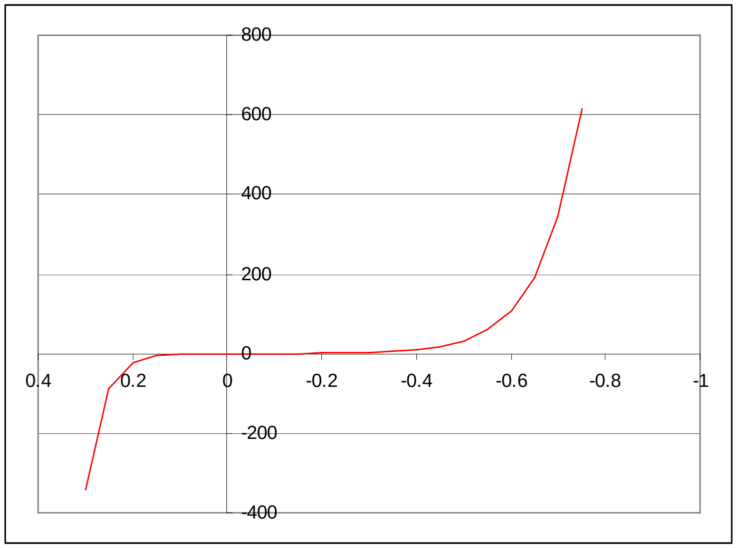
Chapter 3: Problem solutions

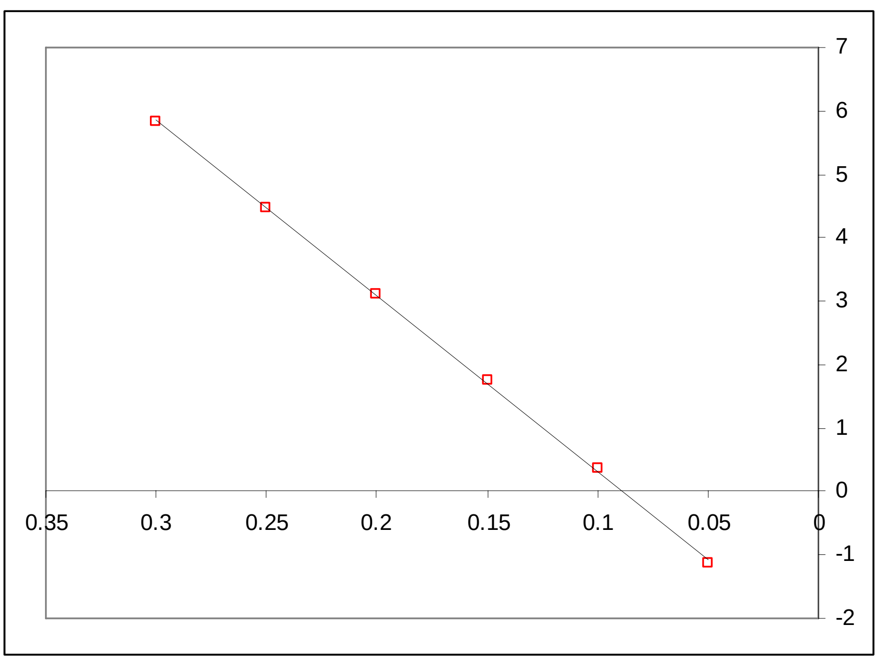
3.1 a. $$j_o = \frac{i_o}{A} = nFk^oC = (1\frac{eq}{mole})(96500\frac{C}{eq})(10^{-7}\frac{cm^2}{\sec})(10^{-6}\frac{mole}{cm^3})$$

$J_o = 9.65x10^{-9}$ A/cm^2

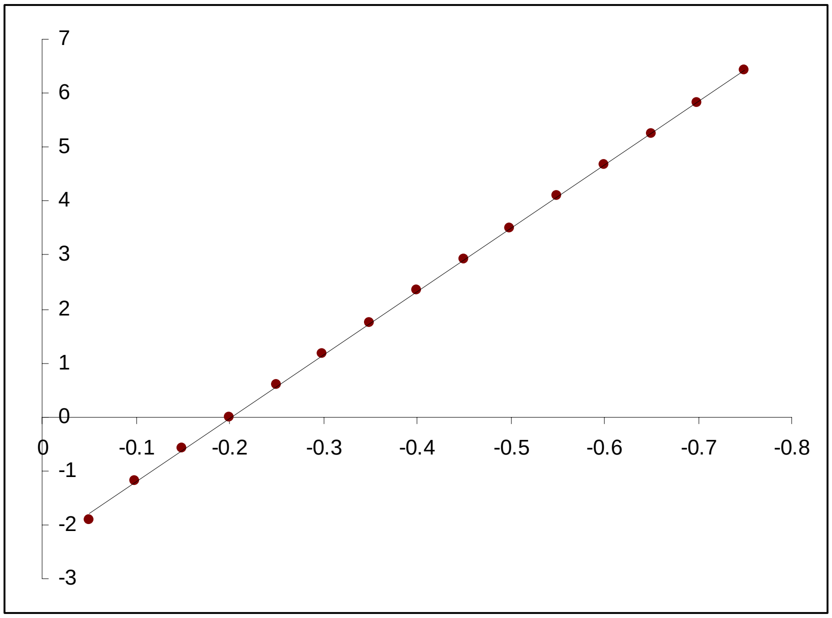
b.



c. Anodic Branch



Cathodic Branch



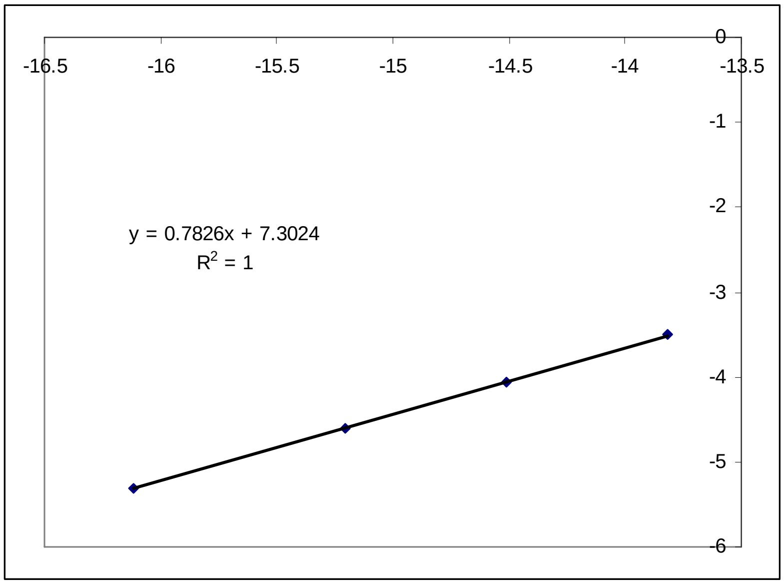
3.7 $$j_o = \frac{i_o}{A} = nFk^o C_O^{*(1-\alpha)} C_R^{*,\alpha}$$

$$\ln(j_o) = \ln(nFk^o C_O^{*(1-\alpha)} C_R^{*,\alpha})$$

$$\ln(j_o) = \ln(nFk^o C_R^{*,\alpha}) + \ln(C_O^{*(1-\alpha)})$$

$$\ln(j_o) = (1-\alpha)\ln(C_O) + \ln(nFk^o C_R^{*,\alpha})$$

Making a plot of $\ln(C_O)$ *vs.* $\ln(j_o)$ will allow determination of α from the slope, and then k^o from the intercept.

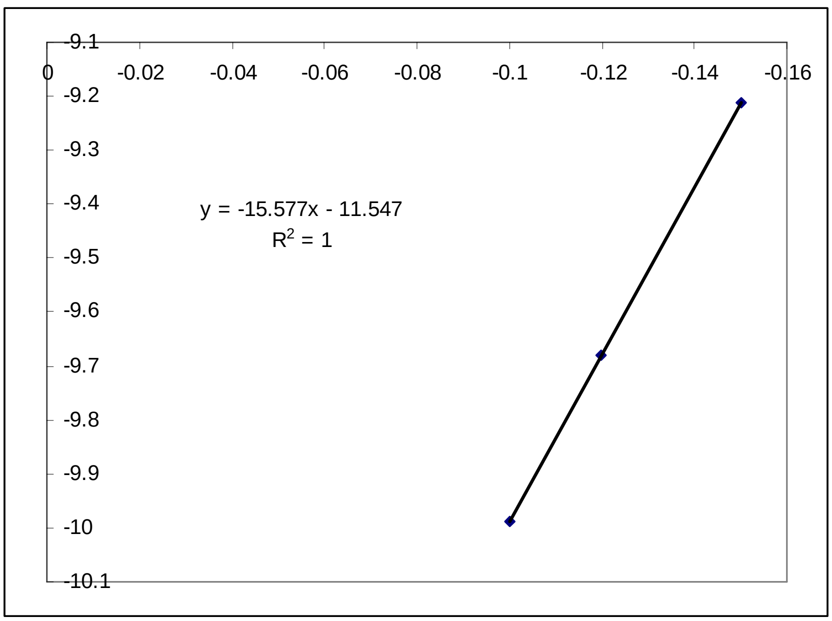


From this analysis, the α is 0.217, and the k_{app}^{o} = 0.378 cm^2/sec. If n_{RDS} is 1, then n' must be 1.

3.11 From this data, determining the i_L is easily determined to be 965 μA. From the concentrations and area of the electrode, the m_o can be determined:

$$i_L = nFAm_oC_O^*$$
$$965x10^{-6}A = \left(\frac{1eq}{mole}\right)\left(\frac{96500C}{eq}\right)(0.1cm^2)m_o\left(\frac{0.01x10^{-3}mole}{cm^3}\right)$$
$$m_o = 0.01cm/\sec$$

The kinetic parameters can be determined from a plot of ln(i) vs. overpotential



The slope = $\frac{-\alpha F}{RT} = -15.577$, and α=0.40

The intercept = ln|i_o| = -11.547, and i_o = 9.66x10^{-6} A

From the exchange current expression, the value of k^o can be determined:

$$i_o = nFAk^oC_O^{*(1-\alpha)}C_R^{*,\alpha}$$
$$9.66x10^{-6}cm^2/\sec = (1)(96500)(0.1cm^2)k^o(0.01x10^{-3}mole/cm^3)^{0.6}(0.01x10^{-3})^{0.4}$$
$$k^o = 1.00x10^{-4}cm^2/\sec$$