PSI Electrochemistry Resources

Combined Activation & Concentration Overpotential

Electrode reaction with mixed activation overpotential η_a and concentration overpotential η_{conc}.

For the sake of simplicity, we consider an anodic reaction in the Tafel regime:

$$i = i_0 \cdot (\frac{c}{c^\infty}) \cdot \exp\left(+ \frac{\eta}{b} \right) \tag{1}$$

where we have introduced the concentration dependence (essentially, it is the exchange current density that is concentration dependent). From the derivation of the concentration overpotential η_c we have the expression

$$\frac{c}{c^\infty} = 1 - \frac{i}{i_{lim}} \tag{2}$$

Inserting into (1) yields

$$i = i_0 \cdot (1 - \frac{i}{i_{lim}}) \cdot \exp\left(+ \frac{\eta}{b} \right) \tag{3}$$

With the expression for current density i_{ct} in the absence of a concentration gradient

$$i_{ct} = i_0 \cdot \exp\left(+ \frac{\eta}{b} \right) \tag{4}$$

we obtain

$$i = (1 - \frac{i}{i_{lim}}) \cdot i_{ct} = i_{ct} - \frac{i_{ct}}{i_{lim}} \cdot i \tag{5}$$

Dividing by ($i_{ct} \cdot i$) and rearranging yields the final expression

$$\frac{1}{i} = \frac{1}{i_{ct}} + \frac{1}{i_{lim}} \tag{6}$$