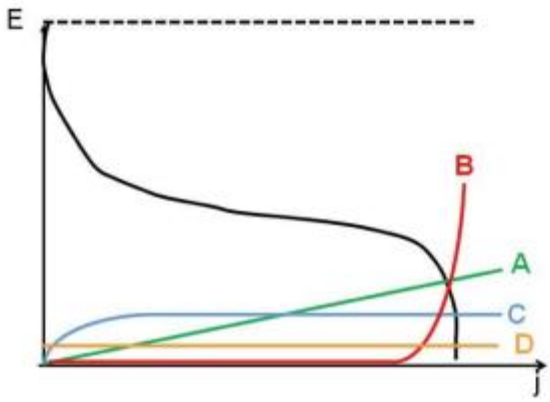
MSE-441 Exercise-3

Exercise 1:

(a) The figure below shows a potential-current plot (black), along with plots of diffrent overpotential losses at increasing currents (A-D). Specify which plots correspond to the thermodynamic losses (standard vs. open-circuit potential), ohmic losses, activation losses, and mass-transfer losses.



Solution:

A = ohmic (linear)

B = mass-transfer (dominates as j→ jlim)

C = activation (dominates at j→ j0)

D = thermodynamic losses (occur at j = 0 and remains constant)

(b) Calculate the concentration overpotential (ηconc) for the cathodic deposition of silver:

Ag+ + e- → Ag

from a solution of 0.1 M AgNO3 in 2 M HNO3 at 25° C using a current density of 10A/m^2 (mass transfer coefficient Km = 10 $^{-5}$ ms $^{-1}$). Assume α_c = 1

Solution:

$$j_{lim,c} = FK_m[Ag]_{bulk}$$

$$j_{lim,c} = 96500\frac{C}{mol\ e^-} \times 1\frac{mol\ e^-}{mol\ Ag} \times 10^{-5}\frac{m}{s} \times 100\frac{mol\ Ag}{m^3} = 96.5\frac{A}{m^2}$$

As this is cathodic current it should be negative → jlim,c= -96.5 A/m^{-2}

$$\eta_{conc} = \frac{RT}{(1-\alpha_a)ZF} ln\frac{|j - j_{lim,c}|}{|j_{lim,c}|} = \frac{8.314\frac{V \cdot C}{mol\ K} \times 298\ K}{96500\frac{C}{mol\ e^-} \times 1\frac{mol\ e^-}{mol}} \ln\left|\frac{-10}{-96.5} - 1\right| = -0.0028\ V$$

(c) Silver is deposited in an electrochemical cell from a solution of AgNO3 in 1 M HNO3 at 25 °C. If the cell operates at 50% of the limiting current density, calculate the total (activation + concentration) cathodic overpotential at this current density. Given jlim =200A m $^{-2}$; j° = 5A m^{-2} ; α = 0.5.

Solution:

For a cathodic reaction, both j and jlim are negative:

$$j_{lim,c} = -200\ \frac{A}{m^2},\ j = -100\ \frac{A}{m^2}$$

Use B-V equation with mass transfer:

$$j = -j^o\left(1 - \frac{j}{j_{lim,c}}\right)e^{\frac{-(1-\alpha_a)ZF}{RT}\eta}$$

Rearrange:

$$\eta = \frac{RT}{(1-\alpha_a)ZF} ln\frac{|j - j_{lim,c}|}{|j_{lim,c}|} + \frac{RT}{(1-\alpha_a)ZF} ln\frac{|j^o|}{|j|}$$

$$\eta = -0.19\ V$$

Activation overpotential:

$$\eta_{act} = \frac{RT}{(1-\alpha_a)ZF} ln\frac{|j^o|}{|j|} = -0.154\ V$$

Concentration overpotential:

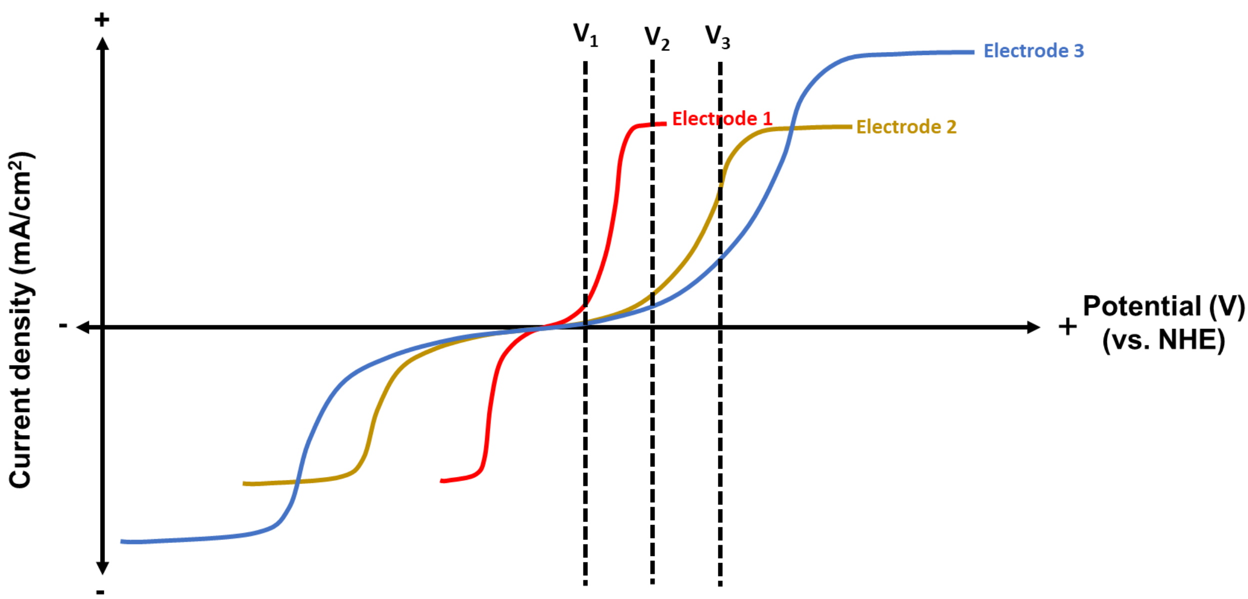
$$\eta_{conc} = \frac{RT}{(1-\alpha_a)ZF} ln\frac{|j - j_{lim,c}|}{|j_{lim,c}|} = -0.036\ V$$

Exercise 2:

Consider a reversible 1:1 O:R, single-electron reaction occurring on the surface of an electrode at standard conditions:

O + e- ↔ R

This same reaction is being performed on three different electrodes, and the corresponding current-voltage plot for each electrode is shown below.



Assume $|j_{lim,a}|$ = $|j_{lim,c}|$ = 2 A/m^2 for Electrodes 1 and 2, and $|j_{lim,a}|$ = $|j_{lim,c}|$ = 2.5 A/m^2 for Electrode 3. At an applied potential of V_1 = 0.03 V, we observe a net current density of j = 0.3 A/m^2 for Electrode 1 and j = 0.02 A/m^2 for Electrode 3. Assume α_a = 0.5 for all electrodes.

Note that the plot is not drawn to scale.

(a) For each electrode, specify the regime(s) (linear, Tafel, or mass transfer-limited) you expect to dominate for each of the three voltages highlighted in bold (V_1, V_2, V_3). Of these nine cases, specify the two cases that most likely represent the transition between two regimes, and indicate the relevant regimes for these two cases.

(b) Approximate the exchange current density j° for Electrodes 1 and 3. (If you are unable to find a solution, you may assume j° = 0.2 mA/cm^2 for Electrode 1 and j° = 0.1 mA/cm^2 for Electrode 3 for the following parts).

(c) Assume j° = 0.1 A/m^2 for Electrode 2. Derive an implicit expression that can be used to approximate the current density j around V_2, with the current density terms arranged on the same side of the equation.

(d) Consider the relative kinetics of the electrodes.

   (i) Quantitatively rank order the electrodes from the most kinetically controlled to the least-kinetically-controlled (lowest to fastest relative kinetics).

   (ii) Comment on whether these rankings are qualitatively reflected in the plots, explaining any discrepancies.

(e) Improvements in the reactor design led to increases in $|j_{lim,c}|$ for all electrodes. How will this improvement affect the j at V_1? Discuss the relative extent of these effects on the three electrodes (which are more strongly or less strongly affected).

a)

Electrode 1 = Tafel
Electrode 2 = Linear
Electrode 3 = Linear

Electrode 1 = Mass transfer limited
Electrode 2 = Tafel
Electrode 3 = Tafel/Linear

Electrode 1 = Mass transfer limited
Electrode 2 = Tafel/mass transfer limited
Electrode 3 = Tafel

b)

$v_1 = 0.03\text{V}$
$j(\text{ Electiode 1}) = \ ?$
$j(\text{ Electrode 3}) = \ ?$

Electrode 1 → Tafel regime, anodic

$$|j_{lim,a}| = |j_{lim,c}| \ = 2\text{A/m}^2, j = 0.3\text{A/m}^2$$

$$\eta = \frac{RT}{\alpha ZF}\ln\frac{j_{lim,a}}{j^0} + \frac{RT}{\alpha zF}\ln\frac{j}{j_{lim,a}-j} \rightarrow \frac{RT}{\alpha zF}\ln\frac{j_{lim,a}}{j^0} = \eta - \frac{RT}{\alpha zF}\ln\frac{j}{j_{lim,a}-j}$$

$$\ln\frac{j_{lim,a}}{j^0} = \frac{\alpha zF}{RT}\eta - \ln\frac{j}{j_{lim,a}-j} \rightarrow \ln\frac{j^0}{j_{lim,a}} = \ln\frac{j}{j_{lim,a}-j} - \frac{\alpha zF}{RT}\eta$$

$$\frac{j^0}{j_{lim,a}} = exp\left(ln\frac{j}{j_{lim,a}-j} - \frac{\alpha zF}{RT}\eta\right) \rightarrow j^0 = j_{lim,a}\frac{e^{ln\frac{j}{j_{lim,a}-j}}}{e^{\frac{\alpha zF}{RT}\eta}} = \frac{j_{lim,a}\,j}{j_{lim,a}-j}e^{-\frac{\alpha zF}{RT}\eta}$$

Plugging in values:

$$j^0 = \frac{(2\ A/m^2)(0.3A/m^2)}{2\ A/m^2 - 0.3\ A/m^2}exp\left(-\frac{0.5(1\ mole^-/mol)(96485\ C/mole^-)}{(8.314\ J/mol.K)(298\ K)}\right) = \ 0.197\ A/m^2 (\text{Electrode 1})$$

Electrode 3 → linear regime

$$|j_{lim,a}| = |j_{lim,c}| = 2.5A/\text{m}^2, j = 0.02A/\text{m}^2$$

$$\eta = j\left[\frac{RT}{j^0\text{z}F} + \frac{RT}{j_{lim,a}\text{z}F} - \frac{RT}{j_{lim,c}\text{z}F}\right] \rightarrow \frac{RT}{j^0\text{z}F} \ = \ \frac{\eta}{\text{j}} \ - \ \frac{RT}{j_{lim,a}\text{z}F} + \frac{RT}{j_{lim,c}\text{z}F}$$

$$\frac{1}{j^0} = \frac{\text{z}F\eta}{RTj} - \frac{1}{j_{lim,a}} + \frac{1}{j_{lim,c}} \rightarrow j^0 = \frac{1}{\frac{\text{z}F\eta}{RTj} - \frac{1}{j_{lim,a}} + \frac{1}{j_{lim,c}}}$$

Plugging in values:

$$j^0 = \frac{1}{\frac{(1\ mole^-/mol)(96485\ C/mole^-)(0.03\ \text{V})}{(8.314\ J/mol.K)(298\ K)(0.02A/\text{m}^2)} - \frac{1}{2.5A/\text{m}^2} + \frac{1}{-2.5A/\text{m}^2}} = \ 0.017A/\text{m}^2 \ (\text{Electrode 3})$$

c) $j^0 = 0.1\text{A/m}^2$

Electrode 2@ v_2 → Tafel linear regime, ∴ $\eta_{\text{Tafel}} \sim \eta_{\text{linear}}$

$$\frac{\mathrm{RT}}{\alpha \mathrm{zF}} l\,n \frac{j_{lim,a}}{j^0} + \frac{\mathrm{RT}}{\alpha \mathrm{zF}} l\,n \frac{j}{j_{lim,a} - j} \approx j\left[\frac{\mathrm{RT}}{j^0 \mathrm{zF}} + \frac{\mathrm{RT}}{j_{lim,a}\mathrm{zF}} - \frac{\mathrm{RT}}{j_{lim,c}\mathrm{zF}}\right]$$

$$\frac{1}{\alpha} ln \frac{j_{lim,a}}{j^0} + \frac{1}{\alpha} ln \frac{j}{j_{lim,a} - j} \approx j\left[\frac{1}{j^0} + \frac{1}{j_{lim,a}} - \frac{1}{j_{lim,c}}\right]$$

$$\frac{1}{\alpha j} ln \left[\frac{j_{lim,a}}{j^0} \cdot \frac{j}{j_{lim,a} - j}\right] = \frac{1}{j^0} + \frac{1}{j_{lim,a}} - \frac{1}{j_{lim,c}}$$

$$ln \left[\frac{j_{lim,a}}{j^0} \cdot \frac{j}{j_{lim,a} - j}\right]^{1/\alpha j} \approx \frac{1}{j^0} + \frac{1}{j_{lim,a}} - \frac{1}{j_{lim,c}}$$

d)

Electrode 1:

$$\frac{j^0}{j_{lim}} = \frac{0.197\ \mathrm{A/m^2}}{2\ \mathrm{A/m^2}} = 0.0985$$

Fastest → Least kinetically controlled

Electrode 2:

$$\frac{j^0}{j_{lim}} = \frac{0.1\ \mathrm{A/m^2}}{2\ \mathrm{A/m^2}} = 0.05$$

Electrode 3:

$$\frac{j^0}{j_{lim}} = \frac{0.017\ \mathrm{A/m^2}}{2.5\ \mathrm{A/m^2}} = 0.0068$$

Slowest → Most kinetically controlled

They are consistent with the plots, since Electrode 3 shows kinetic behavior over a larger range of potentials before leveling off

e)

$$\frac{j}{j^0} = \left[1 - \frac{j}{j_{lim,a}}\right] e^{\frac{\alpha zF}{RT}\eta} - \left[1 - \frac{j}{j_{lim,a}}\right] e^{-\frac{(1-\alpha)zF}{RT}\eta}$$

this term becomes smaller
→ (cathodic) contribution smaller is

<u>Electrode 1:</u> Tafel

$\eta = \frac{RT}{\alpha zF} \ln \frac{j_{lim,a}}{j^0} + \frac{RT}{\alpha zF} \ln \frac{j}{j_{lim,a} - j}$ → No dependence on $j_{lim,c}$ (negligible effect only)

<u>Electrodes 2 and 3:</u> Linear

$\eta = j\left[\frac{RT}{j^0 zF} + \frac{RT}{j_{lim,a} zF} - \frac{RT}{j_{lim,c} zF}\right]$ → Dependence on $j_{lim,c}$ Greater effect of cathodic mass transfer resistance at higher current