PSI Electrochemistry Resources

Derivation of Expression for Concentration Overpotential

We consider the generic electrochemical reaction

$Ox + z \cdot e^- \rightarrow Red$

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

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

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^∞:

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

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

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

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

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

Rearrangement yields

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

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

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

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

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

The limiting current density is (cf. lecture slides)

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

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

$$i = i_{\mathrm{lim}}(1 - \exp(-\frac{zF}{RT}\eta_{\mathrm{c}})) \tag{9}$$

We solve for the concentration overpotential η_{c} and obtain:

$$\eta_{\mathrm{c}} = -\frac{RT}{zF} \cdot \ln(1 - \frac{i}{i_{\mathrm{lim}}}) \tag{10}$$

Since $i < i_{\mathrm{lim}}$, $\eta_{\mathrm{c}} > 0$.