4. Performance characterization of fuel cell systems

(Mench, ch. 4b)

1. Polarization curve
2. Activation polarization
3. Ohmic polarization
4. Concentration polarization
5. Other polarization losses
6. Polarization curve model

(Mench, ch. 2)

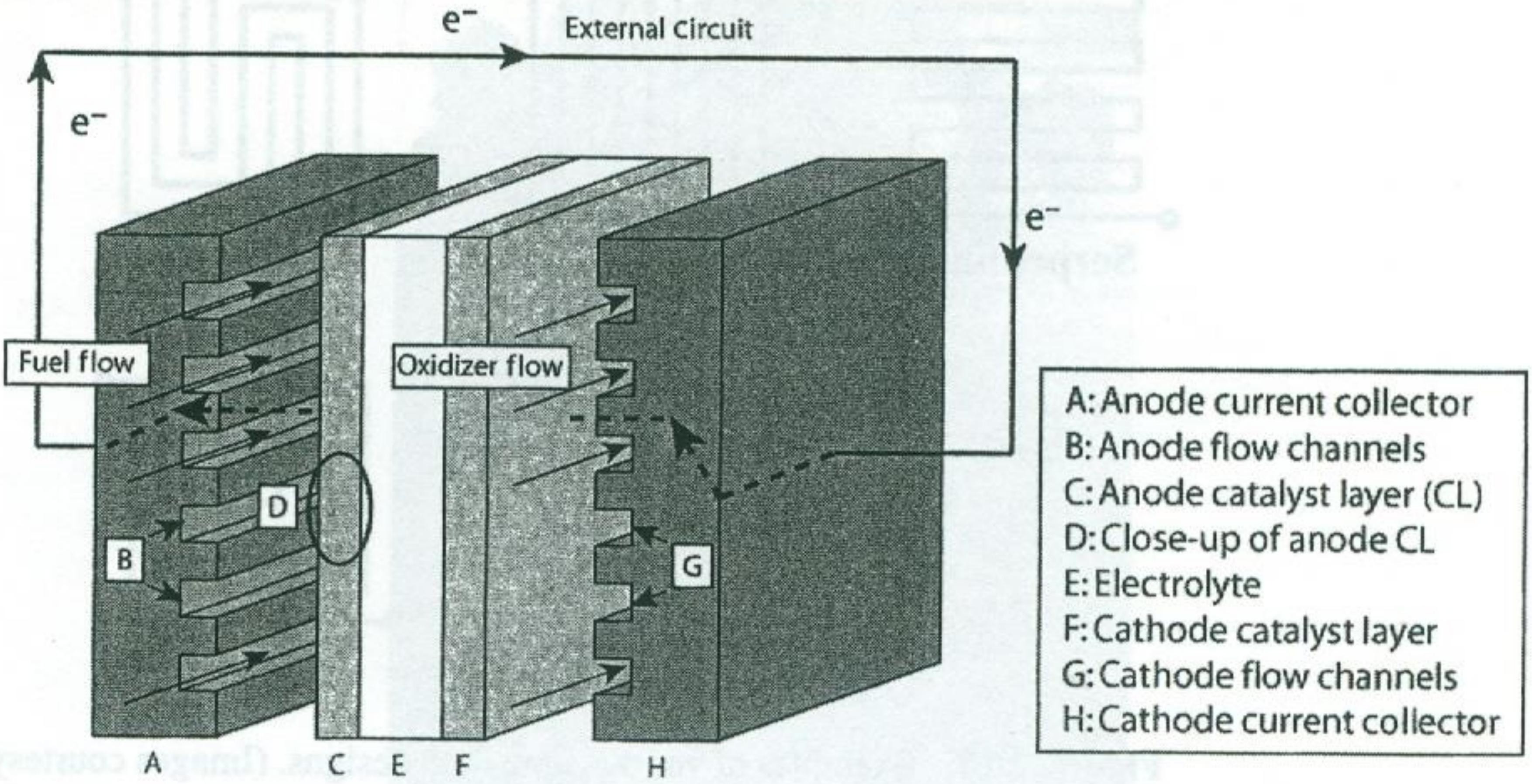


Figure 2.9 Generic fuel cell.

3. Region II: ohmic polarization

-At moderate current densities, a primarily linear region (Region II) → reduction in voltage is dominated by internal ohmic losses (η_r) through the fuel cell, resulting in the nearly linear behavior, although activation and concentration polarization in this region are still present

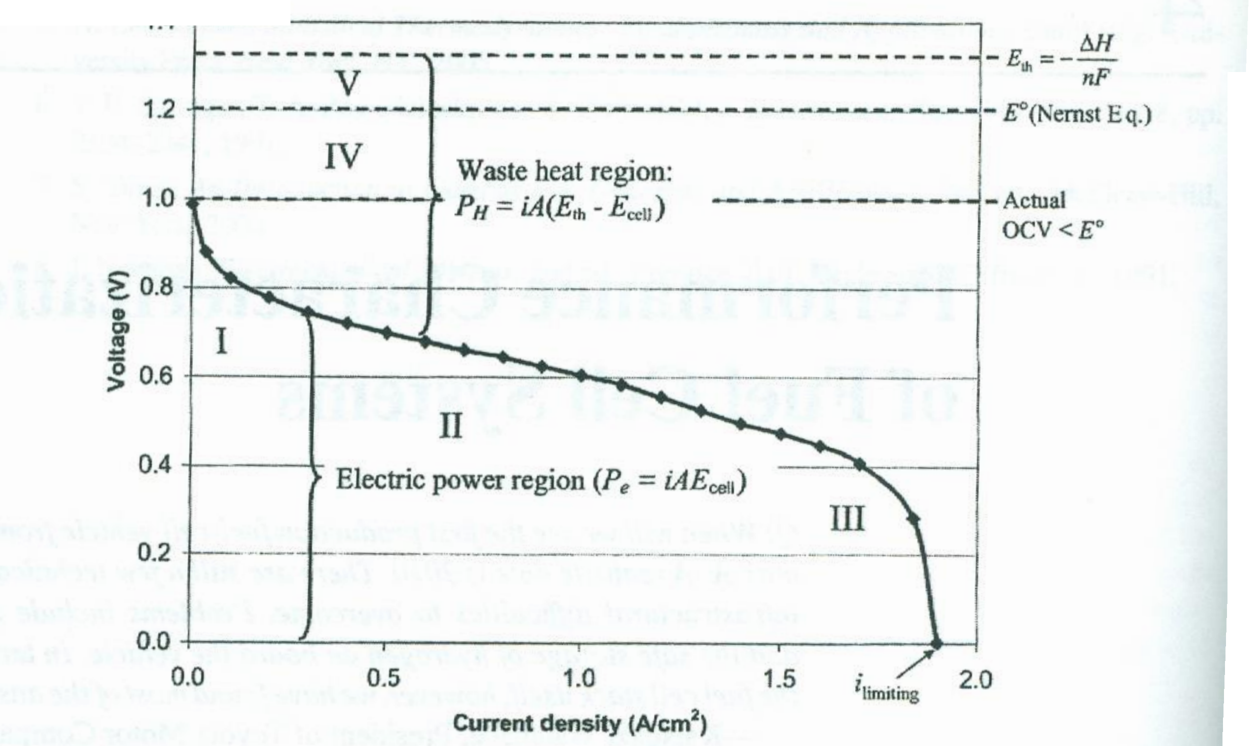


Figure 4.1 Typical polarization curve for fuel cell with significant kinetic, ohmic, concentration, and crossover potential losses.

-Ohmic polarization

$$\eta_r = iA(\sum r_k)$$

each r_k: area-specific resistance of individual cell components, including ionic resistance of the electrolyte, electric resistance of bipolar plates, cell interconnects, contact resistance between parts

-For most fuel cell at the beginning of operating life, ohmic polarization is dominated by ionic conductivity in the main electrolyte and in the catalyst layers

(i) Electronic and ionic resistance

Ohm's law $V = IR = iAR$
Resistivity $\rho = RA/l = \Omega\cdot m$
Conductivity $\sigma = 1/\rho = 1/\Omega\cdot m = S/m$
$V = iAl/\sigma A = il/\sigma = i\rho l$

Table 4.3 Typical Conductivity/Resistivity Values for Selected Fuel Cell Materials

Component	Typical Bulk Through-Plane Conductivity σ_i or σ_e	Typical Thickness	Functional Dependencies
PEFC electrolyte	$\sigma_i = 10$ S/m (hydrated)	50–200 μm	Temperature, water content
SOFC electrolyte	$\sigma_i = 1$–10 S/m (>800°C)	10–300 μm	Temperature, dopants (conductivity through oxygen vacancies)
AFC electrolyte	σ_i on order of 1–100 S/m at operating temperature	0.5–2.0 mm	Ion concentration, temperature, charge number on ion, dielectric constant of solution, mobility, viscosity, degree of ion dissociation, other liquids
MCFC electrolyte	σ_i on order of 1–100 S/m at operating temperature	0.5–2.0 mm	See AFC electrolyte
PAFC electrolyte	σ_i on order of 1–100 S/m at operating temperature	0.5–2.0 mm	See AFC electrolyte
PEFC bipolar plate (graphite)	$\sigma_i = 5000$–20,000 S/m	2–4 mm each	Oxide film (corrosion), materials, coatings
PEFC gas diffusion layer (GDL)	$\sigma_i = 10{,}000$ S/m (much less in plane)	100–300 μm	Approximately constant
PEFC catalyst layer	~1–5 S/m	5–30 μm	Morphology, Nafion and carbon loading, age
Contact resistances for cell	Very low if built well; resistance ~30 mΩ·cm^2	Not available, use area as contact area	Compression, pressure, temperature, age (corrosion), number of cycles, and others, current collector total landing area
Total cell resistance (based on active cell area)	Total resistance < 100 mΩ·cm^2	Not available, use cell superficial active area	See above

-Critical factors governing ohmic losses in a fuel cell

(a) Material conductivity
(b) Material thickness

Example 4.6 Estimate Total Fuel Cell Resistance

Given the experimental polarization data for a SOFC at 700°C from [13], estimate the ionic resistance of the electrolyte. Is this a maximum or a minimum value for the actual ohmic resistance of the electrolyte?

(ii) Contact resistance

$R_{contact}$ (Ω) = $V_{loss}/iA_{contact}$

$A_{contact}$: contact area between two surfaces

(a) State of contact surface, oxidized → resistance↑

(b) Compression pressure from current collector onto electrode or diffusion media

(c) Tolerance and flatness of individual fuel cell bipolar plates

Example 4.7 Cell Ohmic Loss Limiting Current Calculation

Consider an ideal PEFC with only the ionic ohmic losses in the electrolyte and catalyst layers. Ignore kinetic, electronic, and other losses for this problem.The OCV is 1.0V, and the electrolyte conductivity σe is 8.3 S/m. The catalyst layers can be assumed to be 40% ionomer equivalent and 30 μm thick. Consider two cases: (a) The electrolyte is Nafion 112, which is 51 μm thick. (b) The electrolyte is Nafion 117, which is 178 μm thick.

Find the maximum current density that each electrolyte can support, ignoring other polarizations besides ohmic losses.

(iii) Cell assembly

-beyond design point → plastic deformation
-presence of liquid water does not influence the contact resistance since pure water is nonconductive

Example 4.8 Equivalent Ohmic Loss Thermal Network

Draw an equivalent ionic resistance network for a single PEFC.

Example 4.9 Resistance Calculation

Consider a PEFC operating at 0.6 V, 1 A/cm^2, with 500 cm^2 active area electrodes. Nafion 112 (51-μm) electrolyte and a graphite current collectorareused,with3-mm-thick current collection plates, a 200-μm GDL on the anode, and a 300-μm GDL on the cathode. The catalyst layers are 10 μm thick on the anode and 20 μm on the cathode and can be approximated as 0.3 fraction ionomer on the anode and 0.35 fraction ionomer on the cathode. The electrolyte ionic conductivity can be assumed to be 8.3 S/m. The landing to channel area ratio is 1 : 2, and the measured total contact resistance is 30 mΩ·cm^2

(a) Estimate η_R, the voltage loss from resistance. (b) Estimate the percentage of total potential power wasted due to ohmic losses at this condition if E_{th} =1.25 V.

4. Region III: concentration polarization

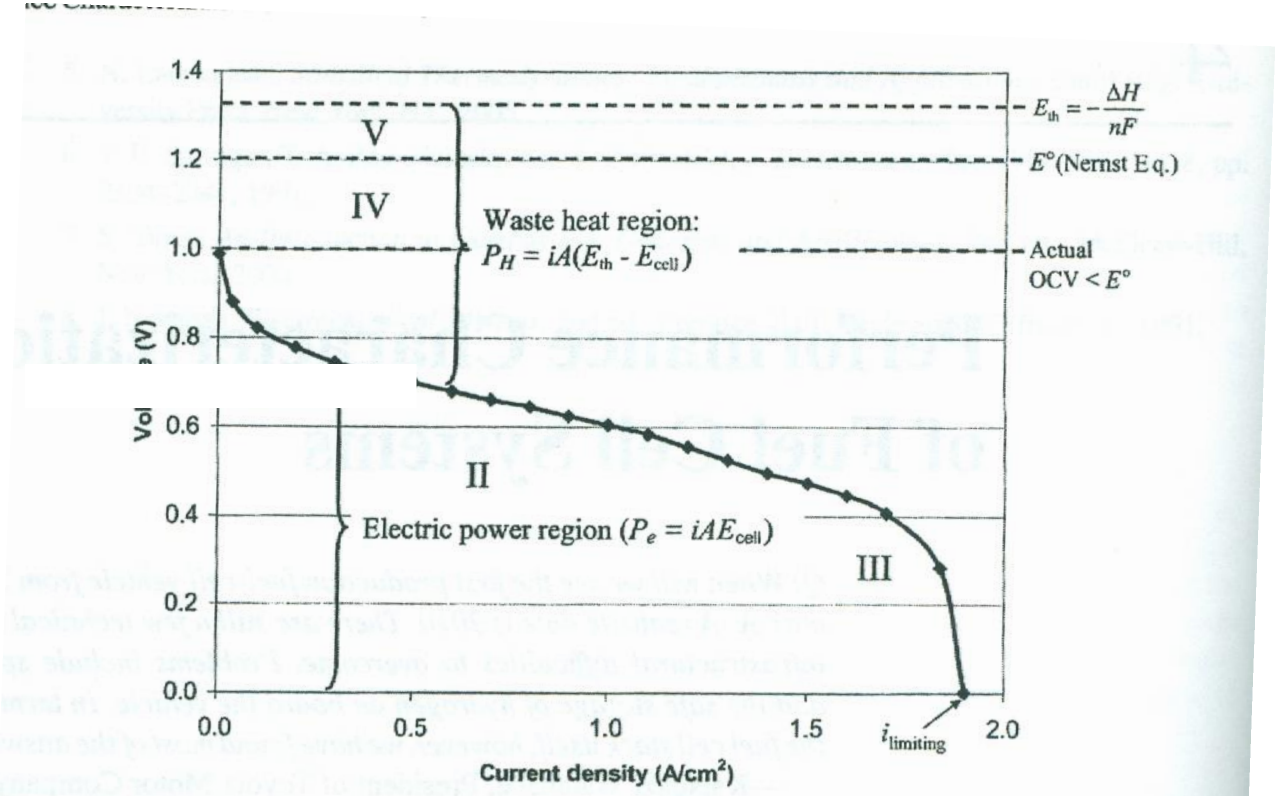


Figure 4.1 Typical polarization curve for fuel cell with significant kinetic, ohmic, concentration, and crossover potential losses.

-a reduction in the reactant surface concentration, which reduces the thermodynamic voltage from the Nernst equation and the exchange current density from the Butler-Volmer equation

-Transport of reactant

-a rate of transport of reactant

$$\dot{n}_{\text{consumed}} = \frac{iA}{nF} \le \dot{n}_{\text{transport}}$$

→ concentration polarization

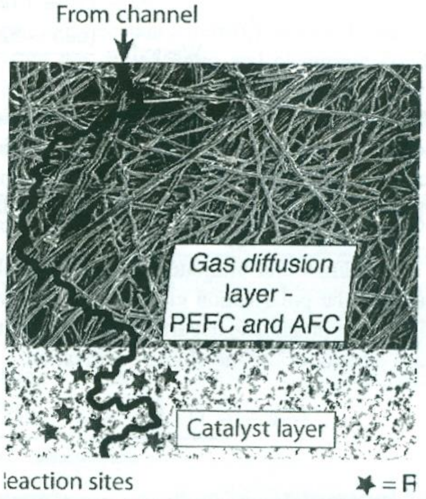


Figure 4.33 Schematic of path through diffusion media to catalyst layer in PEFC.

-Restriction of the rate of transport to the electrode
(a) gas-phase diffusion limitation: diffusion rate…
(b) liquid-phase accumulation and pore blockage limitation: in PEFC, liquid water accumulation and pore blockage in the pores of the electrolyte, diffusion media, or flow channel “flooding”
(c) build-up inert gases: as O_2 consumed in cathode, N_2 mole fraction↑ → inert boundary-layer-restricting reaction
(d) Surface blockage by impurity coverage: CO poisoning

$$i_o = i_{o,\mathrm{ref}}\left(\frac{C}{C*}\right)^{\gamma} = i_o\left(\frac{C}{C*}\right)^{\gamma} \tag{4.31}$$

-from a combination of the thermodynamic(Nernst) and exchange current density dependency (eq.4.31), the voltage adjustment as a result of the hange in oxygen concentration from the reference value(1 atm) on the cathode

$$\Delta V_{s,\mathrm{ref}} = \frac{R_u T}{2F}\ln\left[\frac{C_{O_2,s}}{C_{O_2,\mathrm{ref}}}\right]^{1/2} + \frac{R_u T}{F}\ln\left[\frac{C_{O_2,s}}{C_{O_2,\mathrm{ref}}}\right]^{\gamma_{O_2}} \tag{4.81}$$

γ: oxygen reduction reaction order with respect to O_2 partial pressure at constant overpotential (0.6~0.75 for PEFC)

-assume γ~0.75

$$\Delta V_{s,\mathrm{ref}} = \frac{R_u T}{F}\ln\left[\frac{C_{O_2,s}}{C_{O_2,\mathrm{ref}}}\right]$$

→ 47 mV gain in potential from switching from dry air(21% O_2) to pure oxygen at 353K

-On the anode,

$$\Delta V_{s,\mathrm{ref}} = \frac{R_u T}{2F}\ln\left[\frac{C_{H_2,s}}{C_{H_2,\mathrm{ref}}}\right] + \frac{R_u T}{F}\ln\left[\frac{C_{H_2,s}}{C_{H_2,\mathrm{ref}}}\right]^{\gamma_{H_2}} \tag{4.83}$$

reaction order from hydrogen: 0.25~1

-In practice, the anode hydrogen concentration effect is often neglected for several reasons

(a) Diffusivity of hydrogen is much more rapid than oxygen, especially in higher T fuel cells, so that transport limitation is rare.

(b) HOR kinetics are facile compared to the cathode so that the cathode polarization typically dominates

(c) In PEFC, liquid blockage(electrode flooding) occurs more frequently on the cathode

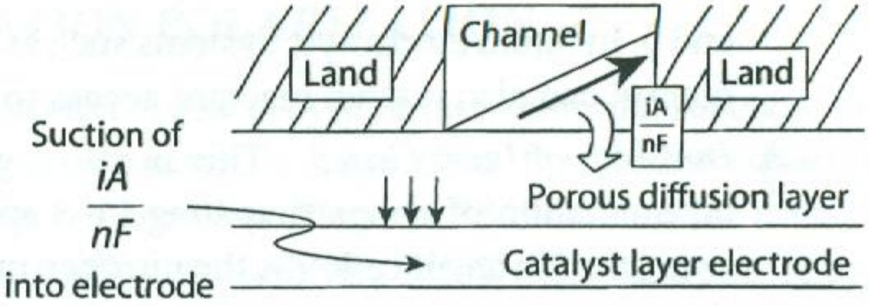


Figure 4.34 Schematic of channel flow suction into catalyst layer of fuel cell.

-At higher current densities, the mass transport limitations can reduce the concentration of the reactants at the catalyst surface to well below the flow field channel concentration and cause a sharp decline in the output voltage → mass concentration polarization (η_m) (Region III)

-Voltage at an electrode for concentration changes in reactant R from some state 2 to state 1

~~ion changes in reactant R from some state 2 to state 1 can be written as~~

$$\Delta V_{C_2-C_1} = \eta_c = V_{C_2} - V_{C_1} = \frac{R_u T}{(n+\gamma)F} \ln\left[\frac{C_{R,s,2}}{C_{R,s,1}}\right] \tag{4.84}$$

-mass-limiting current density (i_l)

assume the surface concentration(c_R) is zero at the limiting state and decreases linearly from state 1 to state 2

$$C_{R,s,2} = C_{R,s,1} - C_{R,s,1}\frac{i}{i_l} = C_{R,s,1}\left[1 - \frac{i}{i_l}\right] \tag{4.85}$$

which we can plug into Eq. (4.84) and show that

$$\Delta V_{C_2-C_1} = \eta_m = -\frac{R_u T}{(n+\gamma)F} \ln\left[1 - \frac{i}{i_l}\right] \tag{4.86}$$

If we assume the reaction occurs only at the catalyst layer interface, which is true for high-current-density mass-transport-limited reactions, and we neglect kinetic effects, we are left with the Nernst equation at each electrode:

$$\eta_m = -\frac{R_u T}{nF} \ln\left[1 - \frac{i}{i_l}\right] \tag{4.87}$$

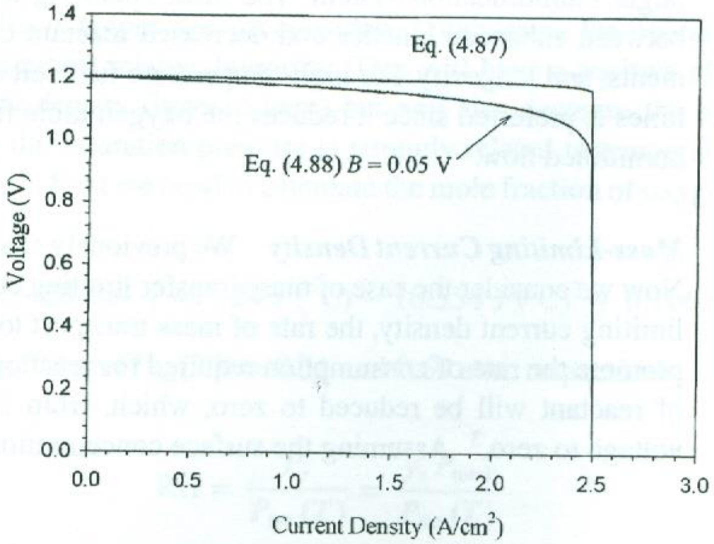


Figure 4.35 Comparison of concentration polarization predicted with Nernst equation and that predicted with semiempirical modification with B factor of 0.05 V at 353 K and $i_l = 2.5$ A/cm^2.

-Semiempirical approach

$$\eta_m = -B \ln\left[1 - \frac{i}{i_l}\right] \tag{4.88}$$

Therefore, the total concentration polarization of the fuel cell can be written as

$$\eta_{m,a} + \eta_{m,c} = -B_a \ \ln\left[1 - \frac{i}{i_{l,a}}\right] - B_c \ \ln\left[1 - \frac{i}{i_{l,c}}\right] \tag{4.89}$$

Anode loss typically negligible for a hydrogen field

Example 4.11 Determine Concentration Polarization

Given the anodic mass-transport limited current density is 15 A/cm^2 and the cathode mass-transport-limited current density is 2.5 A/cm^2, determine the anode and cathode concentration polarization at 0.1 and 1.0 A/cm^2. Assume the B factor is 0.045V on both electrodes and Eq.(4.88) is appropriate and is determined from curve-fit of several polarization curves.

Alternate Empirical Approach Another completely empirical approach to describe the overall fuel cell concentration polarization has been proposed [18–20]:

$$\eta_m = m \ \exp(ni) \tag{4.90}$$

If this equation is used, the constants m and n are typically fit from several polarization curves, and the total (anode + cathode) concentration polarization is included in this single expression. According to [20], typical values of the m constant are around 3×10^{-5} V, and the n constant is around 8×10^{-3} cm^2/mA for a PEFC. Although this expression completely loses physical meaning, it can be used to simply model the complex fuel cell stack mass transport limitations if plentiful polarization curve data are available.

Flow Stoichiometry Until now, we have discussed the flow into a fuel cell and not explored the fact that the concentration of reactant is depleted inside the fuel cell from consumption of reactant. Flow comes into a fuel cell with a molar flow rate of reactant shown in Chapter 2:

$$\dot{n}_{\text{in}} = \lambda \frac{iA}{nF} \tag{4.91}$$

The reactant consumed can be determined from Faraday's law:

$$\dot{n}_{\text{consumed}} = \frac{iA}{nF} \tag{4.92}$$

Therefore the amount of reactant out of a fuel cell is

$$\dot{n}_{\text{in}} - \dot{n}_{\text{consumed}} = (\lambda - 1)\frac{iA}{nF} \tag{4.93}$$

5. Region IV: other polarization losses

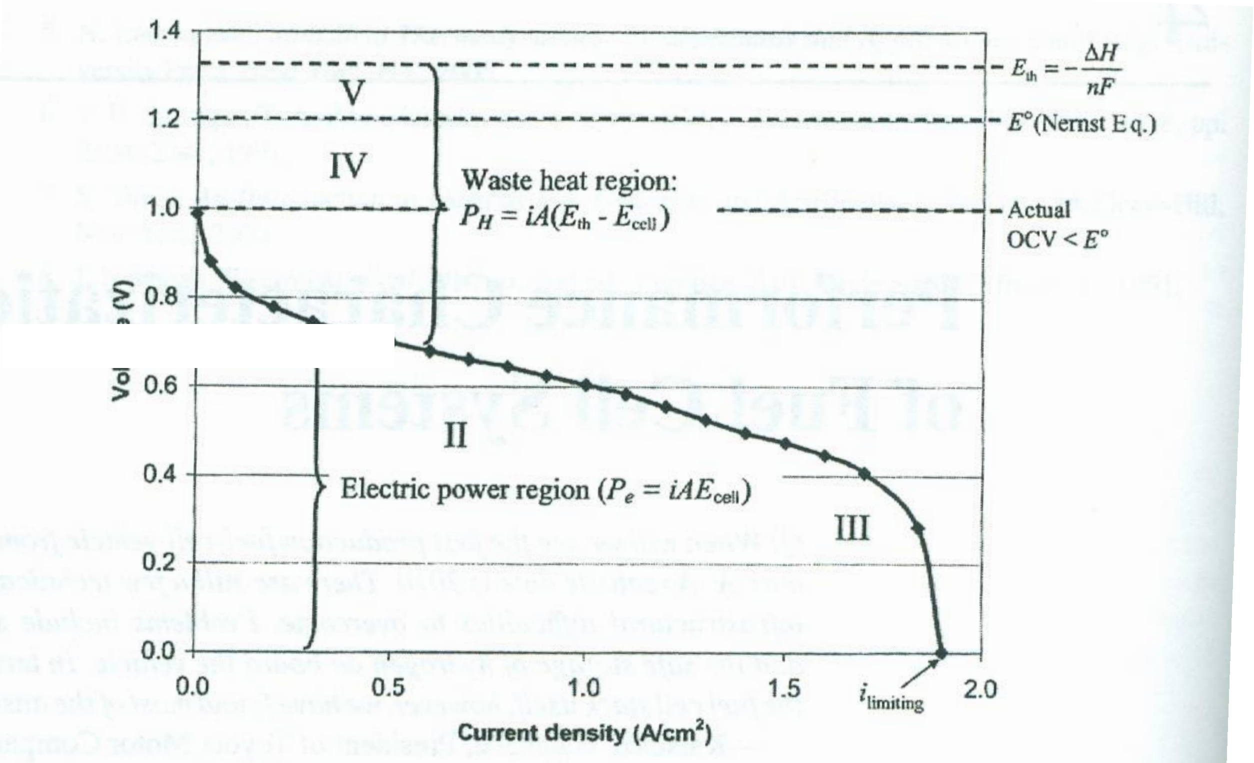


Figure 4.1 Typical polarization curve for fuel cell with significant kinetic, ohmic, concentration, and crossover potential losses.

-the departure from the theoretical OCV

(a) Electrical short circuits in the fuel cell

(b) Crossover of reactants through the electrolyte and subsequent mixed-potential rxn at the opposite electrode

(i) Electrical shorts

-current is short circuited through the electrolyte

transference number (t_i): the ratio of electrolyte ionic conductivities to the total conductivity (ionic + electronic → mixed conductivity of the electrolyte)

$$t_i = \frac{\sigma_i}{\sigma_i + \sigma_e} \tag{4.95}$$

$$E_{OCV} = E^\circ(T, P)_{Nernst} \times \frac{\sigma_i}{\sigma_i + \sigma_e} = E^\circ(T, P) \times t_i$$

(ii) Species crossover

-0.2 V loss at the open circuit in PEFC = ~20% efficiency loss

-DMFC(direct methanol FC) → liquid fuel with water → more readily crossover → actual OCV of 0.7 V (~1.2 V predicted)

-PEFC: anode → negligible oxygen crossover in anode (due to low ORR kinetics). Cathode → higher effect of H_2 crossover → mixed rxn & lowered OCV

$$n'' - D\frac{\partial C}{\partial x} \tag{4.97}$$

-To limit reactant crossover

- Change in material properties of electrolyte (D↓): less permeable to the reactants → porosity, composite

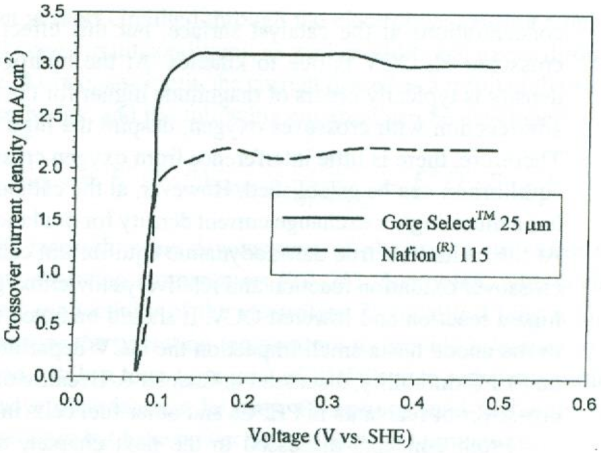


Figure 4.37 Measured hydrogen crossover current density with different electrolyte structures [28]. The crossover current density is measured directly with a hydrogen anode and an inert humidified cathode compartment. The limiting current density of hydrogen oxidation at the cathode is determined to be the crossover current density.

- Use of thicker electrolyte (x↑)
- Alteration of morphology or structure of porous media/or catalyst layers to limit diffusion through electrolyte: diffusion barrier
- Alteration of electrolyte composition to consume crossover before reacting electrode. E.g. Pt in electrolyte
- Recirculation of liquid electrolyte

-Modeling crossover losses

$$R_{\text{short}} = \frac{\delta_{\text{electrolyte}}}{A\sigma_e} \qquad (\Omega) \tag{4.99}$$

Semiempirial basis

crossover current density i_x → cathode current $i + i_x$

cathode kinetic overpotential in the absence of concentration effects

$$\eta_{a,c} = -\frac{R_u T}{\alpha_c F} \ln\left(\frac{i + i_x}{i_{o,c}}\right) \tag{4.101}$$

Example 4.12 Calculating Crossover Losses

In ref. [9], the authors noted a hydrogen crossover loss of 3.3 mA/cm^2 for their automotive H_2 PEFC applications. Calculate the mass crossover rate of hydrogen through the membrane. Also, calculate and plot the cathode activation overpotential loss at open circuit and $1A/cm^2$ as a function of cathodic exchange current density. Assume the cathodic charge transfer coefficient at the cathode is 1.5 at a temperature of 353 K, and the fuel cell has a 50 cm^2 geometric area.

cf. PEFC: 0.1~0.2 V sacrificial to crossover

$I >> i_x$ (high current density) → crossover effect minimized

6. Polarization curve model summary

Returning again to our overall model, we now have a complete representation of the polarization curve. If we know several key paramaters relating to the kinetic, ohmic, and mass transfer processes, we can predict the overall polarization curve of the fuel cell. Much more complex models exist in the literature to cover multidimensional, multiphase, and transient aspects as well as approach the problem from various length scales from molecular to full-size stack simulation. However, the approach taken here does include the most important physicochemical phenomena that affect fuel cell performance:

$$E_{\text{cell}} = E^\circ(T, P) - \eta_{a,a} - \left|\eta_{a,c}\right| - \eta_r - \eta_{m,a} - \left|\eta_{m,c}\right| - \eta_x \tag{4.102}$$

Extension of these relations into multi-dimensional is a matter of additional mathematics, not fundamental understanding.

From Chapter 3

$$E^\circ(T, P) = -\frac{\Delta G}{nF} + \frac{R_u T}{nF} \ln \left[\left(\frac{P_{\text{fuel}}}{P^*_{\text{fuel}}} \right)^{v_{\text{fuel}}} \left(\frac{P_{O_2}}{P^*_{O_2}} \right)^{v_{\text{oxidizer}}} \right] \tag{4.103}$$

The anode and cathode activation polarization losses ($\eta_{a,a}$ and $\eta_{a,c}$) for most fuel cell reactions can be determined from Eq. (4.35), the BV equation or a simplified form [i.e., Eqs. (4.52)–(4.55)].

The ohmic polarization, η_r can be determined from Eq. (4.71), including contact, ionic, and electronic resistances.

The concentration polarization values, $\eta_{m,a}$ and $\eta_{m,c}$ from Eq. (4.86), and the crossover losses can be included by adding either the fuel crossover current density to the cathode current (mass transfer) or an internal short resistor for the case of a mixed conductivity in the electrolyte.

We still cannot fully investigate the concentration polarization without the tools of Chapter 5, which will allow us to predict the mass transfer limiting current density.

Alternative Simplified Empirical Model The complexity of the model shown requires calculation or estimation of many parameters that are themselves functions of operating conditions. Additionally, due to the many complexities and material, geometry, fluid manifolding, and so on, not included in our bulk model, the calculated results often have a large deviation from experimental results. As stated, much more complex computational models exist, but even these have significant deviations from measured results because not every phenomenon can be accurately modeled and many of the transport parameters needed still have significant uncertainty in their values. It must be emphasized that the basic model presented in this chapter is a mere starting point and is not intended as a quantitative or exact solution for all operating fuel cells. Instead, it serves to promote understanding of the underlying physicochemical phenomena that control performance, so that an understanding of the engineering trade-offs in design optimization can be achieved based on the qualitative trends predicted.

Given the error and experimental effort associated with estimation of all the parameters in the analytical model and the complexity and time required for computational simulation, which, ultimately, still relies on the accuracy of the input parameters, there is a need for an entirely empirical approach to quickly characterize performance of fuel cells and stack designs. The following semiempirical model can be used to quickly glean some comparative information:

$$E_{\text{cell}} = E_{\text{OCV}} - A\,\ln(i) - iR - B\,\ln\left(1 - \frac{i}{i_l}\right) \tag{4.104}$$

or, using Eq. (4.90) [20],

$$E_{\text{cell}} = E_{\text{OCV}} - A\,\ln(i) - iR - m\,\exp(ni) \tag{4.105}$$

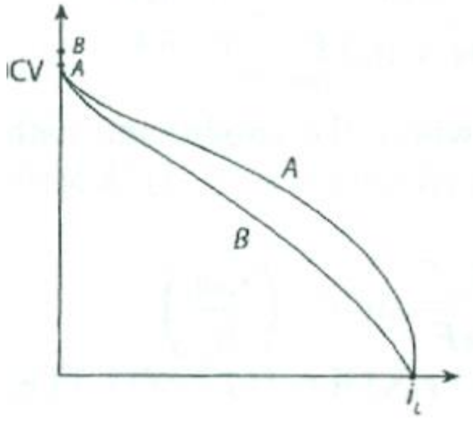
where A, R, B, i_l, m, and n, are parameters taken from curve-fits of experimental data. Each form has fit parameters for activation, ohmic, and concentration polarizations. For the OCV, an empirical equation or constant can be used based on experimental data. This approach is useful to quickly model real fuel cell performance, and by comparison with other similar curve its, the relative impact of the ohmic, concentration, and activation polarizations between different designs can be compared.

Example 4.13 Predicting Change in Polarization Curve Based on our understanding of fuel cell polarizations, we can now diagnose and predict basic polarization curve behavior as a function of the relevant parameters. We should be careful not to generalize too much, as many other minor effects and differently combined variables can lead to similar bulk polarization curve results. Nevertheless, at this stage basic conclusions and predictions can be made based on the understanding of this chapter:

(a) Sketch a typical hydrogen PEFC polarization curve with electrolyte *A*. Then, sketch a polarization curve with the same operating conditions, but with a thicker electrolyte *B*. Be sure to think about all of the effects of this change.

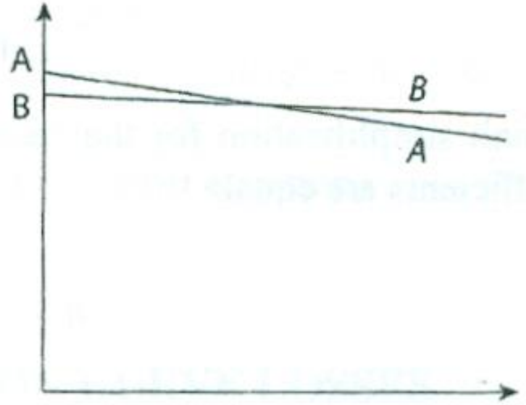
(b) Sketch a typical high-temperature fuel cell (SOFC, MCFC) polarization curve operating at temperature *A*. Then, sketch a polarization curve *B* with elevated temperature conditions. Be sure to think about all of the effects of this change. (Ignore the effects on mass transport region until Chapter 5.)

(c) Sketch the shape of the anode and cathode electrode polarizations versus current for the hydrogen PEFC.



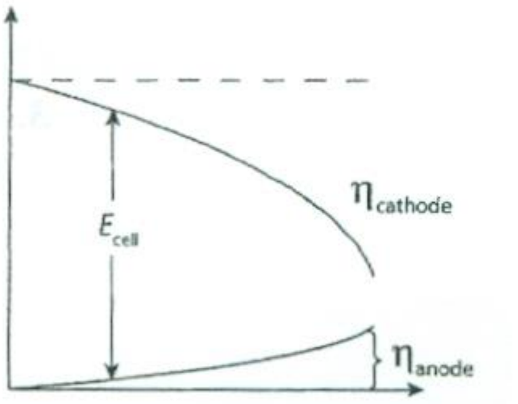
PEFC

B: thicker electrolyte



SOFC, MCFC

B: high T



PEFC

SOFC: solid oxide FC
MCFC: molten carbonate FC