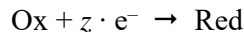


PSI Electrochemistry Resources

Derivation of Expression for Concentration Overpotential

We consider the generic electrochemical reaction



The Nernst equation (for a half-cell reaction) states:

$$E = E^\circ + \frac{RT}{zF} \ln\left(\frac{a_{\text{ox}}}{a_{\text{red}}}\right) \quad (1)$$

The reactant 'Ox' is characterized by its concentration c at the electrode surface. We consider now the Nernst potential of the electrode for case 1 when the concentration at the electrode corresponds to the concentration in the bulk c^∞ :

$$E_1 = E^\circ + \frac{RT}{zF} \ln\left(\frac{c^\infty / c_0}{a_{\text{red}}}\right) \quad (2)$$

where we have replaced the activity a by the concentration c / c_0 ($c_0 = 1 \text{ mol/L}$). In case 2, the concentration of the reactant 'Ox' at the surface of the electrode is $c_{x=0}$:

$$E_2 = E^\circ + \frac{RT}{zF} \ln\left(\frac{c_{x=0} / c_0}{a_{\text{red}}}\right) \quad (3)$$

The concentration overpotential η_c is given by the difference in equilibrium potential between the two cases 1 and 2:

$$\eta_c = E_1 - E_2 = \frac{RT}{zF} \ln\left(\frac{c^\infty / c_0}{a_{\text{red}}}\right) - \frac{RT}{zF} \ln\left(\frac{c_{x=0} / c_0}{a_{\text{red}}}\right) = \frac{RT}{zF} \ln\left(\frac{c^\infty}{c_{x=0}}\right) = -\frac{RT}{zF} \ln\left(\frac{c_{x=0}}{c^\infty}\right) \quad (4)$$

Rearrangement yields

$$\frac{c_{x=0}}{c^\infty} = \exp\left(-\frac{zF}{RT} \eta_c\right) \quad (5)$$

From the lecture slides we note that the current of the reaction is given by

$$i = zFD\left(\frac{c^\infty - c_{x=0}}{\delta}\right) \quad (6)$$

Inserting the expression for $c_{x=0}$ from equation 5, we obtain:

$$i = zFD\left(\frac{c^\infty}{\delta} - \frac{c^\infty}{\delta} \exp\left(-\frac{zF}{RT} \eta_c\right)\right) \quad (7)$$

The limiting current density is (cf. lecture slides)

$$i_{\text{lim}} = zFD\frac{c^\infty}{\delta} \quad (8)$$

Hence, insertion of (8) in (7) yields



$$i = i_{\text{lim}} \left(1 - \exp\left(-\frac{zF}{RT} \eta_c\right) \right) \quad (9)$$

We solve for the concentration overpotential η_c and obtain:

$$\eta_c = -\frac{RT}{zF} \cdot \ln\left(1 - \frac{i}{i_{\text{lim}}}\right) \quad (10)$$

Since $i < i_{\text{lim}}$, $\eta_c > 0$.