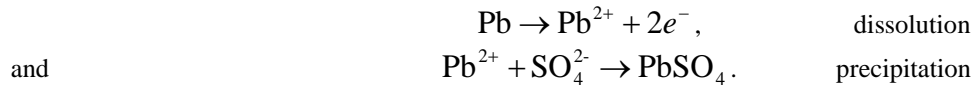


The discharge of the lead-acid battery proceeds through a dissolution/precipitation reaction. These two reactions for the negative electrode are



A key feature is that lead dissolves from one portion of the electrode but precipitates at another nearby spot. The solubility of Pb^{2+} is quite low, around $2 \text{ g} \cdot \text{m}^{-3}$. How then can high currents be achieved in the lead-acid battery?

- Assume that the dissolution and precipitation locations are separated by a distance of 1mm with a planar geometry. Using a diffusivity of $10^{-9} \text{ m}^2/\text{s}$ for the lead ions, estimate the maximum current that can be achieved.
- Rather than two planar electrodes, imagine a porous electrode that is also 1mm thick with made from particles with a radius $10 \mu\text{m}$ packed together with a void volume of 0.5. What is the maximum superficial current here based on the pore diameter?
- What do these results suggest about the distribution of precipitates in the electrodes?

a)

$$\begin{aligned} N_{\text{Pb}^{2+}} &= D \frac{\Delta c}{L} = \frac{D \Delta \rho}{L M} \\ i_{lim} &= nFN_{\text{Pb}^{2+}} = nF \frac{D \Delta \rho}{L M} = (2)(96485) \frac{10^{-9}}{10^{-3}} \frac{2}{207.2} \\ i_{lim} &= 1.9 \times 10^{-3} \text{ A m}^{-2} \end{aligned}$$

b) For a spherical particle

$$\begin{aligned} a &= \frac{3(1 - \varepsilon)}{r} = \frac{3(0.5)}{10^{-5}} = 1.5 \times 10^5 \text{ m}^{-1} \\ I &= aLnF \frac{D\Delta c}{2r} = 42 \text{ A m}^{-2} \end{aligned}$$

c) It is important that the current distribution be uniform through the thickness of the electrode to maximize the utilization of reactants. If the distribution were highly skewed to the front of the electrode, the pores may close, isolating the back of the electrode.

A porous electrode is made from solid material with an intrinsic density of ρ_s . When particles of this material are combined to form an electrode, it has an apparent density of ρ_a . What is the relationship between these two densities and the porosity? Assuming the particles are spherical with a diameter of $5.0 \mu\text{m}$, what is the specific interfacial area? If the electrode made from particles with a density of $2,100 \text{ kg}\cdot\text{m}^{-3}$ is 1 mm thick and has an apparent density of $1,260 \text{ kg}\cdot\text{m}^{-3}$, by what factor has the area increased compared to the superficial area?

a)

$$\rho_a = \frac{\text{mass}}{\text{total volume}} = \frac{\text{mass}}{V_{\text{solid}} + V_{\text{void}}}$$

$$\rho_a = \frac{\rho_s}{1 + \frac{\varepsilon}{1 - \varepsilon}} = \rho_s(1 - \varepsilon)$$

b)

$$a = \frac{6(1 - \varepsilon)}{D} = \frac{6(1 - 0.4)}{5 \times 10^{-6}} = 7.2 \times 10^5 \text{ m}^{-1}$$

c) The surface area A is given by

$$A = A_s L a$$

$$\frac{A}{A_s} = L a = (10^{-3}) 7.2 \times 10^5 = 720$$

Calculate pressure required to force water through hydrophobic gas diffusion layer of PEM fuel cell. The contact angle is 140 degrees and the average pore diameter is 20 μm . Use 0.0627 [N/m] for the surface tension of water.

$$p_c = \frac{2\gamma \cos \theta}{r} = \frac{2(0.0627) \cos(140)}{2 \times 10^{-6}} = -4803 \text{ Pa}$$

the capillary pressure is the pressure of the non-wetting phase minus the pressure of the wetting phases

$$p_c = p_{\text{nw}} - p_{\text{w}}$$

Therefore, the pressure of the water is

$$(-) - 4803 \text{ Pa}$$

or 4803 Pa above the gas pressure.

The separator of a phosphoric acid fuel cell is comprised of micron and sub-micron sized particles of SiC. Capillary forces hold the liquid acid in the interstitial spaces between particles, and this matrix provides the barrier between hydrogen and oxygen. What differential gas pressure across the matrix can be withstood? Assume an average pore size of $1\ \mu\text{m}$, and use a surface tension of $70\ \text{mN}\cdot\text{m}^{-1}$, a contact angle of 10 degrees.

$$p_c = \frac{2\gamma \cos \theta}{r} = \frac{2(0.07) \cos(10)}{1 \times 10^{-6}} = 138\ \text{kPa}$$

The differential pressure (gas over liquid) must be greater than 138 kPa to force the gas across the separator.

The separator used in a commercial battery is a porous polymer film with a porosity of 0.39. A series of electrical resistance measurements are made with various numbers of separators filled with electrolyte stacked together. These data are shown in the table. The thickness of each film is $25\ \mu\text{m}$, the area $2 \times 10^{-4}\ \text{m}^2$, and the conductivity of the electrolyte is $0.78\ \text{S/m}$. Calculate the tortuosity. Why would it be beneficial to measure the resistances with increasing numbers of layers rather than just a single point?

Number of layers	Measured resistance, Ω
1	1.91
2	3.41
3	5.17
4	6.65
5	7.79

$$R_{\Omega} = \frac{nL\tau}{A\kappa\varepsilon}$$

n number of separator films
 L thickness of each film
 κ conductivity of the electrolyte
 ε porosity
 τ tortuosity
 A area

Plot the resistance versus the number of separator films, then fit line to the data. The slope is

$$\frac{dR_{\Omega}}{dn} = \frac{L\tau}{\kappa A\varepsilon} = \text{slope}$$

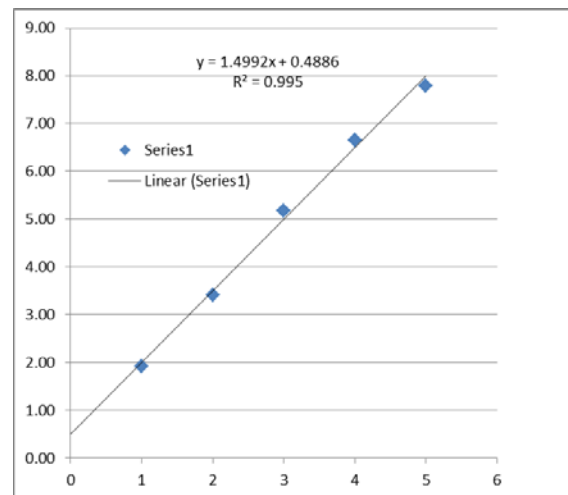
or

$$\tau = \text{slope} \frac{\kappa\varepsilon A}{L}$$

The slope is 1.4992, and therefore the tortuosity is 3.7.

$$\tau = 3.7$$

The resistance does not go to zero when $n=0$ because there is some additional resistance in series. This may be some contact resistance, but by using the slope of the line the effect is eliminated.



To reach the cathode of a proton exchange membrane fuel cell, oxygen must diffuse through a porous substrate. Normally, the porosity (volume fraction available for the gas) is 0.7 and the limiting current is $3000 \text{ A}\cdot\text{m}^{-2}$. However, liquid water is produced at the cathode with the reduction of oxygen. If this water is not removed efficiently, the pores can fill up with water, and the performance decreases dramatically. Use the Bruggeman relationship to estimate the change in limiting current when, because of the build-up of water, only 0.4, and 0.1 volume fraction are available for gas transport.

$$i_{\text{lim}} = 3000 \left(\frac{\varepsilon}{\varepsilon_0} \right)^{1.5}$$

$$\varepsilon=0.4 \quad i_{\text{lim}} = 1300 \text{ A m}^{-2}$$

$$\varepsilon=0.1 \quad i_{\text{lim}} = 160 \text{ A m}^{-2}$$

Calendering of an electrode is a finishing process used to smooth a surface and to ensure good contact between particles of active material. The electrode is passed under rollers at high pressures. If the initial thickness and porosity were 30 μm and 0.3, what is the new void fraction if the electrode is calendared to a thickness of 25 μm ? What effect would this have on transport?

The mass of solids is unchanged

$$m_1 = m_2$$

$$\rho_1(1 - \varepsilon_1)L_1A_1 = \rho_2(1 - \varepsilon_2)L_2A_2$$

There is no change in area, and the solids don't compress, therefore

$$\varepsilon_2 = 1 - \frac{L_1}{L_2}(1 - \varepsilon_1)$$

$$\varepsilon_2 = 1 - \frac{30}{25}(1 - 0.3) = 0.16$$

Electronic conductivity will likely get better because of better contact between particles. The effective conductivity and effective diffusion coefficient will be reduced because of lower porosity and a more tortuous path.

For a cell where $\sigma \gg \kappa$, the reaction proceeds as a sharp front through the porous electrode. Material near the front of the electrode is consumed before the reaction proceeds toward the back of the electrode. This situation is shown in the figure, L_s is the thickness of the separator, L_e the thickness of the electrode, and x_r is the amount of reacted material.

- If the cell is discharged at a constant rate, show how the distance x_r depends on time, porosity, and the capacity of the electrode, q , expressed in C/m^3 .
- What is the internal resistance? Use κ_s and κ for the effective conductivity of the separator and electrode respectively.
- If the cell is ohmically limited, what is the potential during the discharge?

a) The current, I , is a constant.

$$\text{coulombs past} = iAt$$

The capacity of the electrode can also be expressed in coulombs. Let ε be the void fraction and q the capacity per volume

$$\text{coulombs past} = Ax_r(1 - \varepsilon)q$$

$$iAt = Ax_r(1 - \varepsilon)q$$

so

$$x_r = \frac{it}{(1 - \varepsilon)q}$$

b)

internal resistance = resistance of separator + resistance of electrodes

$$R_{int} = \frac{L_s}{\kappa_s} + \frac{x_r}{\kappa}$$

substituting for x_r .

$$R_{int} = \frac{L_s}{\kappa_s} + \frac{it}{(1 - \varepsilon)q\kappa}$$

c)

$$V = U - iR_{int} = U - i \left\{ \frac{L_s}{\kappa_s} + \frac{x_r}{\kappa} \right\}$$

$$V = U - i \left\{ \frac{L_s}{\kappa_s} + \frac{it}{(1 - \varepsilon)q\kappa} \right\}$$

For Tafel kinetics and a one-dimensional geometry an analytic solution is also possible analogous to the one developed for linear kinetics. The solution is presented below for a cathodic process.

$$\frac{i_1}{I} = 2\theta \tan\left(\theta \frac{x}{L} - \psi\right),$$

and

$$\frac{di_1}{dx} = \frac{I}{L} \left\{ \frac{2\theta^2}{\delta} \sec^2\left(\theta \frac{x}{L} - \psi\right) \right\},$$

where

$$\tan \theta = \frac{2\delta\theta}{4\theta^2 - \varepsilon(\delta - \varepsilon)}$$

$$\tan \psi = \frac{\varepsilon}{2\theta}$$

$$\delta = \frac{\alpha_c FIL}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)$$

$$\varepsilon = \frac{\alpha_c FIL}{RT} \frac{1}{\kappa}$$

a. Make two plots of the dimensionless current distribution (derivative of i_1) for Tafel kinetics: one with $K_r=0.1$ and the second with $K_r=1.0$. δ is a parameter, use values of 1, 3, and 10.

Hint: it may be numerically easier to first find the value of θ that corresponds to the desired value for δ .

b. Compare and contrast the results in part (a) with Figure 5.6 and 5.7 for linear kinetics.

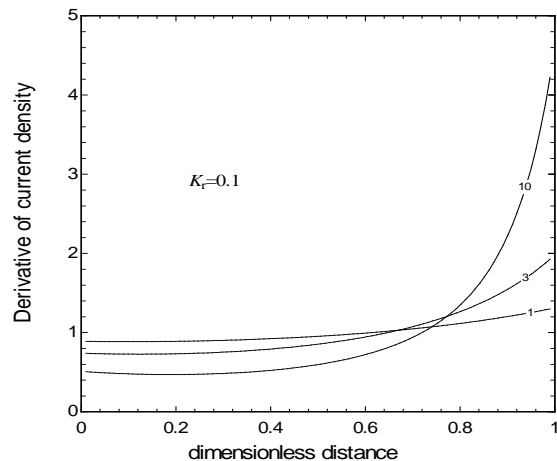
a) compare the above expressions for δ and ε

$$\delta \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)^{-1} = \varepsilon \kappa$$

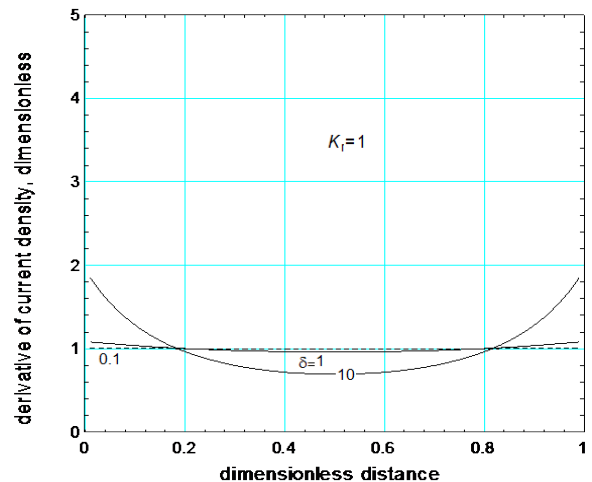
$$\delta = \left(1 + \frac{\kappa}{\sigma} \right) \varepsilon = (1 + K_r) \varepsilon$$

$$\tan \theta = \frac{2\delta\theta}{4\theta^2 - \varepsilon(\delta - \varepsilon)}$$

Find values of θ that correspond to the desired δ .



b)



The curves look very similar to those for linear kinetics, Figures 5.6 and 5.7. The parameter δ , which is proportional to l/A is replaced by v^2 , which is proportional to ai_o . For Tafel kinetics, the distribution becomes more non-uniform as the current is increased.

The two parameters that describe the current distribution in a porous electrode with linear kinetics in the absence of concentration gradients are

$$v^2 = \frac{ai_o(\alpha_a + \alpha_b)FL^2}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right) \quad \text{and} \quad K_r = \frac{\kappa}{\sigma}$$

- a. How can the parameter v^2 be described physically?
- b. For the following conditions sketch out the current distribution $\frac{di_2}{dx}$ across the electrode

$$\begin{array}{ll} K_r=1 & v^2 \gg 1 \\ K_r=1 & v^2 \ll 1 \\ K_r=0.01 & v^2 \gg 1 \end{array}$$

The parameter v^2 is much like the Wagner number.

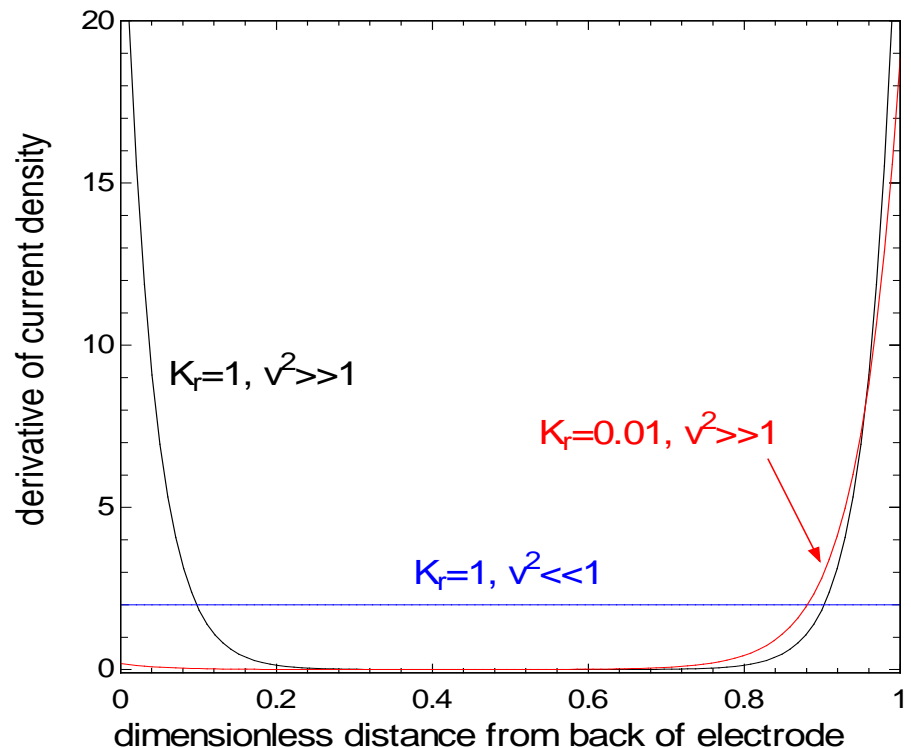
$$v^2 = \frac{ai_o(\alpha_a + \alpha_c)FL^2}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)$$

$$\frac{1}{\text{Wa}} = \frac{i_o(\alpha_a + \alpha_c)FL}{RT} \left(\frac{1}{\kappa} \right)$$

$$v^2 = \frac{\text{ohmic resistance}}{\text{kinetic resistance}}$$

large values of v^2 correspond to small Wa, which leads to a non-uniform distribution

small values of v^2 correspond to large Wa, which suggests a uniform distribution



Problem 5.9 provides the solution for the current distribution in a porous electrode with Tafel kinetics in the absence of concentration gradients. Describe the physical parameters? Compare and contrast these results to the analysis that lead to the Wa for Tafel kinetics found in Chapter 4.

Consider the cathodic case (the anodic situation is similar). There are two parameters

$$\varepsilon = \frac{\alpha_c F (I/A) L}{RT} \left(\frac{1}{\kappa} \right)$$

$$\delta = \frac{\alpha_c F (I/A) L}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)$$

Compare these to the Wa , Equation 4-65.

$$\frac{1}{Wa} = \frac{\alpha_c F |i_{avg}| L}{RT} \left(\frac{1}{\kappa} \right)$$

By inspection δ is very similar to the reciprocal of the Wa .

$$\delta \propto \frac{\text{ohmic resistance}}{\text{kinetic resistance}}$$

small δ results in a uniform current distribution

large δ results in a non-uniform distribution

Analysis of porous electrodes includes both the solution ($1/\kappa$) and the solid ($1/\sigma$) resistances, and thus a second parameter is needed. ε is used. If ε and δ are compared.

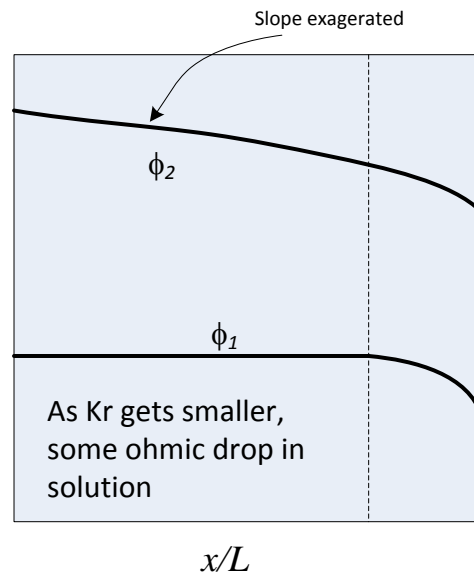
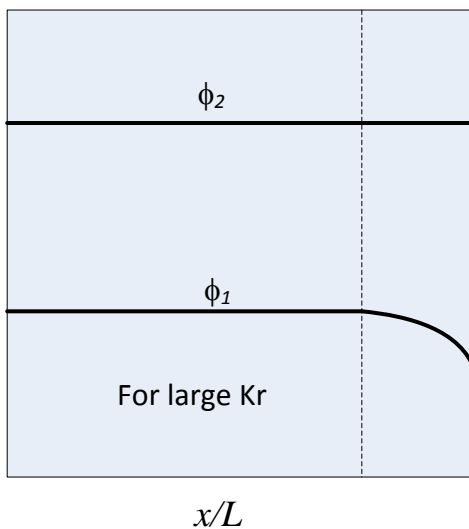
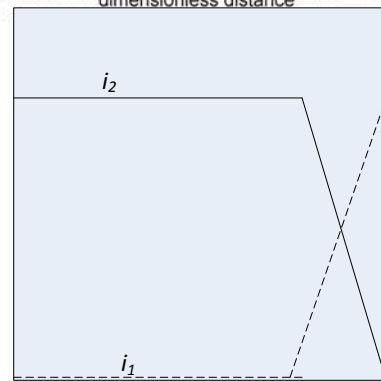
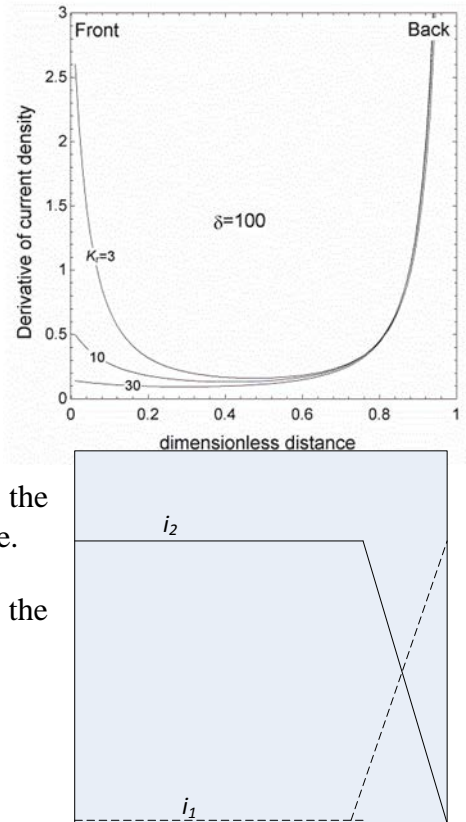
$$\delta = (1 + K_r) \varepsilon$$

where $K_r = \kappa/\sigma$. So either K_r or σ is the second parameter that affects whether the distribution is skewed to the front or to the back of the electrode, which is similar to the linear kinetics case.

On the right is shown the current distribution in a porous electrode for Tafel kinetics. $\delta=100$ and K_r is a parameter. As expected, for such a large value of δ , the current is highly non-uniform. Further, for the values of K_r chosen, the reaction is concentrated near the back of the electrode. Here, the scale of the ordinate has been selected to emphasize the behavior at the *front* of the electrode. Note, that in all cases rather than getting ever smaller at the front of the electrode, the derivative of current density always goes through a minimum and is increasing at the current collector. Physically explain this behavior.

For large values of K_r , ($K_r = \kappa/\sigma$) the reaction is concentrated in the back of the electrode. As is shown in the figure, for a finite K_r , the reaction rate always increases at the front of the electrode rather than going to zero. Further, the increase becomes larger as K_r gets smaller. This behavior can be understood by examining the solution and metal potentials (ϕ_1 and ϕ_2) across the electrode.

Start by assuming that all of the reaction is at the back of the electrode.



Because of the ohmic drop through the electrolyte, the potential at the front of the electrode increases as κ decreases,

$$\nabla \cdot \mathbf{i}_2 \propto \exp(\phi_2 - \phi_1)$$

Thus, we see an exponential increase in current density in the front of the electrode.

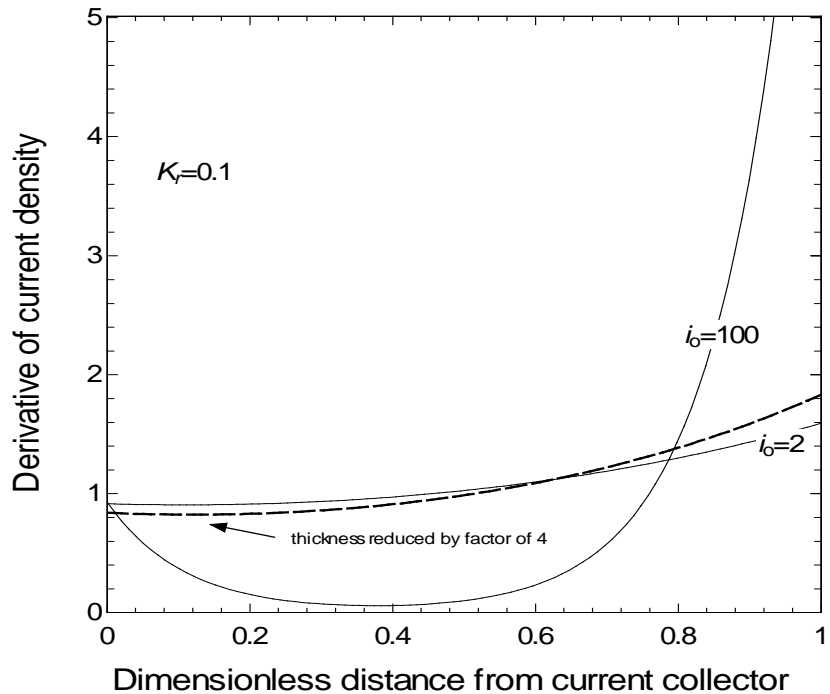
An electrode is produced with a thickness of 1 mm, $\kappa=10 \text{ S}\cdot\text{m}^{-1}$ and $\sigma=100 \text{ S}\cdot\text{m}^{-1}$. The reaction follows linear kinetics, $i_o=2 \text{ A}\cdot\text{m}^{-2}$ and the specific interfacial area is 10^4 m^{-1} . It is proposed to use the same electrode for a second reaction where the exchange current density is much larger, $100 \text{ A}\cdot\text{m}^{-2}$. What would be the result of using this same electrode? What changes would you propose?

As produced the electrode has a relatively uniform current distribution. If the reaction has a higher exchange-current density, the current distribution becomes more non-uniform (see plot). In this case, the middle of the electrode is not being used.

Options to improve the current distribution are

- reduce a , use larger particles, which may be cheaper too.
- reduce the thickness of the electrode.

If the thickness is reduced by a factor of four, the current distribution approaches the original design.



The exchange current density i_o does not appear in the solution for the current distribution for Tafel kinetics (see how ε is defined in problem 9). Why not?

The situation is analogous to the W_a for Tafel kinetics described in Chapter 4.

$$\frac{1}{W_a} = \frac{\alpha_c F |i_{\text{avg}}| L}{RT\kappa}$$
$$\varepsilon = \frac{\alpha_c F (I/A) L}{RT\kappa}$$

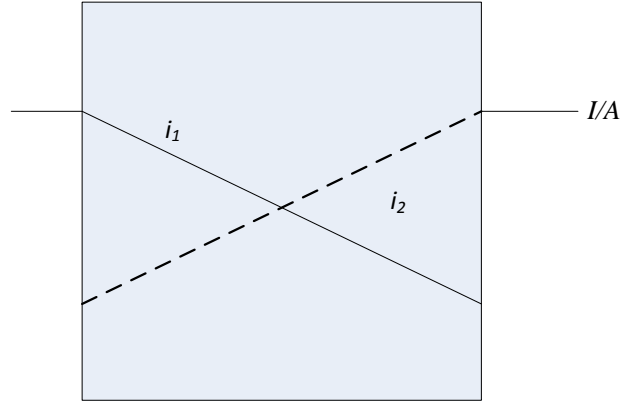
Instead of the average current density, the superficial current density is used. With Tafel kinetics, the charge-transfer resistance decreases with increasing current. Whereas for linear kinetics it is proportional to $1/i_o$.

Rather than the profile shown in Figure 5-7, one might expect that for the case where $\sigma=\kappa$, that the distribution would be uniform and not just symmetric. Show that this cannot be correct. Start by assuming that the profile is uniform; then sketch how i_1 and i_2 vary across the electrode. Then sketch the potentials and identify the inconsistency.

Start by assuming that the current distribution is uniform.

$$i_2 = \frac{I}{A} \left(\frac{x}{L} \right)$$

$$i_1 = \frac{I}{A} \left(1 - \frac{x}{L} \right)$$



Applying Ohm's law

$$i_2 = -\kappa \frac{d\phi_2}{dx}$$

$$i_1 = -\sigma \frac{d\phi_1}{dx}$$

$$\int_0^{\phi_1(x)} d\phi_1 = -\frac{I/A}{\sigma} \int_0^x \left(1 - \frac{x}{L} \right) dx$$

$$\phi_1(x) = -\frac{I/A}{\sigma} \left(x - \frac{x^2}{2L} \right)$$

similarly

$$\phi_2(x) = \phi_2(0) - \frac{I/A}{\kappa} \frac{x^2}{2L}$$

$$\eta_s = \phi_1(x) - \phi_2(x) - U = \phi_2(0) - \frac{I/A}{\kappa} \frac{x^2}{2L}$$

if $\kappa=\sigma$

$$\eta_s = (I/A) \frac{1}{\sigma} \left(\frac{x^2}{2L} - x + \frac{x^2}{2L} \right) - \phi_2(0) - U$$

For the current distribution to be uniform, the surface over potential must be constant, we see however, that η_s is not a constant. Therefore our original assumption of a uniform current distribution is incorrect.

Repeat illustration 5-3 for a more conductive electrolyte, $\kappa=100$ S/m. If it is desired to keep the reaction rate at the back of the electrode no less than 40 % of the front, what is the maximum thickness of the electrode? Additional kinetic data are $\alpha_a = \alpha_c = 0.5$, $i_o = 100$ Am⁻², $a = 10^4$ m⁻¹. Using the thickness calculated, plot the current distribution for solutions with the following conductivities, 100, 10, 1, and 0.1 S/m.

Use equation 5-41

$$0.4 = \frac{1}{\cosh(v)}$$

solve for L from the definition for v^2 , Equation 5.31

$$v^2 \equiv \frac{ai_o(\alpha_a + \alpha_c)FL^2}{RT} \left(\frac{1}{\sigma} + \frac{1}{\kappa} \right) \quad (5-31)$$

$$L = 2.5 \text{ mm}$$

Consider a similar problem to the flooded agglomerate model developed in Section 5.6, except that now a film of electrolyte covers the agglomerate to a depth of δ . Find the expression for the rate of oxygen transport that would replace equation 5-50.

Without the film present,

$$N_{O_2} = \frac{D_{eff} H p_{O_2}}{r_p} (1 - K \coth K)$$

With the film, let c_i be the oxygen concentration at the interface between the agglomerate and the film,

$$N_{O_2} = \frac{D_{eff} c_i}{r_p} (1 - K \coth K)$$

$$N_{O_2} = \frac{(H p_{O_2} - c_i)}{\delta} D_f$$

where D_f is the diffusivity of the film and δ the film thickness.

c_i is expressed as

$$c_i = \frac{N_{O_2} r_p}{D_{eff} (1 - K \coth K)}$$

which is substituted back into the film equation

$$N_{O_2} = \left[H p_{O_2} - \frac{N_{O_2} r_p}{D_{eff} (1 - K \coth K)} \right] \frac{D_f}{\delta}$$

or

$$N_{O_2} = \frac{H p_{O_2} \frac{D_f}{\delta}}{\frac{\delta}{D_f} + \frac{r_p}{D_{eff} (1 - K \coth K)}}$$

$$N_{O_2} = \frac{\frac{D_{eff}}{r_p} (1 - K \coth K) H p_{O_2}}{1 + \frac{\delta D_{eff}}{D_f r_p} (1 - K \coth K)}$$

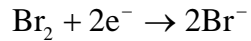
Derive the expression for the effectiveness factor, equation 5-53. What is the expression for a slab rather than a sphere?

$$\eta = \frac{\text{actual reaction rate}}{\text{reaction rate if entire particle at } O_2 \text{ concentration at surface}}$$

$$\eta = \frac{(4\pi r_p^2) \frac{H p_{O_2} D_{eff}}{r_p} (K \coth K - 1)}{(4/3 \pi r_p^3) \left[K^2 H p_{O_2} \frac{D_{eff}}{r_p^2} \right]}$$

$$\eta = \frac{3(K \coth K - 1)}{K^2}$$

A porous flow-through electrode was examined in Chapter 4 for the reduction of bromine in a Zn-Br battery.



The electrode is 0.1 m in length with a porosity of 0.55. What is the maximum superficial velocity that can be used on a 10 mM Br_2 solution if the exit concentration is limited to 0.1 mM? Use the following mass-transfer correlation.

$$\text{Sh} = 1.29 \text{Re}^{0.72}$$

The Re is based on the diameter of the carbon particles, d_p and the superficial velocity, that make up the porous electrode.

$$D_{\text{Br}_2} = 6.8 \times 10^{-10} \text{ m}^2/\text{s} \quad d_p = 40 \text{ } \mu\text{m} \quad v = 9.0 \times 10^{-7} \text{ m}^2/\text{s}$$

$$c_L = c_{in} \exp(-\alpha L)$$

$$\alpha = \frac{ak_c}{v_x \varepsilon}$$

for a spherical particle, $a = \frac{6}{d_p} (1 - \varepsilon) = 67,500 \text{ m}^{-1}$

$$c_L = 0.1 \text{ mM} \quad c_{in} = 10 \text{ mM}$$

L is 0.1m, solve for alpha

$$\alpha = 46.05 \text{ m}^{-1}$$

then solve for the mass-transfer coefficient

$$k_c = 5.49 \times 10^{-5} \text{ m s}^{-1}$$

$$\text{Sh} = 1.29 \text{Re}^{0.72} = \frac{k_c D_p}{D_{\text{Br}_2}} = 3.23$$

$$\text{Re} = \frac{\varepsilon v_x D_p \rho}{\mu} = 3.575$$

$$v_s = \varepsilon v_x = 0.08 \text{ m s}^{-1}$$

Derive equation 5-42. Start with equation 5-36.

The resistance is defined as

$$R_{int} = \frac{\phi_1(L) - \phi_2(0)}{I/A}$$

$$i^* = \frac{K_r}{1+K_r} + \frac{\sinh(vz)+K_r\sinh(v(z-1))}{(1+K_r)\sinh(v)}. \quad (5-36)$$

$y=x/L$, a dimensionless distance

We can write Equation 5-36 as

$$i_2 = \frac{(I/A)\kappa}{\sigma+\kappa} \left\{ 1 + \frac{\sigma/\kappa \sinh(v(1-y)) - \sinh(vy)}{\sinh(v)} \right\}.$$

also from Ohm's law

$$i_2 = -\kappa \frac{d\phi_2}{dx} = -\frac{\kappa}{L} \frac{d\phi_2}{dy}$$

$$\int_0^{\phi_2(1)} d\phi_2 = -\frac{(I/A)\kappa L}{\sigma+\kappa} \int_0^1 \left\{ 1 + \frac{\sigma/\kappa \sinh(v(1-y)) - \sinh(vy)}{\sinh(v)} \right\} dy$$

$$\phi_2(1) = -\frac{(I/A)L}{\sigma+\kappa} \left\{ 1 + \frac{1}{v\sinh(v)} [\sigma/\kappa \cosh(v-1) - \cosh(v) + 1] \right\}$$

For linear kinetics

$$\frac{di_1}{dx} = -\frac{ai_oF}{RT} (\alpha_a + \alpha_c)(\phi_1 - \phi_2)$$

Also, because charge is conserved

$$\frac{di_1}{dx} = -\frac{di_2}{dx}$$

$$\frac{-di_1}{dx} = -\frac{(I/A)}{L} \frac{v\kappa}{\sigma+\kappa} \{ \sigma/\kappa \cosh(v(1-y)) + \cosh(vy) \}$$

since

$$v^2 = (\alpha_a + \alpha_c) \frac{ai_oF}{RT} L^2$$

$$\frac{-di_1}{dx} = \frac{\nu^2}{L^2} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)^{-1} (\phi_1 - \phi_2)$$

solve for $\phi_1 - \phi_2$ at $y=1$,

$$(\phi_1 - \phi_2) = \frac{(I/A)L^2}{\nu^2} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right)^{-1} \frac{1}{L} \frac{\nu\kappa}{(\sigma + \kappa)} \frac{1}{\sinh(\nu)} \left[\frac{\sigma}{\kappa} + \cosh\nu \right]$$

$$\phi_1(y = 1) = \frac{\left(\frac{I}{A}\right)L}{(\sigma + \kappa)} \left\{ 1 + \frac{1}{\sinh(\nu)} \left[\frac{\sigma}{\kappa} \cosh(\nu - 1) - \cosh(\nu) + 1 \right] \right\} -$$

$$\frac{1}{\nu \sinh(\nu)} \frac{\left(\frac{I}{A}\right)L}{(\sigma + \kappa)} (1 + \kappa/\sigma) (\sigma/\kappa + \cosh\nu)$$

$$R_{\text{int}} = \frac{L}{\sigma + \kappa} \left[1 + \frac{2 + \left(\frac{\sigma}{\kappa} + \frac{\kappa}{\sigma} \right) \cosh \nu}{\nu \sinh \nu} \right] \quad (5-42)$$

Rearrange equation 5-57 to provide a *design equation* for a flow-through reactor operating at limiting current. Specifically, provide an explicit expression for L , the length of the reactor, in terms of flow rate, mass-transfer coefficient, and the desired separation

$$c_A = c_{A,in} \exp(-\alpha x)$$

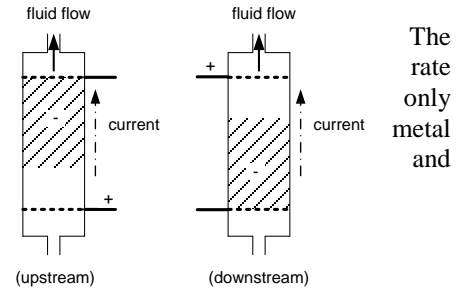
$$\alpha = \frac{ak_c}{v_x \varepsilon}$$

$$\ln \frac{c_A}{c_{A,in}} = -\alpha x = \frac{ak_c}{v_x \varepsilon} x$$

For length L , and $c_{A,o}$ the desired outlet concentration

$$L = \frac{v_x \varepsilon}{ak_c} \ln \frac{c_{A,in}}{c_A} = \frac{v_x \varepsilon}{ak_c} \ln(\text{separation factor})$$

A direct method of removing heavy metals, such as Ni^{2+} , from a waste stream is the electrochemical deposition of the metal on a particulate bed. The goal is to achieve as low a concentration of Ni at the exit for as high a flow as possible. A flow-through configuration is proposed. However, here the negative electrode is porous, and the counter electrode (+) is a simple sheet. Would you recommend placing the counter electrode upstream downstream of the working electrode? Why? For this analysis assume $\sigma \gg \kappa$, and that the reaction at the electrode is mass-transfer limited. Hint: develop an expression for the change in solution potential similar to equation 5-63.



If the reaction is mass-transfer limited, the concentration profile is the same regardless of where the counter electrode is placed.

$$c_A = c_{A,in} \exp(-\alpha x)$$

The current density in solution is different

upstream, the current density is zero at $x=L$

$$i_2 = nFv_x \varepsilon c_{A,in} (\exp(-\alpha x) - \exp(-\alpha L))$$

downstream, the current density is zero at $x=0$

$$i_2 = nFv_x \varepsilon c_{A,in} (1 - \exp(-\alpha x))$$

Using Ohm's law

$$i_2 = -\kappa \frac{d\phi_2}{dx}$$

substitute for i_2 and integrate to find the potential difference

for the upstream placement, we get Equation 5.63

$$\Delta\phi_2 = \frac{nF(v_x \varepsilon)^2 c_{A,in}}{K_{eff} a k_c} = \frac{\beta}{\alpha}$$

In contrast for downstream placement

$$\Delta\phi_2 = \beta \left[-L + \frac{1}{\alpha} (\exp(-\alpha L) - 1) \right]$$

For large L ,

$$\Delta\phi_2 = -\beta L + \frac{\beta}{\alpha}$$

There is an additional term proportional to L . As we try to achieve higher separation by making the electrode larger, the potential difference increases. Thus, upstream placement is preferred.