

POWE

### **PEM Fuel Cell Operations**

# **MECH-526**

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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.





# HYDROGEN CIRCLE



# **CONSUMPTION RATES (FARADAY LAW)**

### ● For the H2/O2 Fuel Cell PER CELL

anode :  $H_2 \rightarrow 2H^+ + 2e^-$ ;  $\rightarrow$  CONSUMPTION=2 ELECTRONS cathode :  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ;  $\rightarrow$  CONSUMPTION=4 ELECTRONS overall :  $H_2 + 1/2O_2 \rightarrow H_2O$ ;  $\rightarrow PRODUCT$ :1MOLE H2  $\rightarrow$  1MOLE H2O=2 ELECTRONS For every mole of REACTANTS  $\rightarrow$  2 moles  $H_2O$ , 2 electron moles of  $H_2$ , 4 electron moles of  $O_2$ CONSUMPTION RATES  $\rightarrow$  GAS REACTANTS

# PEMFC CONSUMPTION/GENERATION PER AMP AND PER CELL

	<i>H</i> 2	<i>O</i> 2	Water(liq)
mol / s	$5.18x10^{-6}$	$2.59x10^{-6}$	$5.18x10^{-6}$
g/s	$10.4x10^{-6}$	$82.9x10^{-6}$	$93.3x10^{-6}$
NL / min	$6.970 x 10^{-3}$	$3.485 x 10^{-3}$	$5.6x10^{-6}$
$Nm^3 / h$	$0.418 \times 10^{-3}$	$0.209 x 10^{-3}$	

#### Standard(?) conditions

15° C International standard atmosphere (in meteorology)
25° C standard temperature in chemical tables
20° C (68° F) some technical handbooks
70° F (21.1° C) (in US)
60° F (15.6° C) in Wikipedia
1 atm: 101.325 kPa: 750 m

1 atm; 101.325 kPa; 750 mmHg; 14.696 psi (??30 inHg; 14.73 psi; 101,6 kPa??)



Normal conditions 0° C (32° F)

## ACTUAL FC STACK FLOW RATES P=1ATM

voltage • In general for real systems: current  $\lambda_f = \text{FUEL ULTIZATION EFF.} = \frac{1}{STOICIOMETRY}$  $S \equiv \text{stoichiometric factor} \equiv \frac{\text{actual fuel supplied}}{\text{exact fuel amount needed for reaction}} \ge 1$  $\frac{\dot{m}(I)\left[\frac{g}{\sec}\right]}{stack} = \frac{I\left[\frac{C/s}{cm^2}\right]A_p\frac{Area}{cell}\left[\frac{cm^2}{cell}\right] \cdot \frac{cells}{stack}}{n\left[\frac{moles of electrons}{moles of reactant}\right]F\left[\frac{C}{moles of electrons}\right] \cdot \frac{1}{\lambda_f} \cdot Mw_{H2}\left[\frac{g}{moles of reactant}\right]$  $\frac{\dot{m}\left[\frac{L}{\min}\right]}{stack} = \frac{\dot{m}\left[\frac{g}{\sec}\right]}{stack} \bullet \frac{1}{Mw_{H2}} \left[\frac{\text{moles of reactant}}{g}\right] \bullet \frac{22.42 \text{Liters}}{\text{mole of reactant}} \bullet \frac{T({}^{0}K)}{273.15} \bullet \frac{1 \text{sec}}{60 \text{ min}}$  $CD = \text{CURRENT DENSITY} = \left[\frac{C/s}{cm^2}\right] = \frac{Amps}{cm^2}$ 

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# "AIR" FLOW CONSUMPTION P=1 ATM



# 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



### **REASONS FOR HIGH CATHODE OVERPOTENTIAL**

- For a PEMFC operating at 1 A/cm<sup>2</sup>,
  - Overpotential at hydrogen electrode is 20 mV
  - Overpotential at oxygen electrode is 400 mV
- The reason for these large differences in overpotential are the exchange current densities  $i_0$ .
  - Exchange current density for hydrogen electro-oxidation is 10<sup>-3</sup> A/cm<sup>2</sup> on smooth platinum electrodes.
  - Exchange current density for oxygen electro-reduction is 10<sup>-9</sup> A/cm<sup>2</sup> on smooth platinum electrodes.
- Oxygen reduction is more complex because
  - Oxygen ions cannot easily accept four electron coming to the orbit.
  - The O-O bond is strong and forms highly stable Pt-O or Pt-OH species.
  - There are at least four intermediate steps/reactions for four electron transfer that we do not know yet.

# **TYPICAL IV CURVE**



Number of electrons involved, n: 2PresFaraday's constant, F: 96,485 C/molGasCurrent loss,  $i_{loss}$ : 0.002 A/cm²TranReference exchange current density,  $i_0$ : 3x10-6 A/cm²Limiting current density,  $i_L$ : 1.6 A/cm²Internal resistance,  $R_i$ : 0.15 Ohm-cm²



Fuel: Hydrogen Oxidant: Air Temperature: 333 K Pressure: 101.3 kPa Gas constant, R: 8.314 J/mol,K Transfer coefficient, α: 1

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# POWER DENSITY VS CURRENT DENSITY



#### Power density = i x V (W/cm<sup>2</sup>)

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### MAJOR ASPECTS OF PEMFC DESIGN

- Method of Connecting cell in Series/Parallel to Obtain Desired Voltag
- Delivery of Reactants to Membrane
- Water management in MEA
- Method of cooling the PEMFC
- Operating pressure in the PEMFC
- Source of pressurized air.
- Source of CO free hydrogen gas
- Systems for water and thermal management in the cells.



First we will start with the details of the connecting cells and details of the polymer membrane, and then will discuss the other above issues.

### **BIPOLAR PLATES**

 Contain over 90% of the volume and 80% of the mass of a fuel cell stack. The bipolar plate is the most expensive part of the fuel cell.

#### • Function

- Collect and conduct the current from the anode of one cell to the cathode of the neighboring cell; connect the cells in series.
- Distribute the "fuel gas" over the anode and "air" over the cathode through the flow field patterns.
- Provide cooling to the stacks depending upon the power generation.
- Keep the reactant gases and cooling fluids unmixed.



# **MONOPOLAR CONSTRUCTION**

- Monopolar construction in which taps at the ANODE electrodes are connected to the CATHODE for current collection purposes. The problems with this design are:
- The electrons must flow across the active area of the electrode to the current collector (taps) at the edge.
- The frame or edge collector of the current must  $\bigcirc$  have electrode conductivity Cat
- The design handles up to 400 cm<sup>2</sup> (size of electrode). Beyond this size, <u>uneven</u>
   <u>CURRENT distribution</u> occurs, as a result of tapering ohmic resistance being high.



#### **Advantage**

A single cell can be disconnected, in case of cell failure without seriously upsetting the performance.

### **Monopolar Stack Configurations**

#### zig-zag configuration



#### flip-flop configuration



#### Adopted From Frano Barbir

#### **BIPOLAR CONSTRUCTION** Electrolyte

- This is a logical stacking of cells to obtain a high voltage. But it suffers from interfacial contact problems, which are solved by applying pressure on the stack using some devices.
- Design of a bipolar plate
  - VERTICAL CHANNELS ARE MADE ON THE ANODES FOR HYDROGEN FLOW
  - HORIZONTAL CHANNELS ARE MADE ON THE CATHODE FOR **OXYGEN/AIR FLOW**
- The channels on bipolar plates compromise optimization of electrical contact. The plate should be thin to reduce electrical resistance, . but this would jeopardize the **<u>rigidity</u>** of the structure. Small channels would reduce gas flow, where cooling is required, and this construction complex makes the and expensive.



#### Advantages

- Bipolar plates are not limited by size
- The current flows perpendicular to the electrode surface and current collection is realized over whole area of electrodes The use of materials of low conductivity is possible
  - The effective area can be greater than  $400 \text{ cm}^2$

#### **Disadvantages**

A single cell failure leads to the malfunction of the stack.

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## **BIPOLAR PLATE AND INTERCONNECTS**



## **Bipolar Stack Configuration**



# FUEL CELL STACK ASSEMBLY



# EXTERNAL MANIFOLDS REACTANT DELIVERY

- Fuel and air are supplied to the fuel cell using this type of construction
- <u>Advantages</u>
- Simplicity
- Disadvantages
- Difficulty in cooling the system
- Probability of the reactants leaking as the gaskets at the edges of the electrodes are not firmly pressed down

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# INTERNAL MANIFOLDS REACTANT DELIVERY

#### **Internal Manifolding Technique**

- In the design, the plates are made larger relative to the electrodes.
- Channels run through the stack that feed fuel and air to the electrodes.
- The reactants are fed in at the ends, where the positive and negative connections are made

### FLOW FIELD PATTERNS IN PEMFCS



#### Flow field orientation



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### **DESIGN CONSIDERATIONS FOR GAS FLOW FIELDS**

- The pressure drop along each channel must be greater than the surface tension so that no water droplet are hold in place.
- The pattern should be such that it should not allow water build up or impurity build up (such as nitrogen) in one or more parallel channels which will otherwise render that flow passage not useful for fuel/oxidant supply near the region of the channel.
- The serpentine passage [in the previous slide] will overcome the above mentioned problem, but will yield very high pressure drop.
- The compromise is several parallel serpentine passages as shown in the previous slide.
- Ballard uses the pattern of having long parallel flow passages so having a reasonable pressure drop to allow no accumulation and stagnant flow area.

# FLOW FIELD PLATE DESIGN: HOW IN THE HECK DOES IT WORK? INTERNAL DISTRIBUTION MANIFOLDS...



# MATERIALS & LEAKAGE

#### Materials for a bipolar plate

- Graphite often used but it is brittle
- Stainless steel corrosion is the main problem in some fuel cells
- Ceramic material used for high temperature fuel cells
- Bipolar plate is a major contributor to the cost of a fuel cell

#### <u>Leakage</u>

- The bipolar plate shown earlier is a simple version, as leaks and gas supply problems are not emphasized.
- The electrodes must be porous to enable gas in, as the edges are unsealed, gas leaks at the edges must be checked

#### This is achieved through:

- Making the electrolyte lager than one or both electrodes
- Fitting a sealing gasket around each electrode.



### DESIRED PHYSICO-CHEMICAL CHARACTERISTICS OF BIPOLAR PLATES

- High surface and bulk electronic conductivity (> 10 S/cm)
- Must be good conductors of heat and compatible with a variety of heat exchanger fluids. Thermal conductivity > 20 W/mK for normal integrated cooling fluids or > 100 W/mK for heat removal from the edges of the plates.
- Permeability to reactant gases must be < 10<sup>-7</sup> mBar L/cm<sup>2</sup>s
- Chemical Stability (years):
  - Resistance to corrosion to acid electrolyte, oxygen, hydrogen, heat and humidity.
- High mechanical strength with thin plates; flexural strength
   > 25 MPa.
- Low material and processing cost (target less than \$10/kW)
- Minimum weight.
- Maintain rigidity and shape without creep at the operating temperature.

### **BIPOLAR PLATE: ISSUES**

- Problems with the Bipolar Plates
  - Many joints and potential problems of leaks of reactant gases and cooling fluid.
  - The anode and cathode gases must be kept separate and fed without leaks to individual anode and cathodes.
  - Entire anode and cathode edge is potentially leak.
- General Construction:
  - Make two halves with channels for reactant gases on one side and the cooling channel on the other side, and join two pieces to make coolant channels and the other sides are then channels for anode and cathode gas flows.



### **BIPOLAR CONSTRUCTION & MATERIALS**

#### **Machined Graphite Plates**

- Graphite is electrically conductive, is easy to machine, and has low density, all attractive features.
- They have, however, the following disadvantages:
  - The machining is time consuming and costly.
  - Careful handling is necessary because the graphite is brittle.
  - Plates need to be a few millimeter thick (since the graphite is porous) to avoid the mixing of reactant gases.
- Carbon-Carbon Composites
  - A composite of carbon and graphitizable resin is made by injection molding. The graphitization process requires heating the parts to 2500°C.
  - The molding is inexpensive while the heating is very expensive.
  - The heating process must be controlled closely to avoid warping, and also requires the plates to be at least a few mm thick.
  - This method is not widely used.

### **BIPOLAR CONSTRUCTION & MATERIALS**

- Injection Molding of Graphite-filled Polymer
  - The polymer has low electric conductivity and hence it is not suitable at present.
- Compression Molding
  - Compression molding of polymer/carbon can increase the electric conductivity.
  - The cycle time is less than machining but more than the injection molding.
- Metal Plates
  - Good conductors, can be machined easily, nonporous, thin plates, and lower volume and weight - all good features.
  - Higher density and prone to corrosion not desirable features.
     Hence, use stainless steel plates with aluminum or other coatings
  - Can be machined like graphite sheets and can be made thin since greater impermeability.
  - The time, energy requirement and cost are high with metal plates.
  - Some manufacturers use today metal plates and some graphite plates since neither are the perfect materials for bipolar plates.

# FUEL CELL STACK BUILDING



#### https://www.youtube.com/watch?v=w5E\_ MAZdO-k

# **GM AND MILITARY FUEL CELLS**

### • <u>https</u>://www.youtube.com/watch?v=r-NGHd4kFkQ







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# FUEL CELL OPERATING CONDITIONS

#### Pressure:

any pressure between atmospheric + pressure drop and 400 kPa, depending on available air supply and desired system efficiency; oxygen up to 1,200 kPa

#### Temperature:

between 50°C and 80°C depending on operating pressure

#### Flow rates:

air: S = 2.0 - 2.5; oxygen: S = 1.2 – 1.5 hydrogen: 1.0 dead end with intermittent purging, up to 1.5 with recirculation reformate: 1.2 – 1.3

#### Humidity of reactants:

air: dry to 100% at stack operating temperature hydrogen: dry to 125%

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## FLOW REACTANTS FLOW THRU MODE / DEAD END MODE



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# CONTROLLING FLOW RATE FLOW THRU MODE...



# CONTROLLING FLOW RATE FLOW THRU VS. DEAD-END



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# **DEAD-END PURGE CONTROL**



#### Purging control

- Timer (every x minutes opened for y seconds)
- Voltage monitor (opened for z seconds if cell voltage drops below V<sub>min</sub>)

# CONTROLLING FLOW RATE DEAD END MODE



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# FUEL UTILIZATION WILOSSES

### • Flow Through

$$\eta_{fu} = \frac{1}{S_{H_2}} = \frac{1}{\frac{\dot{m}_{H_2,CONS} + \dot{m}_{H_2,LOSS}}{\dot{m}_{H_2,CONS}}}$$

• Dead End

 $\eta_{fu} = \frac{\dot{m}_{H2,CONS}}{\dot{m}_{H2,CONS} + \dot{m}_{H2,LOSS} + \dot{m}_{H2,purge}} \bullet DURATION(S) \bullet FREQUENCY(1/S)$ 

### • Oxygen Fraction @ Outlet

 $r_{O2,out} = \frac{S_{AIR,in} - 1}{\frac{S_{AIR,in}}{r_{O2,in}} - 1} = \frac{\text{Theoritical AIR OUT}}{\text{Theoritical O}_2 \text{ Consumption}}$ 

### Effect of operating pressure - 110-cell stack NG2000



Is there an advantage to operate at a higher pressure?



# Temperatures and pressures where water generated is sufficient to fully humidify reactant gases (hydrogen/air)



Figure shows the conditions at which a fuel cell generates enough water for **humidification** of both air and hydrogen (DRY UPPON INLET). ABOVE the line for a given STOIC ratio, the need for humidification of reactant gases is greater than the amount of water generated in the stack.

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# EFFECT OF AIR MASS FLOW RATE S=CONSTANT=2.5



# **EFFECT OF AIR STOIC**

For pure H2, there is no impact of varying the H2 STOIC value.



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# **EFFECT OF FUEL DILUTION**



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# AIR VS OXYGEN



• At given conditions, the expected gain is 0.56 mV/cell. Also with pure O2 does not result in noticeable concentration polarization; therefor the gain at higher current density is even larger than calculated.

## **USE OF PURE OXYGEN VS AIR**



- Used in spacecraft and submarine applications, and substantially improves the performance.
  - The "no loss" open circuit voltage INCREASES due to increase in the partial pressure (see Nernst eq.)
  - The activation overvoltage reduction due to better use of catalyst sites.
  - The limiting current increases thus reducing the concentration losses.
- The change from air to pure oxygen will approximately increase the PEMFC power by about 30%.

# PROBLEM 1A 300 PLATES, 150CM2

 For an anode and a cathode stoichiometry 1.4 and 2.5, respectively. Determine the H2 and air mass flow rate into the fuel cell per amp/cm2 of current.



# PROBLEM 1B/C 300 PLATES, 150CM2

 If the nominal operating point is 0.6V per plate, and 1.2A/cm2, determine stack voltage and electrical power output.

$$V_{stack} = 0.6 \frac{V}{cell} \bullet 300 cells = 180V_{stack}$$

$$I_{stack} = 1.2 \frac{Amps}{cm^2} \bullet 150 cm^2 = 180A$$

$$P = IV = 1.2 \frac{Amps}{cm^2} \bullet 150 cm^2 \bullet 0.6 \frac{V}{cell} \bullet 300 cells$$

$$= 32.400W = 32.4kW$$

 How much total electrical work at 0.6V per plate could be performed with a storage tank with 5 kg of H2, and limitless air.



# PROBLEM 1D 300 PLATES, 150CM2:

 Determine how many plates and plate *power density*, if the fuel cell operates at 0.6 V/plate and current density 1.2 A/cm2 to generate 150 HP for an automotive application.

$$P = 150hp \frac{745W}{hp} = 111.9kW$$

$$I = 1.2 \frac{A}{cm2} \bullet 150cm^{2} = 180A$$

$$V = \frac{111900W}{180A} \bullet 621.7V / stack$$

$$n = \frac{621.7V / stack}{0.6V / plate} = 1036 \ plates / stack$$

$$POWER \ DENSITY \ PER \ PLATE \rightarrow$$

$$P\left[\frac{W / cm^{2}}{plate}\right] = \frac{\frac{111,900W}{150cm^{2}}}{1036 \ plates} = 0.72 \left[\frac{W / cm}{plate}\right]$$

## **PROBLEM 2A** 25 CELL H2/O2 PEM, <u>90W/CM2</u>,@10V

### What is the total stack mass flow rate of hydrogen[g/s]/cm2 if anode STOIC=1.3.



## **PROBLEM 2B 25 CELL H2/O2 PEM, 90W/CM2,@10V**

#### What is total stack generation of water at cathode in [grams/hour]/cm2.



# PROBLEM 2C 25 CELL H2/O2 PEM, 90W/CM2,@10V

• If the theoretical maximum voltage of a single cell is 1.23V, what is the real, voltaic & thermal efficiency of a single cell if we assume "all" cells have same voltage, and 1.3 STOIC;

$$S = Stoichiometry = \frac{\text{Actual Flow}}{\text{Ideal Flow}} > 1.0$$

$$\eta_{real_{absolut}} = \left(\frac{\Delta G}{HHV}\right)_{IDEAL} \bullet \frac{V(i)}{E} \bullet \frac{\frac{i}{nF}}{v_{fuel_{scual}}(mol / \sec)} = \frac{\Delta G}{HHV} \bullet \frac{V(i)}{E} \bullet \frac{1}{S}$$

$$= 0.83 \bullet \frac{1.23}{1.23} \bullet \frac{1}{1.3} = 63.84\%$$

$$\eta_{VOLTAIC} = \frac{\text{Actual Voltage Potential Output}}{\text{Max Voltage Potential Output}}$$

$$= \frac{1.23}{1.23} = 100\%$$

$$\eta_{THERMAL_{IDEAL}} = \frac{\text{Actual Voltage Potential Output}}{\text{Max Voltage Potential INPUT}}$$

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

$$= \frac{-\Delta G}{nF} = \frac{\text{Theoretical Cell Potential}}{\text{Potential Corresponding to H2 Higher Heating Value}} = \frac{1.23}{1.482} = 83\%$$

$$\eta_{THERMAL_{IDEAL}} = \frac{1.23}{1.482} \bullet \frac{1}{S} = 63.84\%$$

### **CONCLUDING REMARKS**

In this lecture, we covered

- Starting with the solid polymer membrane chemistry, the operation of a proton exchange membrane fuel cell was discussed.
- The construction details of basic components of a PEMFC were then covered: Electrolyte, electrodes and electrode structure, and bipolar plates. The selection of various materials and construction features were discussed from the viewpoint of performance, durability and cost point of view.
- Water management issue in a PEMFC and performance characteristics.

In the next lecture, we will cover

- PEMFC cooling and air supply
- Influence of operating parameters on the performance
- CO poisoning
- Some examples of PEMFC systems