

# General Introduction to Fuel Cell Electrochemistry

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## What is fuel cell?

Fuel cell is an electrochemical energy converter.

- It converts chemical energy of fuel (H<sub>2</sub>) directly into electricity.
- Fuel cell is like a battery but with constant fuel and oxidant supply.



# **Fuel cell history**

Invention of fuel cell





Christian Schönbein (1799-1868):

Prof. of Phys. and Chem. in Basel, first observation of fuel cell effect (Dec. 1838, Phil. Mag.)

William Robert Grove (1811 –1896): Welsh lawyer turned scientist, demonstration of fuel cell (Jan. 1839, Phil. Mag.)

First fuel cells as depicted by Grove

1839

# **Fuel cell history**

#### Invention of fuel cell Scientific curiosity



1839

Friedrich Wilhelm Ostwald (1853-1932, Nobel prize 1909): founder of "Physical Chemistry", provided much of the theoretical understanding of how fuel cells operate



Friedrich Wilhelm Ostwald – visionary ideas: "I do not know whether all of us realise fully what an imperfect thing is the most essential source of power which we are using in our highly developed engineering – the steam engine"

Energy conversion in combustion engines
 Iimited by Carnot efficiency
 unacceptable levels of atmospheric pollution VS.
 Energy conversion in fuel cells

direct generation of electricity

highly efficient, silent, no pollution

Transition would be technical revolution Prediction: practical realization could take a long time!

Source: Z. Elektrochemie, Vol. 1, p. 122-125, 1894.

# Fuel cell history

Invention of fuel cell

**Scientific curiosity** 







# Space Applications

PEM Fuel Cells used in Gemini program
Apollo program used alkaline fuel cells
Space Shuttle uses alkaline fuel cells
Renewed interest in PEM fuel cells

First PEM Fuel Cell Grubb and Niedrach (GE)



Gemini Space Program

1960s











#### **Birth of new industry - Ballard stock**



## **Fuel Cell Applications - Demonstrations**

- Automobiles
- Buses
- Scooters
- Bicycles
- Golf-carts
- Distributed power generation
- Cogeneration
- Back-up power
- Portable power
- Space
- Airplanes
- Locomotives
- Boats
- Underwater vehicles



# Why fuel cells

- Promise of high efficiency
- Promise of low or zero emissions
- Run on hydrogen/fuel may be produced from indigenous sources/issue of national security
- Simple/promise of low cost
- No moving parts/promise of long life
- Modular
- Quiet

## What is fuel cell?

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## What is fuel cell?

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It converts chemical energy of fuel (H<sub>2</sub>) directly into electricity.



# **Types of fuel cells**

#### Alkaline

 Acid polymer membrane or Polymer Electrolyte Membrane or Proton Exchange Membrane

PEM

- Phosphoric acid
- Molten carbonate
- Solid oxide
  - Zinc/Air fuel cell is not a fuel cell
  - Direct methanol fuel cell is PEM fuel cell

# **Reactions in fuel cells**



# **Types of fuel cells**

#### Alkaline



 Acid polymer membrane or Polymer Electrolyte Membrane or Proton Exchange Membrane



- Phosphoric acid
- Molten carbonate
- Solid oxide

# Why PEM Fuel Cells?

- Simple
- Quick start-up
- Fast response
- High efficiency
- High power density (kW/kg and kW/l)
- Zero emissions

#### **PEM Fuel Cell Basic Components**



Porous electrode structure Gas diffusion layer surface (carbon fiber paper)



**80** µm

#### **PEM Fuel Cell Basic Components**



**MEA – Membrane Electrode Assembly** 

## **MEA Cross-Section**





#### **PEM Fuel Cell: How does it work?**





# **FUEL CELL STACK**



# **Actual fuel cell stacks**



Teledyne



Ballard





#### **Hydrogenics**



**UTC Fuel Cells** 

#### Fuel cell needs supporting equipment/balance-of-plant



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## Actual fuel cell system



## **Understand the difference between:**



#### **Fuel Cell Theory - Thermodynamics**

#### **Basic reactions**

Hydrogen side: anode – hydrogen oxidation Oxygen side: cathode – oxygen reduction

Mnemonic: reduction of oxygen on cathode: red-cat

Anode reaction:	$H_2 \rightarrow 2e^- + 2H^+$	oxidation
Cathode reaction:	$^{1/_2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$	reduction
Overall reaction:	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	

Same as combustion of hydrogen

## **Heat of Formation**

Combustion of hydrogen is an exothermic reaction – heat is generated

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

How much heat?

From the tables: Heat of formation:  $\Delta H = (h_f)_{H2O} - (h_f)_{H2} - \frac{1}{2}(h_f)_{O2} = -286 - 0 - 0 = -286 \text{ kJ/mol}$ 

 $\Delta$  means difference between products and reactants

mol is a measure of quantity
1 mol of hydrogen contains 2 grams of hydrogen (2.0159 to be more precise)
1 mol of oxygen contains 32 grams of oxygen
1 mol contains 6.022 x 10<sup>23</sup> molecules (Avogadro's number)

In a fuel cell both heat and electricity are generated.

But how much electricity?

Can all heat be converted into useful work (electricity)?

Remember 2<sup>nd</sup> law of thermodynamics? Remember entropy?

For mechanical processes:  $W = Q - T\Delta S$ 

For chemical reactions:  $\Delta G = \Delta H - T \Delta S$ 

 $\Delta G$  = Gibbs free energy

 $\Delta$  means difference between products and reactants

 $\Delta G = 237.2 \text{ kJ/mol}$  (at 25°C)

## **Theoretical cell voltage**


## **Theoretical cell voltage – function of temperature**



# **Theoretical Fuel Cell Efficiency**



Ideal cell Voltage at different temperature and pressure

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

$$\frac{\Delta G}{nF} = \frac{\Delta H}{nF} - \frac{T\Delta S}{nF} \quad At \ 25^{\circ}C \quad \frac{\Delta G}{nF} = 1.23 \ V \quad \frac{\Delta H}{nF} = 1.482 \ V \quad \frac{T\Delta S}{nF} = 0.252 \ V$$

$$E_{T} = 1.482 - 0.000845T \qquad Note: \ \Delta H \ and \ \Delta S \ are \ f(T)$$
For T<373K  $E_{T} \approx 1.482 - 0.000845T$ 

All of the above considerations were at ambient pressure P = 1 atm, P = 101.3 kPa; P = 1.013 bar, P = 14.698 psi; P = 0 psig

Does the ideal voltage change with pressure?

**Unfortunately – yes!** 

A little bit of basic thermodynamics

 $-dG = V_m dP$ 

For an ideal gas:

 $PV_{m} = RT$  $- dG = RT \frac{dP}{P}$  $- G = -G_{0} + RT \ln \frac{P}{P_{0}}$ 

Fuel cell reaction:  $H_2 + \frac{1}{2} O_2 \rightarrow H_2 O_2$ 

$$\frac{-\Delta G}{nF} = \frac{-\Delta G_0}{nF} + \frac{RT}{nF} ln \left(\frac{P_{H_2} \cdot P_{O2}^{0.5}}{P_{H_2O}}\right)$$

**Nernst Equation** 

$$\mathbf{E}_{\mathbf{P}} = \mathbf{E}_{\mathbf{0}} + \frac{\mathbf{RT}}{\mathbf{nF}} ln \left( \frac{\mathbf{P}_{\mathbf{H}_{2}} \cdot \mathbf{P}_{\mathbf{O}_{2}}^{\mathbf{0.5}}}{\mathbf{P}_{\mathbf{H}_{2}\mathbf{O}}} \right)$$

## Summary

Ideal fuel cell voltage

$$\begin{split} & \mathsf{E}_{0} = \mathsf{E}_{1atm,298.15K} = 1.23 \text{ V} \\ & \mathsf{E}_{\mathsf{P},\mathsf{T}} = 1.482 - 0.000845\mathsf{T} + \frac{\mathsf{RT}}{2\mathsf{F}} \ln\!\!\left(\frac{\mathsf{P}_{\mathsf{H}_{2}} \cdot \mathsf{P}_{\mathsf{O}_{2}}^{0.5}}{\mathsf{P}_{\mathsf{H}_{2}\mathsf{O}}}\right) \\ & \mathsf{E}_{\mathsf{P},\mathsf{T}} = 1.482 - 0.000845\mathsf{T} + 0.0000431\mathsf{T} \ln\!\!\left(\frac{\mathsf{P}_{\mathsf{H}_{2}} \cdot \mathsf{P}_{\mathsf{O}_{2}}^{0.5}}{\mathsf{P}_{\mathsf{H}_{2}\mathsf{O}}}\right) \end{split}$$

**Caution: valid only for low temperatures** 

This is voltage at 0 current So called open circuit voltage (OCV) Ideal Cell voltage: 1.23 V  $(H_2/O_2 \text{ at } 25^{\circ}\text{C}, 1 \text{ atm})$ 

Function of temperature, pressure and concentration of reactants:At 80°C:1.186 VAir instead of O2:1.174 V

Actual voltage is always lower!



Ideal Cell voltage: 1.23 V  $(H_2/O_2 \text{ at } 25^\circ\text{C}, 1 \text{ atm})$ 

Function of temperature, pressure and concentration of reactants:At 80°C:1.186 VAir instead of O2:1.174 V

Actual voltage is always lower!



### **Relationship between current and voltage**

**Butler-Volmer equation** 

$$i = i_0 \left\{ exp \left[ \frac{-\alpha F(E - E_r)}{RT} \right] - exp \left[ \frac{(1 - \alpha)F(E - E_r)}{RT} \right] \right\}$$

- i<sub>0</sub> = exchange current density
- $\alpha$  = charge transfer coefficient
- F = Faraday's constant
- R = gas constant
- T = temperature
- E = potential
- **E**<sub>r</sub> = reversible potential

### Factors affecting the exchange current density

- Catalyst
- Roughness/actual surface area
- Temperature
- Reactants concentration

Pressure

$$\mathbf{i}_{0} = \mathbf{i}_{0}^{\text{ref}} \mathbf{a}_{c} \mathbf{L}_{c} \left(\frac{\mathbf{P}_{r}}{\mathbf{P}_{r}^{\text{ref}}}\right)^{\gamma} exp\left[-\frac{\mathbf{E}_{C}}{\mathbf{RT}}\left(1 - \frac{\mathbf{T}}{\mathbf{T}_{\text{ref}}}\right)\right]$$

 $i_0^{ref}$  = exchange current density at reference conditions (T,P) in A/cm<sup>2</sup> Pt surface  $a_c$  = catalyst specific area (for Pt theoretically: 2,400 cm<sup>2</sup>/mg practically: 600-1,000 cm<sup>2</sup>/mg in electrode: 420-700 cm<sup>2</sup>/mg

 $L_c$  = catalyst loading (today 0.3 to 0.5 mg/cm<sup>2</sup>)  $E_c$  = activation energy (66 kJ/mol) R = universal gas constant (8.314 J/molK)

 $\gamma$  = pressure coefficient (0.5 to 1.0)

#### $\alpha$ = charge transfer coefficient

 $\alpha \;\cong \textbf{1}$ 

```
Notes: in some literature n\alpha is used instead of \alpha
n = 2 for the anode and n = 4 for the cathode
Larminie&Dicks suggest \alpha_a = 0.5 and \alpha_c = 0.1 to 0.5
Newman specifies \alpha in a range between 0.2 and 2.0
```

```
\alpha is an empirical factor
it should be distinguished from a symmetry factor \beta
\beta may be used for single-step reaction with n=1
\beta_{Rd} + \beta_{Ox} = 1 or \beta_{Ox} = 1 - \beta_{Rd}
for metallic surfaces \beta \cong 0.5
```

```
\begin{array}{l} \alpha_{Rd} + \alpha_{Ox} \neq 1 \\ \alpha_{Rd} + \alpha_{Ox} = n/\nu \\ n = number \ of \ electrons \ involved \\ \nu = number \ of \ times \ the \ rate-determining \ step \ must \ occur \ for \\ the \ overall \ reaction \ to \ occur \ once^* \end{array}
```

\*E. Gileadi, *Electrode kinetics for Chemists, Chemical Engineeris and Material Scientists*, VCH Publishers, New York, 1993

### **Relationship between current and voltage**

**Butler-Volmer equation** 

$$i = i_0 \left\{ exp \left[ \frac{-\alpha F(E - E_r)}{RT} \right] - exp \left[ \frac{(1 - \alpha)F(E - E_r)}{RT} \right] \right\}$$

 $\alpha$  = charge transfer coefficient

$$i = i_0 \left\{ exp \left[ \frac{-\alpha_{Rd} F(E - E_r)}{RT} \right] - exp \left[ \frac{\alpha_{Ox} F(E - E_r)}{RT} \right] \right\}$$

$$i = i_0 \left\{ exp \left[ \frac{-\alpha_{Rd} F(E - E_r)}{RT} \right] - exp \left[ \frac{\alpha_{Ox} F(E - E_r)}{RT} \right] \right\}$$
  
(E - E<sub>r</sub>) = overpotential

On the fuel cell anode:

$$\mathbf{i}_{a} = \mathbf{i}_{0} \left\{ exp \left[ \frac{-\alpha_{Rd,a} F \left( \mathbf{E}_{a} - \mathbf{E}_{r,a} \right)}{RT} \right] - exp \left[ \frac{\alpha_{Ox,a} F \left( \mathbf{E}_{a} - \mathbf{E}_{r,a} \right)}{RT} \right] \right\}$$

**E**<sub>r,a</sub> = 0 definition of zero potential – hydrogen electrode

$$\begin{aligned} (\mathsf{E}_{\mathsf{a}} - \mathsf{E}_{\mathsf{r},\mathsf{a}}) &> 0 \\ \mathsf{i}_{\mathsf{a}} &= -\mathsf{i}_{\mathsf{0}} \exp\!\!\left[\frac{\alpha_{\mathsf{Ox},\mathsf{a}}\mathsf{F}\!\left(\!\mathsf{E}_{\mathsf{a}} - \!\mathsf{E}_{\mathsf{r},\mathsf{a}}\right)}{\mathsf{R}\mathsf{T}}\right] \\ &\quad \mathsf{negative sign means current is leaving the electrode} \\ &\quad \mathsf{negative reaction} \end{aligned}$$

$$i = i_0 \left\{ exp \left[ \frac{-\alpha_{Rd} F(E - E_r)}{RT} \right] - exp \left[ \frac{\alpha_{Ox} F(E - E_r)}{RT} \right] \right\}$$
  
(E - E<sub>r</sub>) = overpotential

On the fuel cell anode:

$$\mathbf{i}_{a} = \mathbf{i}_{0} \left\{ exp \left[ \frac{-\alpha_{Rd,a} F \left( \mathbf{E}_{a} - \mathbf{E}_{r,a} \right)}{RT} \right] - exp \left[ \frac{\alpha_{Ox,a} F \left( \mathbf{E}_{a} - \mathbf{E}_{r,a} \right)}{RT} \right] \right\}$$

**E**<sub>r,a</sub> = 0 definition of zero potential – hydrogen electrode

$$\begin{aligned} (\mathsf{E}_{\mathsf{a}} - \mathsf{E}_{\mathsf{r},\mathsf{a}}) &> 0 \\ \mathsf{i}_{\mathsf{a}} &= -\mathsf{i}_{\mathsf{0}} \exp\!\!\left[\frac{\alpha_{\mathsf{Ox},\mathsf{a}}\mathsf{F}\!\left(\!\mathsf{E}_{\mathsf{a}} - \!\mathsf{E}_{\mathsf{r},\mathsf{a}}\right)}{\mathsf{R}\mathsf{T}}\right] \\ &\quad \mathsf{negative sign means current is leaving the electrode} \\ &\quad \mathsf{- oxidation reaction} \end{aligned}$$

On the fuel cell cathode:

$$\mathbf{i}_{c} = \mathbf{i}_{0} \left\{ exp \left[ \frac{-\alpha_{Rd,c} F(\mathbf{E}_{c} - \mathbf{E}_{r,c})}{RT} \right] - exp \left[ \frac{\alpha_{Ox,c} F(\mathbf{E}_{c} - \mathbf{E}_{r,c})}{RT} \right] \right\}$$

$$E_{r,c} = 1.23 V$$

$$(E_c - E_{r,c}) < 0$$

$$i_c = i_{0,c} exp \left[ \frac{-\alpha_{Rd,c} F(E_c - E_{r,c})}{RT} \right]$$

Types of losses in fuel cell:

- Activation losses (activation polarization)
- Resistive (Ohmic) losses
- Mass transfer losses (concentration polarization)
- Internal current and fuel crossover

### **Activation polarization losses**

Tafel equation: ∆V<sub>act</sub> = a + b · *log*(i)

(empirical)

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

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

- i = current density (mA/cm<sup>2</sup>)
- i<sub>0</sub> = exchange current density (mA/cm<sup>2</sup>)
- R = universal gas constant = 8.314 J/mol
- T = temperature of the process (K)
- $\alpha$  = charge transfer coefficient
- n = number of electrons involved (2)

$$\Delta V = -\frac{RT}{\alpha F} ln(i_0) + \frac{RT}{\alpha F} ln(i)$$

$$a = -\frac{RT}{\alpha F} \ln(i_0) = -2.3 \frac{RT}{\alpha F} \log(i_0)$$

$$b = 2.3 \frac{RT}{\alpha F}$$

Tafel slope

### **Activation polarization losses**



### **Resistive losses**

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

 $\begin{array}{l} \mbox{I = current (Amps)} \\ \mbox{R = resistance (Ohms)} \\ \mbox{i = current density (A/cm<sup>2</sup>)} \\ \mbox{R}_{i} \mbox{= aerial resistance (Ohm-cm<sup>2</sup>)} \end{array}$ 

ρ = resistivity (Ohm-cm)
d = distance, length (cm)
A = cross sectional area (cm<sup>2</sup>)
R<sub>i</sub> = R·A

**Resistance through:** 

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





### **Concentration polarization or mass transport losses**



Alternative way to express concentration polarization

Voltage gain/loss  
(Nernst equation)
$$\Delta V = \frac{RT}{nF} ln \left( \frac{C_B}{C_s} \right)$$
Fick's First Law of Diffusion:
$$N = \frac{D \cdot (C_B - C_S)}{\delta} A$$
$$N = \frac{I}{nF}$$
$$N = \frac{I}{nF}$$
$$i = \frac{nF \cdot D \cdot (C_B - C_S)}{\delta}$$
Limiting current  $C_S = 0$ 
$$i_L = \frac{nF \cdot D \cdot C_B}{\delta}$$
$$\frac{C_S}{C_B} = 1 - \frac{i}{i_L}$$
Voltage loss due to concentration polarization:
$$\Delta V = \frac{RT}{nF} ln \left( \frac{i_L}{i - i_L} \right)$$

### **Voltage losses compared**



# Actual fuel cell voltage

$$\mathbf{V}_{cell} = \mathbf{E}_{T,P} - \Delta \mathbf{V}_{act} - \Delta \mathbf{V}_{res} - \Delta \mathbf{V}_{conc}$$

Losses occur on both anode and cathode:

$$\mathbf{V}_{\text{cell}} = \mathbf{E}_{\text{T,P}} - \left( \Delta \mathbf{V}_{\text{act}} \right)_{\text{an}} - \left( \Delta \mathbf{V}_{\text{act}} \right)_{\text{ca}} - \Delta \mathbf{V}_{\text{res}} - \left( \Delta \mathbf{V}_{\text{conc}} \right)_{\text{an}} - \left( \Delta \mathbf{V}_{\text{conc}} \right)_{\text{ca}} + \left( \Delta \mathbf{V}_{\text{co$$

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

## Potential Distribution in H<sub>2</sub>/Air Fuel Cell





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### **Power density vs. current density**

Power density = V-i (W/cm<sup>2</sup> or mW/cm<sup>2</sup>)



### Cell potential vs. power density



#### Internal currents and fuel crossover



Hydrogen consumption in fuel cell

Faraday's law:

I = nFN (Amps = Amp-second/mol x mol/s)



Hydrogen consumption in fuel cell:  $N_{H_2} = I/(2F)$ 

Oxygen consumption in fuel cell:  $N_{O2} = \frac{1}{2} N_{H2} = \frac{1}{4F}$ 

Water generation in fuel cell:  $N_{H2O} = I/(2F)$ 

Internal currents and fuel crossover

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.





### efficiency Cell potential vs. power density





Hydrogen in = hydrogen converted into current + hydrogen loss

$$\mathbf{N} = \frac{\mathbf{I} + \mathbf{I}_{\text{loss}}}{2\mathbf{F}} \implies \eta = \frac{\mathbf{V}_{\text{cell}}}{1.482} \frac{\mathbf{I}}{\mathbf{I} + \mathbf{I}_{\text{loss}}} = \frac{\mathbf{V}_{\text{cell}}}{1.482} \frac{\mathbf{i}}{\mathbf{i} + \mathbf{i}_{\text{loss}}}$$

In some cases excess hydrogen is fed into the fuel cell – some H<sub>2</sub> is wasted



### Fuel cell efficiency vs. power density



**Additional slides** 






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





## **Operating pressure**

$$V_{cell} = \underbrace{\mathsf{E}_{\mathsf{T},\mathsf{P}}}_{\mathsf{C}} - \frac{\mathsf{RT}}{\alpha\mathsf{F}} \ln \left( \frac{\mathsf{i} + \mathsf{i}_{\mathsf{loss}}}{\mathsf{i}_0} \right) - \mathsf{i} \cdot \mathsf{R}_{\mathsf{i}} + \frac{\mathsf{RT}}{\mathsf{n}\mathsf{F}} \ln \left( 1 - \frac{\mathsf{i}}{\mathsf{i}_\mathsf{L}} \right)$$



$$V_{\text{cell},\text{P=3}} = \text{E}_{\text{T},\text{P=3}} - \frac{\text{RT}}{\alpha\text{F}} \ln \left(\frac{\text{i} + \text{i}_{\text{loss}}}{\text{i}_{0,\text{P=3}}}\right)$$

$$V_{\text{cell},\text{P=3}} = \text{E}_{\text{T}} + \frac{\text{RT}}{4\text{F}} \ln(\text{P}_{3}) + \frac{\text{RT}}{1 \cdot \text{F}} \ln(\hat{\textbf{i}}_{0,\text{P=3}}) - \frac{\text{RT}}{1 \cdot \text{F}} \ln(\hat{\textbf{i}} + \hat{\textbf{i}}_{\text{loss}})$$

$$V_{\text{cell},\text{P}=1} = \text{E}_{\text{T}} + \frac{\text{RT}}{4\text{F}} \ln(\text{P}_{1}) + \frac{\text{RT}}{1 \cdot \text{F}} \ln(\text{i}_{0,\text{P}=1}) - \frac{\text{RT}}{1 \cdot \text{F}} \ln(\text{i} + \text{i}_{\text{loss}})$$

$$V_{\text{cell},\text{P=3}} - V_{\text{cell},\text{P=1}} = \frac{\text{RT}}{4\text{F}} \ln\left(\frac{3}{1}\right) + \frac{\text{RT}}{\text{F}} \ln\left(\frac{3}{1}\right)$$

 $V_{cell,P=3} - V_{cell,P=1} = 0.039 V$  (at 60°)



# Air vs. O2 MEA Perf. - Origin of Transport Losses





# **Evidence of Mass Transport Losses**



Fig. 5 For air operation, in Ballard Mark 5E hardware, the kinetic benefit of a PtCr alloy cathode is masked by mass transport losses. The comparative performance of the PtCr alloy and a pure Pt cathode electrocatalyst is shown using air, helox (21%  $O_2$  in helium) and  $O_2$  as oxidants and  $H_2$  as fuel. The MEAs (< 1 mg Pt cm<sup>-2</sup>) are based on catalysed substrates bonded to Nafion 115 membrane electrolyte. The cell is operated at 80°C, in hydrogen/air, helox, oxygen, 308/308 kPa, 1.5/2, 2, 10 stoichiometry, full internal membrane humidification

Source: T.P. Ralph and M.P. Hogarth, Platinum Metals Review, Vol. 46, No. 1, pp. 3-14, 2002

#### Constant current Constant voltage Constant resistance Constant power Variable power



### What else can affect the 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!

Reduced theoretical voltage

$$E_{T,P} = -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right) + \frac{RT}{nF} ln \left[\frac{P_{H2}P_{O_2}^{0.5}}{P_{H_2O}}\right]$$
$$E_{T,P} = 1.482 - 0.000845T + 0.0000431T ln \left(P_{H_2}P_{O_2}^{0.5}\right)$$

- Reduced theoretical voltage
- More hydrogen permeation through the membrane



T. Sakai, et al., J. Electrochem. Soc., Vol. 133, No. 1, pp. 88-92, 1986

- Reduced theoretical voltage
- More hydrogen permeation through the membrane
- Faster kinetics Reduced activation losses (exchange current density)

$$\dot{i}_{0} = \dot{i}_{0}^{\text{ref}} a_{c} L_{c} \left(\frac{P_{r}}{P_{r}^{\text{ref}}}\right)^{\gamma} exp\left[-\frac{E_{C}}{RT}\left(1-\frac{T}{T_{\text{ref}}}\right)\right]$$

- Reduced theoretical voltage
- More hydrogen permeation through the membrane
- Reduced activation losses (exchange current density)
- Improved conductivity of materials 1



T.A. Zawodzinski, Jr., C. Lopez, R. Jestel, J. Valerio, and S. Gottesfeld, *J. Electrochem. Soc.* 140, 1981, 1993

- Reduced theoretical voltage
- More hydrogen permeation through the membrane
- Reduced activation losses (exchange current density) 1
- Improved conductivity of materials 1
- Mass transport properties (diffusion coefficients) 1

$$D_{ij}^{eff} = \frac{a}{p} \left( \frac{T}{\sqrt{T_{c,i} T_{c,j}}} \right)^{b} \left( p_{c,i} p_{c,j} \right)^{1/3} \left( T_{c,i} T_{c,j} \right)^{5/12} \left( \frac{1}{M_{i}} + \frac{1}{M_{j}} \right)^{1/2} \varepsilon^{1.5}$$

- Reduced theoretical voltage
- More hydrogen permeation through the membrane
- Reduced activation losses (exchange current density) 1
- Improved conductivity of materials
- Mass transport properties (diffusion coefficients) 1
- Tightly related to relative humidity of the reactant gases 1



- Reduced theoretical voltage
- More hydrogen permeation through the membrane
- Reduced activation losses (exchange current density)
- Improved conductivity of materials 1
- Mass transport properties (diffusion coefficients) 1
- Tightly related to relative humidity of the reactant gases 1
- Stack compression 1



#### Effect of operating temperature on fuel cell performance



Q. Yan, H. Toghiani, H. Causey. Steady state and dynamic performance of proton exchange membrane fuel cells (PEMFCs) under various operating conditions and load changes, Journal of Power Sources, 2006

## Effect of operating temperature - 10-cell stack



## **Freeze tolerance test**



# **Definition of Operating Temperature**

- cell surface (where)
- cell inside (where and how)
- heating pad
- coolant in
- coolant out
- reactants out



## **Operating temperature**



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## What else can affect the polarization curve?

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

# Summary

Voltage losses: Activation polarization Ohmic (resistive losses) Concentration polarization or mass transport losses Internal currents and reactants crossover

**Resulting polarization curve:** 

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

Effect of operating pressure Effect of oxygen vs. air Effect of operating temperature

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

PEM Specific Issues – Water transport, gas diffusion

# PEM Fuel Cell: Membrane/Electrode Processes





Materials Science and Technology Division



Fig. 1. Isopiestic sorption of vapor-phase water in N, C, and D membranes at 30°C.

Source: T.A. Zawodzinski, et al., J. Electrochem. Soc., Vol. 140, No. 7, pp. A1981-A1985, 1993

# **Qualitative Picture of Transport in Nafion**



## Water content and conductivity



Fig. 1. Isopiestic sorption of vapor-phase water in N, C, and D membranes at 30°C.



Fig. 4. Conductivity of N, C, and D membranes at 30°C as a function of state of membrane hydration.

Source: T.A. Zawodzinski, et al., J. Electrochem. Soc., Vol. 140, No. 7, pp. A1981-A1985, 1993



Fig. 2. Isopiestic sorption of vapor-phase water in N, C, and D membranes at  $30^{\circ}$ C, with uptake expressed as percent of dry weight.



Fig. 5. Conductivity of N, C, and D membranes, immersed in water, as a function of temperature.

# Nafion conductivity

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Nafion conductivity: ~0.1 S/cm
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1/conductivity = resistivity = 10 Ohm-cm

Nafion 115 thickness: 5 mils = 0.0127 cm

Resistance = 10 Ohm-cm x 0.0127 cm = 0.127 Ohm-cm<sup>2</sup>

At 1 A/cm<sup>2</sup> it would cause 0.127 V loss

Nafion conductivity is a function of water content and temperature!

## Nafion resistivity – function of membrane thickness?



Figure 3. In situ specific resistivity of Nafion membranes of different thicknesses at (O) 50°C and  $(\oplus)$  60°C at zero current.

- unisotropic structure
- resistance from the electrodes
- thickness of the membrane in the cell different from measured before assembly

Source: F.N. Buchi and G.G. Scherer, J. Electrochem. Soc., Vol. 148, No. 3, pp. A181-A188, 2001

# Cell Resistance and Performance: PEM Thickness Effects



Electro-osmotic drag removes water from the anode side. With thicker membranes, back diffusion of water is difficult - the anode side loses water content.



Materials Science and Technology Division

### **Membrane resistance – function of current density**



Figure 2. In situ resistances of Nafion membranes with different thicknesses (from 60 to 240  $\mu$ m) as functions of current density at 60°C. The thicknesses and composition of membranes are indicated in the figure.

Figure 4. Resistance of the individual sheets, in a  $H_2/O_2$  fuel cell with four Nafion 112 sheets as a function of current density at a cell temperature of 60°C.

Source: F.N. Buchi and G.G. Scherer, J. Electrochem. Soc., Vol. 148, No. 3, pp. A181-A188, 2001

# Water Issues

- For PerFluoro Sulfonate lonomers (PFSI) and some sulfonated aromatic systems
- Humidification requirement
  - conductivity requires contact with liquid water or water vapor at > ~80 RH.
  - Water management system
    - > FC system cost ↑
    - > specific power  $\downarrow$
- Dimensional changes in membrane with water content
  - stresses at electrode/membrane interface and at the gasket
  - electrode debonding from membrane with CCM
  - buckling and cracking of carbon paper from shrinking membrane



# Water Issues (continued)

- Electro-Osmotic water Drag (EOD)
  - Each proton transported drags 1 to 5 water molecules
    - > Both aromatic sulfonates and PFSI: EOD increases with increasing temperature and water content.
  - Necessitates anode humidification system for hydrogen & reformate.
  - Degrades system efficiency for DMFC
- Water requirement makes for poor dynamic response of stack
  - Chasms of dry-out (conductivity loss) or flooding on either side of the operating point.
  - Water content depends on diffusion, evaporation, condensation.
    - > non-linear and slow response of system to current changes.
- Need for faster diffusion of cathode water back to anode => thinner membranes
  - manufacturing, fuel permeation, lifetime problems
- Wanted: conductivity without water


## **Permeation of gases through the membrane**

Permeability is a product of diffusivity and solubility:

$P_m = D \times S$		
$cm^2/s \times mol/cm^3 atm = \frac{mc}{cm \cdot s \cdot a}$	$\frac{d}{dtm}  \text{or}  \frac{mol \cdot cm}{cm^2 \cdot s \cdot atm}$	
For ideal gas: $Pv_m = RT$ ; at standard conditions $v_m = 0.024 \text{ m}^3/\text{mol}$ $v_m = 24,060 \text{ cm}^3/\text{mol}$		
$\frac{\text{cm}^{3} \cdot \text{cm}}{\text{cm}^{2} \cdot \text{s} \cdot \text{atm}} \qquad 1 \text{ atm} = 75 \text{ cmH}$	Ig $\frac{\text{cm}^{3} \cdot \text{cm}}{\text{cm}^{2} \cdot \text{s} \cdot \text{cmHg}} = 10^{10} \text{ barrers}$	
Example:	$P_{\rm m} = 1.5 \times 10^{-11}  {\rm mol} \cdot {\rm cm}^{-1} {\rm s}^{-1} {\rm atm}^{-1}$	
$D_{H2} = 6.65 \times 10^{-7} \text{ cm}^2/\text{s}$ $S_{H2} = 2.2 \times 10^{-5} \text{ mol/cm}^3 \text{atm}$	$1.5 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-1} \text{s}^{-1} \text{atm}^{-1} \times 24,060 \text{ cm}^{3}/\text{mol} =$ = 3.6 \times 10^{-7} \text{ cm}^{3} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \text{atm}^{-1} = = 3.6 \text{s} 10^{-7} \text{ cm}^{3} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \text{atm}^{-1} / 75 \text{ cm} \text{Hg/atm} = = 4.8 \text{s} 10^{-9} \text{ cm}^{3} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \text{cm}^{-1} \text{Hg} = 48 \text{ Barrers}	

## **Permeation rate**, N (mol/s)

$N = P_m \cdot A \cdot \Delta P/d$	
$N = I/nF$ $N_V$	$= N.24060 (cm^3/mol) = 0.125 \times I cm^3/s$
$i = I/A = nF P_m \Delta P/d$	$N_V = 7.5 \text{ cm}^3/\text{min}/\text{Amp}$
Example: $P_m = 1.5 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-1} \text{s}^{-1} \text{atm}^{-1}$ $A = 100 \text{ cm}^2$ $d = 51 \ \mu\text{m} = 0.0051 \text{ cm}$ $\Delta P = 1 \text{ atm} \text{ (partial pressure)}$	$N = 2.94 \times 10^{-7} \text{ mol/s}$ I = nFN = 0.057  A $i = I/A = 0.00057 \text{ A/cm}^2 = 0.57 \text{ mA/cm}^2$
Additional variable (complication) $D_{H2} = f(T) = 0.0041e^{-2602/T}$	5.00E-06 4.00E-06 3.00E-06 2.00E-06 1.00E-06 0.00E+00 0 20 40 60 80 100 120 temperature (°C)

## Permeation of gases through Nafion



Fig. 7. Arrhenius plots of permeability coefficients ( $P_m$ ) of oxygen for the dried and 35 w/o hydrated Nafions. Data obtained previously (8) for the 35 w/o hydrated Nafion by a volumetric method, estimated values for water (8), and literature values for PTFE (20) are shown for comparison.



Fig. 2. Arrhenius plots of permeability coefficients ( $P_m$ ) of hydrogen, oxygen, and nitrogen for the acid- and K<sup>+</sup>-form dried membrane (Nafion 125).

Source: T. Sakai, et al., J. Electrochem. Soc., Vol. 133, No. 1, pp. 88-92, 1986

## More information about PEM fuel cells:

Frano Barbir **PEM Fuel Cells: Theory and Practice** Elsevier/Academic Press, 2005 ISBN 978-0-12-078142-3

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