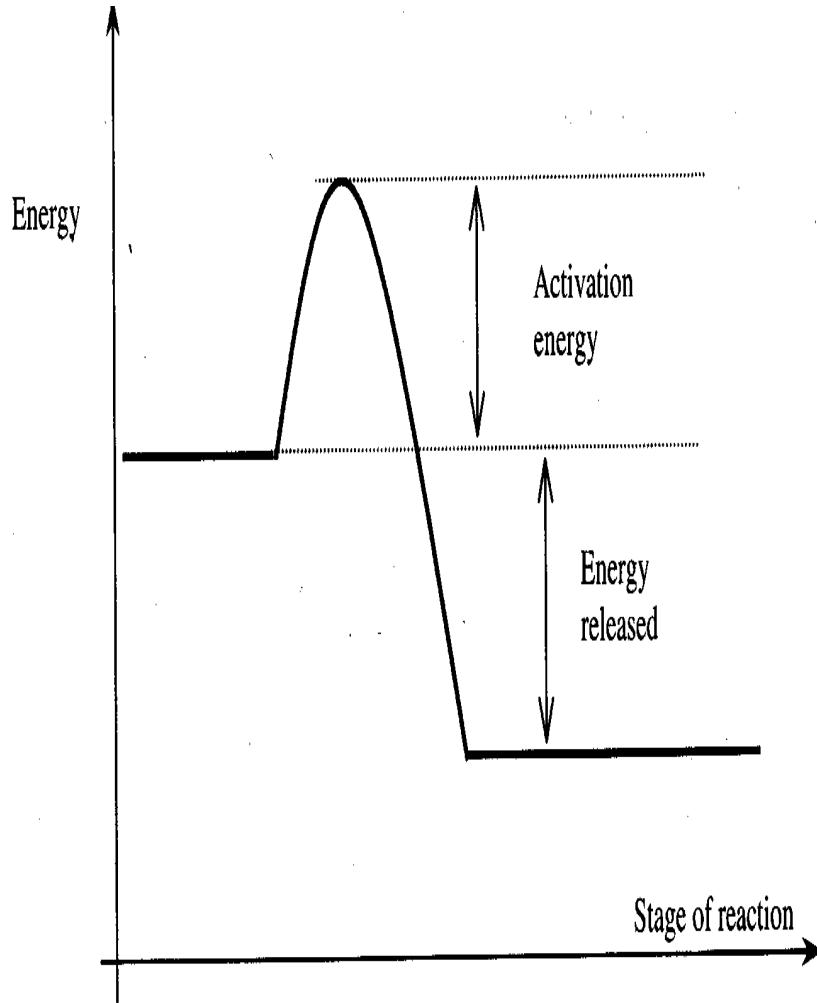
$$\Delta G_{System} = \Delta H_{System} - T \Delta S_{System}$$

if  $\Delta G_{System} < 0 \rightarrow$  spontaneous (**Exergonic**)  $\rightarrow$  form more products

if  $\Delta G_{System} > 0 \rightarrow$  non-spontaneous (**Endergonic**)  $\rightarrow$  form more starting materials

# “CLASSICAL” ENERGY DIAGRAM

## WHAT LIMITS CURRENT?



- Although energy is released, ‘activation energy’ must be supplied to get over the ‘energy’ hill’. (similar to mechanical inertia)
- If molecular energy is low, then chemical reactions will proceed slowly.
- Increase reaction rates:
  - **Use of Catalyst**
  - **Raising Temperatures**
  - **Increasing Electrode Area: Impacts rate at which “electrons” are removed on surface of electrode.**
  - **Area is increased with highly porous electrodes**

# HEAT OF REACTION

- ◉ Combustion is an 'EXOTHERMIC' process (heat is released)



- ◉ Heat (or enthalpy) of a reaction is the DIFFERENCE between the heats of formation of products and reactants: i.e.:

$$\Delta H = (h_f)_{H_2O} - (h_f)_{H_2} - 1/2(h_f)_{O_2}$$

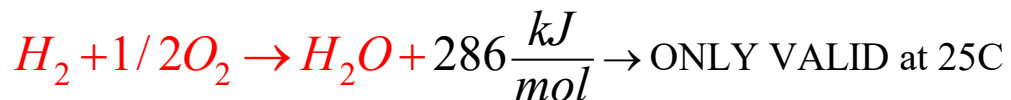
$(h_f)_{H_2O}$  = Heat of Formation of Liquid Water is -286 kJ/mol at 25C

$(h_f)_{H_2}$  = Heat of Formation of base element  $H_2$  is 0

$(h_f)_{O_2}$  = Heat of Formation of base element  $O_2$  is 0

$$\Delta H = -286 \frac{\text{kJ}}{\text{mol}} - 0 - 0$$

$$= -286 \frac{\text{kJ}}{\text{mol}} \rightarrow \text{Negative sign means HEAT is being released}$$



# H<sub>2</sub> HIGHER VS LOWER HEATING

- ◉ If 1 MOLE of Hydrogen is fully combusted with ½ MOLE of Oxygen and allowed to cool to 25C at 1 ATM, there will be only liquid remaining. 286 kJ/Mole of heat will be transferred. This is known as the *hydrogen's HIGHER heating value*.
- ◉ However, If 1 MOLE of Hydrogen is fully combusted with EXCESS Oxygen and allowed to cool to 25C at 1 ATM, product will be in form of vapor and unburned O<sub>2</sub> and/or N<sub>2</sub>. 241 kJ/Mole of heat will be transferred. This is known as the *hydrogen's LOWER heating value*.
- ◉ The difference is known as the *HEAT of EVAPORATION*

$$H_{fg} = 286 - 241 = 45 \text{ kJ} / \text{mol}$$



# THEORETICAL ELECTRICAL WORK

- ⦿ Since there is NO COMBUSTION, Hydrogen heating value is used as a measure on energy input in a fuel cell. This is the **MAXIMUM** amount of thermal energy that may be extracted.
- ⦿ *But not all this thermal energy can be converted to **ELECTRICAL ENERGY** to do work.*
- ⦿ The portion of the reaction enthalpy that can be converted to electricity is constrained by the **GIBBS** free energy relationship.

# GIBBS:

## 237.36 KJ/MOLE—WORK, 48.66 KJ/MOLE--HEAT

- Consider Gibbs and Enthalpies and Entropies of formation at **25C**.

$$\Delta G_{\text{System}} = \Delta H_{\text{System}} - T \Delta S_{\text{System}}$$

	$h_f \frac{\text{kJ}}{\text{mol}}$	$s_f \frac{\text{kJ}}{\text{mol} - \text{K}}$
$H_2$	0	0.13066
$O_2$	0	0.20517
$H_2O - \text{Liquid}$	-286.02	0.06996
$H_2O - \text{Vapor}$	-241.98	0.18884

DIFFERENT VALUES AT  
DIFFERENT  
TEMPERATURES

$$\Delta H = (h_f)_{H_2O} - (h_f)_{H_2} - 1/2(h_f)_{O_2} = -286.02$$

$$T \Delta S = (s_f)_{H_2O} - (s_f)_{H_2} - 1/2(s_f)_{O_2}$$

$$= (25 + 273)K \cdot (0.06996 - 0.13066 - 1/2 \cdot 0.20517) = -48.65893 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G_{\text{System}} = \Delta H_{\text{System}} - T \Delta S_{\text{System}} = -286.02 - (-48.65893) = -237.36 \frac{\text{kJ}}{\text{mol}}$$

# FUEL CELL EFFICIENCY

# FUEL CELL EFFICIENCY H<sub>2</sub>/O<sub>2</sub> FUEL CELL--MAX

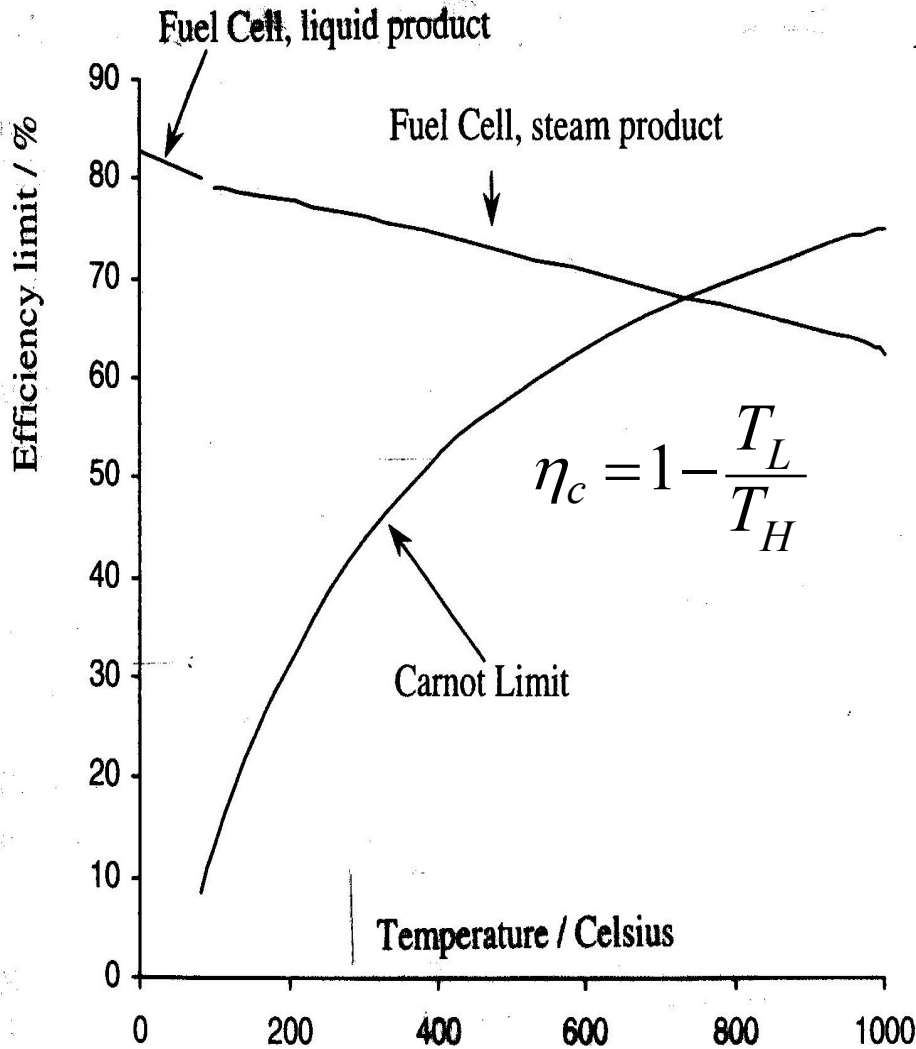
- Various efficiencies are defined related to fuel cells.
- The *thermodynamic fuel cell efficiency* is defined as the ratio of the electric energy produced divided by the enthalpy change of electrochemical reaction or energy released in burning the fuel, i.e., the calorific value or the enthalpy of formation:

$$\eta_{cell\ max} = \frac{\text{Work Output Desired}}{\text{Work Input Required}}$$
$$\eta_{cell\ max} = \frac{W_e}{-\Delta h_f} = \frac{-\Delta g_f}{-\Delta h_f} = \frac{\text{Gibbs Free Energy(THEORETICAL)}}{\text{H2 Higher Heating Value}} = \frac{237.34\text{kJ} / \text{mol}}{286.02\text{kJ} / \text{mol}} = 83\% @ 23C$$

- Higher heating value (HHV) or “enthalpy” accounts for all energy available for combustion.

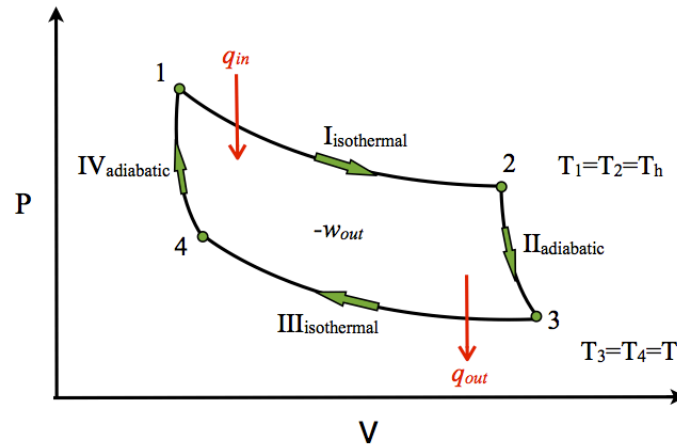


# EFFICIENCY

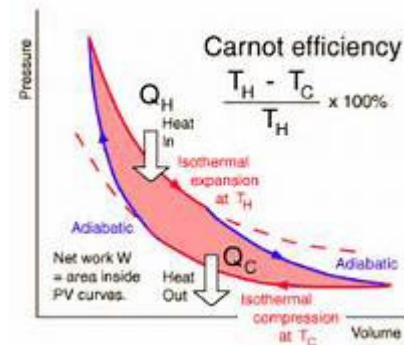


Recall from THERMODYNAMICS that a Carnot efficiency is the maximum efficiency that a heat engine may have operating between two temperatures.

Carnot efficiency does not apply to fuel cells because a fuel cell is NOT a heat engine; rather it is an electrochemical energy converter.



# THEORY VS REALITY



- **Theoretical** Graph suggest that *lower fuel cell operating temperatures* are better; contrary to heat engines governed by Carnot Efficiency.
- But actual **fuel cell transport & chemical losses** are nearly always “**LESS**” at higher temperatures. So in practice, fuel cell voltages are **higher** at higher temperatures.
- Waste heat from higher temperature fuel cells is more useful than from lower temperature fuel cells; thus higher thermal efficiency for Combined Heat and Power (CHP) applications .

# ***HYDROGEN-OXYGEN FUEL CELL VOLTAGE***



- Theoretically, the expected output voltage for the cell is **1.23V @ 25C**. (Different for other temperatures)
- Why then does a fuel cells give lower voltage?
- This is caused by the “***over-potential***” of the reactions at the two electrodes; mass transport limitations, ohmic losses etc. Mostly caused by the ***oxygen reduction reaction (cathode)*** which is irreversible.
- Four electrons arriving (or racing) at the ***cathode***, cannot be simultaneously be added in the oxygen ion orbit.

# ***HYDROGEN-CHLORINE FUEL CELL VOLTAGE*** ***(FUEL CELLS JUST USE FREE GIBBS ENERGY TO PRODUCE ELECTRICITY)***

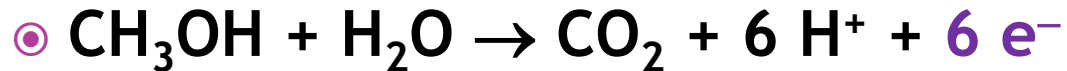
- A combination of two half cells can be used to build fuel cells.
- For example, we can have hydrogen and chlorine combine to make a fuel cell.
- $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2 \text{HCl}$
- Here for the half cells,
- $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2 \text{e}^-$
- $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$
- Voltage is 1.30 V, and the fuel cell gives 1.30 V.



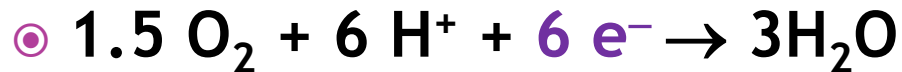
# METHANOL FUEL CELL



- Reaction on the Anode:



- Reaction on the Cathode:



- Six electrons are involved in the half reaction and

- $\Delta \bar{g}_f^0 = - 698.2 \text{ kJ/mol}$

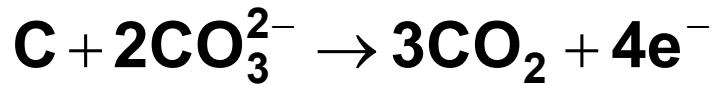
- Hence, reversible open circuit voltage is given by

$$E^0 = \frac{-\Delta \bar{g}_f^0}{6F} = \frac{-(-698.2 \times 10^3 \text{ kJ/mol})}{6 \times 96485 \text{ C}} = 1.21 \text{ V}$$

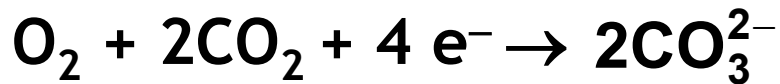
# CARBON FUEL CELL

Overall Reaction:  $C + O_2 \rightarrow CO_2$  (500-700°C operating T)

Reaction on the Anode:



Reaction on the Cathode:



Four electrons are involved in the half reaction and

$$\Delta \bar{g}_f^0 = -394.36 \text{ kJ/mol}$$

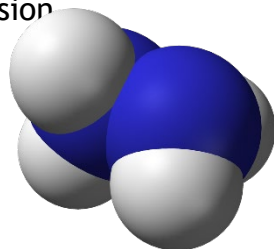
Hence, reversible open circuit voltage is given by

$$E^0 = \frac{-\Delta \bar{g}_f^0}{4F} = \frac{-(-394.4 \times 10^3 \text{ J/mol})}{4 \times 96485 \text{ C}} = 1.02 \text{ V}$$

# OTHER HEATS/FREE ENERGY/EFF. CANDIDATE FUELS

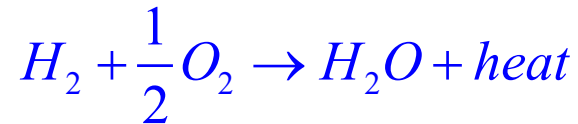
Fuel	Reaction	n	$-\Delta\bar{h}_f$	$-\Delta\bar{g}_f$	$E_0$	$\frac{\Delta g_f}{\Delta h_f} = \%$
Hydrogen	$2H_2 + O_2 \rightarrow 2H_2O$	2	286.02	237.34	1.229	82.97
Methane	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	8	890.8	818.4	1.066	91.87
Propane	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	20	2221.1	2109.3	1.093	94.96
Hydrazine	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$	4	622.4	602.4	1.560	96.77
Zinc	$Zn + 0.5O_2 \rightarrow ZnO$	2	348.1	318.3	1.650	91.43
Sodium	$4Na + 2H_2O + O_2 \rightarrow 4NaOH$	1	326.8	300.7	3.120	92.00

About two million tons of hydrazine hydrate were used in foam blowing agents in 2015. Additionally, hydrazine is used in various **rocket fuels** and to prepare the gas precursors used in **air bags**. Hydrazine is used within both nuclear and conventional electrical **power plants** steam cycles as an **OXYGEN SCAVENGER** to control concentrations of dissolved oxygen in an effort to reduce corrosion



# H2 HIGHER HEATING VALUE (HHV)

- ◉ The overall fuel cell reaction of hydrogen is the same as the combustion reaction of hydrogen, i.e.:



- ◉ Combustion is an exothermic process (heat is released), and the **ENTHALPY** of a chemical reaction is the difference between the **heats of formation** of products and reactants. So:

$$\Delta H = (h_f)_{H_2O} - (h_f)_{H_2} - \frac{1}{2}(h_f)_{O_2} = -286 \text{ kJ} / \text{mol}(\text{negative}) \rightarrow \text{Heat Released}$$

$$(h_f)_{H_2O} = -286.02 \text{ kJ} / \text{mol} @ 25C$$

$$(h_f)_{H_2} = (h_f)_{O_2} = 0 \rightarrow \text{BASIC ELEMENT}$$

- ◉ The enthalpy of hydrogen combustion reaction is also called the **“HYDROGEN HIGHER HEATING VALUE (HHV)”**
  - ALL ENERGY AVAILABLE FOR COMBUSTION

# ***H<sub>2</sub>/O<sub>2</sub> FUEL CELL PERFORMANCE PARAMETERS***

$\Delta\bar{g}_f$ , maximum open circuit EMF (reversible voltage), and efficiency limit (ref. HHV—Higher Heating Value) for hydrogen fuel cells

Form of water product	Temp °C	$\Delta\bar{g}_f$ kJ/gmole	Max EMF $E^0$ V	Max Efficiency $\eta_{cell}$
Liquid	25	-237.34	1.23V	83%
Liquid	80	-228.2	1.18V	80%
Gas	100	-225.3	1.17V	79%
Gas	200	-220.4	1.14V	77%
Gas	400	-210.3	1.09V	74%
Gas	600	-199.6	1.04V	70%
Gas	800	-188.6	0.98V	66%
Gas	1000	-177.4	0.92V	62%

# H2 LOWER HEATING VALUE (LHV)

- The difference between HHV and LHV is the heat of evaporation at 25C:i.e.:

$$\begin{aligned} H_{fg} &= HHV - LHV \rightarrow \text{HEAT of VAPORIZATION} \\ &= (286 - 241) \text{ kJ / mol} \\ &= 45 \text{ kJ / mol} \end{aligned}$$

$$\eta_{\text{Efficiency THERMAL}} = \frac{V}{E_{HHV} = \frac{HHV}{nF}} = \frac{V}{1.482 @ 25C} \rightarrow \text{Product Leaves as LIQUID (HHV)}$$

$$\eta_{\text{Efficiency}} = \frac{V}{E_{LHV} = \frac{LHV}{nF}} = \frac{V}{1.2489 @ 25C} \rightarrow \text{Product Leaves as VAPOR (LHV)}$$

- The conversion of a liquid to a vapor requires heat and is called the “**latent heat of vaporization**”. Implies that “**more**” energy can be recovered if the product water vapor is condensed to liquid form.
- For automotive combustion engines, using the LHV to compute efficiency is OK. But for **LTPEM fuel cells we always use the HHV to compute efficiency**

$$\eta_{\text{max}} = \frac{\text{useful WORK OUT}}{\text{total ENERGY IN}} = \frac{\Delta G}{\Delta H} = \frac{237.34 \text{ kJ / mol}}{286.02 \text{ kJ / mol}} = 83\%, \text{ or}$$

$$\eta_{\text{max}} = \frac{\text{useful POTENTIAL OUT}}{\text{total POTENTIAL IN}} = \frac{\frac{\Delta G}{nF}}{\frac{\Delta H}{nF}} = \frac{1.23V}{1.482V} = \frac{\text{theoretical cell potential (VOLTAIC)}}{\text{HHV thermoneutral potential (THERMAL)}} = 83\%$$

# MAXIMUM POSSIBLE EFFICIENCY

- If **1 MOLE of Hydrogen** is fully combusted with **½ MOLE of Oxygen** and allowed to cool to 25C at 1 ATM, there will be only liquid remaining. **286 kJ/Mole of heat** will be transferred. This is known as the *Hydrogen's HIGHER Heating Value (HHV)*.
- For H<sub>2</sub>/O<sub>2</sub> fuel cell, overall reaction is (GIBBS=max work possible)



$$\eta_{MAX\_VOLTAIC} = \frac{237.36}{286.02} \left[ \frac{\text{kJ}}{\text{mol}} \right] = 82.98\%$$

at 25C and 1 ATM, Based upon **H<sub>2</sub> HHV**

$$\eta_{REAL\_VOLTAIC} = \frac{\eta_{ACTUAL} = \frac{E[V / cell]}{\Delta G = nF}}{\eta_{MAX\_VOLTAIC}}$$



# REAL (PRACTICAL) FC EFFICIENCY

- Real fuel cell efficiency must always be less than the reversible thermodynamic efficiency due to: 1) Voltage Losses and 2) Fuel Utilization Losses. Real efficiency can be calculated as:

$$\eta_{real} = (\eta_{THERMAL}) \times (\eta_{VOLTAGE})$$

$\eta_{THERMAL}$  → Not all enthalpy contained in the FUEL can be converted into useful work  $\left(\frac{V(i)}{\frac{\Delta H}{nF}}\right) \cdot \eta_{fuel}$

$\eta_{VOLTAGE}$  → Losses due to fuel cell irreversible kinetic effects

$$\equiv \frac{V(i)}{E} = \frac{\text{real operating voltage as function of current draw}}{E = \frac{\Delta G}{nF} = \text{reversible cell voltage}}$$

$\eta_{fuel}$  → accounts for the fact that not all fuel provided to a fuel cell will participate in the reaction

$$\equiv \frac{\text{exact fuel 'needed' to generate electric current}}{\text{total fuel provided}} = \frac{\frac{i}{nF}}{v_{reactant}}$$

$$= \frac{\frac{i(\text{amps} = C/s)}{n(\frac{\text{mole-electron}}{\text{mole reactant}}) \cdot F(C/\text{mole-electron})}{v_{fuel}(\text{mole reactant/sec})}}{\frac{1}{S}}; \text{ let } S \equiv \text{stoic factor} = \frac{\text{actual fuel supplied}}{\text{exact fuel amount needed for reaction}} \geq 1$$



$$\eta_{real\_absolute} = \eta_{real} = \frac{(\eta_{THERMAL}) \times (\eta_{VOLTAGE})}{0.83} \text{ (ON 100\% SCALE)}$$

The total fuel cell efficiency is still 40-50% with all these factors, and is higher than any fossil fuel power generation by steam or gas turbine including micro turbines.

PRESSURE  
TEMPERATURE  
CONCENTRATION

# EFFECT OF PRESSURE / TEMPERATURE

**NOTE: PRESSURE IN ATM, CRITICAL**

Note: Partial Pressure of Liquid Water is 1.0.

- For the hydrogen/oxygen fuel cell reaction, the **NERNST** equation governs fuel cell performance as below:

$$\Delta G = \Delta G_o + \bar{R}_g T_{abs} (K) \ln\left(\frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.50}}\right), (\Delta G_o)_{1atm,25C} = -237.340 \text{ kJ / mole}$$

$$E = E_{o_{1atm,25C}} + \frac{\bar{R}_g T_{abs} (K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right); E_{o_{1atm,25C}} = \frac{(-\Delta G_o)_{1atm,25C}}{nF} = 1.23V$$

*P* = partial pressure of reactant or product species

- Only valid for gaseous products and reactants.
- Higher reactant pressure, the cell potential (E) is higher (**open circuit voltage or EMF**).
- If reactants are diluted, e.g. air, their partial pressure is **proportional** to their **concentration** and thus the cell potential is lower.

# PARTIAL PRESSURE COMPUTATION

⊙ Consider Air at 0.10 MPa.

$$N_2 = 78\%,$$

$$P_{N_2} = 0.78 \times 0.1 \text{ MPa} = 0.078 \text{ MPa}$$

$$O_2 = 20.9\%$$

$$P_{O_2} = 0.209 \times 0.1 \text{ MPa} = 0.0209 \text{ MPa}$$

$$Ar = 0.908\%$$

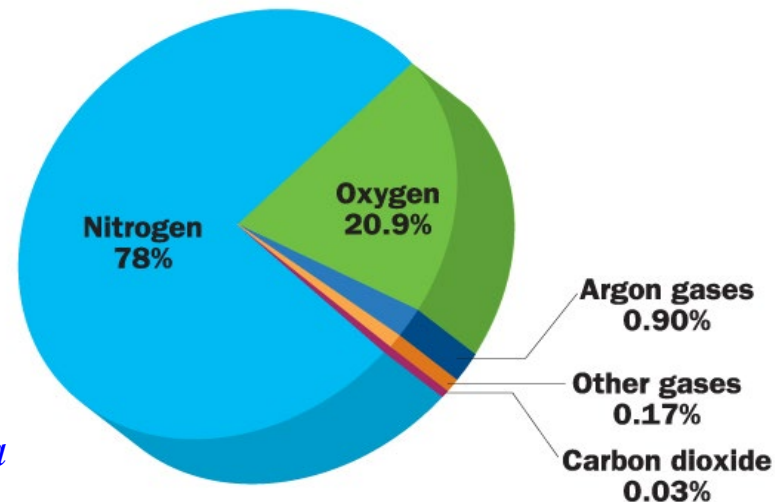
$$P_{Ar} = 0.00908 \times 0.1 \text{ MPa} = 0.000908 \text{ MPa}$$

$$CO_2 = 0.03\%$$

$$P_{CO_2} = 0.0003 \times 0.1 \text{ MPa} = 0.00003 \text{ MPa}$$

$$\text{Other} = 0.17\%$$

$$P_{\text{other}} = 0.0017 \times 0.1 \text{ MPa} = 0.00017 \text{ MPa}$$



# CELL PRESSURE EXAMPLE

- Consider H<sub>2</sub>-O<sub>2</sub> cell at 25C with H<sub>2</sub> at 3 ATM, and “air” at 5 ATM. Potential cell voltage is:

$$E = E_0(T) + \frac{\bar{R}_g T_{abs} (K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right); E_0(T_{abs} = 298.15K) = E_o = \frac{-\Delta G}{nF} = 1.229$$

example: let  $T=298.15K$ ,  $\bar{R}_g \equiv$  Ideal Gas Constant =  $8.314 \frac{J}{mol - K}$

$$\frac{\bar{R}_g T_{abs} (K)}{nF} = \frac{\bar{R}_g}{n} = \frac{\frac{J}{mole\ of\ reactant - K}}{\frac{moles\ of\ electrons}{mole\ of\ reactant}} \cdot \frac{T_{abs} = K}{F = \frac{C}{moles\ of\ electrons}} =$$

$$= 1.229 + \frac{(8.314)(298.15)}{(2)(96485)} \ln\left(\frac{(3 \cdot 1)(5 \cdot 0.21)^{0.5}}{1}\right)$$

$$= 1.229V + 0.014425V = \frac{1.2434V}{cell}$$



- Not much of an increase for the extra work and expense of pressurizing the fuel cell stack! Unless cost is not a driving factor, but performance is important.**
- Consider 120 cell stack?

**NOTE: PRESSURE IN ATM, CRITICAL**

$$\Delta V = \frac{0.014425V}{cell} \cdot 120 \frac{cells}{stack} = \frac{1.731V}{stack}$$

$$\Delta \eta_{eff} = \frac{0.014425V}{1.23V} = +1.2\%$$

# EFFECT OF TEMPERATURE

- The theoretical cell potential changes with temperature:

1<sup>st</sup> Law

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

GIBBS

$$E_{th}(T) = \left( \frac{-\Delta G_{th}}{nF} \right)_{@T=?} = \left( - \left( \frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF} \right) \right)_{@T=?}$$

Although the theoretical voltage decreases with temperature, in general higher cell temperatures result in higher cell potential; because actual *transport & chemical losses* decrease with temperature. **More in next chapter!**

Change of Enthalpy, Gibbs, and S for H<sub>2</sub>/O<sub>2</sub> FC w/Temperature:

T(K)	$\Delta H(kJ/mol)$	$\Delta G(kJ/mol)$	$\Delta S(kJ/mol)$	$E_{th}(V)$
298.15	-286.02	-237.34	-0.16328	1.230
333.15	-284.85	-231.63	-0.15975	1.200
353.15	-284.18	-228.42	-0.15791	1.184
373.15	-283.52	-225.24	-0.15617	1.167

# TEMPERATURE DEPENDENCE

⊙ Enthalpy and Entropy can be expressed as:

$$\Delta H_{th} = \Delta H_{298.15} + \Delta a(T - 298.15) + \Delta b\left(\frac{T^2 - 298.15^2}{2}\right) + \Delta c\left(\frac{T^3 - 298.15^3}{3}\right)$$

$$\Delta S_{th} = \Delta S_{298.15} + \Delta a \ln(T / 298.15) + \Delta b(T - 298.15) + \Delta c\left(\frac{T^2 - 298.15^2}{2}\right)$$

$$\Delta a = a_{H_2O} - a_{H_2} - 1/2a_{O_2}$$

$$\Delta b = b_{H_2O} - b_{H_2} - 1/2b_{O_2}$$

$$\Delta c = c_{H_2O} - c_{H_2} - 1/2c_{O_2}$$

	<i>a</i>	<i>b</i>	<i>c</i>
$H_2$	28.91404	-0.00084	$2.01 \times 10^{-6}$
$O_2$	25.84512	0.012987	$-3.9 \times 10^{-6}$
$H_2O_{(g)}$	30.62644	0.009621	$1.18 \times 10^{-6}$
$H_2O_{(l)}$	75.42646	0	0

## IDEAL FUEL CELL VOLTAGE

$$E_{th}(T) = \frac{-\Delta G_{th}}{nF} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right)$$

## GENERAL EXPRESSION

At temperatures < 100C, changes in enthalpy and entropy are very small.

But at higher temperatures, such as Solid Oxide Fuel Cells, they must not be neglected.



# LOW TEMPERATURE APPROXIMATION

$$T=25C=298.15K$$



IN GENERAL FOR TEMPERATURE & PRESSURE

$$E(T, P)_{\text{PER CELL}} = E_{th}(T) + \frac{\overline{R}_g T_{abs}(K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right) \rightarrow \text{NO LOSSES}$$

$$E(T, P)_{\text{PER CELL}} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right) + \frac{\overline{R}_g T_{abs}(K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

LOW TEMPERATURES

$$E_{th}(T) = \frac{-\Delta G_{th}}{nF} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right);$$

VALID:  
T < 100C

$$\left(\frac{\Delta H_{th} = -286.02}{nF}\right)_{298.15} = -1.482V; \frac{\Delta S_{th} = -0.16328}{nF} = -0.000845 \frac{V}{K}; \frac{\overline{R}_g}{nF} = 0.0000431 \frac{V}{K},$$

$$E_{th}(T, P)_{\text{PER CELL}} = 1.482 - 0.000845T + 0.0000431T \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

$$= 1.482V - 0.000845 \frac{V}{K} (298.15) + 0.0000431T \frac{V}{K} \ln(1)$$

$$= 1.482 - 0.2519 + 0$$

$$= 1.23006 @ 25C, 1ATM$$

EXAMPLE

# TEMPERATURE, PRESSURE, & CONCENTRATION

- Concentration gradients occur when a reactant is rapidly consumed at the electrode by the electrochemical reaction.



$$\Delta V_{\text{concentration}} = \frac{RT_{\text{abs}}}{nF} \ln \left( \frac{C_B}{C_s} \right)$$

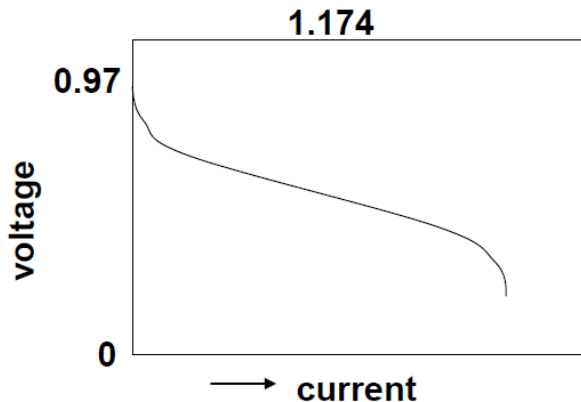
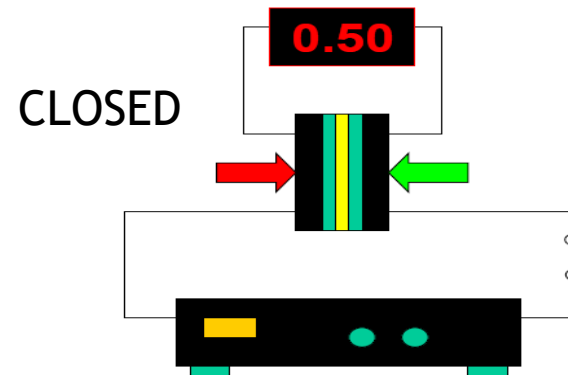
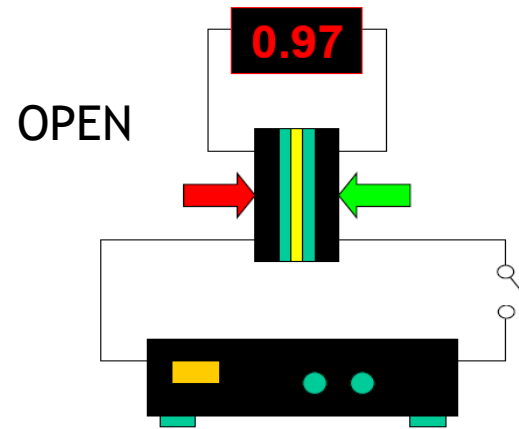
$C_B$  = bulk concentration of reactant, mol/cm<sup>3</sup>

$C_s$  = reactant concentration at catalyst surface, mol/cm<sup>3</sup>

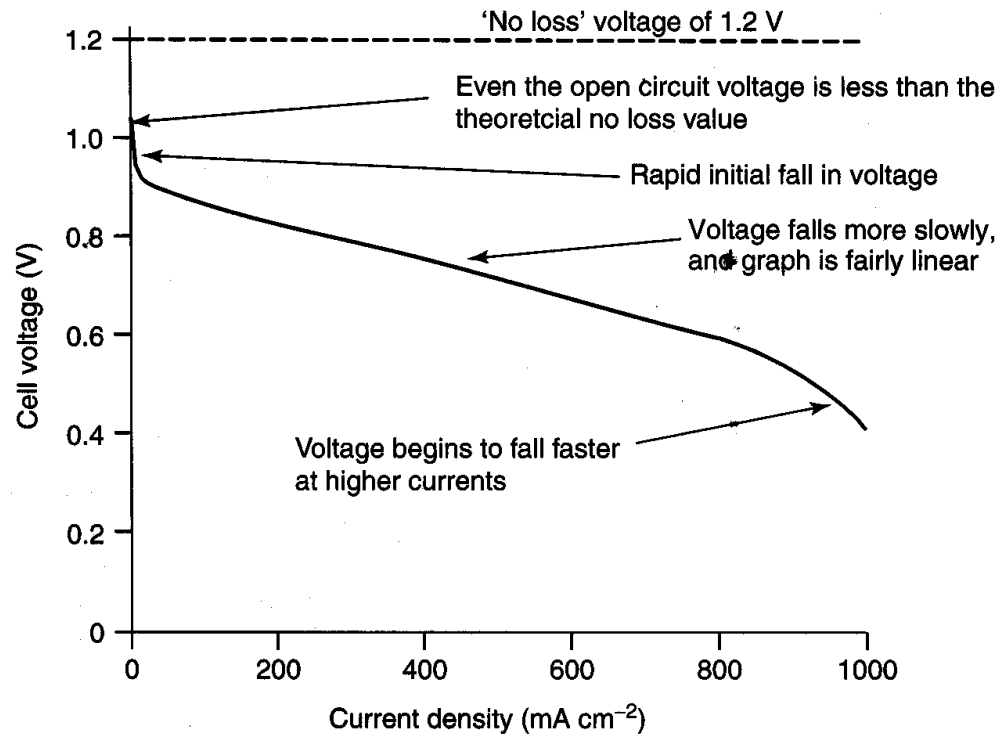
$$E(T, P)_{\text{PER CELL}} = - \left( \frac{\Delta H_{th}}{nF} - \frac{T \Delta S_{th}}{nF} \right) + \frac{R_{H_2} T_{abs}}{nF} \ln \left( \frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}} \right) + \frac{RT_{abs}}{nF} \ln \left( \frac{C_B}{C_s} \right)$$

# VOLTAGE LOSSES

- For a fuel cell with reactants, **but NO LOAD**, will NOT generate any current. So we expect cell voltage to be at least to theoretical (i.e. 1.23).
- But this **OPEN CIRCUIT VOLTAGE (OCV)** is not, and is usually less than 1. Thus there are losses.
- When the circuit is closed, the voltage drops even more.



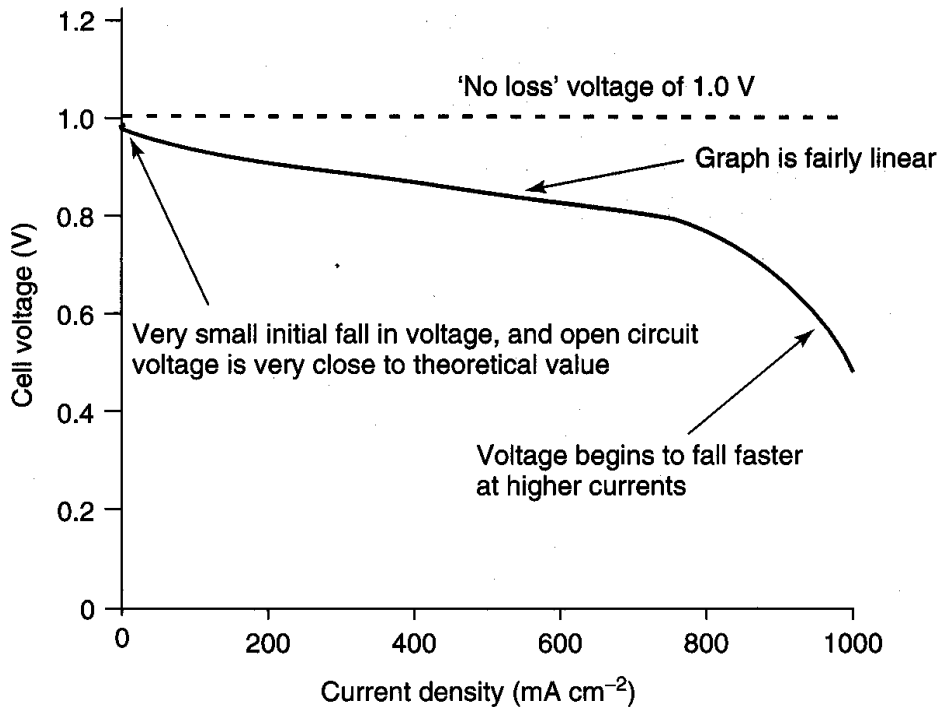
# VOLTAGE VERSUS CURRENT DENSITY BEHAVIOR- LOW TEMPERATURE FC



PEMFC  
operating at  
70°C

- ❑ The open circuit voltage is less than the theoretical value.
- ❑ There is rapid initial fall in voltage.
- ❑ The voltage then falls less slowly, and more linearly.
- ❑ There is sometimes a higher current density at which the voltage falls rapidly.

# VOLTAGE VERSUS CURRENT DENSITY BEHAVIOR- HIGH TEMPERATURE FC



**SOFC  
operating at  
800°C**

- The open circuit voltage is less than the theoretical value.
- The voltage then falls less slowly, and more linearly.
- At a higher current density, the voltage falls rapidly.

# LOSSES

(A.K.A. POLARIZATION/OVER POTENTIAL)

- ⊙ Difficulties in Reactions Reaching Reaction Sites
  - Activation Losses
- ⊙ Fuel Crossover & Internal Currents
- ⊙ Internal Electrical and Ionic Resistance
- ⊙ Electrochemical Reaction Kinetics
  - Mass Transport or Concentration Losses

# ACTIVATION POLARIZATION

- ◉ “*SOME*” voltage difference from equilibrium is needed to get the electrochemical reaction started. (similar to mechanical inertia)
- ◉ **Activation Losses** are caused by the slowness of the chemical reaction taking place at the surface of the electrodes.
- ◉ A portion of actual generated voltage is lost in **driving the chemical reaction** that transfers the electrons to or from the electrodes. This voltage drop is **highly nonlinear**, and temperature usually has a large influence on this type of overvoltage.





# ACTIVATION LOSSES –TAFEL EQUATION

- Based on experimental results, Tafel in 1905 correlated the OVERVOLTAGE at the surface of an electrode as follows.

$$\eta = \Delta V = E - V = A \ln\left(\frac{i}{i_0}\right); i > i_0$$

where the constant A is higher for a slower electrochemical reaction,  $i_0$  is the *exchange current density* when the overvoltage begins to move from zero. The faster the chemical reaction, higher is the value of exchange current density.

- Exchange current density is a measurement of the electrode readiness to perform (current per surface area).
- McDougall and others have now provided a theoretical basis for the Tafel equation and provided the formula for the constant A as follows.

# ACTIVATION LOSSES –TAFEL EQUATION

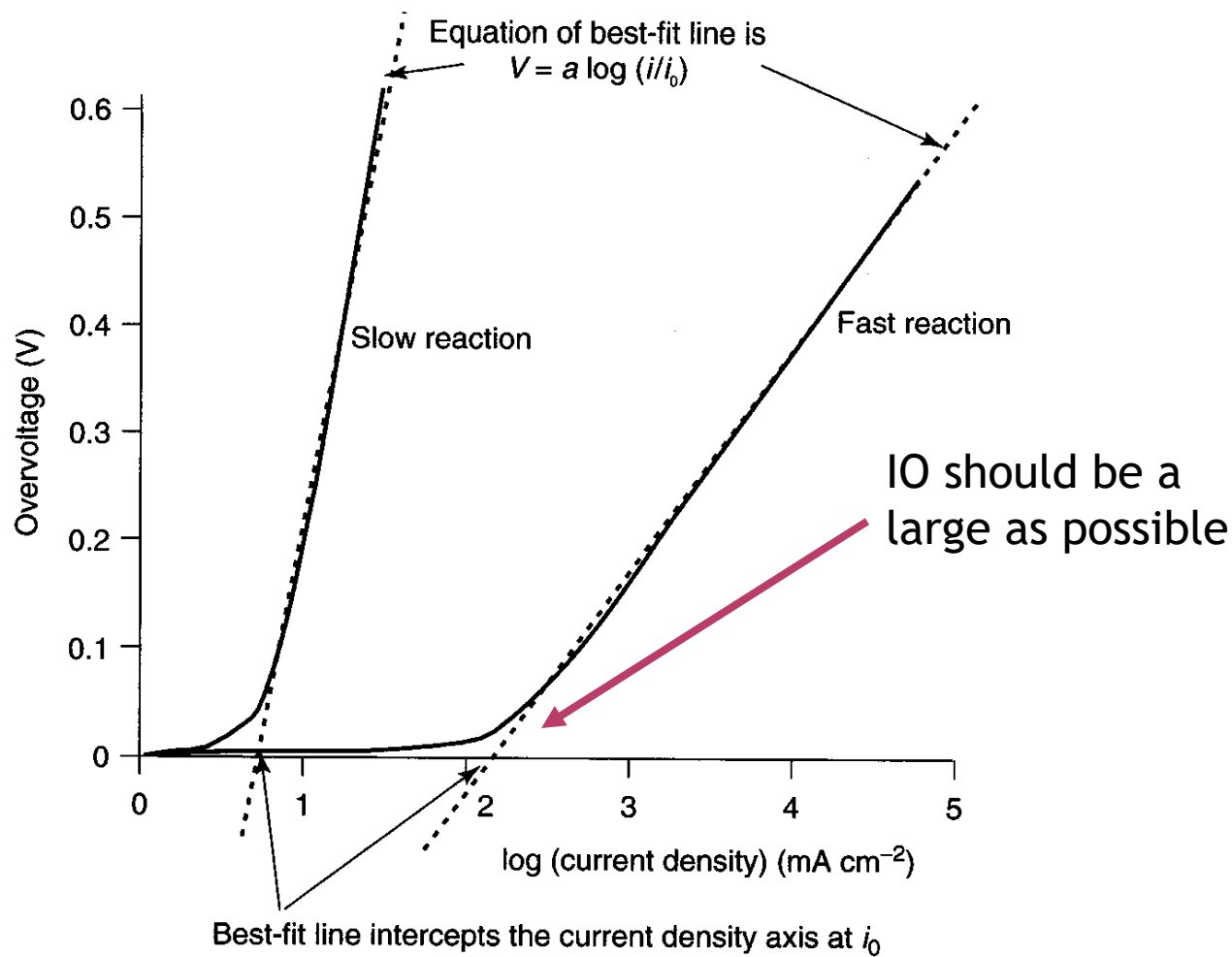
$$A = \frac{RT}{\alpha F}$$

where the constant  $\alpha$  is called *charge transfer coefficient*. Its value depends upon the reaction involved and the material of the electrode.

For the hydrogen electrode,  $\alpha \approx 0.5$  for most electrode materials. For the oxygen electrode,  $\alpha$  varies between 0.1 and 0.5.

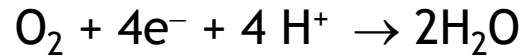
Note that while increasing T will increase A linearly (and hence the overvoltage), the effect of increase in T is significantly higher on  $i_0$  (several order of magnitudes, thus reducing overvoltage), and hence every attempt should be made to make the exchange current density  $i_0$  as high as possible. The  $i_0$  also depends upon several parameters in addition to the electrode material.

# TAFEL PLOTS FOR SLOW AND FAST REACTIONS

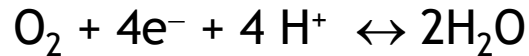


# ACTIVATION LOSSES –TAFEL EQUATION

- Let us review  $i_0$ : At the oxygen electrode of a PEMFC or PAFC, the reaction taking place is

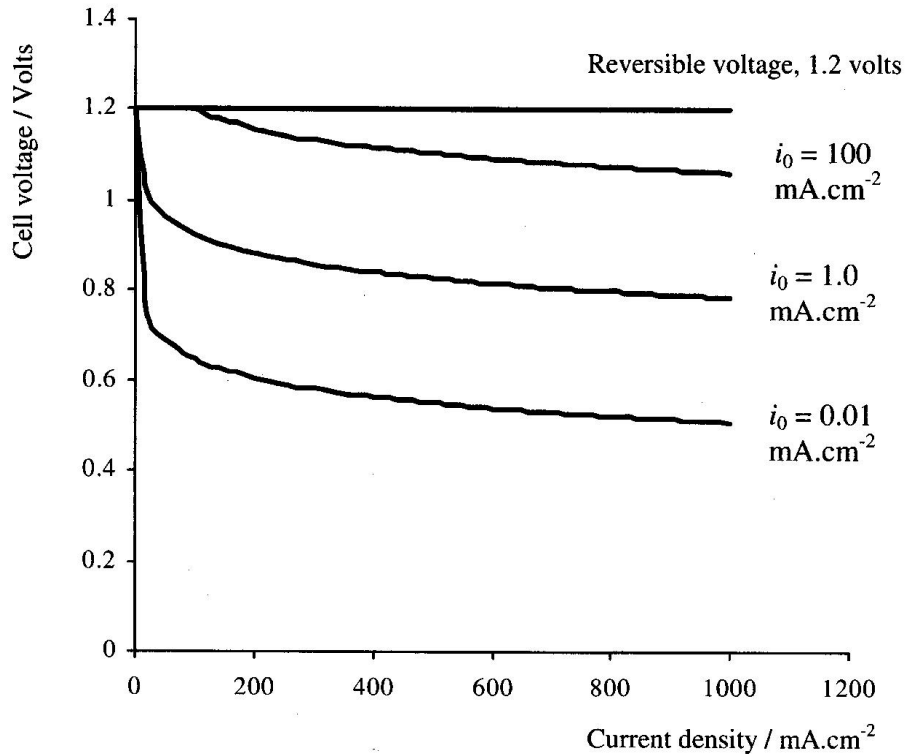


- At zero current density, there is no effective current generated, but the *chemical activity is taking place in forward and reverse directions* (continued flow of electrons from and to the electrode) in equilibrium as below.



- Hence, larger  $i_0$  means that the surface of the electrode is more active, and the current in one given direction is more likely to flow. Since the electrons flow preferentially in one given direction (from anode to cathode via outside circuit) in a fuel cell, the larger  $i_0$  will reduce the overvoltage losses.

# ACTIVATION LOSSES –TAFEL EQUATION



Let us consider an idealized situation of other losses in the fuel cell negligible except for the activation overvoltage. In that case, the voltage generated is the ideal EMF (E minus activation overvoltage) and is shown here.

**Figure 3.4** Graphs of cell voltage against current density, assuming losses are due only to the activation overvoltage at one electrode, for three different values of exchange current density  $i_0$ .

# TAFEL EQUATION – BUTLER-VOLLMER EQUATION

- ◉ *Tafel equation*

$$V = E - A \ln\left(\frac{i}{i_0}\right) = E - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right)$$

$$\Delta V = E - V = A \ln\left(\frac{i}{i_0}\right)$$

- ◉ This equation indicates that  $\Delta V = E - V = \eta$  = overvoltage is needed to cause the current flow  $i$  to or from an electrode and thus it is a measure of the thermodynamic irreversibility of the electrode reaction. By recasting in terms of  $I$ , we get

$$i = i_0 \exp\left(\frac{\alpha F \Delta V}{RT}\right) \quad \eta = \Delta V = E - V$$

- ◉ This equation is called the *Butler-Vollmer equation*. It shows a small change in  $\eta = \Delta V$  can cause a large change in the current flow  $i$ . **For a PEMFC,  $E = 1.23$  volts,  $A = 0.06$  volts and  $i_0 = 0.04$  mA/cm<sup>2</sup>.** The current flowing through a cell can be calculated by using this equation.

# ACTIVATION LOSSES –TAFEL EQUATION

- ⦿ The smaller is exchange current density  $i_0$ , the larger is the voltage drop.
- ⦿ For larger values of  $i_0$  such as  $100 \text{ mA/cm}^2$ , there is no voltage drop up to the current density  $i \leq 100 \text{ mA/cm}^2$ .
- ⦿ The impact of  $i_0$  is much more significant as the current density  $i$  increases.
- ⦿ At the low current densities, there is a sharp drop in voltage for the PEM fuel cell.
- ⦿ The **exchange current density  $i_0$**  is dependent upon the catalyst used on carbon electrodes, and the surface smoothness or roughness of the electrodes.



# EXCHANGE CURRENT DENSITY

The *exchange current density*  $i_0$  is dependent upon the catalyst used on carbon electrodes, and the surface smoothness or roughness of the electrodes. For example, the following table summarizes the value of  $i_0$  for various catalysts on the *smooth* hydrogen electrode of a PEMFC or PAFC.

Exchange Current Density: Elevated Pressures

$$i_0 = i_0 \left( \frac{P_{high}}{P_{low}} \right)^{0.75}$$

Metal	$i_0, \text{A/cm}^2$
Pb	$2.5 \times 10^{-13}$
Zn	$3 \times 10^{-11}$
Ag	$4 \times 10^{-7}$
Ni	$6 \times 10^{-6}$
Pt	$5 \times 10^{-4}$
Pd	$4 \times 10^{-3}$

# ACTIVATION LOSSES –TAFEL EQUATION

- There is a great variation in  $i_0$  with different catalysts.
- Platinum has one of the highest values of  $i_0$ .
- For an oxygen electrode,  $i_0 = 10^{-8}$  A/cm<sup>2</sup>, a much lower value than that at the hydrogen electrode (far worse effect than the lowest curve in Fig. 3.4).
- For real electrodes, the surface is rough, and the actual surface area is at least  $10^3$  larger than that for the smooth surface area. For PEMFC,  $i_0 = 0.1$  mA/cm<sup>2</sup> at cathode and 200 mA/cm<sup>2</sup> at the anode.
- Since  $i_0$  is much larger on the anode side compared to the cathode side, generally we **neglect** the overvoltage on the **anode side** in the **PEMFC** and **PAFC**.
- In contrast, the anode overvoltage is not negligible for the Direct Methanol Fuel Cell (DMFC), and the total activation overvoltage for this fuel cell is given by:

$$\text{Activation Voltage Drop } \Delta V = A_{anode} \ln\left(\frac{i}{i_{0a}}\right) + A_{cathode} \ln\left(\frac{i}{i_{0c}}\right)$$

# REDUCING ACTIVATION VOLTAGE

As we discussed, increasing the exchange current density  $i_0$  will reduce the activation overvoltage. The exchange current density  $i_0$  can be increased as follows:

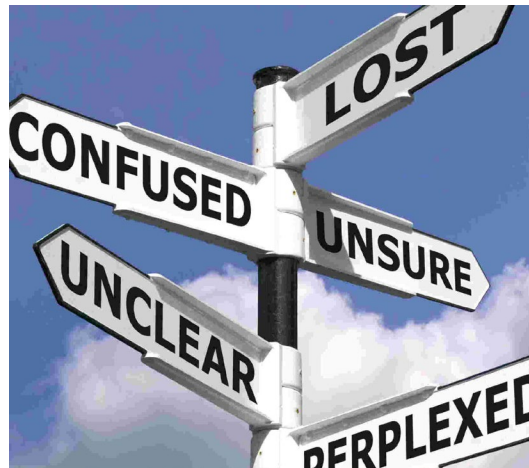
- Raise the cell operating temperature, in general.
- Use more effective catalyst such as platinum compared to silver, which increases the number of catalyst sites for reaction.
- Increase the roughness of the electrode surfaces, which increases the nominal surface area of the electrode several orders of magnitude.
- Increase the reactant concentration such as flowing more concentrated OXYGEN instead of air; similarly flow more concentrated hydrogen in a reformed fuel. With increased reactant concentration, the **catalysts sites are more effectively occupied by the reactants** as well as also increases the reversible open circuit voltage.
- Increase the **system pressure**, which increases the catalyst sites as well as also increases the reversible open circuit voltage.

# ACTIVATION LOSSES



⊙ Thus the overvoltage irreversibility is the most important irreversibility and a cause for voltage drop:

- at the cathode for the  $H_2/O_2$  fuel cell
- at the cathode and anode for the Direct Methanol Fuel Cell
- less important at high temperatures and pressures



**A FUEL CELL OPERATES AT 60C AND AMBIENT PRESSURE.  
EXCHANGE CURRENT DENSITY IS 0.0005 MA/CM2. ASSUME  
CHARGE TRANSFER COEFFICIENT TO BE 1.0. CALCULATE:**

*A. Activation voltage losses at 1.5 A / cm<sup>2</sup>.*

$$\eta = \Delta V = E - V = A \ln\left(\frac{i}{i_0}\right); i > i_0, A = \frac{RT}{\alpha F}$$

$$R = 8.314 J / mol - K, \alpha = 1, F = 96,485 C / mol$$

$$A = \frac{8.314 J / mol - K \cdot 333 K}{96,485 C / mol} = 0.02869 V (J / C)$$

$$\Delta V = 0.02869 V \ln\left(\frac{1,500}{0.0005}\right) = 0.4279 V$$

# FUEL CROSSOVER



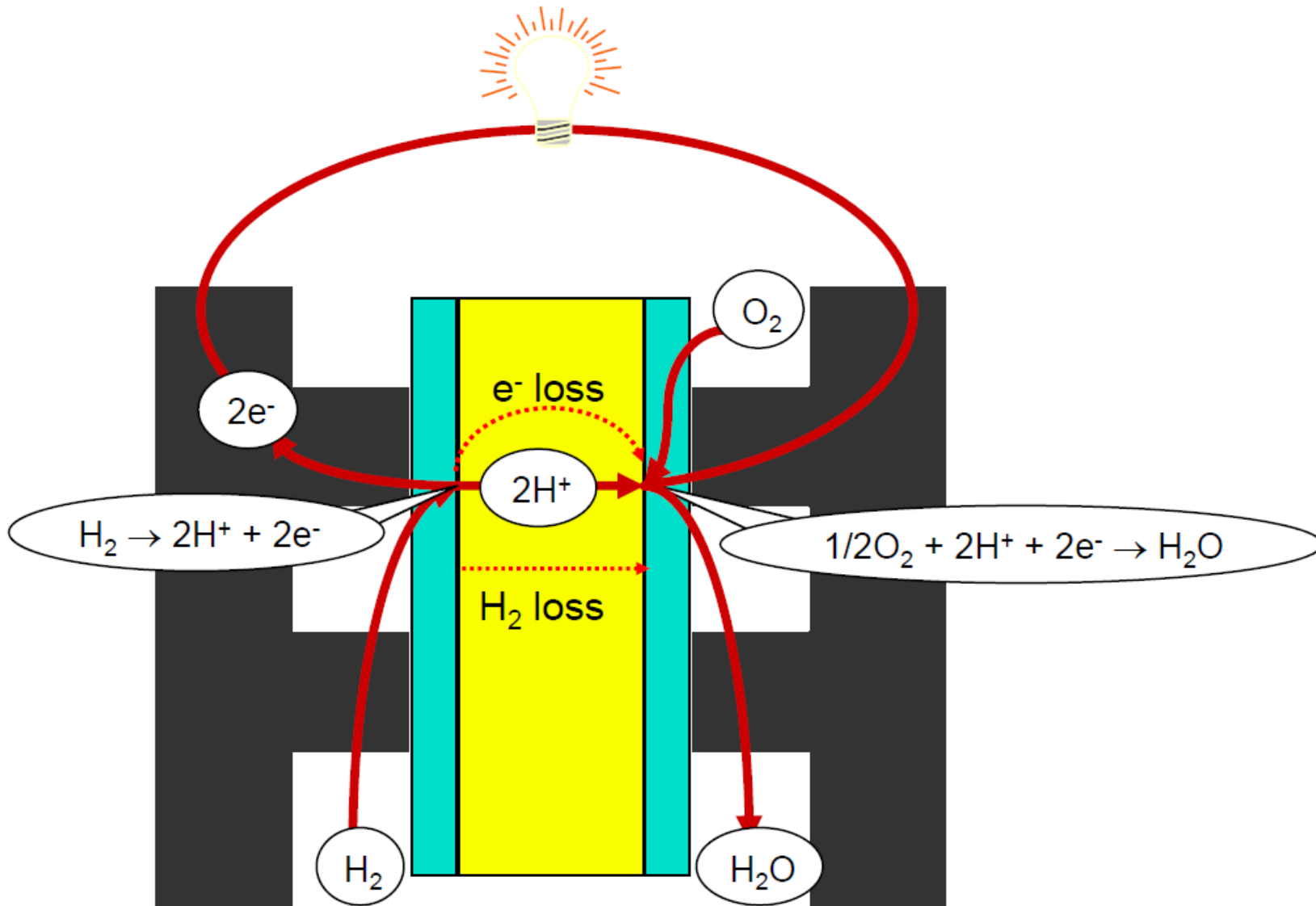
- ◉ *Fuel Crossover and Internal currents.*  
The electrolyte is supposed to pass only ions ( $H^+$ ,  $OH^-$ ,  $O^=$ , etc.) and not fuel or electrons. Generally a small amount of fuel diffuses and electron flows from the anode to the cathode side. This effect is particularly important for low temperature fuel cells.

# **FUEL CROSSOVER AND INTERNAL CURRENTS**

- ◉ Fuel crossover refers to the fuel directly diffusing from anode to cathode. This diffused fuel then reacts with the oxygen on the cathode side without generating any electricity and is thus wasted.
- ◉ Internal current refers to the electrons conducting through the electrolyte from the anode to the cathode side, and this current is then not available for external electrical circuit. Generally, the electrolyte material is chosen such that it allows ion conduction and very small electron conduction.
- ◉ Both fuel crossover and internal currents are essentially equivalent and have the identical effect whether you lose one molecule of hydrogen fuel or two electrons!



# Internal currents and fuel crossover



# CELL VOLTAGES AT LOW CURRENT DENSITIES

Current density (mA cm <sup>-2</sup> )	Voltage (V)
0	1.2
0.25	1.05
0.5	1.01
1.0	0.97
2.0	0.92
3.0	0.90
4.0	0.88
5.0	0.87
6.0	0.86
7.0	0.85
8.0	0.84
9.0	0.83

If the internal current density is 1.0 mA cm<sup>-2</sup>, then the open circuit voltage will drop to 0.97 V

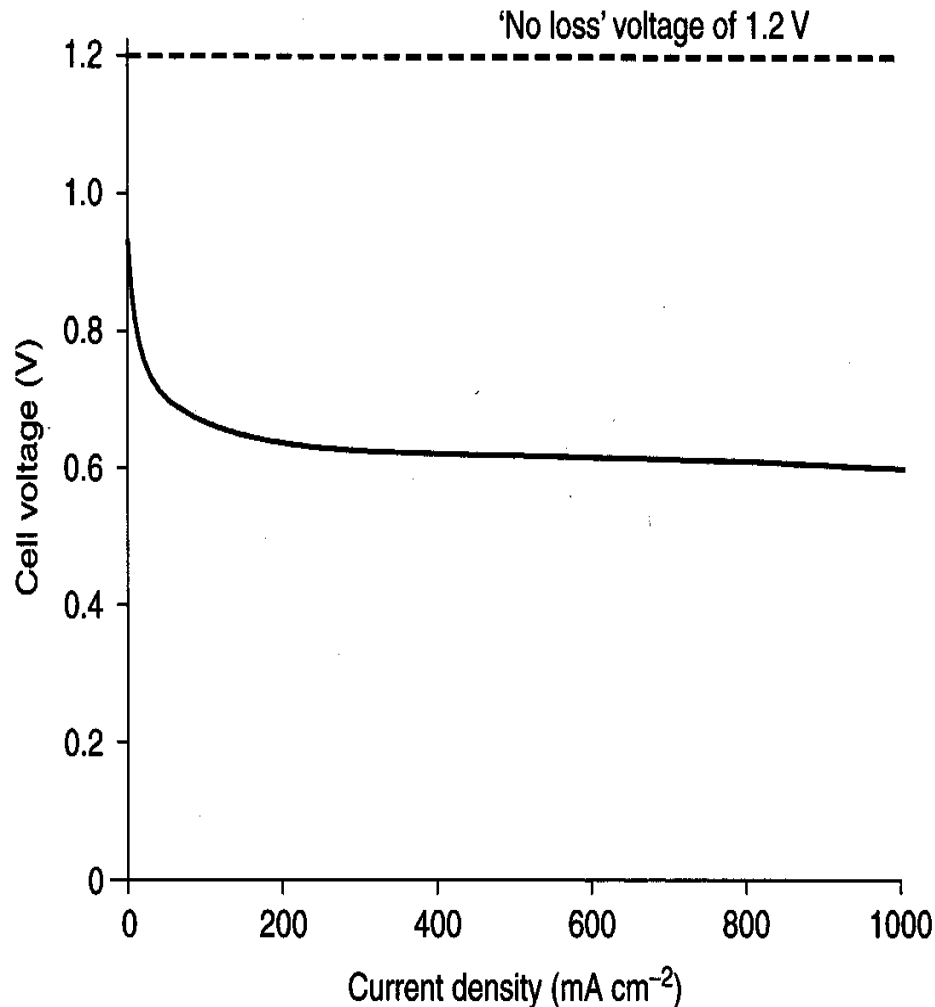
# FUEL CROSSOVER LOSS

- ◉ The reduction in the voltage produced due to fuel crossover and internal current ( $i_n$ ) is taken into account in the same manner as for the overvoltage where the current density  $i$  of the cell is replaced by  $i + i_n$  (slide 13).

$$V = E - A \ln \left( \frac{i + i_n}{i_0} \right), \quad A = \frac{RT}{\alpha F}$$

- ◉ For a PEMFC, using typical values:  $E = 1.23 \text{ V}$ ,  $A = 0.06 \text{ V}$ ,  $i_0 = 0.04 \text{ mA/cm}^2$  and  $i_n = 3 \text{ mA/cm}^2$ , we obtain the following V-I curve.

# FUEL CELL VOLTAGE USING ACTIVATION AND FUEL CROSSOVER/INTERNAL CURRENT LOSSES



*Hydrogen crossover is a function of membrane permeability, membrane thickness, and hydrogen partial pressure, i.e. hydrogen concentration difference across the membrane as the main driving force.*

*A very low **OPEN CIRCUIT VOLTAGE (OCV)** (i.e. no external current) well below 0.9 may indicate either a hydrogen leak or an electrical short.*

# INTERNAL CURRENTS & CROSSOVER

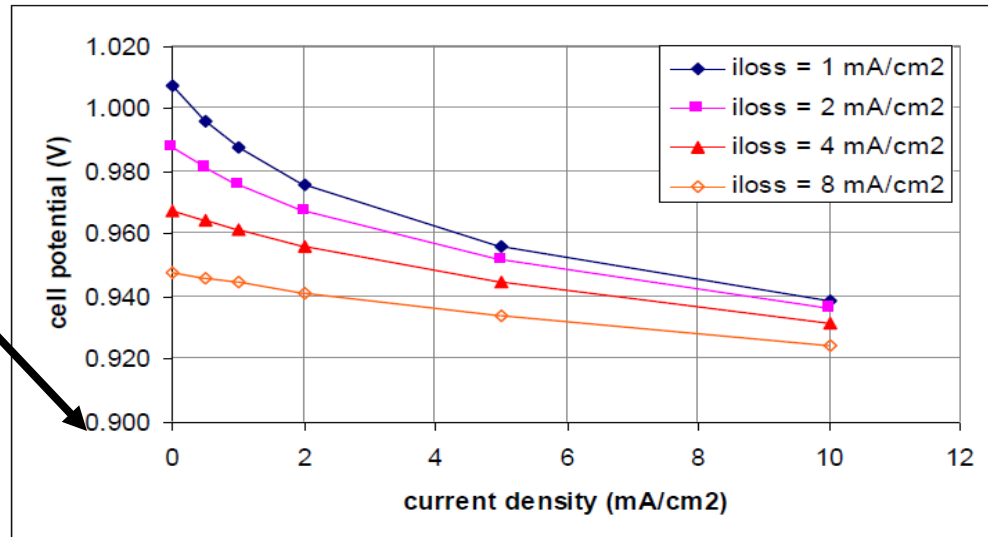
$$\frac{I_{loss} \left[ \frac{\text{Coulombs}}{\text{sec}} = \frac{\text{Amp} \cdot \text{sec}}{\text{sec}} = \text{Amp} \right]}{\text{cell}} = n \left[ \frac{\text{moles of electrons}}{\text{moles of reactant}} \right] \cdot F \left[ \frac{\text{Coulombs}}{\text{moles of electrons}} \right] \cdot \frac{N \left[ \frac{\text{moles of reactant}}{\text{sec}} \right]}{\text{cell}}$$

Both internal currents and hydrogen crossover mean loss of current:

$$I_{loss} = 2FN_{loss}$$

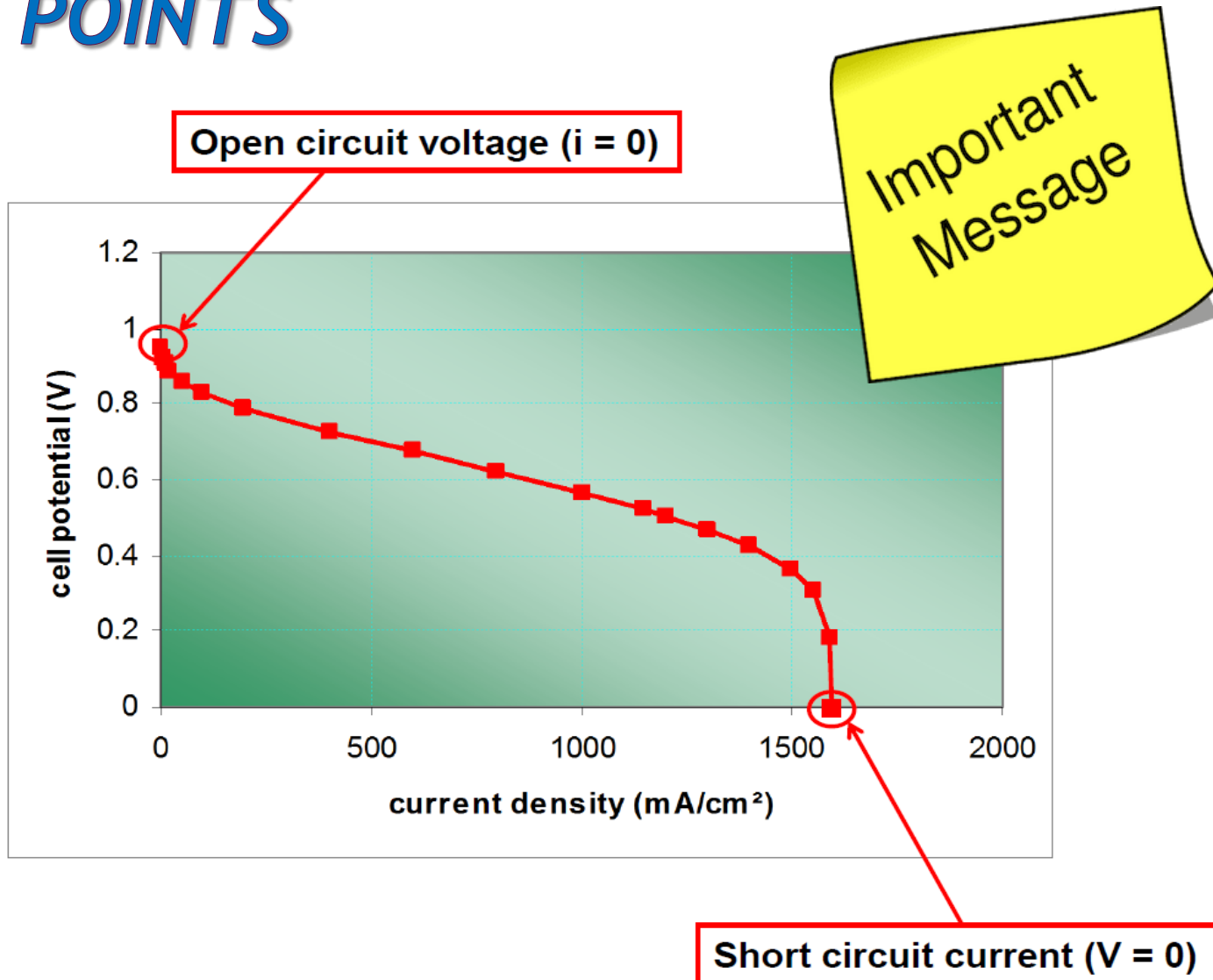
This means that even at 0 external current there is hydrogen consumption.

$$V_{cell} = E_{T,P} - \frac{RT}{\alpha F} \ln \left( \frac{i + i_{loss}}{i_0} \right)$$



$$i_{loss} = i_0 \cdot \exp \left[ \frac{E_{T,P} - V_c}{\frac{RT}{\alpha F}} \right]$$

# FUEL CELL POLARIZATION CURVE: KEY POINTS



Adopted From Frano Barbir

# CROSSOVER CURRENT @ OCV

- Consider the H<sub>2</sub>/O<sub>2</sub> fuel cell operating at STP with an open circuit: **Surface area of the electrode (or electrolyte) = 10 cm<sup>2</sup>**, **hydrogen consumption (flow rate per cell) = 0.0034 cm<sup>3</sup>/sec.** Determine the **H<sub>2</sub> crossover current.** MOLAR VOLUME

$$STP: T = 273.15K(0C), P = 101,300Pa (101.3kPa)$$

IDEAL GAS

$$v \left[ \frac{m^3}{kg} \right] = \frac{V}{m} \left[ \frac{m^3}{kg} \right] = \frac{RT}{P}, \bar{v} \left[ \frac{m^3}{mole} \right] = \frac{V}{n} \left[ \frac{m^3}{mole} \right] = \frac{\bar{R}T}{P};$$

$$R = \frac{\bar{R}}{MW_{H_2}} = \frac{8.3144 \frac{J}{mol-K}}{2.016 \frac{g}{mole}} = 4.1242 \frac{J}{g-K}$$

$$\bar{v} = \frac{V}{n} \left( \frac{m^3}{mole} \right) = \frac{8.3144 \frac{J}{mol-K} \cdot 273.15K}{101,300Pa} = 0.0224189 \frac{m^3}{mole} \cdot \frac{1000L}{m^3} = 22.42 \frac{Liters}{mole}$$

$$\rho \left[ \frac{g}{m^3} \right] = \frac{P}{RT} = \left[ \frac{101,300Pa \left( \frac{N}{m^2} \right)}{4.1242 \frac{J(N-m)}{g-K} \cdot 273.15K} \right] = 89.92 \frac{g}{m^3} \cdot \frac{1kg}{1000g} = 0.08992 \frac{kg}{m^3}$$

$$\dot{m} = \frac{0.0034 \frac{cm^3}{s}}{cell} \cdot \frac{0.001L}{cm^3} = \frac{3.4 \times 10^{-6} \frac{L}{s}}{cell}$$

H<sub>2</sub> CONSUMPTION FLOW RATE/cell

$$\frac{\dot{N}_{H_2}}{cell} = \frac{\dot{m}}{\bar{V}} = \frac{\frac{3.4 \times 10^{-6} \frac{Liter}{s}}{cell}}{22.42 \frac{Liter}{mole}} = \frac{1.5165 \times 10^{-7} \frac{moles \text{ of reactant}}{s}}{cell} @ STP$$



# CONTINUE....

## H2 CONSUMPTION FLOW RATE/cell

$$\frac{\dot{N}_{H_2}}{\text{cell}} = \frac{\dot{m}}{\bar{V}} = \frac{3.4 \times 10^{-6} \frac{L}{s}}{22.42 \frac{\text{Liters}}{\text{mole}}} = \frac{1.5165 \times 10^{-7} \frac{\text{moles of reactant}}{s}}{\text{cell}}$$

## H2 CROSOVER CURRENT

$$\dot{N}_{H_2} = \frac{i \frac{C}{s} [\text{amps}]}{n \left[ \frac{\text{moles of electrons}}{\text{mole of reactant}} \right] F \left[ \frac{C}{\text{mole of electrons}} \right]} = \frac{\text{mole of reactant}}{\text{sec}}$$

$$i = \dot{N}_{H_2} n F = \frac{1.5165 \times 10^{-7} \frac{\text{moles of reactant}}{s}}{\text{cell}} \cdot 2 \frac{\text{moles of electrons}}{\text{mole of reactant}} \cdot 96,485 \frac{C}{\text{mole of electrons}}$$

$$= \frac{0.029263 \frac{C}{s} (\text{Amps})}{\text{cell}} = 29 \text{mA per cell}$$

# PEMFC OCV (OPEN CIRCUIT VOLTAGE)

- ◉ Compute ***Voltage Reduction*** due to CROSSOVER Current: Assume
- ◉ PEMFC, using typical values:  $E = 1.23 \text{ V}$ ,  $A = 0.06 \text{ V}$ ,  $i_0 = 0.4 \text{ mA/cm}^2$

CURRENT DENSITY:  $i = \frac{i}{A} = \frac{29 \text{ mA}}{10 \text{ cm}^2} = 2.9 \text{ mA/cm}^2$

$$\Delta V = V_n - E = -A \ln \left( \frac{i_n}{i_0} \right)$$

$$= -0.06 \ln \left( \frac{2.9}{0.4} \right) \text{ V}$$

$$= -0.11886 \text{ V / cell}$$

For a 100 cell stack, this is 11.9 Volts/stack.

# CONSUMPTION RATES (FARADAY LAW)

⊙ For the H<sub>2</sub>/O<sub>2</sub> Fuel Cell PER CELL

anode:  $H_2 \rightarrow 2H^+ + 2e^-$ ; → CONSUMPTION=2 ELECTRONS

cathode:  $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ ; → CONSUMPTION=4 ELECTRONS

overall:  $H_2 + 1/2O_2 \rightarrow H_2O$ ; → PRODUCT:1MOLE H<sub>2</sub> → 1MOLE H<sub>2</sub>O=2 ELECTRONS

For every mole of REACTANTS → 1 moles H<sub>2</sub>O, 2 electron moles of H<sub>2</sub>, 4 electron moles of O<sub>2</sub>

CONSUMPTION RATES → GAS REACTANTS FOR EACH CELL

$$\dot{m}_{H_2} \left[ \frac{g}{sec} \right] = \frac{I}{2F} \left[ \frac{\text{moles of } H_2 \text{ Reactant}}{sec} \right] \cdot M_{W_{H_2}} \left[ \frac{g}{\text{moles of } H_2} \right]$$

$$\dot{m}_{O_2} \left[ \frac{g}{sec} \right] = \frac{I}{4F} \left[ \frac{\text{moles of } O_2 \text{ Reactant}}{sec} \right] \cdot M_{W_{O_2}} \left[ \frac{g}{\text{moles of } O_2} \right]$$

$$\dot{m} [SLM] = \frac{I}{nF} \left[ \frac{\text{moles}}{sec} \right] \cdot \frac{22.42 \text{ Liters}}{\text{mole}} \cdot \frac{60 \text{ sec}}{\text{min}} \rightarrow \text{LITERS PER MINUTE@0C/101.3kPa}$$



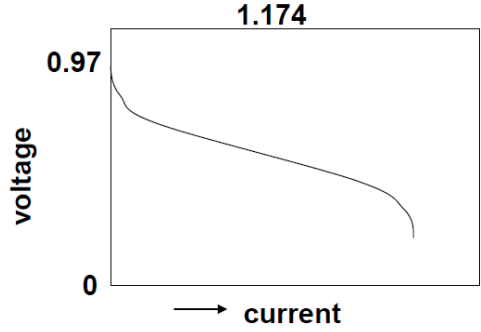
GENERATION RATES → LIQUID PRODUCTS

$$\dot{m}_{H_2O} \left[ \frac{g}{sec} \right] = \frac{I}{2F} \left[ \frac{\text{moles of } H_2O \text{ Product}}{sec} \right] \cdot M_{W_{H_2O}} \left[ \frac{g}{\text{moles of } H_2O} \right]$$

$$\dot{m} [SLM] = \frac{I}{nF} \left[ \frac{\text{moles}}{sec} \right] \cdot M_{W_{H_2O}} \left[ \frac{g}{\text{mole}} \right] \cdot \frac{60 \text{ sec}}{\text{min}} \cdot \frac{1}{\rho_{H_2O} \frac{g}{m^3}} \cdot \frac{1000L}{m^3}; (\dot{m} = \rho Q, Q = \frac{\dot{m}}{\rho})$$

# ACTUAL FC STACK FLOW RATES

◉ In general for real systems:



$$\lambda_f \equiv \text{FUEL UTILIZATION EFF.} = \frac{1}{S} = \frac{1}{\text{STOICHIOMETRY}}$$

$S \equiv$  stoichiometric factor  $\equiv \frac{\text{actual fuel supplied}}{\text{exact fuel amount needed for reaction}} \geq 1$   
 = 1 for dead ended stacks

$$\frac{\dot{m}(I) \left[ \frac{g}{\text{sec}} \right]}{\text{stack}} = \frac{I \left[ \frac{C/s}{\text{cm}^2} \right] A_p \frac{\text{Area} \left[ \frac{\text{cm}^2}{\text{cell}} \right] \cdot \frac{\text{cells}}{\text{stack}}}{n \left[ \frac{\text{moles of electrons}}{\text{moles of reaction}} \right] F \left[ \frac{C}{\text{moles of electrons}} \right]} \cdot \frac{1}{\lambda_f} \cdot M_{w_{H_2}} \left[ \frac{g}{\text{moles of reaction}} \right]$$

$$\frac{\dot{m} \left[ \frac{L}{\text{min}} \right]}{\text{stack}} = \frac{\dot{m} \left[ \frac{g}{\text{sec}} \right]}{\text{stack}} \cdot \frac{1}{M_{w_{H_2}}} \left[ \frac{\text{moles of reaction}}{g} \right] \cdot \frac{22.42 \text{ Liters (@ 0C)}}{\text{mole of reaction}} \cdot \frac{60 \text{ sec}}{\text{min}} \cdot \frac{T(K)}{273.15}$$

$$I^* = CD \equiv \text{CURRENT DENSITY} = \left[ \frac{C/s}{\text{cm}^2} \right] = \frac{\text{Amps}}{\text{cm}^2}$$

# “AIR” FLOW CONSUMPTION/STACK

$$\frac{\dot{m}(I) \left[ \frac{g}{sec} \right]}{stack_{O_2}} = \frac{I \left[ \frac{C/s}{cm^2} \right] A_p \frac{Area}{cell} \left[ \frac{cm^2}{cell} \right] \cdot \frac{cells}{stack}}{n \left[ \frac{\text{moles of electrons}}{\text{moles of reactant}} \right] F \left[ \frac{C}{\text{moles of electrons}} \right]} \cdot S_{Air} \cdot Mw_{O_2} \left[ \frac{g}{\text{moles of reactant}} \right]$$

$n = 4$

$$\frac{\dot{m} \left[ \frac{L}{min} \right]}{stack_{AIR}} = \frac{\dot{m} \left[ \frac{g}{sec} \right]}{stack_{O_2}} \cdot \frac{1}{p_{O_2}} \frac{1}{Mw_{O_2}} \left[ \frac{\text{moles of reactant}}{g} \right] \cdot \frac{22.42 \text{ Liters (@ } 0C)}{\text{mole of reactant}} \cdot \frac{60 \text{ sec}}{\text{min}} \cdot \frac{T(K)}{273.15}$$

$p_{O_2} \equiv$  partial pressure oxygen in air = 0.21

# EXIT CONDITIONS

## EXIT H2 MASS FLOW

$$\begin{aligned}\frac{\dot{m}_{H2out}}{cell} &= \dot{m}_{H2in} - \dot{m}_{H2CONSUMPTION} \\ &= S_{H_2} \frac{I}{2F} M_{H_2} - \frac{I}{2F} M_{H_2}, \rightarrow g / \text{sec} \\ &= (S_{H_2} - 1) \frac{I}{2F} M_{H_2} \text{ g/sec per cell}\end{aligned}$$

## EXIT AIR/N2 MASS FLOW

$$\begin{aligned}\frac{\dot{m}_{AIRout}}{cell} &= \dot{m}_{O_2OUT} + \dot{m}_{N_2IN} \text{ (Nitrogen does not participate in the reaction)} \\ &= \left[ (S_{O_2} - 1)M_{O_2} + S_{O_2} \frac{1 - r_{O_2in}}{r_{O_2in}} M_{N_2} \right] \frac{I}{4F} \text{ g/sec per cell}\end{aligned}$$

## EXIT OXYGEN VOLUME FRACTION

$$r_{O_2out} = \frac{O_2_{OUT}}{AIR_{IN}} = \frac{S_{O_2} - 1}{\frac{S_{O_2}}{r_{O_2in}} - 1}; \quad r_{O_2in} = 0.21 \text{ Normally}$$

Consider a H<sub>2</sub>/O<sub>2</sub> fuel cell stack of 300 plates and plate area of 100 cm<sup>2</sup>.

Determine the hydrogen mass flow rate as a function of the current density (A/cm<sup>2</sup>) assuming a fuel utilization of 95%.

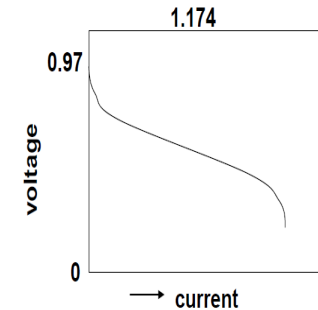
SOLUTION

$$\frac{\dot{m}(I) \left[ \frac{g}{\text{sec}} \right]}{\text{stack}} = \frac{I \left[ \frac{C/s}{\text{cm}^2} \right] A_p \frac{\text{Area} \left[ \frac{\text{cm}^2}{\text{cell}} \right] \cdot \text{cells}}{\text{stack}}}{n \left[ \frac{\text{moles of electrons}}{\text{moles of reactant}} \right] F \left[ \frac{C}{\text{moles of electrons}} \right]} \cdot \frac{1}{\eta_f} \cdot M_{w_{H_2}} \left[ \frac{g}{\text{moles of reactant}} \right]$$

$$\frac{\dot{m}(I) \left[ \frac{g}{\text{sec}} \right]}{\frac{\text{stack}}{\frac{\text{Amps}}{\text{cm}^2}}} = \frac{A_p \left[ \frac{\text{cm}^2}{\text{cell}} \right] \cdot \text{cells}}{nF} \cdot \frac{1}{\text{stack}} \cdot \frac{1}{\lambda_f} \cdot M_{w_{H_2}} \left[ \frac{g}{\text{moles of reactant}} \right]$$

$$\frac{\dot{m}(I) \left[ \frac{g}{\text{sec}} \right]}{\frac{\text{stack}}{\frac{\text{Amps}}{\text{cm}^2}}} = \frac{100 \frac{\text{cm}^2}{\text{cell}} \cdot 300 \frac{\text{cells}}{\text{stack}}}{2 \left[ \frac{\text{moles of electrons}}{\text{moles of reactant}} \right] \cdot 96,485 \frac{C(= A - \text{sec})}{\text{moles of electrons}}} \cdot \frac{1}{0.95} \cdot \frac{2.016g}{\text{moles of reactant}}$$

$$\frac{\dot{m}(I) \left[ \frac{g}{\text{sec}} \right]}{\frac{\text{Amps}}{\text{cm}^2}} = 0.333 \frac{g/\text{sec}}{\text{Amps}/\text{cm}^2} = 0.333 \frac{g/\text{sec}}{CD} \text{ per stack, } CD = \text{CURRENT DENSITY} = \frac{\text{Amps}}{\text{cm}^2}$$





# RESISTIVE LOSSES (OHMIC)

Ohmic law:  $\Delta V = I \cdot R = i \cdot R_i$

$I$  = current (Amps)

$R$  = resistance (Ohms)

$i$  = current density ( $A/cm^2$ )

$R_i$  = aerial resistance ( $Ohm \cdot cm^2$ )

$$R = \rho \frac{d}{A}$$

$\rho$  = resistivity ( $Ohm \cdot cm$ )

$d$  = distance, length (cm)

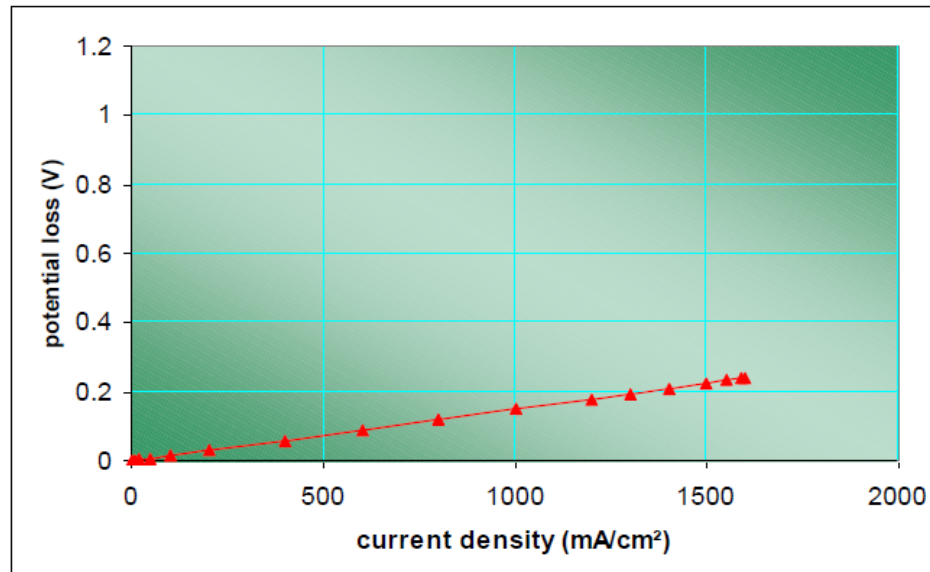
$A$  = cross sectional area ( $cm^2$ )

$$R_i = R \cdot A$$

Resistance through:

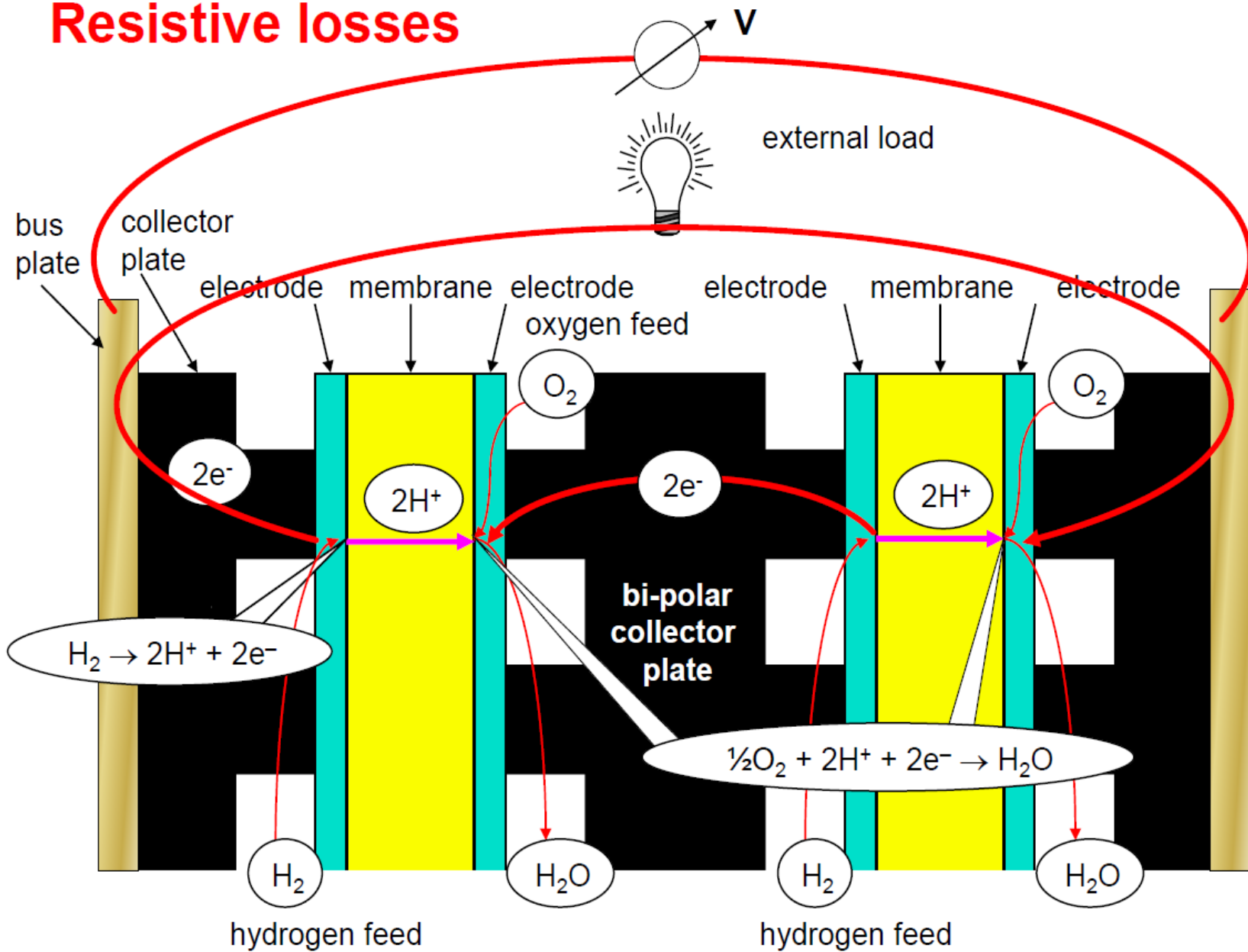
- Membrane (ionic)
- Electrodes
- Bi-polar plates
- Interfacial contacts

$$R_i = R_{i,i} + R_{i,e} + R_{i,c}$$



Adopted From Frano Barbir

# Resistive losses



Adopted From Frano Barbir

# OHMIC LOSSES

- ◉ The losses in the voltage generated due to electrical resistance of ion flow through the electrolyte is most important. The amount of this voltage drop is proportional to current flow rate.

$$\Delta V = IR$$

- ◉ There are two currents through the electrolyte: **the current (ion) flow rate  $i$**  and the **internal current  $i_n$** , both in mA/cm<sup>2</sup>
- ◉ The electrical resistance of electrodes and the cell interconnects or bipolar plates is generally small. Here, we will neglect them considering them as a second order of magnitude.
- ◉ Since we represent all losses in terms of the current density, we represent ohmic losses also in terms of current density based on the surface area of the “smooth” plate of the cell electrode/electrolyte.

$$\Delta V = (i + i_n)r$$

where  $i$  is the current density in mA/cm<sup>2</sup>,  $i_n$  is the internal current density in mA/cm<sup>2</sup>, and  $r$  is the area specific resistance (ASR) in kΩ·cm<sup>2</sup>.

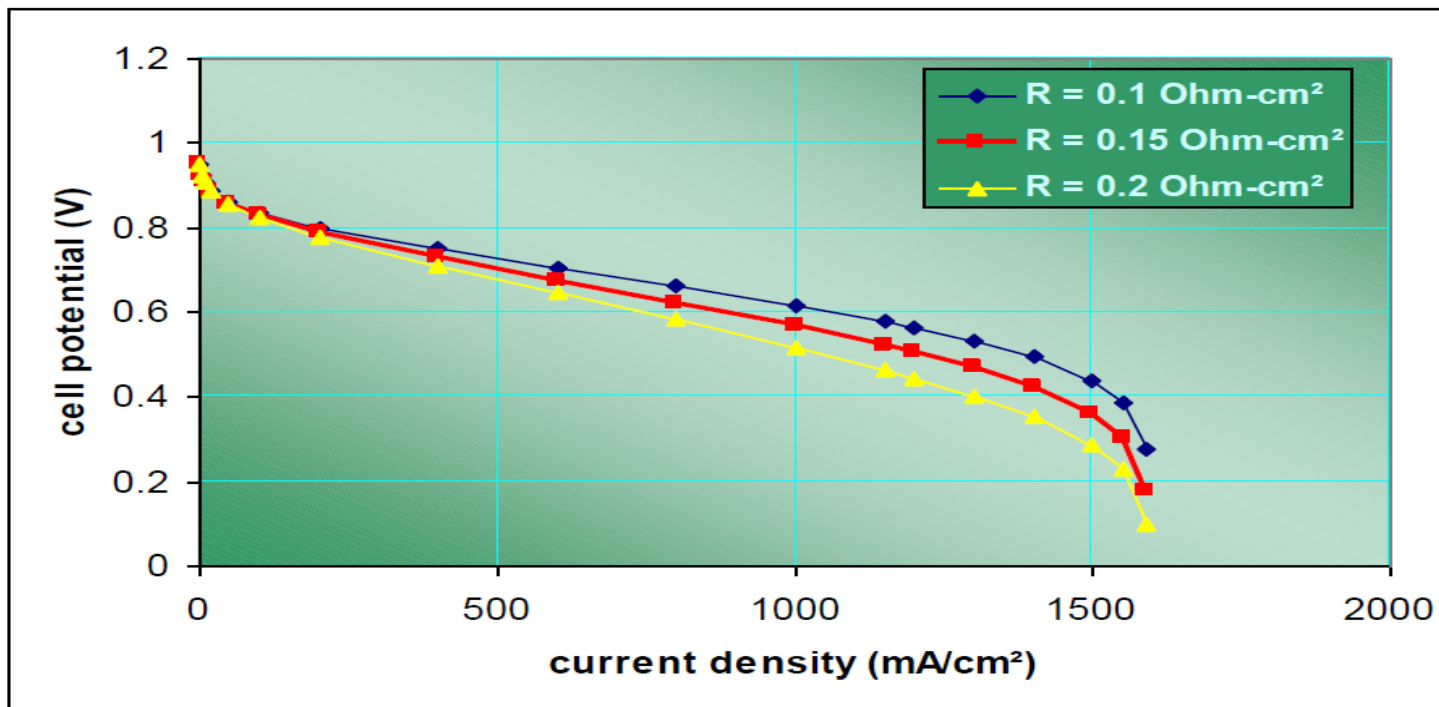
- ◉ The ‘**OHMIC**’ voltage loss is important in all types of the fuel cells, but more important in SOFC due to high temperatures > 800C.

# ***METHODS TO REDUCE INTERNAL RESISTANCE***

- ◉ Choose the electrode material with the highest possible electrical conductivity.
- ◉ Select good design and use of appropriate materials for the bipolar plates or cell interconnects.
- ◉ Make the electrolyte ***as thin as possible*** keeping into consideration that it may support electrodes and/or needs to be wide enough to allow a circulating flow of electrolyte, particularly when the electrolyte is in liquid form. It must be robust enough to prevent any shorting of one electrode to another through the electrolyte.

# IMPACT OF RESISTANCE

$$V_{\text{cell}} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{\text{loss}}}{i_0}\right) - i \cdot R_i + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right)$$



$i$  = external current density

$i_{\text{loss}}$  = current density loss due to fuel crossover and internal currents

$i_l$  = limiting current density prior to short circuit current (0 Volts)

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**IF THE RESISTIVE LOSSES AT 1.5 A/CM<sup>2</sup> ARE 50% OF THE ACTIVATION LOSSES, CALCULATE THE CELL RESISTANCE, RI.**

*B. Resistive voltage losses at 1.5 A / cm<sup>2</sup> and 50% Activation Losses.*

$$\eta = \Delta V = E - V = A \ln\left(\frac{i}{i_0}\right); i > i_0, A = \frac{RT}{\alpha F}$$

$$R = 8.314 J / mol - K, \alpha = 1, F = 96,485 C / mol$$

$$A = \frac{8.314 J / mol - K \cdot 333 K}{96,485 C / mol} = 0.02869 V (J / C)$$

$$\Delta V = 0.02869 V \ln\left(\frac{1,500}{0.0005}\right) = 0.4279 V$$

$$\begin{aligned} \Delta V_R &= 0.50 \cdot 0.4279 V \\ &= 0.2139 V = IR \end{aligned}$$

$$R = \frac{0.21394 V}{1.5 A / cm^2} = 0.14262 \Omega - cm^2$$

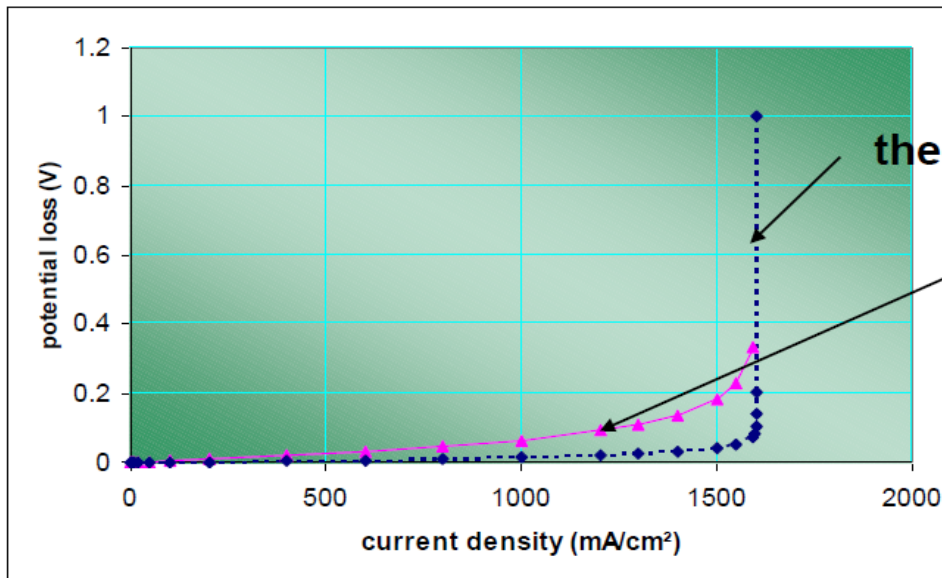
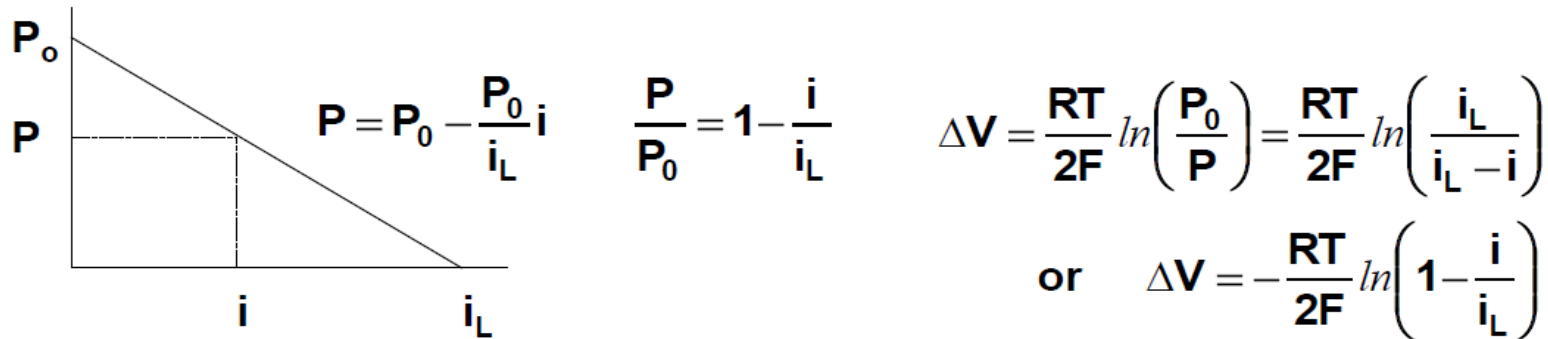


# MASS TRANSPORT/CONCENTRATION POLARIZATION

- ◉ The reaction concentration at the catalyst surface depends on the current density (mA/cm<sup>2</sup>). (i.e. The **HIGHER** the **CURRENT DENSITY**, the **LOWER** the surface Concentration)
- ◉ The surface concentration reaches zero when the rate of consumption becomes equal to the diffusion rate; in other words, the **reactants are consumed at the same rate as it is reaching the surface.**
- ◉ Thus, the concentration of reactant and the catalyst surface is equal to zero.
- ◉ The current density at which this happens is called the **LIMITING CURRENT DENSITY.** (cathode anode)
- ◉ A fuel cell can't produce **MORE THAN** the limiting current because there are no more reactants at the catalyst surface. (**Every fuel cell has different limiting value**)
- ◉ In case of oxygen, its partial pressure will go down with consumption. In the case of hydrogen, if there are other components present, its partial pressure will go down. **If pure hydrogen flows along the anode, its pressure will go down due to pressure drop associated with the flow.**



# TRANSPORT POLARIZATION & LIMITING CURRENT DENSITY



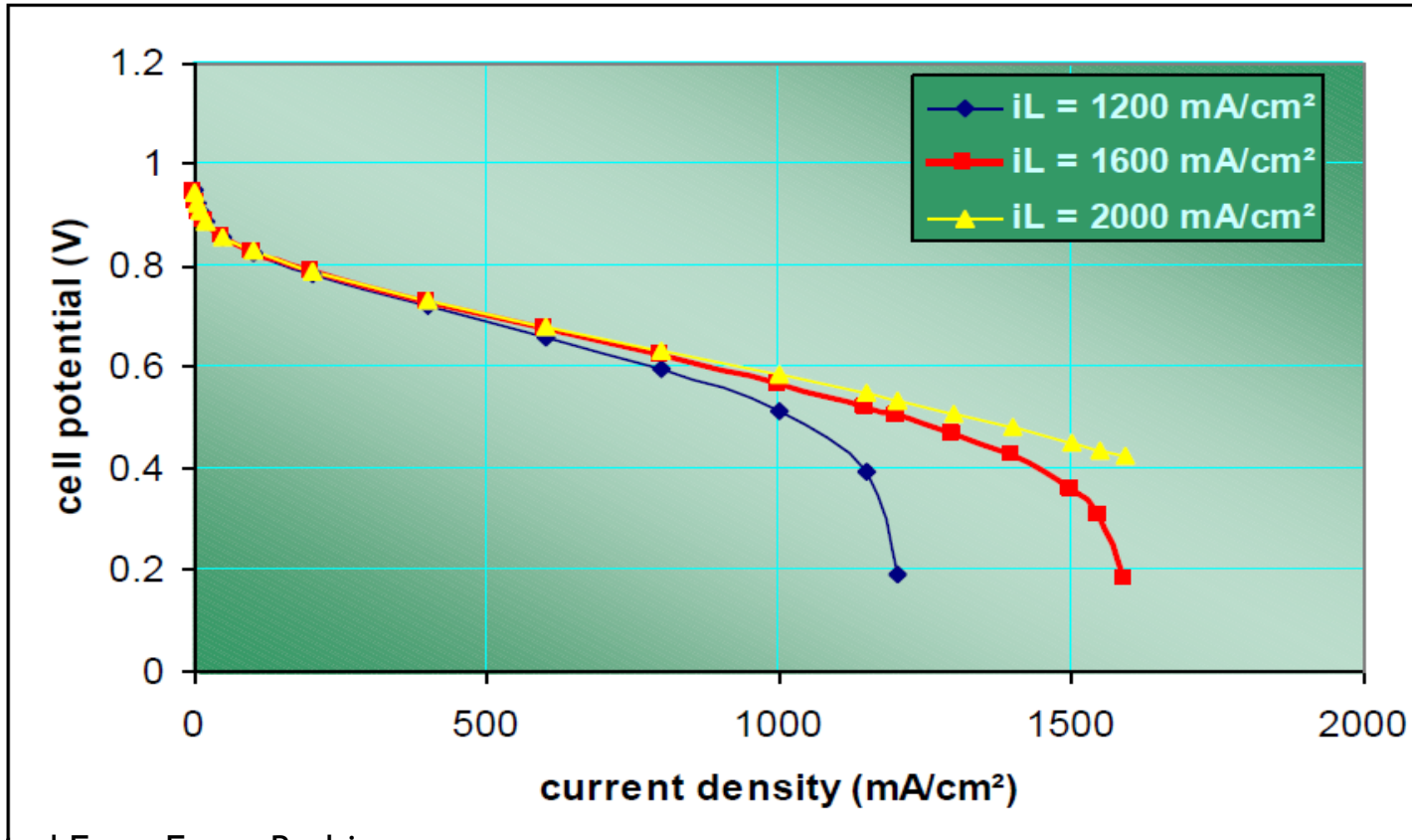
theoretical  
 more realistic

$$\Delta V_{\text{conc}} = C \cdot \exp\left(\frac{i}{d}\right)$$

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# EFFECT OF LIMITING CURRENT DENSITY

$$V_{\text{cell}} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{\text{loss}}}{i_0}\right) - i \cdot R_i + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right)$$



# COMPUTE CELL VOLTAGE AT 60C, 1BAR, 500 MA/CM2

Cell Voltage at 60C 1Bar, 500mA/cm<sup>2</sup>

$$i_0 = 0.003 \text{ mA/cm}^2, i_{\text{loss}} = 1.2 \text{ mA/cm}^2, i_L = 800 \text{ mA/cm}^2$$

$$\alpha = 0.5, R_i = 0.15 \Omega \text{ - cm}^2, A = \frac{RT}{\alpha F}$$

$$R = 8.314 \text{ J/mol - K}, F = 96,485 \text{ C/mol}$$

$$A = \frac{8.314 \text{ J/mol - K} \cdot 333 \text{ K}}{0.5 \cdot 96,485 \text{ C/mol}} = 0.05739 \text{ V (J/C)}$$

$$\begin{aligned} V_{\text{cell}} &= E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{\text{loss}}}{i_0}\right) + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right) - iR \\ &= E_{T,P} - 0.05739 \text{ V} \ln\left(\frac{500 + 1.2}{0.003}\right) + \frac{8.314 \cdot 333}{2 \cdot 96,485} \ln\left(1 - \frac{500}{800}\right) - 0.500 \cdot 0.15 \\ &= E_{T,P} - 0.690 - 0.01472 - 0.075 \\ &= E_{T,P} - 0.07797 \end{aligned}$$

$$\begin{aligned} E(T, P)_{\text{PER CELL}} &= -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right)_{60\text{C}} + \frac{R_{H_2} T_{\text{abs}}(K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right) \\ &= \frac{-(-284850 \frac{\text{J}}{\text{mol}} - 333 \text{ K}(-159.75 \frac{\text{J}}{\text{mol - K}}))}{2 \cdot 96,485 \text{ C/mol}} + \frac{8.314 \cdot 333}{2 \cdot 96,485 \text{ C/mol}} \ln\left(\frac{1 \cdot 0.21^{0.50}}{1}\right) \\ &= 1.2 - 0.03756 - 0.01195 = 1.15049 \end{aligned}$$

$$\begin{aligned} V_{\text{cell}} &= E_{T,P} - 0.07797 \\ &= 1.15049 - 0.07797 \\ &= 1.07252 \text{ V} \end{aligned}$$

# CELL VOLTAGE AT 6 BAR

## EXCHANGE CURRENT DENSITY

### PROPORTIONAL TO PRESSURE INCREASE

Cell Voltage at 60C, 6Bar, 500mA/cm<sup>2</sup>

$$i_0 = 6 \bullet 0.003 \text{mA} / \text{cm}^2, i_{loss} = 1.2 \text{mA} / \text{cm}^2, i_L = 800 \text{mA} / \text{cm}^2$$

$$\alpha = 0.5, R_i = 0.15 \Omega - \text{cm}, A = \frac{RT}{\alpha F}$$

$$E(T, P)_{\text{PER CELL}} = - \left( \frac{\Delta H}{nF} - \frac{T\Delta S}{nF} \right)_{60C} + \frac{R_{H_2} T_{abs} (K)}{nF} \ln \left( \frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}} \right)$$

$$E(T, P)_{\text{PER CELL}} = - \left( \frac{\Delta H}{nF} - \frac{T\Delta S}{nF} \right)_{60C} + \frac{R_{H_2} T_{abs} (K)}{nF} \ln \left( \frac{6 * (6 * 0.21)^{0.5}}{1} \right)$$

$$V_{cell} = E_{T,P} - \frac{RT}{\alpha F} \ln \left( \frac{i + i_{loss}}{i_0} \right) + \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right) - iR$$

# ACTUAL FUEL CELL VOLTAGE

$$V_{\text{cell}} = E_{\text{T,P}} - \Delta V_{\text{act}} - \Delta V_{\text{res}} - \Delta V_{\text{conc}}$$

Losses occur on both anode and cathode:

$$V_{\text{cell}} = E_{\text{T,P}} - (\Delta V_{\text{act}})_{\text{an}} - (\Delta V_{\text{act}})_{\text{ca}} - \Delta V_{\text{res}} - (\Delta V_{\text{conc}})_{\text{an}} - (\Delta V_{\text{conc}})_{\text{ca}}$$

$$(\Delta V_{\text{act}})_{\text{an}} \ll (\Delta V_{\text{act}})_{\text{ca}}$$

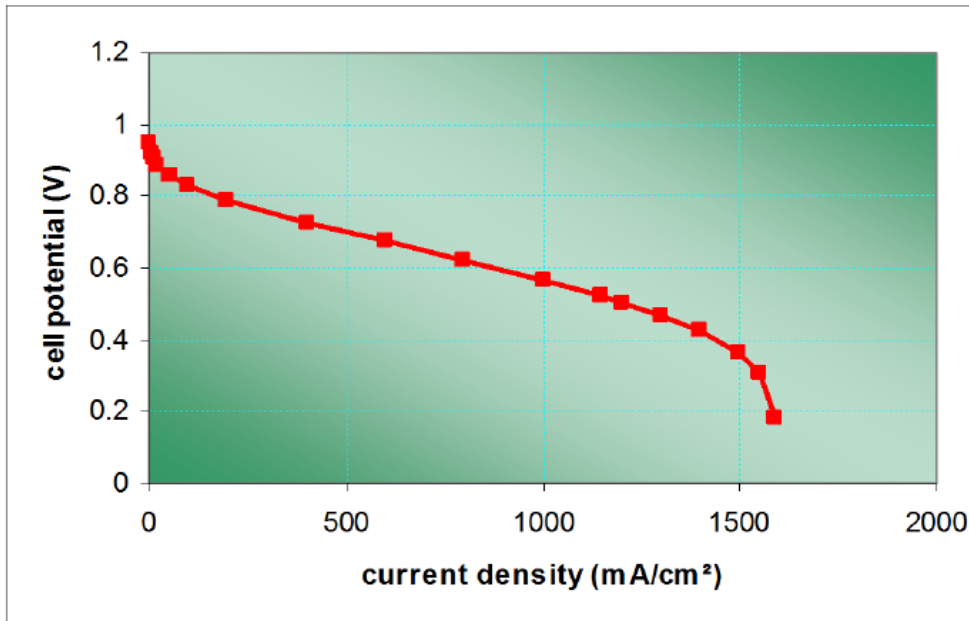
$$V_{\text{cell}} = E_{\text{T,P}} - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right) - i \cdot R_i + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right)$$

Strictly (mathematically):

$$\frac{1}{\alpha} = \frac{1}{\alpha_a} + \frac{1}{\alpha_c} \quad i_0 = i_{0,a}^{\alpha/\alpha_a} \cdot i_{0,c}^{\alpha/\alpha_c}$$

$$V_{cell} = E(T, P) - \Delta V_{act} - \Delta V_{crossover} - \Delta V_{resistive} - \Delta V_{mass\ transfer}$$

# TYPICAL IV CURVE



**Fuel: Hydrogen**

**Oxidant: Air**

**Temperature: 333 K**

**Pressure: 101.3 kPa**

**Gas constant, R: 8.314 J/mol,K**

**Transfer coefficient,  $\alpha$ : 1**

**Number of electrons involved, n: 2**

**Faraday's constant, F: 96,485 C/mol**

**Current loss,  $i_{loss}$ : 0.002 A/cm²**

**Reference exchange current density,  $i_0$ :  $3 \times 10^{-6}$  A/cm²**

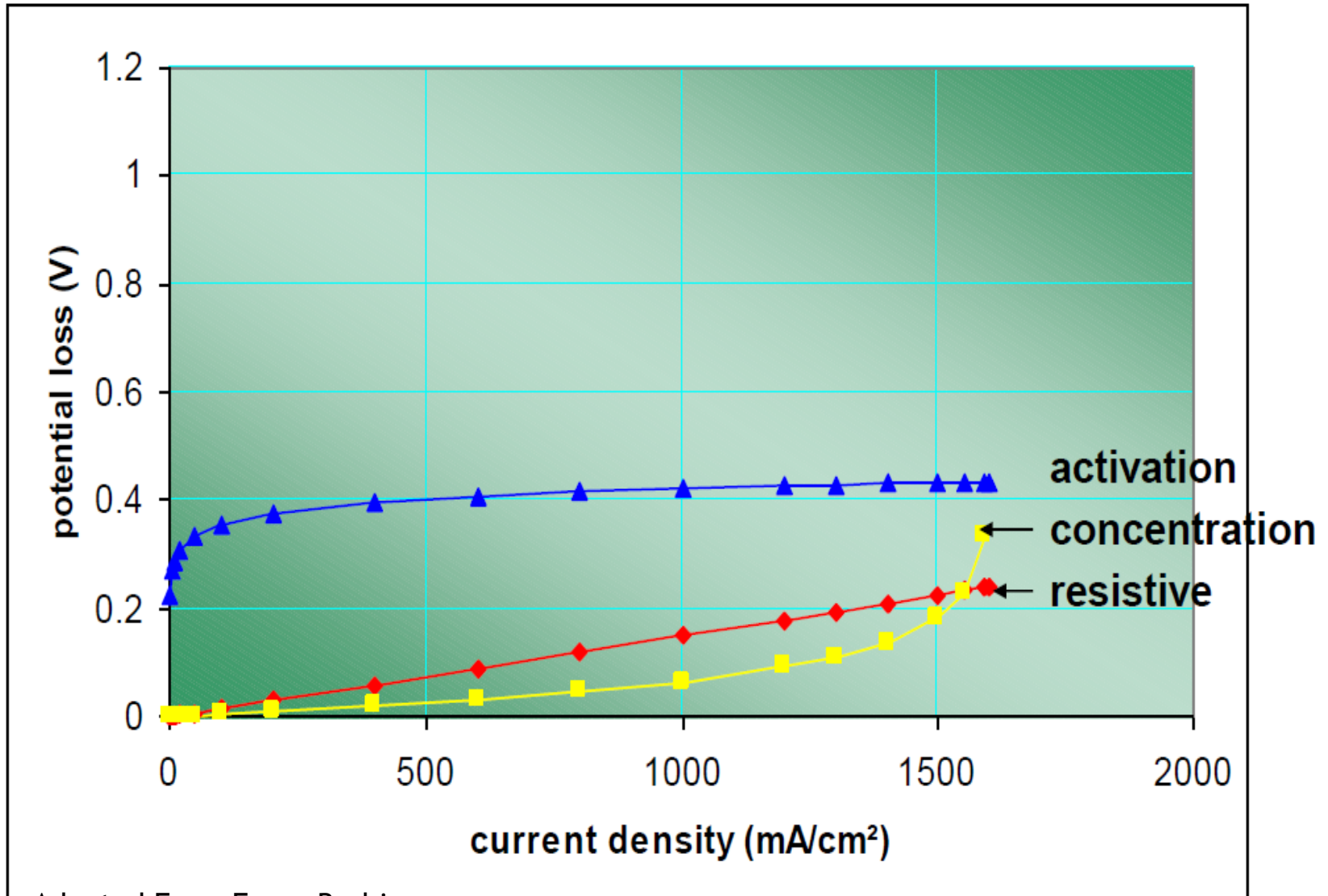
**Limiting current density,  $i_L$ : 1.6 A/cm²**

**Internal resistance,  $R_i$ : 0.15 Ohm-cm²**

Adopted From Frano Barbir



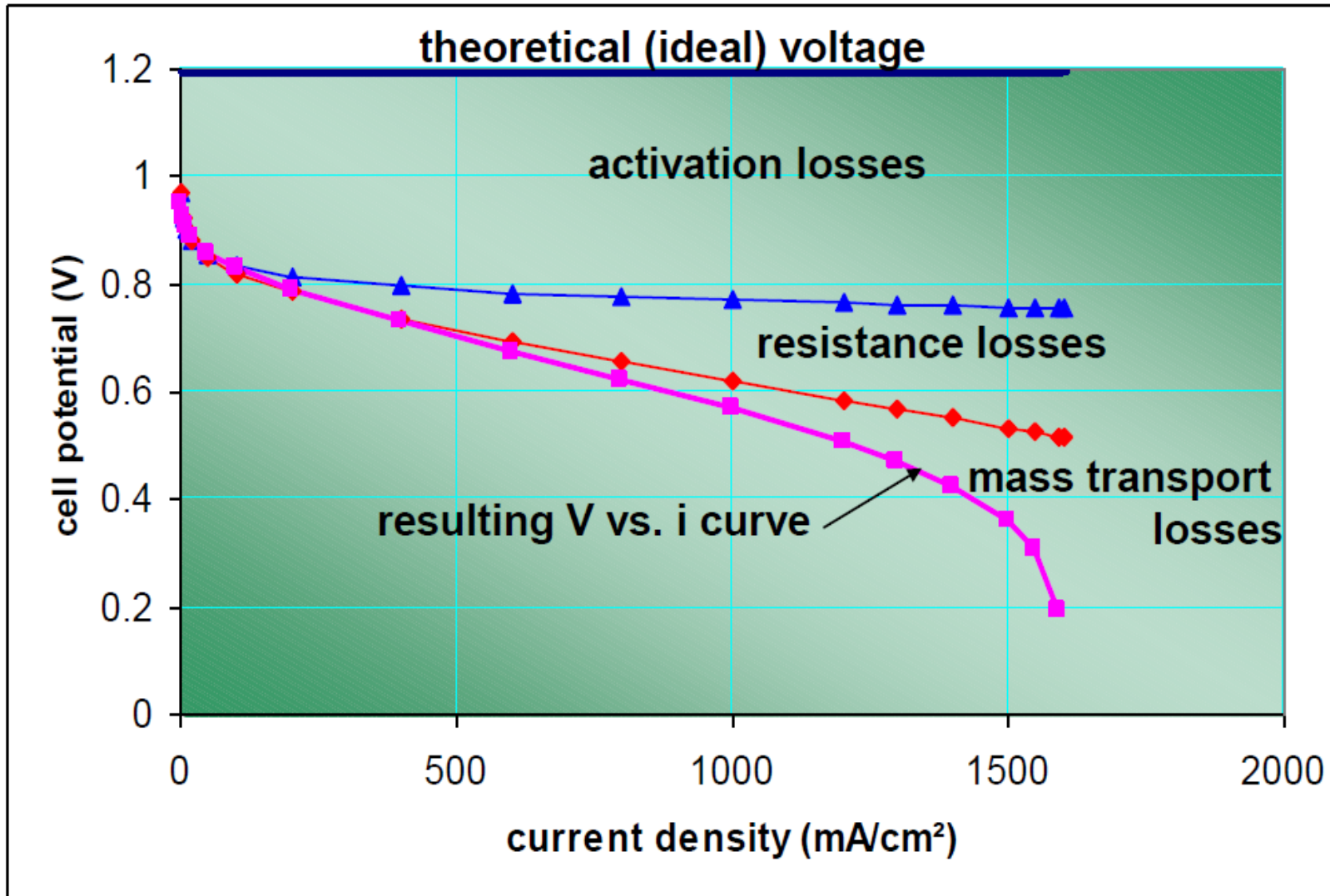
# LOSS COMPARISON



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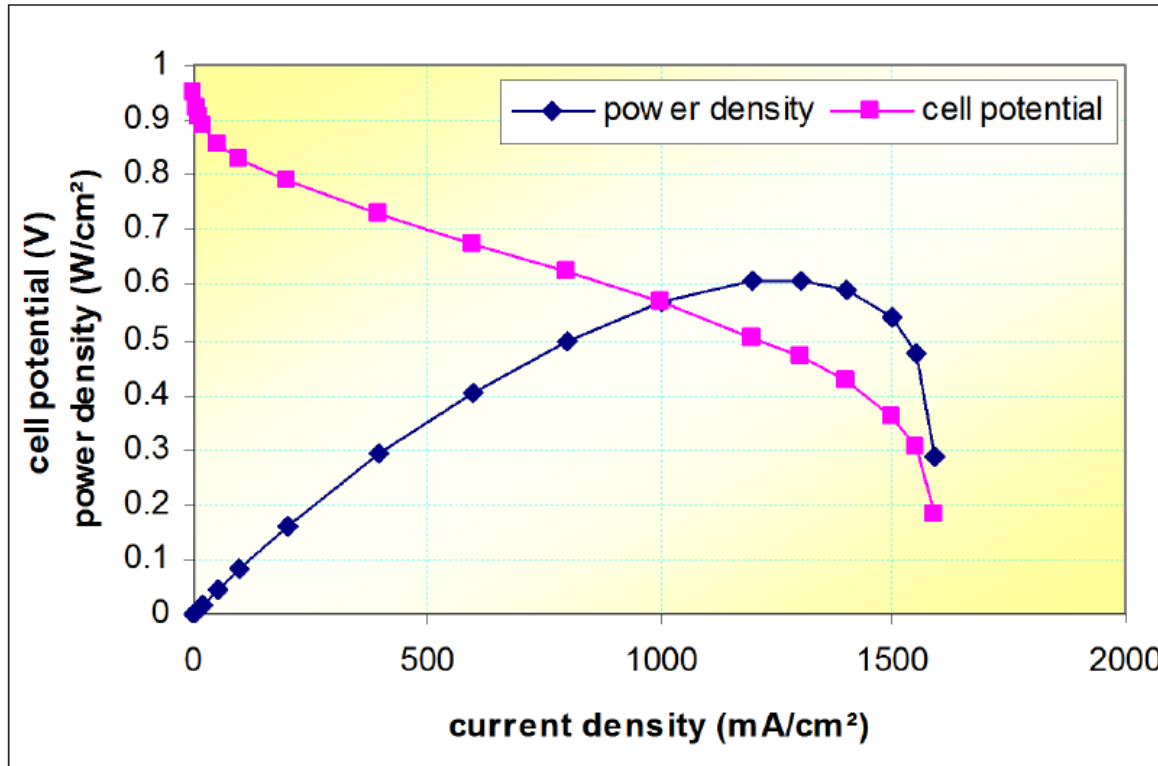


# FUEL CELL POLARIZATION CURVE



Adopted From Frano Barbir

# POWER DENSITY VS CURRENT DENSITY



$$\text{Power density} = i \times V \text{ (W/cm}^2\text{)}$$

Adopted From Frano Barbir

# TOTAL LOSSES THROUGH A FUEL CELL



- The losses in the cell voltage that we have discussed are
  - Activation losses
  - Losses due to fuel crossover and internal currents
  - Ohmic losses
  - Mass transport or concentration losses
- We have derived the expressions for the **activation losses, ohmic losses and mass transport losses**, all of which depend upon the current density  $i$ . We also mentioned that there is an **internal current flowing through the electrolyte from electrode-to-electrode**, which is generally measured in the open circuit voltage experiments. The total losses then are given by

$$V_{cell} = E_{T,P} - iR_i - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{loss}}{i_0}\right) + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right), i + i_{loss} > i_0, i < i_L$$

$$E(T, P)_{PER CELL} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right) \rightarrow SLIDE 35 + \frac{R_{H_2} T_{abs} (K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right) \rightarrow Week\#1, Lecture 2$$

$R_i \equiv$  total cell internal resistance (ionic, electronic & contact resistance:  $\Omega cm^{-2}$ )

- This equation is valid ONLY when  $i + i_{loss} > i_0$ . and when the limiting current density is NOT exceeded, i.e., when  $i < i_L$ .

# VOLTAIC AND THERMAL EFFICIENCY

Cell Voltage at 60C 1Bar, 500mA/cm<sup>2</sup>

$$i_0 = 0.003 \text{mA} / \text{cm}^2, i_{\text{loss}} = 1.2 \text{mA} / \text{cm}^2, i_L = 800 \text{mA} / \text{cm}^2$$

$$\alpha = 0.5, R_i = 0.15 \Omega - \text{cm}^2, A = \frac{RT}{\alpha F}$$

$$R = 8.314 \text{J} / \text{mol} - \text{K}, F = 96,485 \text{C} / \text{mol}$$

$$A = \frac{8.314 \text{J} / \text{mol} - \text{K} \cdot 333 \text{K}}{0.5 \cdot 96,485 \text{C} / \text{mol}} = 0.05739 \text{V} (\text{J} / \text{C})$$

$$V_{\text{cell}} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{\text{loss}}}{i_0}\right) + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right) - iR$$

$$= E_{T,P} - 0.07797$$

$$E(T, P)_{\text{PER CELL}} = -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right)_{60\text{C}} + \frac{R_{H_2} T_{\text{abs}} (\text{K})}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

$$= 1.20 - 0.01195 = 1.18805$$

$$V_{\text{cell}} = E_{T,P} - 0.07797$$

$$= 1.18805 - 0.07797 = 1.11008$$

$$\eta_v = \frac{1.11008}{-\left(\frac{\Delta G}{nF} = \frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right)_{60\text{C}}} = 92.5\%,$$

$$= 1.20 \text{V}$$

$$\eta_{\text{th}} = \frac{1.11008}{\left(\frac{-\Delta H}{nF}\right)_{60\text{C}}} = 75\% \cdot \frac{i}{i + i_{\text{loss}}} \cdot \frac{1}{S_{H_2}}$$

$$= 1.476$$

# SUMMARY

## Voltage losses:

Activation polarization

Ohmic (resistive losses)

Concentration polarization or mass transport losses

Internal currents and reactants crossover

## Resulting polarization curve:

$$V_{\text{cell}} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{\text{loss}}}{i_0}\right) - i \cdot R_i + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right)$$

Effect of operating pressure

Effect of oxygen vs. air

Effect of operating temperature

Fuel cell efficiency:  $\eta = \frac{V_{\text{cell}}}{1.482}$

Considering Losses

$$\eta = \frac{V_{\text{CELL}}}{1.482} \cdot \frac{i}{(i + i_{\text{loss}})}$$

# A COMPARISON OF VARIOUS VOLTAGE DROPS IN A FUEL CELL

Causes of Voltage Drops	PEMFC	SOFC	Comments
<ul style="list-style-type: none"> <li>• <b>Activation</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Most important</b></li> <li>• <b>Important at cathode, not at anode.</b></li> <li>• <b>The larger the <math>i_0</math>, smaller is this drop.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Not important</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>At high P, high T, high reactant concentration, this drop becomes small.</b></li> <li>• <b>With the change in load, the activation losses do not change instantly, but slowly.</b></li> </ul>
<b>Fuel crossover/ Internal current</b>			
<ul style="list-style-type: none"> <li>• <b>Ohmic Losses</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Important for the total operating range of <math>i</math>.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>More important for the total operating range of <math>i</math>.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>With the change in load, the ohmic loss affects the voltage drop immediately.</b></li> </ul>
<ul style="list-style-type: none"> <li>• <b>Mass Transport and Concentration Change</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Extremely important when <math>i</math> approaches <math>i_l</math>.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Extremely important when <math>i</math> approaches <math>i_l</math>.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Extremely nonlinear.</b></li> </ul>
	<ul style="list-style-type: none"> <li>• <b>Ohmic and activation losses are about the same order of magnitude in operation.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>Most voltage drop is due to ohmic losses during the operation.</b></li> </ul>	



# ***IMPACTING POLARIZATION CURVE***

Operational conditions.

- Operating pressure
- Flow rates of reactants
- Operating temperature
- Humidity of reactants

**Fluid mechanics**

**Fluid mechanics/chemistry**

**Heat transfer**

**Psychrometry**

**Thermodynamics** of moist gases

**We must know some basics!**

**We must know fuel cell inner working!**

# ***WHAT ELSE?***

- ⦿ Unsteady conditions (flooding/drying)
- ⦿ Contaminants
- ⦿ Crossover Leaks
- ⦿ Aging (loss of catalyst surface, cross leaks, change in membrane properties)



# CONCLUDING REMARKS

- The fundamental performance behavior of a fuel cell can be explained by the going through the basic thermodynamics and electrochemistry of the fuel cells.
- The Nernst equation provides the relationship between the open circuit voltage and the operating partial pressure of the reactants and products. Influence of all parameters associated with the Nernst equation were discussed in details to explain the performance behavior of fuel cells.
- The actual voltage obtained from a fuel cell with load is different than the ideal voltage from the thermodynamics. This is due to losses associated with the operation, fuel cell materials used, and the design. These losses are: **activation, fuel crossover and internal current leakage, ohmic, and mass transport or concentration losses**. These losses were discussed in detail with some explanation of physical phenomena.

# A 100 CM2 5 CELL H2/O2 FUEL CELL STACK OPERATES AT 0.5 A/CM2 AND 0.0018 G/S. WHAT IS THE MAXIMUM CURRENT (A) THAT COULD BE GENERATED?

A 100 cm<sup>2</sup> 5 cell H<sub>2</sub>/O<sub>2</sub> fuel cell stack operates at 0.5 A/cm<sup>2</sup> and 0.0018 g/s.

What is the maximum current (A) that could be generated?

$$\frac{\dot{m}(I) \left[ \frac{\text{g}}{\text{sec}} \right]}{\text{stack}} = \frac{I \left[ \frac{\text{C/s}}{\text{cm}^2} \right] A_p \frac{\text{Area}}{\text{Plate}} \left[ \text{cm}^2 \cdot \frac{\# \text{ plates}}{\text{stack}} \right]}{n \left[ \frac{\text{moles of electrons}}{\text{moles of reactant}} \right] F \left[ \frac{\text{C}}{\text{moles of electrons}} \right]} \cdot \frac{1}{\lambda_f} \cdot M_{w_{H_2}} \left[ \frac{\text{g}}{\text{moles of reactant}} \right]$$

$$I_{MAX} = \frac{\dot{m} \cdot n \cdot F \cdot \lambda_f}{A_p \cdot \# \text{ plates} \cdot M_{w_{H_2}}} = \frac{0.0018 \text{ g/s} \cdot 2 \cdot 96,485 \cdot 1}{100 \cdot 5 \cdot 2.016} = 0.344 \text{ A/cm}^2$$

So stack's operating point is not possible. A stack's MAX current output is always determined by the H<sub>2</sub> flow rate.

# ASSUME NO CONCENTRATION/CROSS-OVER LOSSES, FIND CELL VOLTAGE AT 1.5A/CM2, AND 0.5A/CM2, $I_0=0.0005 \text{ MA/CM}^2$

C. Cell Voltage at 1.5 A/cm<sup>2</sup>

$$V_{cell} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{loss}}{i_0}\right) + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right) - iR$$

$$A = \frac{RT}{\alpha F}$$

$$R = 8.314 \text{ J / mol - K}, \alpha = 1, F = 96,485 \text{ C / mol}$$

$$A = \frac{8.314 \text{ J / mol - K} \cdot 333 \text{ K}}{1 \cdot 96,485 \text{ C / mol}} = 0.02869 \text{ V (J / C)}$$

For Low Temperatures (T=60C=333K)

$$E_{th}(T)_{PER CELL} = -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right)_{60C}; \text{Eqn.2-18 / Table 2-4}$$

$$= \frac{-(-284850 \frac{\text{J}}{\text{mol}} - 333 \text{ K}(-159.75 \frac{\text{J}}{\text{mol - K}}))}{2 \cdot 96,485 \text{ C / mol}} = 1.20 \text{ V}$$

$$V_{cell_{1.5A/cm^2}} = 1.20 \text{ V} - 0.02869 \text{ V} \ln\left(\frac{1,500}{0.0005}\right) - 1.5 \text{ A / cm}^2 \cdot 0.07132 \Omega - \text{cm}^2$$

$$= 1.20 \text{ V} - 0.42789 \text{ V} - 0.10698 \text{ V}$$

$$= 0.66513 \text{ V}$$

$$V_{cell_{0.5A/cm^2}} = 1.20 \text{ V} - 0.02869 \text{ V} \ln\left(\frac{500}{0.0005}\right) - 1.5 \text{ A / cm}^2 \cdot 0.07132 \Omega - \text{cm}^2$$

$$= 1.20 - 0.3964 - 0.10698$$

$$= 0.69665 \text{ V}$$

# E=0.7V/C, H2 STOIC=1.5, A=100 CM2 FIND EFF, MASS FLOW, POWER, CELLS

$$\eta_v = \frac{0.7}{1.23} = 57\%, \quad \eta_{th} = \frac{0.7}{1.428} = 49\%$$

$$\frac{\dot{m}}{\text{cell}} = \frac{I(A/cm^2) \cdot \text{Area}}{nF} \cdot S_{H_2} \cdot M_{H_2}$$

$$= \frac{0.5(C-S/cm^2) \cdot 100cm^2}{2 \frac{\text{mole of electron}}{\text{mole of reactant}} \cdot 96,485C / \text{mole of reactant}} \cdot 2.016g/mol \rightarrow \text{Exact Consumption Rate}$$

$$\frac{\dot{m}}{\text{cell}} \left( \frac{g/sec}{\text{cell}} \right)_{INLET} = 0.000522 \frac{g/sec}{\text{cell}} \cdot S_{H_2}$$

$$= 0.00078 \frac{g/sec}{\text{cell}}$$

$$\frac{\dot{m}}{\text{cell}} \left( \frac{g/sec}{\text{cell}} \right)_{EXIT} = 0.000522 \frac{g/sec}{\text{cell}} \cdot (S_{H_2} - 1)$$

$$= 0.00026 \frac{g/sec}{\text{cell}}$$

$$P = V \cdot I \cdot A \cdot n$$

$$n = \frac{P}{V \cdot I \cdot A} = \frac{90,000W}{0.7V / \text{cell} \cdot 0.5A / cm^2 \cdot 100cm^2} = 2,572 \text{ cells}$$

$$P'' = \frac{90,000W}{100 \frac{cm^2}{\text{plate}} \cdot 2572 \text{ plates}} = 0.35W / cm^2$$

# PROBLEM 1

- ⊙ A given fuel cell operates at 150A and 0.55VDC with an overall resistance of 3 milli ohms at 1.4 A/cm<sup>2</sup> current density. Find: a) Potential Loss, b) Total electrical work produced in 2h, and c) Rate of ohmic heat dissipation from the cell in W.

$$\begin{aligned}V &= IR \\ &= 150\text{amps} \bullet 0.003\Omega \\ &= 0.45V\end{aligned}$$

$$\begin{aligned}\dot{W}_e &= \Delta t \bullet P_e = 3600 \frac{\text{sec}}{\text{hr}} \bullet 2\text{hr} \bullet 150\text{amps} \bullet 0.55\text{VDC} \\ &= 594J\end{aligned}$$

$$\begin{aligned}\text{Ohmic Dissipation Rate} &= I^2 R \\ &= 150^2 \bullet 0.003\Omega \\ &= 67.5W\end{aligned}$$

# PROBLEM 2

- Determine the fuel utilization efficiency for a 300 plate fuel cell stack with 120 A current output and a hydrogen flow rate through the stack of 0.5 g/s of hydrogen

$$\frac{\dot{m}_{H_2} \left[ \frac{g}{sec} \right]}{cell} = \frac{I}{2F} \left[ \frac{\text{moles of } H_2 \text{ Reactant}}{sec} \right] \cdot M_{W_{H_2}} \left[ \frac{g}{\text{moles of } H_2} \right]$$

$$\dot{m} = n(\text{cells}) \cdot \frac{i}{nF} \cdot M_{W_{H_2}}$$

$$= 300 \text{ cells} \cdot \frac{120 \text{ A} / \text{ cells}}{2 \frac{\text{mole of electron}}{\text{mole of reactant}} \times 96,485 \frac{\text{A} \cdot \text{s}}{\text{mole of electron}}} \cdot \frac{2.016 \text{ g}}{\text{mole of reactant}}$$

$$= 0.3761 \text{ g} / \text{s} = 10.4472 \times 10^{-6} \frac{\text{g} / \text{s}}{\text{Amp} \cdot \text{cell}} \rightarrow \text{Exact Consumption Rate}$$

$$\lambda = \text{Fuel Utilization} = \frac{1}{\text{Stoic}} = \frac{\text{ideal mass consumed}}{\text{actual mass supplied}}$$

$$\lambda = \frac{0.3761 \text{ g} / \text{s}}{0.5 \text{ g} / \text{s}} = 75.22\%$$

$$S = 1.33$$

# PROBLEM 3

- A H<sub>2</sub>/O<sub>2</sub> Fuel Cell polarization curve has the following parameters.

Parameter	Value
T	333K
P	101.3 kPa
i <sub>o</sub>	0.002mA/cm <sup>2</sup>
R	0.21 Ohm-cm <sup>2</sup>
i <sub>L</sub>	2000mA/cm <sup>2</sup>
i <sub>Loss</sub>	1.2 mA/cm <sup>2</sup>

- Determine the efficiency at 0.6V and 0.7V.

# EFFECT OF TEMPERATURE

- The theoretical cell potential changes with temperature:

1<sup>st</sup> Law

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

GIBBS

$$E_{th}(T) = \left( \frac{-\Delta G_{th}}{nF} \right)_{@T=?} = \left( - \left( \frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF} \right) \right)_{@T=?}$$

Although the theoretical voltage decreases with temperature, in general higher cell temperatures result in higher cell potential; because actual *transport & chemical losses* decrease with temperature. **More in next chapter!**

Change of Enthalpy, Gibbs, and S for H<sub>2</sub>/O<sub>2</sub> FC w/Temperature:

T(K)	$\Delta H(kJ/mol)$	$\Delta G(kJ/mol)$	$\Delta S(kJ/mol)$	$E_{th}(V)$
298.15	-286.02	-237.34	-0.16328	1.230
333.15	-284.85	-231.63	-0.15975	1.200
353.15	-284.18	-228.42	-0.15791	1.184
373.15	-283.52	-225.24	-0.15617	1.167



# TEMPERATURE DEPENDENCE

⊙ Enthalpy and Entropy can be expressed as:

$$\Delta H_{th} = \Delta H_{298.15} + \Delta a(T - 298.15) + \Delta b\left(\frac{T^2 - 298.15^2}{2}\right) + \Delta c\left(\frac{T^3 - 298.15^3}{3}\right)$$

$$\Delta S_{th} = \Delta S_{298.15} + \Delta a \ln(T / 298.15) + \Delta b(T - 298.15) + \Delta c\left(\frac{T^2 - 298.15^2}{2}\right)$$

$$\Delta a = a_{H_2O} - a_{H_2} - 1/2a_{O_2}$$

$$\Delta b = b_{H_2O} - b_{H_2} - 1/2b_{O_2}$$

$$\Delta c = c_{H_2O} - c_{H_2} - 1/2c_{O_2}$$

	<i>a</i>	<i>b</i>	<i>c</i>
$H_2$	28.91404	-0.00084	$2.01 \times 10^{-6}$
$O_2$	25.84512	0.012987	$-3.9 \times 10^{-6}$
$H_2O_{(g)}$	30.62644	0.009621	$1.18 \times 10^{-6}$
$H_2O_{(l)}$	75.42646	0	0

## IDEAL FUEL CELL VOLTAGE

$$E_{th}(T) = \frac{-\Delta G_{th}}{nF} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right)$$

## GENERAL EXPRESSION

At temperatures < 100C, changes in enthalpy and entropy are very small.

But at higher temperatures, such as Solid Oxide Fuel Cells, they must not be neglected.

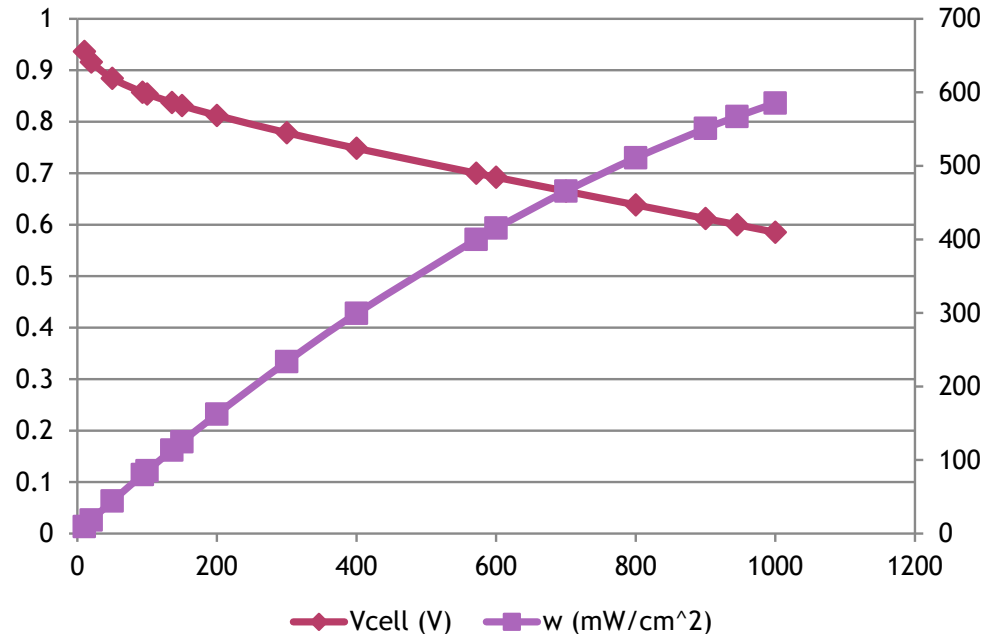
# PROBLEM 3: SOLUTION

$$V_{cell} = E_{T,P} - iR_i - \frac{RT}{\alpha F} \ln\left(\frac{i + i_{loss}}{i_0}\right) + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right), i + i_{loss} > i_0, i < i_L$$

$$E(T,P)_{PER\ CELL} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right) \rightarrow SLIDE\ 35 + \frac{R_{H_2} T_{abs}(K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right) \rightarrow Week\#1, Lecture\ 2$$

$R_i \equiv$  total cell internal resistance (ionic, electronic & contact resistance:  $\Omega cm^{-2}$ )

E(T,P)	1.200615	
i(mA/cm2)	Vcell(V)	w(mW/cm2)
10	0.93645	9.364497
20	0.915967	18.31935
50	0.884144	44.20718
<b>93.33013</b>	<b>0.857115</b>	<b>79.99468</b>
100	0.853705	85.37054
<b>135.4345</b>	<b>0.837363</b>	<b>113.4078</b>
150	0.831276	124.6915
200	0.812148	162.4295
300	0.778633	233.5898
400	0.748351	299.3406
<b>571.393</b>	<b>0.7</b>	<b>399.9753</b>
600	0.692184	415.3101
700	0.665192	465.6343
800	0.638527	510.8217
900	0.611978	550.7805
<b>945.066</b>	<b>0.6</b>	<b>567.0395</b>
1000	0.58535	585.3504



# PROBLEM 3: SOLUTION - EFF.

Considering Losses

$$\eta = \frac{V_{CELL}}{1.482} \cdot \frac{i}{(i + i_{loss})} \cdot \frac{\Delta G}{HHV}$$

$$\eta_{0.7} = \frac{0.7}{1.482} \cdot \frac{571.393}{(571.393 + 1.2)} = 0.4713 \cdot \frac{\Delta G}{HHV}$$

$$\eta_{0.6} = \frac{0.6}{1.482} \cdot \frac{945.066}{(945.066 + 1.2)} = 0.4043 \cdot \frac{\Delta G}{HHV}$$

Efficiency at 20% of nominal power

Considering Losses

$$\eta = \frac{V_{CELL}}{1.482} \cdot \frac{i}{(i + i_{loss})} \cdot \frac{\Delta G}{HHV}$$

$$\eta_{0.7@20\%} = \frac{0.857115}{1.482} \cdot \frac{93.33013}{(93.33013 + 1.2)} = 0.57101 \cdot \frac{\Delta G}{HHV}$$

$$\eta_{0.6@20\%} = \frac{0.83763}{1.482} \cdot \frac{135.4345}{(135.4345 + 1.2)} = 0.56006 \cdot \frac{\Delta G}{HHV}$$

E(T,P)	1.200615	
i(mA/cm <sup>2</sup> )	V <sub>cell</sub> (V)	w(mW/cm <sup>2</sup> )
10	0.93645	9.364497
20	0.915967	18.31935
50	0.884144	44.20718
<b>93.33013</b>	0.857115	<b>79.99468</b>
100	0.853705	85.37054
<b>135.4345</b>	0.837363	<b>115.4078</b>
150	0.831276	124.6915
200	0.812148	162.4295
300	0.778633	233.5898
400	0.748351	299.3406
<b>571.393</b>	<b>0.7</b>	<b>399.9753</b>
600	0.692184	415.3101
700	0.665192	465.6343
800	0.638527	510.8217
900	0.611978	550.7805
<b>945.066</b>	<b>0.6</b>	<b>567.0395</b>
1000	0.58535	585.3504

# PROBLEM 3.2

Problem 3.2			
V <sub>cell</sub>	0.8	0.6	V
i	0.2	0.8	A/cm <sup>2</sup>
A	100		cm <sup>2</sup>
Solution			
k	0.333333		
V <sub>0</sub>	0.866667	V	

Find:

- Max power at what voltage
- Cell voltage and current density at ½ max power
- Efficiency @ max power
- Efficiency at ½ max power

Assume linear polarization curve:

$$V_{cell} = V_0 - k \cdot i, k \equiv slope = \frac{V_1 - V_2}{i_2 - i_1} = \frac{0.8 - 0.6}{0.8 - 0.2} = \frac{1}{3}$$

$$V_0 = V_{cell} + k \cdot i = 0.8 + \left(\frac{1}{3}\right) \cdot 0.2 = 0.8 + \frac{0.2}{3} = 0.87$$

$$V_{cell}(i) = 0.87 - \frac{i}{3}$$

$$w = VI = i\left(0.87 - \frac{i}{3}\right) = 0.87i - \frac{i^2}{3} \rightarrow \text{Quadratic}$$

$$\frac{dw}{di} = 0.87 - \frac{2i}{3}, \frac{dw}{di} = 0, i_{max} = \frac{0.87 \cdot 3}{2}$$

$$w_{max} = 0.87 \cdot \frac{0.87 \cdot 3}{2} - \frac{\left(\frac{0.87 \cdot 3}{2}\right)^2}{3} = 1.135 - 0.5677 = 0.5673 \frac{W}{cm^2}$$

$$W_{max} = 0.5673 \frac{W}{cm^2} \cdot 100 cm^2 = 56.73 W$$

$$i_{max} = \frac{0.87 \cdot 3}{2}$$

$$V_{cell}(i) = 0.87 - \frac{i}{3}$$

$$V_{max} = 0.87 - \frac{0.87 \cdot 3}{2} = 0.435 V$$

# PROBLEM 3.2-CONT

$$w = VI = i(0.87 - \frac{i}{3}) = 0.87i - \frac{i^2}{3} \rightarrow \text{Quadratic}$$

$$i^2 - 3 \cdot 0.87i + 3w = 0$$

@1/2 Max, need to find current given work

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$i_{1,2} = \frac{3 \cdot 0.87 + \sqrt{(3 \cdot 0.87)^2 - 4 \cdot 3w}}{2}, w = 0.28365$$

$$i_1 = \frac{3 \cdot 0.87 + \sqrt{6.8121 - 3.4038}}{2} = 2.2280A$$

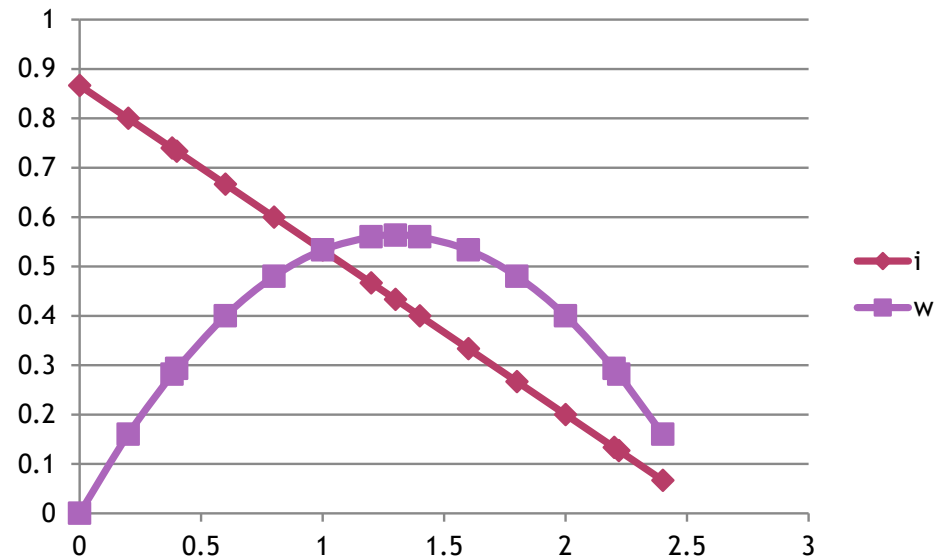
$$i_2 = \frac{3 \cdot 0.87 - \sqrt{6.8121 - 3.4038}}{2} = 0.3819A$$

Find:

- Max power at what voltage
- Cell voltage and current density at 1/2 max power
- Efficiency @ max power
- Efficiency at 1/2 max power

Note that work is quadratic and has two "i" values for 1/2 power

	i	V	w	EFF
	0	0.866667	0	0.584795
	0.2	0.8	0.16	0.539811
wmax/2	0.380761	0.739746	0.281667	0.499154
	0.4	0.733333	0.293333	0.494827
	0.6	0.666667	0.4	0.449843
	0.8	0.6	0.48	0.404858
	1	0.533333	0.533333	0.359874
	1.2	0.466667	0.56	0.31489
wmax	1.3	0.433333	0.563333	0.292398
	1.4	0.4	0.56	0.269906
	1.6	0.333333	0.533333	0.224921
	1.8	0.266667	0.48	0.179937
	2	0.2	0.4	0.134953
	2.2	0.133333	0.293333	0.089969
wmax/2	2.219239	0.12692	0.281667	0.085641
	2.4	0.066667	0.16	0.044984



# PROBLEM 3.3

## LOW PRESSURE

$$E_{th}(T, P)_{\text{PER CELL}} = 1.482 - 0.000845T + 0.0000431T \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

$$E_{th}(T = 298.15K, P = 300 / 101.3)_{\text{PER CELL}} = 1.200558V$$

$$i_0 = i_0^{ref} a_c L_c \left(\frac{P_r}{P_r^{ref}}\right)^\gamma \exp\left[-\frac{E_c}{RT} \left(1 - \frac{T}{T_{ref}}\right)\right], P_r = 0.21 \cdot 300kPa, P_r^{ref} = 101,3kPa$$

$$i_0(L_c = 0.4mg / cm^2) = 2.94E - 07$$

$$i_0(L_c = 2.0mg / cm^2) = 1.47E - 06$$

## COMPUTE CURRENT DENSITY @ $V_{cell} = 0.9V$

$$V_{cell} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right) \rightarrow \text{neglect crossover, mass transfer, and "ir" losses}$$

$$i = i_0 \exp\left(-\left(V_{cell} - E_{T,P}\right) \frac{\alpha F}{RT}\right), F = 96485 \frac{C}{mol}, R = 8.314 \frac{J}{mol \cdot K}$$

$$i(L_c = 0.4mg / cm^2) = 0.010359508 mA / cm^2 = i(L_c = 2mg / cm^2)$$

## NOW VOLTAGE INCREASE WITH INCREASED CATALYST LOADING @ Same Current Density

$$V_{cell} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i = 0.010359508}{i_0 = 1.47E - 06}\right), E_{T,P} = 1.200558V$$

$$V_{cell}(L_c = 2mg / cm^2) = 0.946202$$

$$\Delta V_{cell} = 0.946202 - 0.90 = 0.046202 \frac{V}{cell}$$

Problem 3.3	
$i_0^{ref}$	1.00E-10A/cm <sup>2</sup>
$T_{ref}$	298.15K
$P_{ref}$	101.3kPa
$V$	0.9V
$a_c$	640cm <sup>2</sup> /mg
$L_c$	0.4mg/cm <sup>2</sup>
$P$	300kPa
$T$	333.15K
$E_c$	66kJ/mol
$R$	8.314J/molK
$\gamma$	0.75
$\alpha$	1
$F$	96485

What is cell voltage increase for increased cathode Pt loading from 0.4 to 2.0mg/cm<sup>2</sup>?

Assume same current density.

# PROBLEM 3.4

Parameter	Value
$i_0$	0.003 A/cm <sup>2</sup>
$\alpha$	0.5
$R_i$	0.015 Ohm-cm <sup>2</sup>
$T$	338K
$P_1$	1 Bar
$P_2$	6 Bar

- a. Find cell voltage at 1 A/cm<sup>2</sup> at 1Bar and at 6Bar (Anode & Cathode)

$$V_{cell} = E_{T,P} - iR_i - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right)$$

Exchange Current Density: Elevated Pressures

$$i_0 = i_0 \left(\frac{P_{high}}{P_{low}}\right)^{0.75}$$

In General

$$E(T,P)_{PER\ CELL} = -\left(\frac{\Delta H_{th}}{nF} - \frac{T\Delta S_{th}}{nF}\right) \rightarrow SLIDE\ 35 + \frac{R_{H_2} T_{abs}(K)}{nF} \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

LOW PRESSURE

$$E_{th}(T,P)_{PER\ CELL} = 1.482 - 0.000845T + 0.0000431T \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

$$V_{cell}(@1Bar) = 0.708$$

$$V_{cell}(@6Bar) = 0.825$$

$$\Delta V = 0.117$$

# PROBLEM 3.5

Problem 3.5	
T	353.15K
P	1atm
$i_0$	0.0012mA/cm <sup>2</sup>
alpha	1
VOC	0.975V
i	0

Find:

- Theoretical cell voltage
- When OCV=0.975V, find current density due to hydrogen crossover or due to internal currents.

LOW PRESSURE

$$E_{th}(T, P)_{\text{PER CELL}} = 1.482 - 0.000845T + 0.0000431T \ln\left(\frac{P_{H_2} P_{O_2}^{0.50}}{P_{H_2O}}\right)$$

$$E_{th}(T = 353.15K, P = 1Atm)_{\text{PER CELL}} = 1.1836$$

$$V_{cell} = E_{T,P} - iR_i - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right)$$

SO AT OCV:

$$V_{OCV\ cell} = E_{T,P} - \frac{RT}{\alpha F} \ln\left(\frac{i_{loss}}{i_0}\right)$$

$$i_{loss} = i_0 \exp\left(-\left(V_{OCV\ cell} - E_{T,P}\right) \frac{\alpha F}{RT}\right), F = 96485 \frac{C}{mol}, R = 8.314 \frac{J}{mol-K}$$

$$= 0.0012 \frac{mA}{cm^2} \cdot \exp\left(-\left(0.975 - 1.1836\right) \frac{J}{C} \frac{1.0 \cdot 96485 \frac{C}{mol}}{8.314 \frac{J}{mol-K} \cdot 353.15K}\right)$$

$$i_{loss} = 1.1383 \frac{mA}{cm^2} \text{ per cell}$$



# PROBLEM 3.6

Problem 3.6		
A	100	cm <sup>2</sup>
m_dot_H2	0.0018	g/s
F	96485	As/mol
M_H2	2.0159	g/mol

Determine limiting current density.

$$I_L = \frac{2F\dot{m}}{M_{H_2}} = \frac{2 \cdot 96485 \cdot 0.0018 \text{ g/s}}{2.0159} = 172.3 \text{ A}$$

$$\frac{I_L}{A} = \frac{172.3 \text{ A}}{100 \text{ cm}^2} = 1.72 \frac{\text{A}}{\text{cm}^2}$$

# ***FUEL CELL PERFORMANCE***

- Fuel Cell STACK total voltage depends on the number of cells in a stack. Voltage per cell is 0.6 - 0.7 volts.
- Cell current depends on the AREA (the size) of a cell and is same for EACH CELL.
- Cell power density is power (VI) per unit volume of the cell, W/Liter.
- Specific power is defined as power per unit mass, W/kg.

# AN EXAMPLE

## Input Data and Problem

Fuel cell plate area =  $1 \text{ m} \times 1 \text{ m} = 1 \text{ m}^2$

Current density (operating point) =  $0.4 \text{ A/cm}^2$  (amps/cm<sup>2</sup>)

Voltage per cell =  $0.7 \text{ V}$

How many cells do we need for  $120 \text{ V}$ ?

How much is the total power generated?

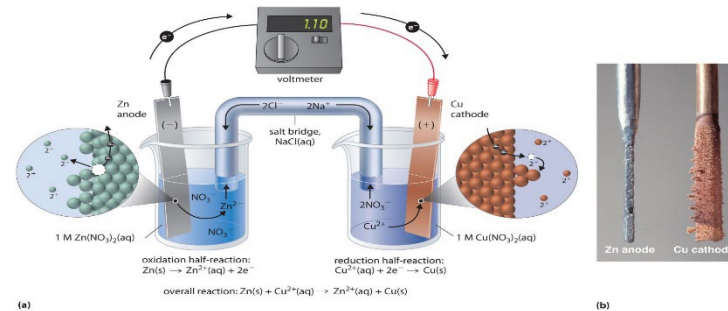
## Solution

No. of cell =  $120 \text{ V} / 0.7 \text{ V per cell} = 171.4$  or 172 cells

Total current produced =  $0.4 \text{ A/cm}^2 \times (100 \text{ cm})^2 = 4000 \text{ A}$

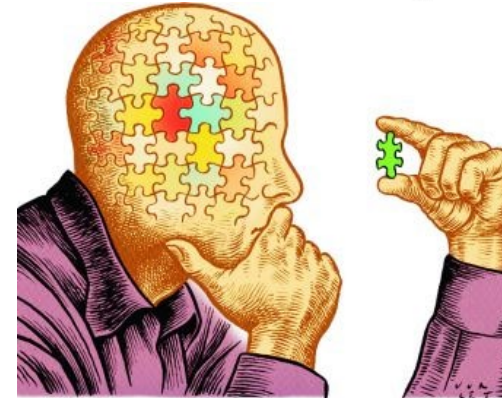
Power produced =  $0.7 \text{ V/cell} \times 172 \text{ cells} \times 4000 \text{ A}$   
 $= 481.6 \times 10^3 \text{ W} = 481.6 \text{ kW}$

# FINAL THOUGHT...



(a)

(b)



- Fuel cell **electrical potential** is obtained by converting the **“chemical free energy potential”** of the (Reactants - Products) to electric energy.
- This chemical potential is impacted by pressure, temperature, and can also be impacted by **“CONCENTRATION”** differences between Anode and Cathode, even with same chemical species, e.g. **Biological Fuel Cells**.

- Galvanic Cells Video; [CLICK HERE](#)
- HOMEWORK-Read Chapter #2, Prob. 2,3,4,Quiz1-10.
  - <https://video.search.yahoo.com/yhs/search?fr=yhs-mozilla-002&hsimp=yhs-002&hspart=mozilla&p=galvanic+cell#id=49&vid=9a02969d155c40e55d91d6b23e554164&action=view>

