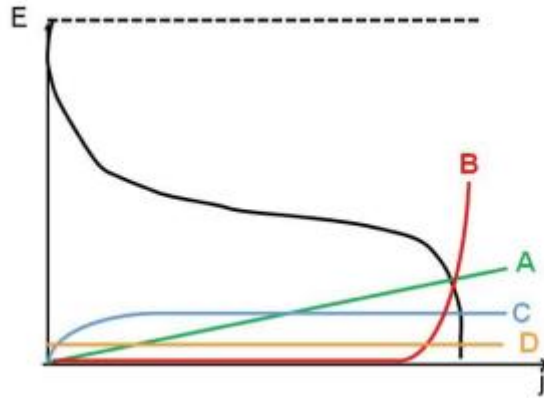


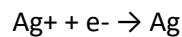
MSE-441 Exercise-3

Exercise 1:

- (a) The figure below shows a potential-current plot (black), along with plots of different 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.



- (b) Calculate the concentration overpotential (η_{conc}) for the cathodic deposition of silver:

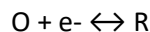


from a solution of 0.1 M AgNO_3 in 2 M HNO_3 at 25 °C using a current density of 10 A m^{-2} (mass transfer coefficient $k_m = 10^{-5} \text{ m s}^{-1}$). Assume $\alpha_c = 1$

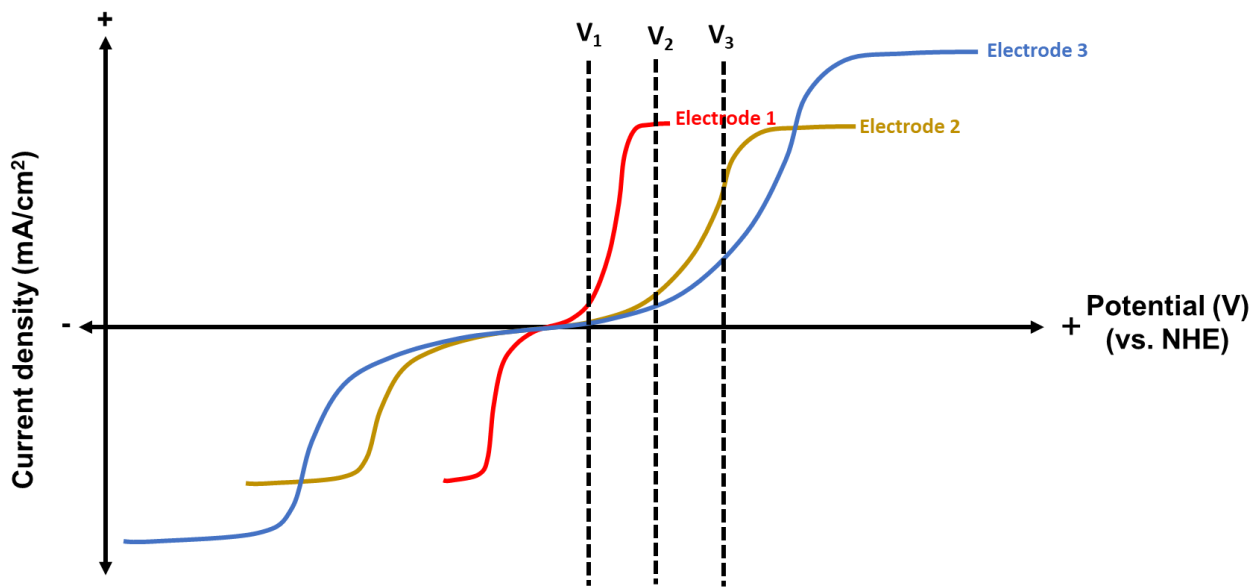
- (c) Silver is deposited in an electrochemical cell from a solution of AgNO_3 in 1 M HNO_3 at 25 °C. If the cell operates at 50% of the limiting current density, calculate the total (activation + concentration) cathodic overpotential at this current density. Given $j_{\text{lim}} = 200 \text{ A m}^{-2}$; $j^\circ = 5 \text{ A m}^{-2}$; $\alpha = 0.5$.

Exercise 2:

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



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



Assume $|j_{lim,a}| = |j_{lim,c}| = 2 \text{ A/m}^2$ for Electrodes 1 and 2, and $|j_{lim,a}| = |j_{lim,c}| = 2.5 \text{ A/m}^2$ for Electrode 3. At an applied potential of $V_1 = 0.03 \text{ V}$, we observe a net current density of $j = 0.3 \text{ A/m}^2$ for Electrode 1 and $j = 0.02 \text{ A/m}^2$ for Electrode 3. Assume $\alpha_a = 0.5$ 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 $j^\circ = 0.2 \text{ mA/cm}^2$ for Electrode 1 and $j^\circ = 0.1 \text{ mA/cm}^2$ for Electrode 3 for the following parts).
- (c) Assume $j^\circ = 0.1 \text{ A/m}^2$ 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).