Basic Fuel Cell Reactions

The overall reaction of a PEM fuel cell is: $H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$

This reaction is the same as the reaction of hydrogen combustion, which is an exothermic process (energy is released):

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

The heat, typically given in terms of enthalpy, of a chemical reaction is the difference between the heats of formation of products and reactants:

$$\Delta H = \left(h_f\right)_{H_2O} - \left(h_f\right)_{H_2} - \frac{1}{2}\left(h_f\right)_{O_2} = -286 kJ/g - 0 - 0 = -286\frac{kJ}{mol}$$

Heat of formation of liquid water: -286 kJ/mol at 25°C and at atmospheric pressure.

$$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O(l) + 286 kJ/mol$$

Reference: PEM fuel cells: theory and Practice, Frano Barber, Elsevier Academic Press, 2005

Hydrogen HHV and LHV

Hydrogen heating value is used as a measure of energy input in a fuel cell.

Hydrogen heating value: the amount of heat that may be generated by a complete combustion of 1 mol of hydrogen = the enthalpy of hydrogen combustion reaction = 286 kJ/mol

The result of combustion is liquid water at 25°C and the value of 286 kJ/mol is considered as Higher Heating Value (HHV).

If the combustion is done with excess oxygen and allowed to cool down to 25°C, the product will be in the form of vapor mixed with unburned oxygen. The resulting heat release is measured to be 241 kJ/mol, known as Lower Heating Value (LHV).

$$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O(g) + 241 kJ/mol$$

The difference between HHV and LHV is the heat of evaporation of water at 25°C:

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

Theoretical Electrical Work

Not all the hydrogen’s energy can be converted into electricity.

The portion of the reaction enthalpy that can be converted to electricity corresponds to Gibbs free energy:

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

ΔS is the difference between entropies of products and reactants:

$$\Delta S = \left(S_f\right)_{H_2O} - \left(S_f\right)_{H_2} - \frac{1}{2}\left(S_f\right)_{O_2}$$

At 25^{o}C and at one atmosphere

	h_f (kJ/mol)	s_f (kJ/mol)
Hydrogen	0	0.13066
Oxygen	0	0.20517
Water (liquid)	-286.02	0.06996
Water (Vapor)	-241.98	0.18884

48.68 kJ/mol is converted into heat.

$$\Delta G = -286.02 - 298 \times \left(0.06996 - 0.13066 - \left(0.5 \times 0.20517\right)\right) = -237.36 kJ/mol$$

Theoretical Fuel Cell Potential

Electrical work: $W_e = n_e F E = -\Delta G$

n_e = 2 (two electron per molecule); *F =96,485 Coulombs/electron-mol.*

The theoretical potential of fuel cell at 25°C and at one atmosphere:

$$E = \frac{-\Delta G}{n_e F} = \frac{237,340 J/mol}{2 \times 96,485 As/mol} = 1.23 Volts$$

Temperature Effect:

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

$$E = -\left(\frac{\Delta H}{n_e F} - \frac{T\Delta S}{n_e F}\right)$$

$$h_T = h_{298.15} + \int_{298.15}^{T} C_P dt$$

$$S_T = S_{298.15} + \int_{298.15}^{T} \frac{1}{T} C_P dt$$

$$C_P = a + bT + cT^2$$

a, b and c are empirical Coefficients, different for each gas

Theoretical Fuel Cell Potential

	a	*b*	*c*
H_2	28.91404	-0.00084	2.01E-06
O_2	25.84512	0.012987	-3.9E-06
H_2O (g)	30.62644	0.009621	1.18E-06

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

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

	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O(l)$	-286.02	-0.1633	-237.34
$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O(g)$	-241.98	-0.0444	-228.74

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

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

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

For T=298.15, E = 1.23 Volts

For T=373.15, E = 1.167 Volts

Theoretical Fuel Cell Efficiency

$$\eta = \frac{\Delta G}{\Delta H} = \frac{237.34}{286.02} = 0.83$$

$$\eta = \frac{\Delta G}{\Delta H_{LHV}} = \frac{228.74}{241.98} = 0.945$$

$$\eta = \frac{-\Delta G}{-\Delta H} = \frac{\dfrac{-\Delta G}{n_e F}}{\dfrac{-\Delta H}{n_e F}} = \frac{1.23}{1.482} = 0.83$$

Potential corresponding to hydrogen’s higher heating value

Theoretical Fuel Cell Potential

Effect of Pressure:

The change in Gibbs free energy may be shown to be: $\Delta G = V_m dP$

Where V_m *= molar volume,* m^3*/mol and* P *= pressure, Pa*

For an ideal gas: $PV_m = RT$

Therefore:

$$dG = RT\frac{dP}{P}$$

$$G = G^o + RT\ln\frac{P}{P_o}$$

G^o : Gibbs free energy at standard temperature, 25°C and at one atmosphere

Theoretical Fuel Cell Potential

Equilibrium of a gas mixture:

For a chemical reaction occurring at constant pressure and temperature, the reactant gases *A* and *B* form products *M* and *N*.

$$aA + bB \Leftrightarrow mM + nN$$

Where *a*, *b*, *m* and *n* are stoichiometric coefficients.

The change in the Gibbs energy

$$\Delta G = mG_M + nG_N - aG_A - bG_B$$

Where g is in molar quantity (kJ/mol)

$$\Delta G = \Delta G^o + RT\ln\left[\frac{\left(\frac{P_M}{P_o}\right)^m \left(\frac{P_N}{P_o}\right)^n}{\left(\frac{P_A}{P_o}\right)^a \left(\frac{P_B}{P_o}\right)^b}\right]$$

In terms of standard Gibbs energy. The reference pressure is usually taken as 1 atm.

Theoretical Fuel Cell Potential

Equilibrium of a gas mixture:

$$\Delta G = \Delta G^o + RT \ln \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

$$\Delta G = \Delta G^o + RT \ln Q$$

Q: Reaction coefficient for the pressures

$$Q = \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

The change in Gibbs energy of a reaction involving gases is:

$$\Delta G = \Delta G^o + RT \ln Q$$

Theoretical Fuel Cell Potential

For a hydrogen-oxygen fuel cell, the overall reaction stoichiometry is

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

The Nernst equation becomes:

$$\Delta G = \Delta G^o + \frac{RT}{n_e F}\ln\frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}}$$

$$E = E^o + \frac{RT}{n_e F}\ln\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}$$

When liquid water is produced in a fuel cell: $P_{H_2O} = 1$

For higher reactant pressures the cell potential is higher

Theoretical Fuel Cell Potential

Air vs oxygen:

$$\Delta E = E_{O_2} - E_{air} = \frac{RT}{n_e F}\ln\frac{P_{O_2}}{P_{air}} = \frac{RT}{n_e F}\ln\left(\frac{1}{0.21}\right)^{0.5}$$

At 80^{o}C , the voltage loss becomes 0.012V. In practice, this is much higher.

Effect of Pressure

The Nernst equation is given by

$$E = E^o - \frac{RT}{n_e F}\ln\frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}}$$

Or

$$E = E^o - \frac{RT}{n_e F}\ln\frac{\frac{P_{H_2O}}{P_o}}{\frac{P_{H_2}}{P_o}\frac{P_{O_2}^{1/2}}{P_o}}$$

Where P_o is the standard pressure, 0.1 MPa. If the pressure on both cathode and the anode is approximately same, P then we can write

$$P_{H_2} = \alpha P; P_{O_2} = \beta P; P_{H_2O} = \delta P$$

then

$$E = E^o - \frac{RT}{2F}\ln\left(\frac{\delta}{\alpha\beta^{\frac{1}{2}}}\right) - \frac{RT}{4F}\ln(P)$$

Fuel and Oxidant Utilization

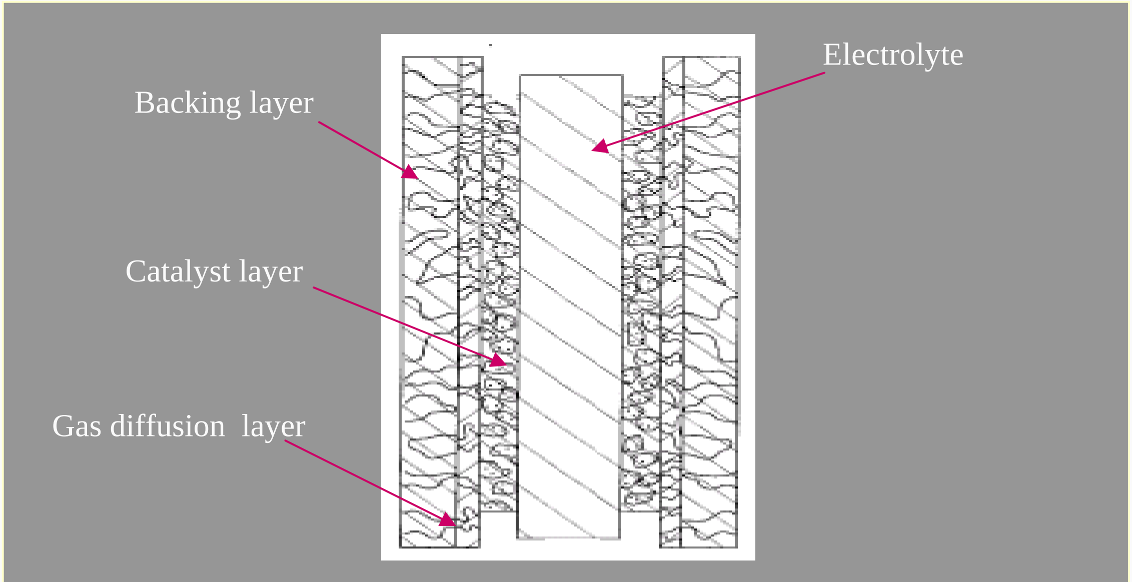
As air passes through a fuel cell, the oxygen is used and so the partial pressure will reduce. Similarly, the fuel partial pressure will often decline, as the portion of the fuel reduces and reaction products increase, *i.e,* α and β decrease where as δ increase. This results in the increase of magnitude of

$$\frac{RT}{2F}\ln\left(\frac{\delta}{\alpha\beta^{\frac{1}{2}}}\right)$$

Making the voltage E to fall. This will vary within the cell - worst at the fuel outlet as the fuel is used. Since it is not possible for different parts of the cell to have different voltages, the current varies. The current density will be lower nearer the exit where the fuel concentration is lower. The RT term in the equation also shows that the drop in E due to fuel utilization is greater in high temperature fuel cells.

Electrochemical Kinetics

A chemical reaction involves both a transfer of electrical charge and a charge in Gibbs energy. The electrochemical reaction occurs at the interface between the electrode and electrolyte.



Typical Electrode Design

The charge must overcome an activation energy barrier in moving from electrolyte to an electrode. The magnitude of the barrier determines the rate of reaction. The *Butler-Volmer* equation gives the current density, that is derived from transition state theory of electrochemistry.

Electrochemical Kinetics

The general half-reaction expression for the *oxidation* of a reactant is:

$$Ox + ne^- \rightarrow R$$

Where reactant *R* loses electrons and becomes *Ox*, the product of oxidation, and *n* is the number of electrons that are transferred in the reaction. For the opposite direction, *Ox* gains electrons, undergoing reduction to form R in the half-reaction.

$$R \rightarrow Ox + ne^-$$

On an electrode at equilibrium conditions, both processes occur at equal rates and the currents produced by two reactions balance each other, giving no net current from the electrode

$$Ox + ne^- \Leftrightarrow R$$

Source: Fuel cell technology Handbook - Chapter 3.

Electrochemical Kinetics

Single-step Electrode reactions

Considering only one direction of the reaction, the current produced is

$$I = nA \cdot F \cdot J$$

Where I is the current (in amperes), A is the active area of the electrode (cm^2), F is the Faraday's constant (the charge per mole of electrons= 96,485 (coulombs/mole e$^-$) and j is the flux of reactants reaching the surface (mole/sec). The current density (per unit area) is

$$i = nF \cdot j$$

The current is produced from the reactants that reach the surface of the electrode and lose or gain electrons. The flux is determined by the rate of conversion of the surface concentration of the reactant. For the forward reaction (subscript f), the flux arising from the reduction of Ox is

$$j_f = k_f [Ox]_o$$

Forward rate coefficient

Surface concentration of the reactant

Electrochemical Kinetics

Single-step Electrode reactions

For the backward reaction (subscript *b*), the flux produced by the oxidation of R is

$$j_b = k_b[R]_o$$

Backward rate coefficient

The net flux is

$$j = j_f - j_b$$

The net current density that appears on the electrode when the current is produced is given by

$$i = n\left(Fk_f[Ox]_o - Fk_b[R]_o\right)$$

Electrochemical Kinetics

Butler-Volmer Equation

From the Transition state theory (refer to any physical chemistry book), the heterogeneous rate coefficient, *k*. is a function of the Gibbs energy of activation and is given by

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta \overline{G}^{\neq}}{RT} \right)$$

Boltzmann's constant

(1.38049x10^{-23} j/^{o}K)

Plank's constant (6.621x10^{-34} Js)

Gibbs energy of activation (kJ/mol)

Because an electrochemical reaction occurs in the presence of an electrical field, the Gibbs energy of activation consists of both chemical and electrical terms

Reduction $\Delta \overline{G}^{\neq} = \Delta \overline{G}_c^{\neq} + nF\Delta\phi$

Oxidation $\Delta \overline{G}^{\neq} = \Delta \overline{G}_c^{\neq} - n(1-\beta)F\Delta\phi$

Change in electrical potential

Transfer coefficient (0.5)

Electrochemical Kinetics

For a reduction reaction

$$k_f = \frac{k_B T}{h}\exp\left(\frac{-\Delta\overline{G}^{\neq}_{c,f}}{RT}\right)\exp\left(\frac{-n\beta F\Delta\phi}{RT}\right)$$

Chemical Component Electrical Component

With the over potential is defined as $\eta = \Delta\phi - \Delta\phi_{rev}$

For a hydrogen-oxygen fuel cell, the reversible potential of the anode is 0 V; at the cathode it is +1.23 V at 25°C.

$$k_f = \frac{k_B T}{h}\exp\left(\frac{-\Delta\overline{G}^{\neq}_{c,f}}{RT}\right)\exp\left(\frac{-n\beta F\Delta\phi_{rev}}{RT}\right)\exp\left(\frac{-n\beta F\eta}{RT}\right)$$ Reduction

$$k_b = \frac{k_B T}{h}\exp\left(\frac{-\Delta\overline{G}^{\neq}_{c,f}}{RT}\right)\exp\left(\frac{-n(1-\beta)F\Delta\phi_{rev}}{RT}\right)\exp\left(\frac{-n(1-\beta)F\eta}{RT}\right)$$ Oxidation

Electrochemical Kinetics

Butler-Volmer Equation

when the electrode is in equilibrium and at its reversible potential, the overpotential and external current are both zero. In this case, the exchange current density, i_o is defined as

$$nF[Ox]_o k_{o,f} = nF[R]_o k_{o,b} \equiv i_o (A/cm^2)$$

The current density is given by

$$i = i_o\left[\exp\left(\frac{-n\beta F\eta}{RT}\right) - \exp\left(\frac{-n(1-\beta)F\eta}{RT}\right)\right] \qquad \eta = \Delta\phi - \Delta\phi_{rev}$$

Reduction term

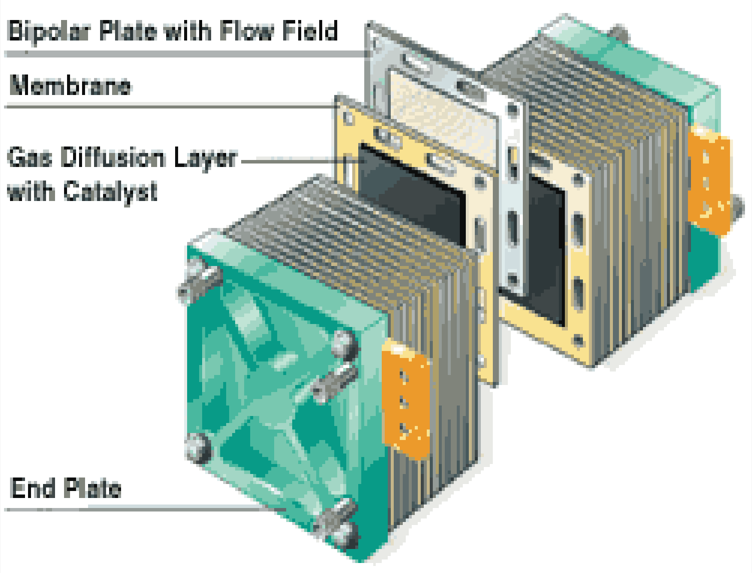
Oxidation term

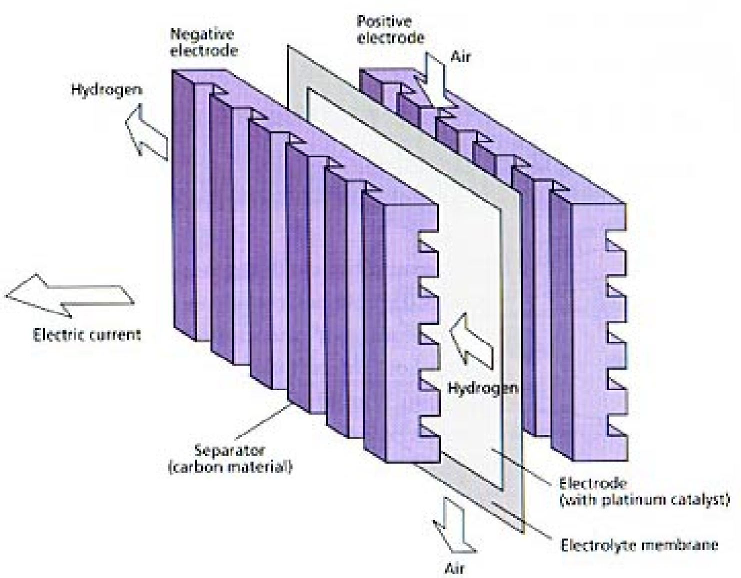
If η > 0 then the oxidation component becomes large and the reduction reaction on the on the electrode becomes small. The net current density is negative, which corresponds to a net oxidation reaction where electrons leave the anode of the fuel cell. In operating fuel cells, because of the cathode reaction of oxygen reduction requires a more significant overpotential (η) than the anode reaction. For hydrogen-oxygen fuel cell, the reversible potentials at the anode and cathode are 0V and 1.23 V respectively.

Fuel Cell Components

Fuel Cell Components Impact on Performance

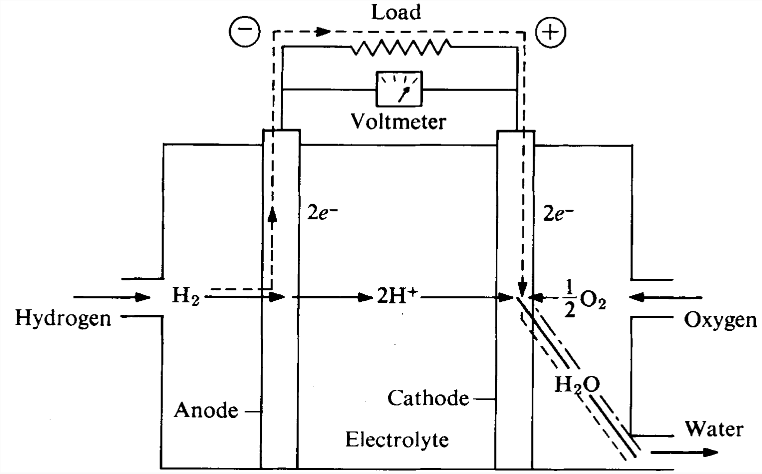
The proton exchange membrane fuel cell (PEMFC)





Special plastic membrane used as the electrolyte + electrodes (anode & cathode) is called the membrane electrode assembly (MEA). It is not thicker than a few hundred microns. When supplied with fuel and air , generates electric power at cell voltages around 0,7V and power densities up to about 1 W/cm^2 electrode area.

The Proton Exchange Membrane Fuel Cell (PEMFC)



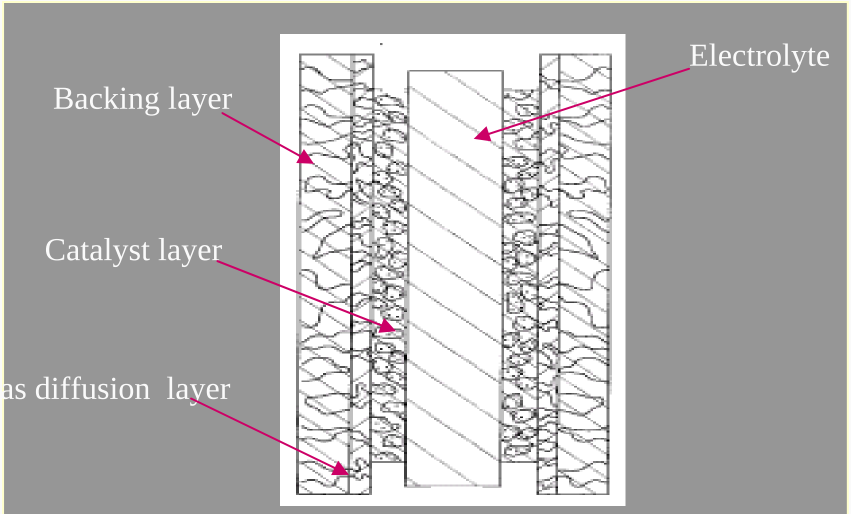
$H_2 \rightarrow 2H^+ + 2e^-$ Anode ($E_r = 0$ V)

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow 1H_2O$ Cathode ($E_r = 1.23$ V)

The electrochemical reactions take place at the anode and the cathode catalyst layer respectively. The best catalyst is platinum. The catalyst is used at the rate of about 0.2 mg/cm^2. The basic raw material cost of platinum for a 1- kW PEMPC cell is about $10 - a small portion of the total cost.

The PEM Fuel Cell

The gas diffusion layer and backing layer (substrate) at the ***anode*** allows hydrogen to reach the reactive zone within the electrode. Upon reaching, protons migrate through the ion conducting membrane, and electrons are conducted through the gas diffusion layer and ultimately to the electric terminals of the fuel stack. The substrate therefore has to be porous to allow gas and electrically conducting. Not all of the chemical energy supplied to the MEA by reactants is converted into electric power. Heat will also be generated and the substrate also acts as a heat conductor to remove heat from the reactive zones of the MEA.



Membrane Electrode Assembly (MEA)

Water is formed at the cathode. If the water is in liquid form, there is a risk of liquid blocking the pores within the substrate and consequently gas access to the reactive zone. The oxidant used in most applications is air, therefore, 80% of the gas present is inert. Fuel cell operation will result in depletion of oxygen towards the active cathode catalyst.

The membrane acts as a proton conductor, thus requires it to be well humidified. Because the proton conduction process relies on membrane water. As a consequence, an additional water flux from anode to cathode is present and is associated with the migration of protons. Humidity is often provided with the anode gas by pre-humidifying the reactant.

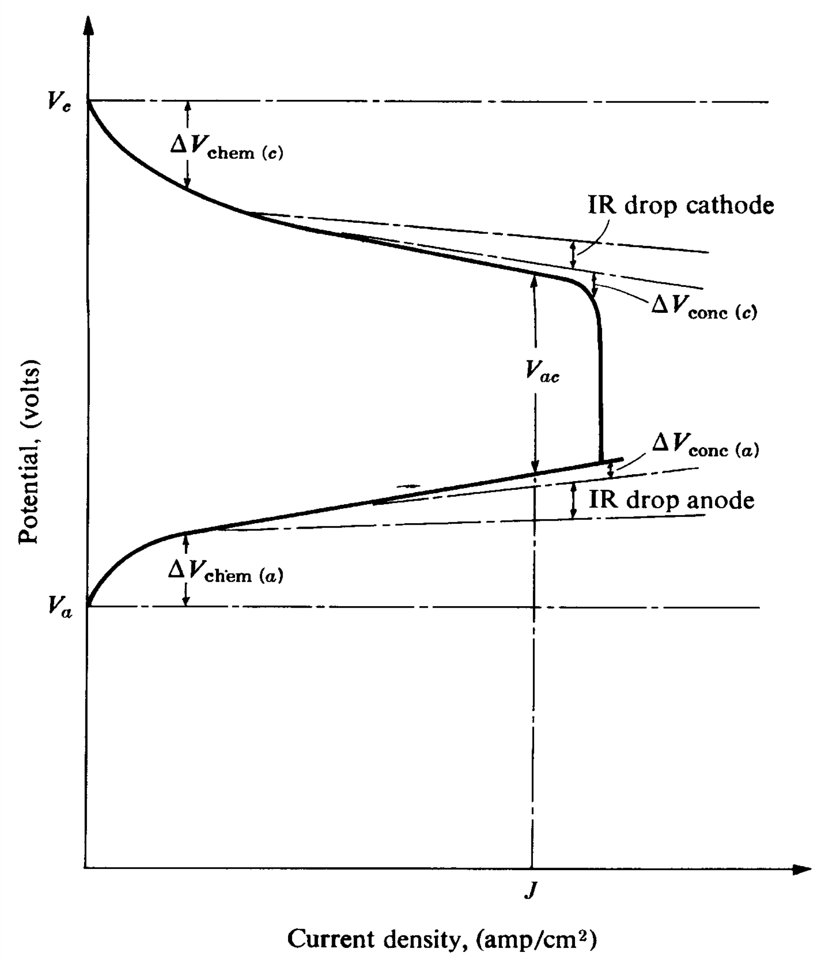
The PEM Fuel Cell

MEA Component	Task/effect
Anode Substrate	Fuel supply and distribution, Electron conduction, heat removal from reaction zone, water supply into electrocatalyst
Anode catalyst layer	Catalysis of anode reaction, proton conduction into membrane, electron conduction into substrate, water and heat transport
Proton exchange membrane	Proton conduction, water transport, electronic insulation
Cathode catalyst layer	Catalysis of cathode reaction, oxygen transport to reaction sites, proton conduction from membrane to reaction sites, electron conduction from substrate to reaction zone, water removal from reaction zone into substrate and heat removal.
Cathode substrate	Oxidant supply and distribution, electron conduction towards reaction zone, heat removal and water transport

Source: Fuel cell technology handbook, Chapter 4

Factors Limiting Fuel Cell Performance

The losses that takes place at electrodes are generally attributed to some form of polarization - a term used to denote the difference between the theoretical voltage of a given electrode and the experimental voltage when the current is drawn from the cell. The losses are classified in three categories: Chemical polarization. Concentration polarization and resistance polarization.



The theoretical value of the open circuit voltage of a hydrogen-oxygen fuel cell is given by

$$V = E = \frac{-\Delta \bar{g}_f}{2F}$$

This gives a value of about 1.23 V for a cell operating at 298K.

$$V_{ac} = V - \Delta V_{conc(c)} - \Delta V_{chem(c)} - \Delta V_{conc(a)} - \Delta V_{chem(a)} - \sum IR$$

Chemical Polarization

It is customary to express the voltage drop due to chemical polarization by strictly empirical equation, called the ***Tafel equation*** as

$$\Delta V_{chem} = a' + b' \ln J$$

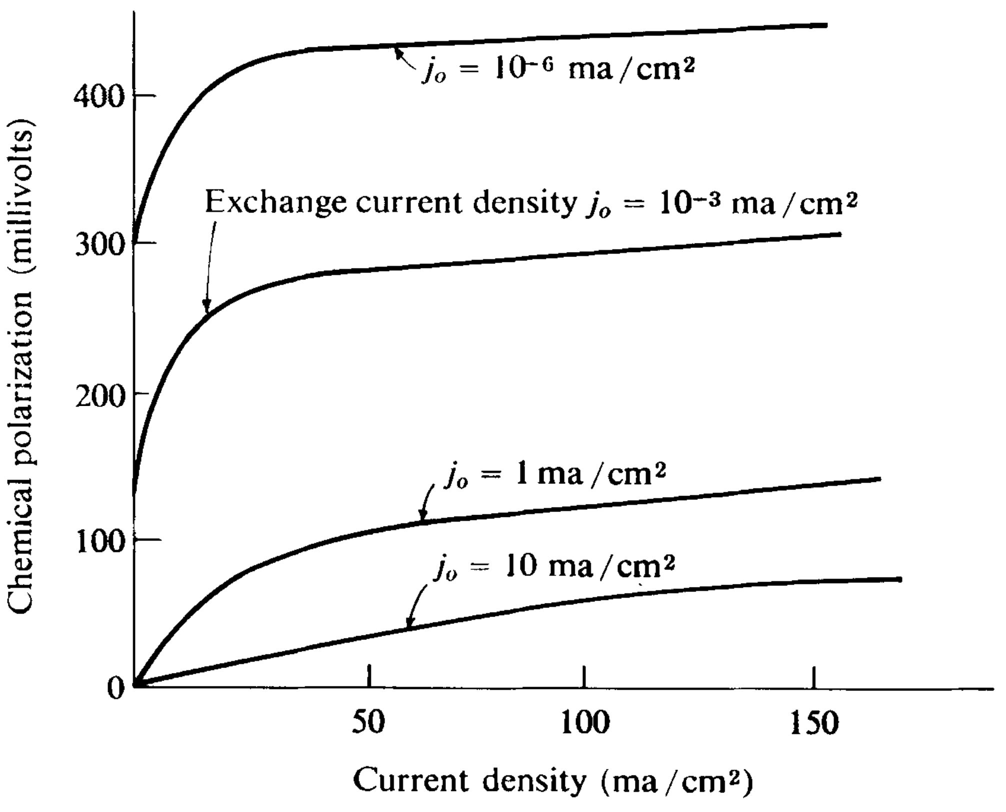
$$a' = \frac{-RT}{\alpha n F \ln(j_o)}$$

$$b' = \frac{-RT}{\alpha n F}$$

Where J is the apparent current density at the electrode, α and j_o are kinetic parameters, the former being a constant that represents the fraction of ΔV_{chem} that aids a reaction in proceeding (For a hydrogen electrode, its value is about 0.5 for a great variety of electrode materials and for the oxygen electrode it is between 0.1 and 0.5. The best possible value of b` will have little impact), the later being the exchange current density, intimately related to the height of the activation energy barrier. Gas diffusion electrode reduces the chemical polarization by maximizing the three-phase interface of gas-electrode-electrolyte. The small pores create large reactive surface areas per unit geometrical area and allow free entrance to reactants and exit to products. Increases in pressure and temperature will also generally decrease chemical polarization.

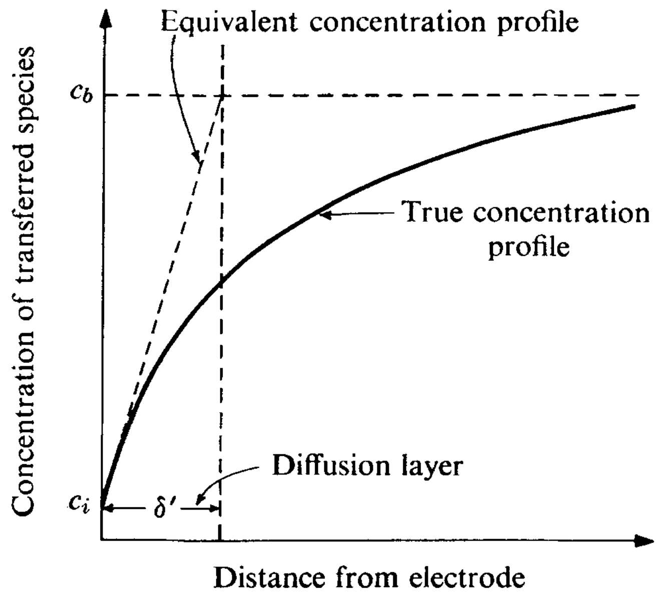
Chemical Polarization

The effect of current density and the exchange current density on chemical polarization loss



Concentration Polarization

After current begins to flow in an electrochemical cell, there is a loss of potential due to inability of the surrounding material to maintain the initial concentration of the bulk fluid. This uneven concentration produces a back *EMF* which opposes the voltage that a fuel cell would deliver under completely reversible conditions. The concentration of electrolyte in the vicinity of an electrode during reaction should be maintained at the desirable condition.



$$\Delta V_{conc(c)} = \frac{RT}{nF} \ln\left(\frac{c_{if}}{c_b}\right)$$

c_b : average concentration in bulk electrolyte

c_{if} : concentration at the interface

$$\Delta V_{conc(c)} = \frac{RT}{nF} \ln\left(\frac{J_L}{J_L - J}\right)$$

$$J_L = \frac{nFD}{\delta'} c_b$$

$$\Delta V_{conc(a)} = \frac{RT}{nF} \ln\left(\frac{J_L + J}{J_L}\right)$$

D: diffusion coefficient

Resistance Polarization

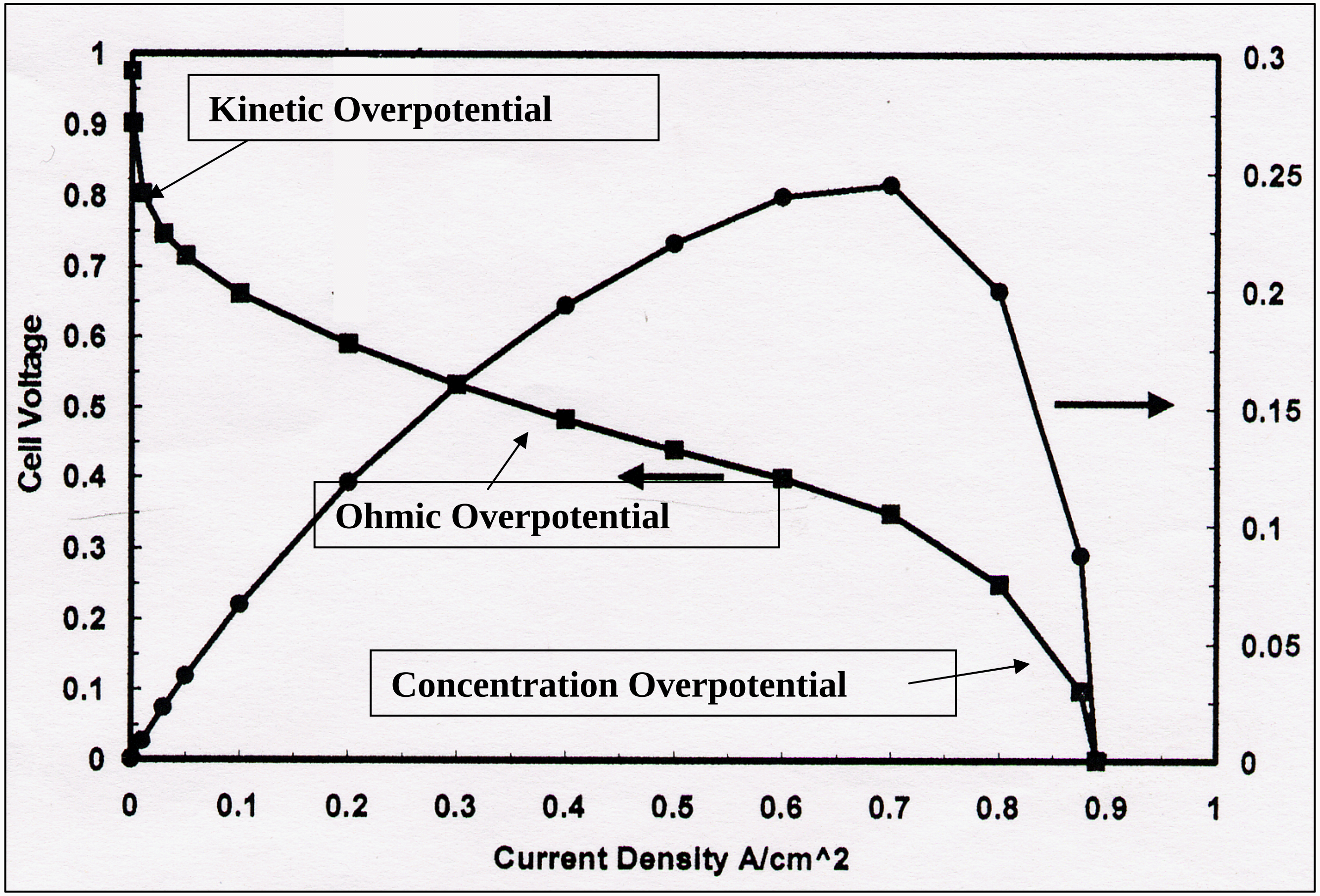
When an electrochemical reaction occurs at an electrode there is generally a significant change in the specific conductivity of electrolyte which involves an additional loss of potential.

Hydrogen-oxygen fuel cells employing concentrated solutions of potassium or sodium hydroxide as electrolytes show that resistance polarization is negligibly low even at fairly high current densities.

Ohmic Losses: $V = IR$

In most fuel cells the resistance is mainly caused by the electrolyte, through the cell interconnects or bipolar plates. Reducing these internal resistances can be accomplished by the use of electrodes with the highest possible conductivity, good design and use of appropriate materials for the bipolar plates and cell interconnects and making electrolyte as thin as possible.

Typical Fuel Cell Polarization Curves



Heat Transfer

In cells with high current densities, it is often important to calculate the heat transfer within a fuel cell.

1) The electrochemical reaction producing the current in the cell is not adiabatic which gives rise to a reversible heat transfer whose magnitude is T∆S.

2) Some of the fuel reacts chemically with the oxidizer rather than electrochemically to generate an irreversible heat transfer.

3) The cell operates at some voltage less than the theoretical open circuit voltage with the difference manifesting itself as I^2R and $I\ \Delta V$ heat in the cell (I is the current drawn and R and ΔV represent irreversible resistances and voltage drops).

$$\dot{Q}_t = \dot{Q}_{rev} + \underset{\substack{\uparrow \\ \text{Generally small}}}{\dot{Q}_{chem(irr)}} + \dot{Q}_{\Delta V} = \frac{1}{nF}\left[T\Delta S + +nF\left(V_{ac} - V\right)\right]$$