Q-1
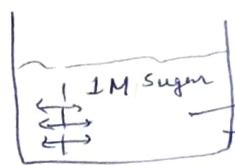
1> Diffusion :→ Due to Conc^n gradient of ions in solution

$$j_i = -D \frac{\partial c_i}{\partial x}$$

Migration : due to electrostatic potential gradient in electrolyte

molar flux due to migration $= -z_i u_i F c_i \nabla \phi$

2> Self Diffusion Coeff

when there is no net diffusion of molecules (Uniform sol^n).

Uniform sol^n
No net diffusion

But there is ~~some~~ random movement of molecules, resulting in self diffusion coefficient.
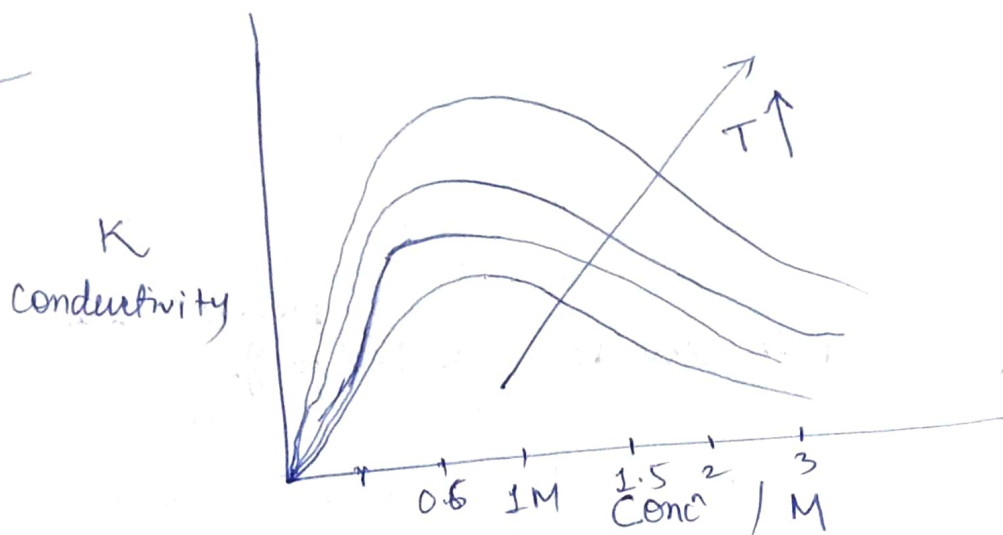
Chemical diffusion coeff

Due to net diffusion of molecules in solution (due to Conc^n gradient)

$$D_{Chemical} = D_{self} \left(1 + \underbrace{\frac{d \ln f_+}{d \ln c_+}}_{} \right)$$

Thermodynamic factor

fick's law uses chemical diffusion coefficient.

(3)

K
Conductivity

0.6 1M 1.5 2 3
         Conc° / M

---

(4) KCl is commonly used because transference no. is nearly 0.5 $[t_+ = 0.49, \quad t_- = 0.51]$ hence the junction potential is zero (or near 0)

---

(5) $t_+ \rightarrow$ fraction of current carried by '+ve' ion, when there is no conc^n gradient.

$t_+ = 1 \longrightarrow$ Nafion Membrane
                     Solid State Electrolyte with fixed or immobile -ve ions.

$t_+ = 0$ Anion exchange membrane (+ve ions are immobile)

---

(6) Thermodynamic factor,

$$= 1 + \frac{d\ln f_\pm}{d\ln c}$$

$f \rightarrow$ fugacity of ion in solution

$c \rightarrow$ conc° of ion

(7) We prefer PEIS because, we want a fixed voltage of battery while doing EIS. If we do GIEIS, effectively we are charging or dis charging the cell & potential im most Battery will drift due to ocv ($f.(soc)$). Perturbation is kept small because to maintain linearity of the system. ($I \propto V$). It ensures accurate and reliable impedance measurement.

(8) Cottrell Eqn,

describes time dependent current response of a system under diffusion controlled condition after a potential step is applied at a planar electrode.

(9)

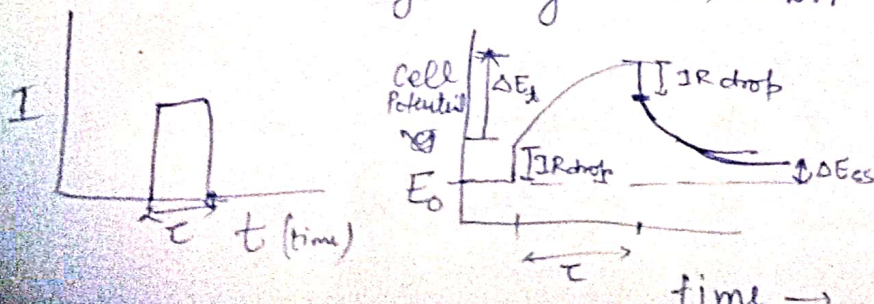$$i(t) = \frac{nFAc^{\circ}\sqrt{D}}{\sqrt{\pi t}}$$

→ bulk conc^n of electroactive species ($\frac{mol}{cm^3}$)

→ Diff. Coff (cm^2/s)

A → Electrode Area (cm^2),

(9)

$$i(t) \propto \frac{1}{\sqrt{t}}$$

(10) GITT Protocol →

Small current pulse applied for a short duration, followed by long relaxation period

$$D = (\quad)\left(\frac{\Delta E_t}{\Delta E_{ss}}\right)^2$$

Diffusion Coeff
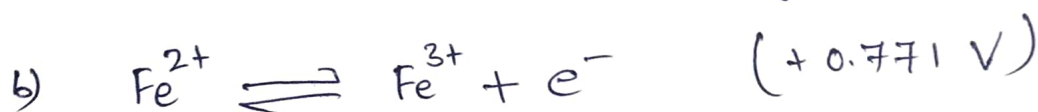
Q② Pourbaix Diagram , (E vs PH)

a) $Fe \rightleftharpoons Fe^{2+} + 2e^-$ $(-0.44 v)$

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{[Fe^{2+}]}{a_{Fe}} \right)$$

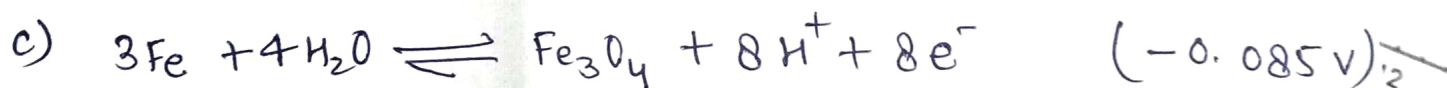$$= -0.44 - \frac{0.0591}{n} \log \left(\frac{1}{[Fe^{2+}]} \right)$$

∵ $[Fe^{2+}] = 1 M$, $\log 1 = 0$

∴ $E = -0.44 V$ { Horizontal line)

b) $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ $(+0.771 V)$

$$E = 0.771 + \frac{0.0591}{1} \log \left(\frac{[Fe^{3+}]}{[Fe^{2+}]} \right)$$

$E = 0.771 V$ { Horizontal line }

c) $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 8H^+ + 8e^-$ $(-0.085 v)_{\overline{2}}$

$$E = -0.085 - \frac{0.0591}{8} \log \left([H^+]^8 \right)$$

$E = -0.085 - 0.0591 pH$

sloped line { slope $= -0.0591$ }
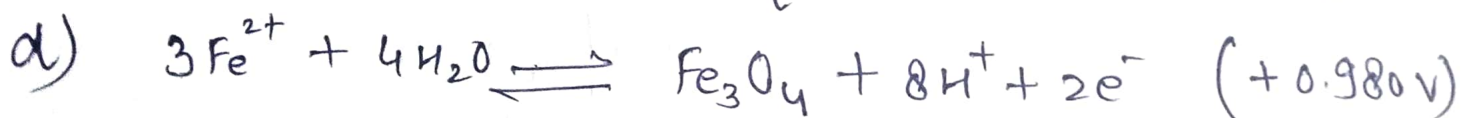
d) $3Fe^{2+} + 4H_2O \rightleftharpoons Fe_3O_4 + 8H^+ + 2e^-$ $(+0.980 v)$

$$E = 0.980 - \frac{0.0591}{2} \log \left(\frac{1}{[H^+]^8} \right)$$

$$= \underset{\text{Intercept}}{0.980} - \underset{\text{slope}}{0.2364} pH$$

sloped line

e)

$$2 Fe^{2+} + 3H_2O \rightleftharpoons Fe_2O_3 + 6H^+ + 2e^- \qquad (+0.728v)$$

$$E = 0.728 - \frac{0.0591}{2} \log\left(\frac{1}{[H^+]^6}\right)$$

$$E = \underset{\text{Intercept}}{0.728} - \underset{\text{slope}}{0.1773} \, pH$$

f)
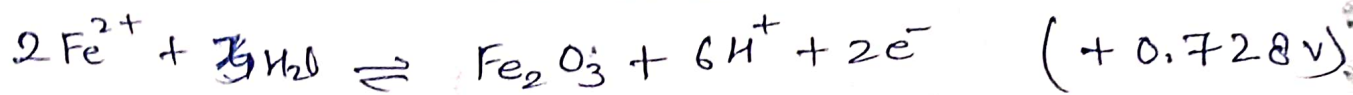
$$2 Fe^{3+} + 3H_2O \rightleftharpoons Fe_2O_3 + 6H^+$$

we will find the potentials using eq(b) & eq(e)

$$2 \times \left(Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \right) \longrightarrow (\Delta G_1) \qquad (+0.771V)$$

$$2Fe^{2+} + 3H_2O \rightleftharpoons Fe_2O_3 + 6H^+ + 2e^- \rightarrow (\Delta G_2) \quad (+0.728\,V)$$

___

$$2 Fe^{3+} + 3H_2O \rightleftharpoons Fe_2O_3 + 6H^+$$
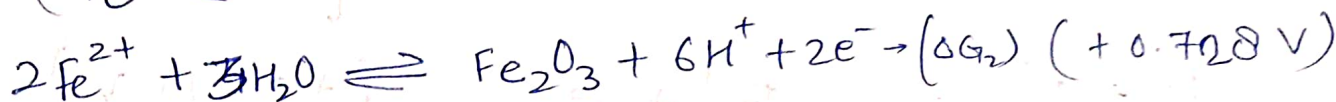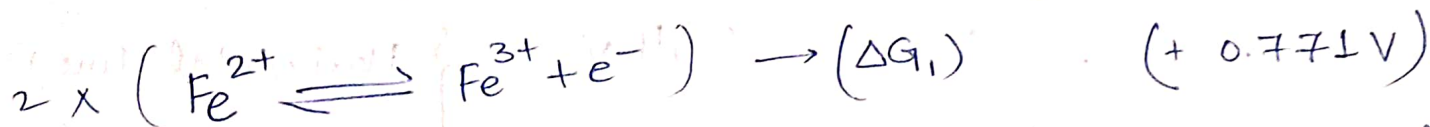
$$\Delta G = \Delta G_2 - 2\Delta G_1$$

$$-2FU^\circ = -\{(0.728 - 2\times0.771)F\}$$

$$-2FU^\circ = -2F\cdot(0.728) - 2\{-1\cdot F(0.771)\}$$

$$U^\circ = +0.043 \ v$$

Solubility ← $K_{sp} = \dfrac{[Fe_2O_3]^1 [H^+]^6}{[H_2O]^3 [Fe^{3+}]^2_1} = [H^+]^6$

Since

$$K_{sp} = e^{\frac{nFU_\theta}{RT}}$$

$$K_{sp} = e^{\frac{2\times 96485 \times (+0.043)}{8.314 \times 298}} = \cancel{}$$

$$K_{sp} = \frac{}{} = [H^+]^6$$

$$[H^+] = \cancel{0.572}\ 1.7475$$

$$PH = -\log[H^+] = 0.242$$

so, we will get a vertical line at

$$PH = -0.242$$

g) $Fe_3O_4 + 3H_2O \rightleftharpoons 3Fe_2O_3 + 2H^+ + 2e^-$ $\qquad (+0.221\ V)$

$$E = +0.221 - \frac{0.0591}{2} \log\left(\frac{1}{[H^+]^2}\right)$$

$$E = 0.221 - 0.0591\ PH$$

h) $3HFeO_2^- \rightleftharpoons Fe_3O_4 + H_2O + OH^- + 2e^-$ $\qquad (-1.819\ V)$

$$E = -1.819 - \frac{0.0591}{2} \log\left(\frac{1}{[OH^-]}\right)$$

$$= -1.819 - 0.02955\ POH$$

$$= -1.819 - 0.02955\ (14 - PH)$$

$$= \cancel{-2.2327} + 0.0295\ PH$$

$$28.47 = \frac{[H^+]^6}{(28.47)^{1/6}}$$

$$[H^+] = (28.47)^{1/6}$$

$$\log^{(1.74)}$$
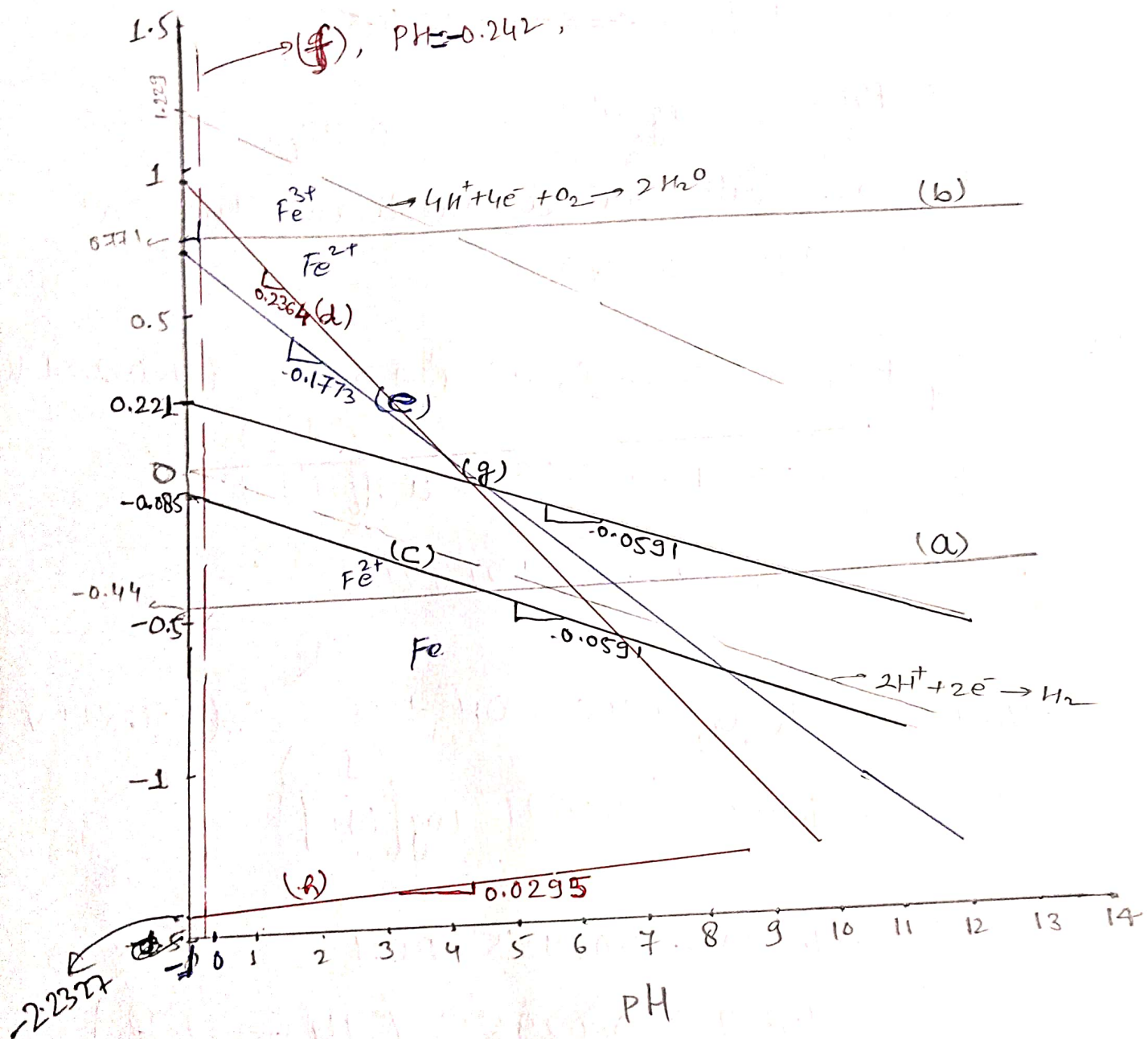
Refer to ppt uploaded for detailed analysis of pourbaix diagram.

③

$$Z_{Q_2} = \frac{1}{(j\omega)^n Q_2}$$

@ Impedance Response

⊗ Note: If it was pure capacitor C, then

$$Z_{cap} = \frac{1}{j\omega C}$$
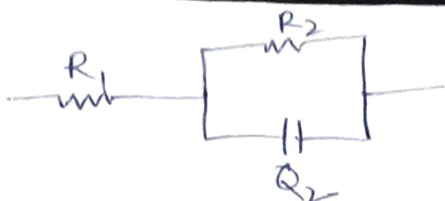
$$Z = R_1 + Z_{parallel}$$

$$Z_1 = R_1$$

$Z_{parallel}$ = parallel sum of R_2 & Z_{Q_2}

$$Z_{Q_2} = \frac{1}{Q_2(j\omega)^n}$$

$$Z_{parallel} = \frac{R_2 \cdot \frac{1}{Q_2(j\omega)^n}}{R_2 + \frac{1}{Q_2(j\omega)^n}}$$

$$\therefore \boxed{Z = R_1 + \frac{R_2 \cdot \frac{1}{Q_2(j\omega)^n}}{R_2 + \frac{1}{Q_2(j\omega)^n}}}$$

where n = constant phase element

$$n \approx 0.8 - 0.95 \quad [n < 1]$$

for pure capacitor, $n = 1$

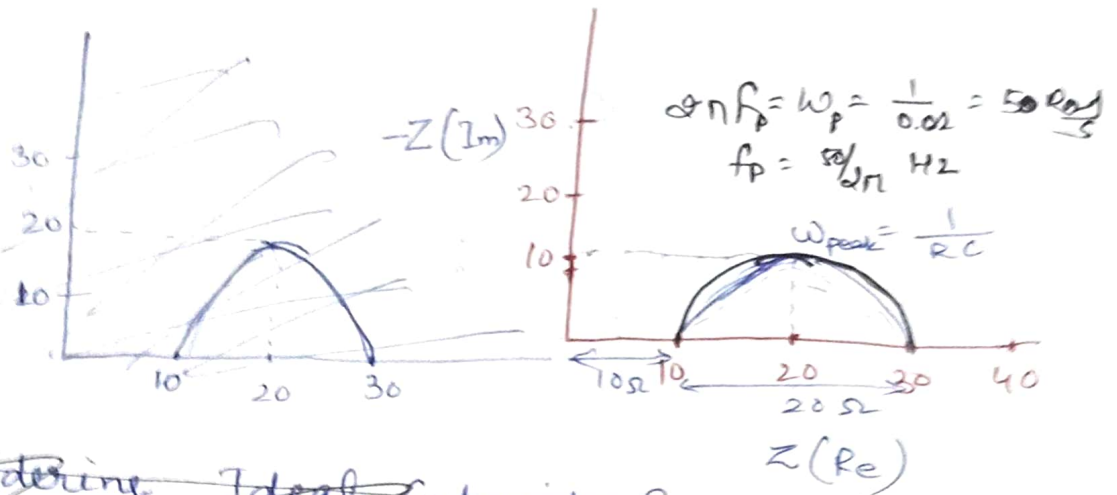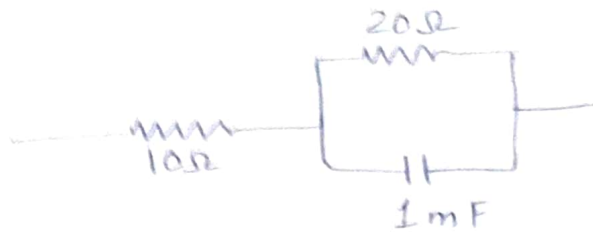ⓑ   At $\omega \to \infty$,   capacitor offers zero impedanc
$$\boxed{Z = R_1}$$ current will $\cancel{\text{be}}$ not flow through R_2

At $\omega = 0$,   capacitor offer ∞ impedance. All
current flow through R_2

$$\boxed{Z = R_1 + R_2}$$

20Ω

10Ω

$1\,mF$

$-Z(I_m)$

36

20

10

10 20 30

$2\pi f_p = W_p = \dfrac{1}{0.02} = 50\,\text{rad/s}$

$f_p = \dfrac{50}{2\pi}\ H_z$

$W_{peak} = \dfrac{1}{RC}$

10Ω 10 20 30 40

20Ω

$Z(Re)$

~~ponse plotted is~~ considering ~~Ideal capacitor~~ $[\,Q = C \,, \quad n = 1\,]$

~~for Real capacitor~~ ~~[n < 1]~~, ~~coordinate of~~

peak frequency ~~will be less than 10~~

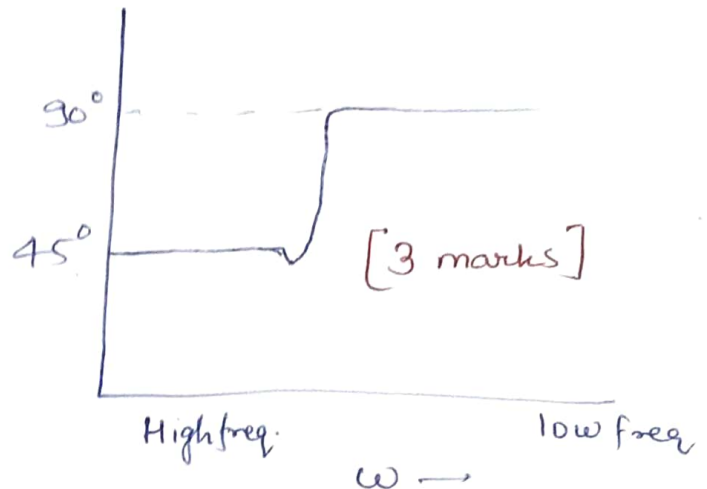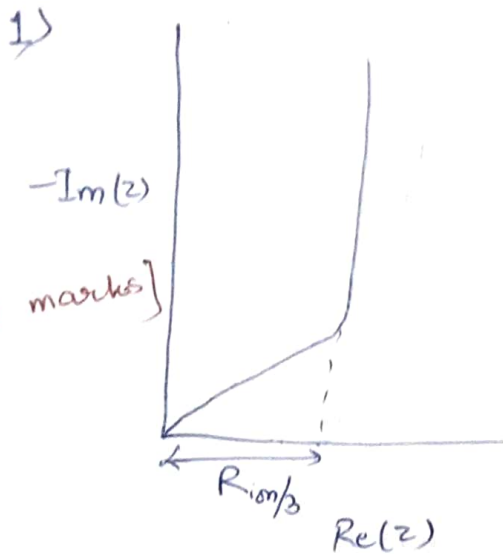depending on value of n $f_p = \dfrac{50}{2\pi} = 7.9577$

(d) Time Constant :

$$\tau = R_2 \times Q_2$$

$$= 20\Omega \times 1\,mF$$

$$= 20\ mS$$

$$\boxed{\tau = 0.02\ S}$$

1)

for derivation, Refer Quiz ③ Question 1 solution
uploaded on Moodle

[10 marks for derivation]

$$Z = \frac{R_{ion} \coth \sqrt{i\omega R_{ion} C_{dl}}}{\sqrt{i\omega R_{ion} C_{dl}}}$$

$-Im(z)$

[marks]

$R_{ion}/3$

$Re(z)$

$90°$

$45°$

[3 marks]

High freq.   low freq

$\omega \longrightarrow$

Bode Plot

At $\omega \to \infty$, $\coth\left(\sqrt{i\omega R_{ion} C_{dl}}\right) \approx 1$

$$Z = \frac{R_{ion} \coth \sqrt{i\omega R_{ion} C_{dl}}}{\sqrt{i\omega R_{ion} C_{dl}}}$$

$$Z = \sqrt{\frac{R_{ion}}{\omega C_{dl}}} \cdot \frac{1}{\sqrt{i}}$$

[3 marks]

$$Z_{\omega \to \infty} = \sqrt{\frac{R_{ion}}{\omega C_{dl}}} \cdot \frac{1}{\sqrt{2}} (1-i)$$

$45°$ line behaviour

At $\omega = 0$

$$\coth(x) = \frac{1}{x} + \frac{x}{3} + \cdots$$

[2 marks]

$$Z = \frac{R_{ion}}{\sqrt{i\omega R_{ion} C_{dl}}}\left[\frac{1}{\sqrt{i\omega R_{ion} C_{dl}}} + \frac{\sqrt{i\omega R_{ion} C_{dl}}}{3} \cdots\right]$$

$$= \frac{R_{ion}}{i\omega R_{ion} C_{dl}} + \frac{R_{ion}}{3} = \frac{R_{ion}}{3} + \frac{1}{i\omega C_{dl}}$$

($90°$ line, Capacitive

③ → find R_{ion} from Nyquist plot

Make symmetric cell using identical electrodes (same thickness, porosity loading) and a separator. Using blocking electrolyte (No intercalation, $R_{ct} = 0$)

Get Nyquist Response, find $2 \dfrac{R_{ion}}{3}$ (2 identical electrodes)

[5 marks]

$$R_{ion} = \dfrac{d}{A \, K_{eff}} = \dfrac{d}{A \, K \, \dfrac{E}{T}} \quad \begin{array}{l} d \rightarrow \text{thickness of electrode} \\ E \rightarrow \text{porosity} \\ T \rightarrow \text{Tortuosity} \\ K \rightarrow \text{Conductivity of pure electrolyte} \end{array}$$

↙ Area of electrode

Note : thickness (d) is of electrode only [excluding cu foil]

Q.⟨5⟩

ⓐ From plot given,

$i \approx 180 \ A/m^2$

Ourpotential $\approx 0.5 \ V$

[5 marks]

$$\underset{[A]}{i} = \underset{[F]}{C_{de}} \times \underset{[V/s]}{\nu}$$
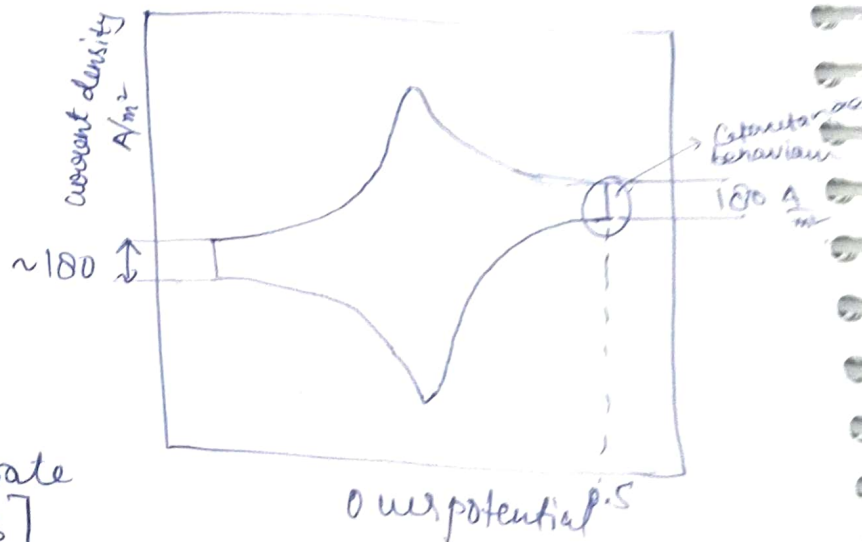
↙ ↓ scan rate

scan rate is needed for Calculation of areal Capacitance $\left[\dfrac{F}{m^2}\right]$ of Since scan rate not given Everyone who attempted it nicely, will get full marks

(b)

$$\Delta E_p \simeq \frac{0.059}{n}$$

$$n = \frac{0.059}{0.058} \simeq 1$$

$$\boxed{n = 1}$$

(6) $\quad \dfrac{\partial c}{\partial t} = D \dfrac{\partial^2 c}{\partial x^2} \quad\underline{\hspace{1cm}}$ ⓪

$\quad$ Let $\eta = \dfrac{x}{g(t)} \quad\underline{\hspace{1cm}}$ ①

$\quad \dfrac{\partial c}{\partial t} = \dfrac{\partial c}{\partial \eta}\dfrac{\partial \eta}{\partial t} \;=\; \dfrac{-x\,g'}{g^2}\dfrac{\partial c}{\partial \eta} \quad\underline{\hspace{1cm}}$ ②

$\quad \dfrac{\partial c}{\partial x} = \dfrac{\partial c}{\partial \eta}\cdot\dfrac{\partial \eta}{\partial x} \;=\; \dfrac{1}{g}\dfrac{\partial c}{\partial \eta}$

$\quad \dfrac{\partial^2 c}{\partial x^2} = \dfrac{1}{g^2}\dfrac{\partial^2 c}{\partial \eta^2} \quad\underline{\hspace{1cm}}$ ③

② & ③ $\longrightarrow$ ⓪

$\therefore \quad \dfrac{-x g'}{g^2}\dfrac{\partial c}{\partial \eta} = \dfrac{D}{g^2}\dfrac{\partial^2 c}{\partial \eta^2}$

$\quad \dfrac{\partial^2 c}{\partial \eta^2} + \dfrac{x g'}{D}\dfrac{\partial c}{\partial \eta} = 0$

$\quad x = \eta\, g \quad\longrightarrow$ from eqn ①

$\quad \dfrac{\partial^2 c}{\partial \eta^2} + \dfrac{\eta g g'}{D}\dfrac{\partial c}{\partial \eta} = 0$

Let $\quad \dfrac{g g'}{D} = C_1$

$\boxed{\dfrac{\partial^2 c}{\partial \eta^2} + \eta C_1 \dfrac{\partial c}{\partial \eta} = 0}$

Let $\quad \dfrac{\partial c}{\partial \eta} = \phi \qquad\Rightarrow\qquad \boxed{\dfrac{\partial \phi}{\partial \eta} + \eta C_1\, \phi = 0}$

$\qquad\qquad \displaystyle\int \dfrac{\partial \phi}{\phi} = -\int \eta\, C_1\, \partial \eta$

$\qquad\qquad \ln \phi = -C_1 \dfrac{\eta^2}{2} + \ln C_2$

at $\eta=0$ $\phi=0$ $\rightarrow$ $C_2=0$

$\qquad\qquad \phi = C_2\, e^{-C_1 \eta^2/2} \qquad\Rightarrow\qquad \boxed{\dfrac{dc}{d\eta} = C_2\, e^{-C_1 \eta^2/2}}$

$$erf(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-\eta^2} d\eta$$

comparing: $\quad c_2 = \frac{2}{\sqrt{\pi}} \quad , \quad c_1 = 2$

$$\therefore \quad \frac{c - c_\infty}{} $$

$$\boxed{c = c_\infty \, erf(\eta^2)'}$$ [5 marks] {For full derivation}

Those who have only shown steps from Fuller, will get 2 marks

(B) $\quad g g' = \frac{1}{2}(g^2)' = D c_1$

$\qquad (g^2)' = 2 D c_1$

$\qquad\qquad g^2 = 2 D c_1 t + c_3 = 4 D t + c_3$

$\qquad\qquad$ at $\quad t = 0, \quad g = 0 \quad \therefore c_3 = 0$

$\qquad\qquad g = \sqrt{4 D t} = 2\sqrt{D t}$

[5 marks]

$$\boxed{c = c_\infty \, erf(\eta^2)} = c_0 \, erf\left(\frac{x^2}{4 D t}\right)$$

(C)

(c) System will not reach steady state
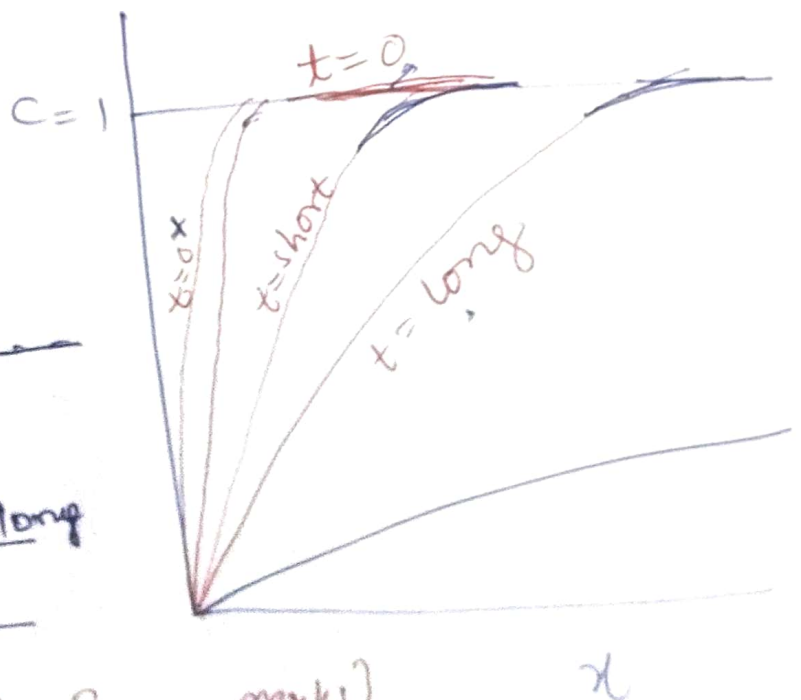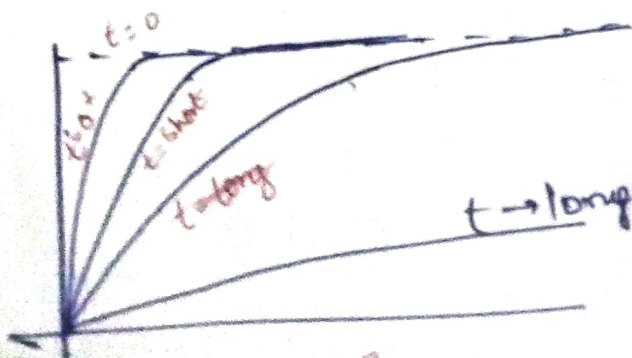
[3 + 2 marks] → for S.S. answer

$$J = D \frac{dc}{dx}$$

$$\frac{i}{nF} = D \cdot \frac{1}{g} \frac{dc}{d\eta}$$

$$i = \frac{Dnf}{g} \frac{dc}{d\eta}\Big|_{\eta=0}$$

$$= \frac{Dnf}{g} \, c_\infty \, \frac{d}{d\eta}\left(\text{erf}(\eta^2)\right)\Big|_{\eta=0}$$

$$= \frac{Dnf}{2\sqrt{Dt}} \, c_\infty \cdot \frac{2}{\sqrt{\pi}}$$

$$\boxed{i = \frac{nF\sqrt{D}\,c^\infty}{\sqrt{\pi t}}} \qquad [5\ \text{marks}]$$

(7) @ At 100% SOC $\quad \left(\begin{array}{l}\text{Anode @ } x=0.9 \\ \text{Cathode @ } y=0.5\end{array}\right)$

Anode ≈ 0.07 V

Cathode $= 4.2$ $\qquad\qquad$ [2 marks]

$V_{cell} = 4.2 - 0.07 = 4.13$ V

(b) At 0% SOC

Anode $(x = 0.1) = 0.2$ V

Cathode $(y = 0.98) = 3.59$ V

$V_{cell} = 3.59 - 0.2 \approx 3.39$ V

$\qquad\qquad$ [3 marks]

(c)

At 50% SOC

Anode ~~range~~ $x = 0.1 - \boxed{0.9}$
Cathode: $y = 0.98 + 0.5$ → 0% SOC

At 50% SOC

$$y_{\text{cathode}} = 0.5 + \frac{0.48}{2} = \underline{0.74}$$ → 2 marks

Cathode potential = 3.8 V

$$(\because \Delta y \, 0 - 100\% = 0.48 \quad (0.98 - 0.5))$$

$$\text{Anode}, x = 0.1 + \frac{0.8}{2} = \underline{0.5}$$ → 2 marks

$$(\because \Delta x \, (0 - 100\%) = 0.8)$$

Anode potential = 0.1 V

$$V_{\text{cell}} @ 50\% SOC = \underset{3.8 \rightarrow 0.1}{\underline{0.74 - 0.5 = 0.24 V}} = \underline{3.7 V}$$ → 1 mark

d) ← 4.13 — 1 mark

Voltage [2 marks] ← 3.7

2 marks ~ 3.4

4.2

100%   50%   0%
SOC
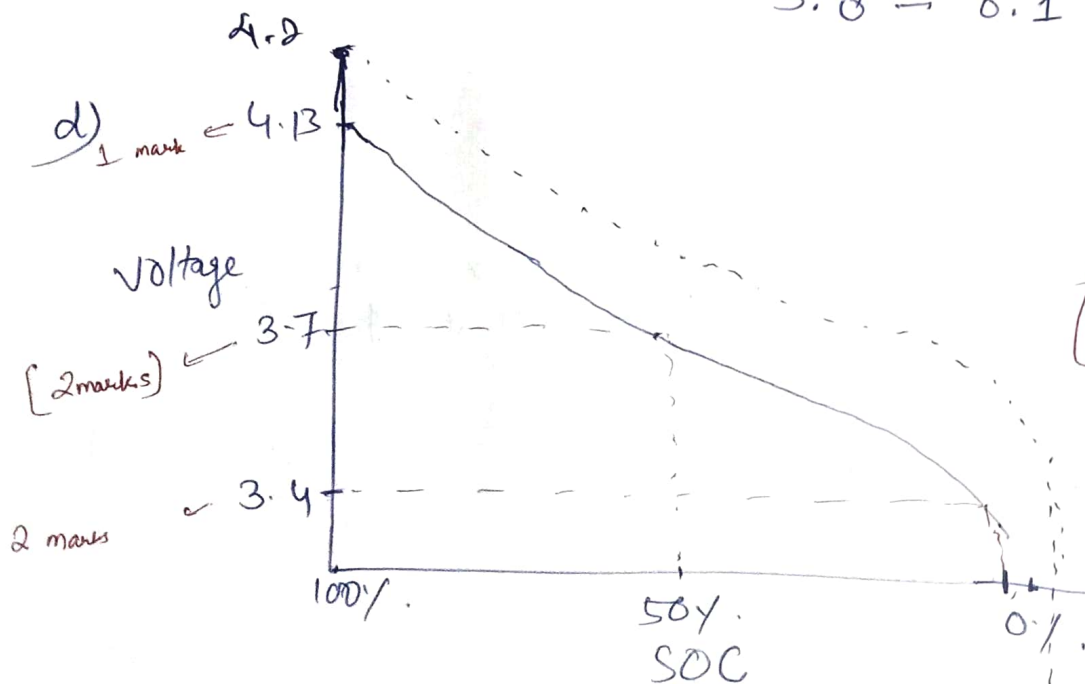
[5 Total marks]

(e)

At 0% SOC, Anode = 0.2 V
Cathode = 3.59 V

when 50% Anode particles are lost,
charging the battery upto 50% SOC will

correspond to 100% SOC of ~~original~~ Anode $(0.07V)$.
But Cathode will be at 50% SOC $(3.80 V)$ at that time.
Maximum Cell voltage will be, $(3.80 - 0.07 = 3.73 V)$
when we further charge battery (since cathode
is half empty), Anode potential will go down
further and will cross below 0V at some
SOC, and plating will start.

[5 marks]

[3 marks for Plot
2 marks for Plating]