3.53 Model Solutions to Test 1 2001

1. (a) $i = i_0 \exp(-\alpha n f \eta)$

$\therefore \ln i = \ln i_0 - \frac{\alpha n F}{RT}(\mathcal{E} - \mathcal{E}^{eq})$

from Fig. 3.4.5, $\mathcal{E}^{eq} = 1.62\ V$
for $C_{Mn^{4+}} = 10^{-2}\ M$ & $C_{Mn^{3+}} = 10^{-2}\ M$ $\quad A = \pi\left(\frac{0.08}{2}\right)^2 = 5.03\times10^{-3}\ cm^2$

$\mathcal{E}$	log j	$\mathcal{E}-\mathcal{E}^{eq}$	j	i	ln i
1.60	−4.75	−0.02	1.78×10^{-5}	8.95×10^{-8}	−16.23
1.40	−4.00	−0.22	1.00×10^{-4}	5.03×10^{-7}	−14.50
1.20	−2.90	−0.42	1.26×10^{-3}	6.33×10^{-6}	−11.97

fit ln i vs $(\mathcal{E}-\mathcal{E}^{eq}) \Rightarrow \ln i = -16.58 - 10.65(\mathcal{E}-\mathcal{E}^{eq})$

$\Rightarrow i_0 = \exp(-16.58) = 6.32\times10^{-8}\ A$

to get i_0 for $C_{Mn^{4+}} = 0.4\ M$ and $C_{Mn^{3+}} = 0.353\ M$, we must get to k_0 first

$$k_0 = \frac{i_0}{AnFC_O^{1-\alpha}C_R^{\alpha}} = \frac{6.32\times10^{-8}}{(5.03\times10^{-3})(1)(96485)\left(\frac{10^{-2}}{10^3}\right)^{1-0.24}\left(\frac{10^{-2}}{10^3}\right)^{0.24}}$$

$= 1.30\times10^{-5}\ cm/s$

now i_0 when $C_{Mn^{4+}} = 0.4\ M$ and $C_{Mn^{3+}} = 0.353\ M$:

$$i_0 = nFAk^0 C_O^{1-\alpha} C_R^{\alpha}$$
$$= (1)(96485)(5.03\times10^{-3})(1.30\times10^{-5})\left(\frac{0.4}{10^3}\right)^{0.76}\left(\frac{0.353}{10^3}\right)^{0.24}$$
$$= 2.45\times10^{-6}\ A$$

b) plateau in current density at $\approx \log j \approx -2.4$

$\therefore j_l \approx 10^{-2.4} = 3.93 \times 10^{-3}\ A/cm^2$

c) at small η, $i - \eta$ is linear and $i = -\frac{i_o F}{RT}\eta$

$$\therefore \eta = \frac{RT}{F}\frac{i}{i_o} = \frac{RT}{F}\frac{3.53\, i_o}{i_o}$$

$$= \frac{8.314 \times 298}{96485} \times 3.53 = 90.6\ mV$$

d) assume $10^{-4}\ A/cm^2$ is "large" $\therefore$ neglect back rxn

from Fig. 3.4.5, $E = 1.4\ V$ when $j = 10^{-4}\ A/cm^2$

$\therefore \eta = E - E^{eq} = 1.4 - 1.62 = -0.22\ V$

This is for **reduction** of $Mn^{4+} \rightarrow Mn^{3+}$

what about **oxidation** of $Mn^{3+} \rightarrow Mn^{4+}$?

for oxidation $\eta = \frac{RT}{(1-\alpha)F}\ln i_o - \frac{RT}{(1-\alpha)F}\ln i$

for reduction $i = i_o e^{-\alpha f \eta}$ at large η

for oxidation $i = i_o e^{(1-\alpha)f\eta}$

for identical value of i, η scales as follows

$$i = i_o e^{-\alpha f \eta} = i_o e^{(1-\alpha)f\eta}$$

$$\Rightarrow -\alpha f \eta_c = 1 - \alpha f \eta_a \Rightarrow \eta_a = -\frac{\alpha}{1-\alpha} = \frac{-0.24}{0.76}$$

$$\therefore \eta_a = (-0.316)(-0.22) = 69\ mV$$

2. (a) $R_{ct} = \dfrac{RT}{nFi_0}$ $\qquad i_0 = nFAk^\circ C_0^{1-\alpha}$

- from data set we can determine k° and α
- use $i/i_d = F_1(\lambda) \xrightarrow{\text{Fig. 5.52}} \lambda$, where $\lambda = k_f t^{1/2} / D_0^{1/2}$
- you know $t = \tau$ and D_0 is given $\Rightarrow$ get k_f
- since $k_f = k^\circ \exp\left\{-\dfrac{\alpha n F}{RT}(E - E^{\circ\prime})\right\}$

fit $\ln k_f$ vs $E - E^{\circ\prime}$ $\qquad k_f = \lambda\left(\dfrac{6.66\times10^{-5}}{3.53}\right)^{1/2} = 4.34\times10^{-3}\lambda$

i/i_d	λ	k_f	$\ln k_f$	$E - E^{\circ\prime}$
0.1	0.06	2.61×10^{-4}	−8.25	−0.141
0.3	0.22	9.56×10^{-4}	−6.95	−0.191
0.7	0.78	3.39×10^{-3}	−5.69	−0.216
0.9	1.95	8.47×10^{-3}	−4.77	−0.239

by least squares, $\ln k_f = -13.43 - 35.65(E - E^{\circ\prime})$

$\therefore \ln k^\circ = -13.43 \Rightarrow k^\circ = 1.47\times10^{-6}$ cm/s

$\therefore i_0 = (1)(96485)(0.01)(1.47\times10^{-6})\left(\dfrac{3.53\times10^{-3}}{10^3}\right)^{(1-0.915)}$

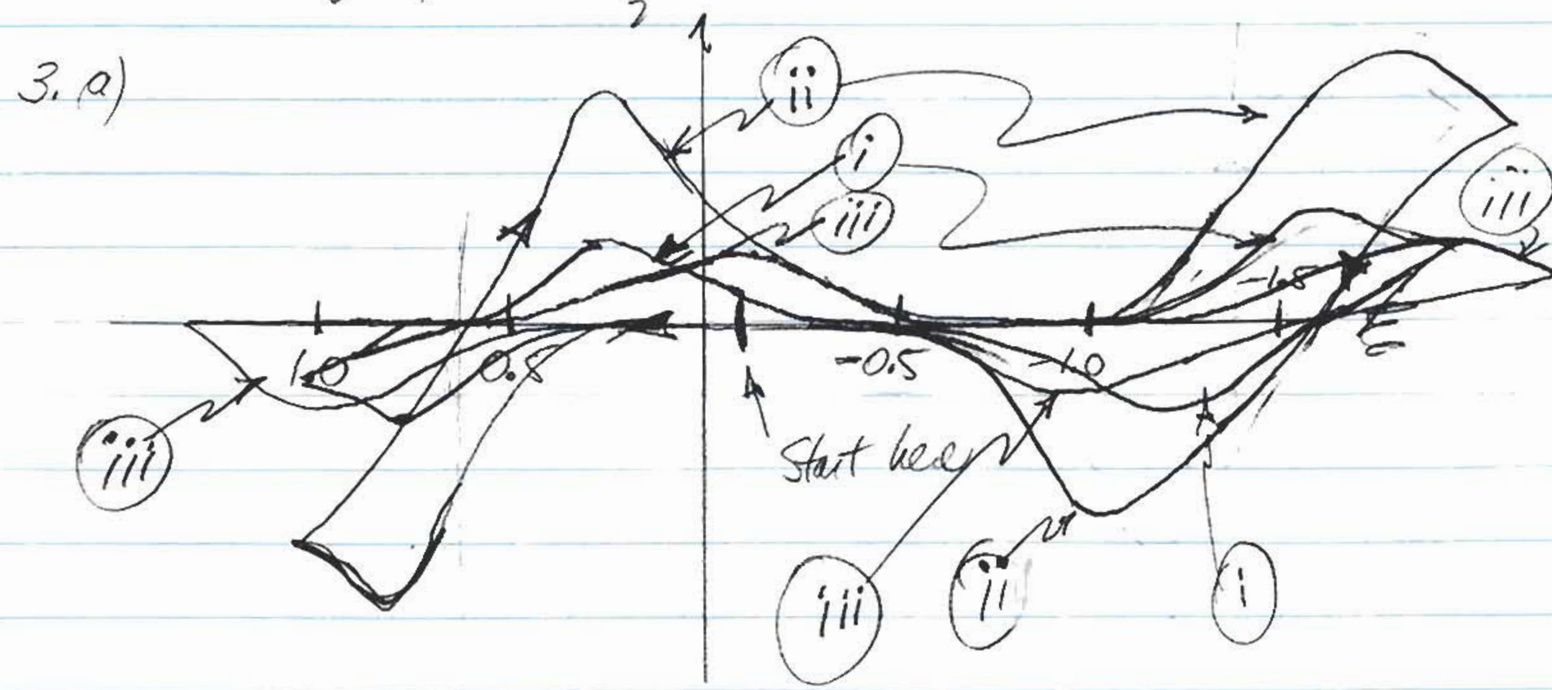
$-\dfrac{\alpha n F}{RT} = -35.65 \Rightarrow \alpha = \dfrac{35.65\,RT}{nF} = \dfrac{(35.65)(8.314)(298)}{(1)(96485)} = 0.915$

$i_0 = 4.88\times10^{-4}$ A

$$\therefore\ R_{ct} = \frac{(8.314)(298)}{(1)(96485)(4.88\times10^{-4})} = 53\ \underline{\Omega}$$

(b) – look at Fig. 5.5.2 ⇒ as $\lambda \to \infty$, $i/i_d \to 1$
– choose $\lambda = 10$ & get value of k_f
– using k_f in eq. 5.5.27 gives i_d at $\tau = 3.53$ s

3. (a)



(b) – WE material affects binding energy of electron & hence facility to transfer it to reacting species
– facility of redox couple influenced by chemical composition & microstructure (e.g., polyxtal, single xtal, glassy)