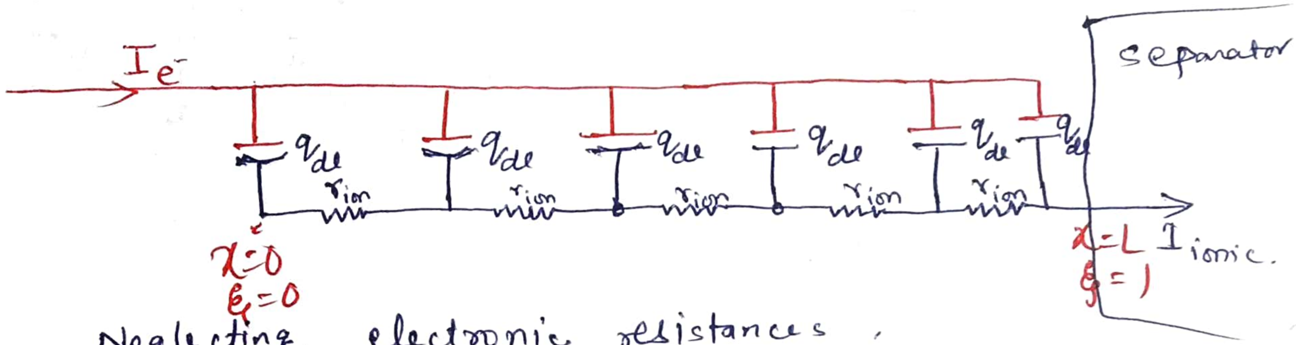
Quiz-3 Solution

Q1

To derive:

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

(a) Transmission line Model:



Neglecting electronic resistances,

b

$$\sum q_{dl} = Q_{dl}$$

$$\sum r_{ion} = R_{ion}$$

(b) Variable: potential across the thickness of electrode.

~~Param~~

(c) Conservation law;
Charge Balance;

Through a resistance r_{ion} Ionic Current (In − Out) = change in Capacitive Current

$$\underbrace{-\frac{\partial}{\partial x}\left\{-K_{eff}\frac{\partial \phi}{\partial x}\right\}}_{A/m^3} = i_{cdl} := c\,\frac{d\phi}{dt}$$

$$c \frac{d\phi}{dt} = K_{eff} \frac{\partial^2 \phi}{\partial x^2}$$

$$\boxed{\frac{d\phi}{dt} = \frac{K_{eff}}{c} \frac{\partial^2 \phi}{\partial x^2}}$$

Non dimensionalize

Let $\xi = \frac{x}{L}$

$$\therefore \frac{\partial \phi}{\partial t} = \frac{K_{eff} A}{A \times C L \times L} \frac{\partial^2 \phi}{\partial \xi^2}$$

$A \times C \times L = Q \longrightarrow$ Total capacitance of electrode

$$\frac{K_{eff} A}{L} = \frac{1}{R_{ion}}$$

$$\therefore \boxed{\frac{\partial \phi}{dt} = \frac{1}{R_{ion} Q} \frac{\partial^2 \phi}{\partial \xi^2}}$$

Boundry Conditions:

At $x = 0$ (Near Current Collector), Ionic flux is zero.

$$-K_{eff} \frac{\partial \phi}{\partial x}\bigg|_{x=0} = 0$$

(1) or

$$-K_{eff} \frac{\partial \phi}{\partial \xi}\bigg| = 0$$

(b) At $x = L$ $(\xi = 1)$ [Near Separator]

$$\phi = 1$$

(d) Laplace Transform

$$L\left\{ \frac{\partial \phi}{\partial t} = \frac{1}{R_{ion} Q} \frac{\partial^2 \phi}{\partial \xi^2} \right\}$$

$$s \Phi = \frac{1}{R_{ion} Q} \frac{d^2 \Phi}{d \xi^2}$$

$$\frac{d^2 \Phi}{d \xi^2} = R_{ion} Q s \Phi$$

$$\frac{d^2 \Phi}{d \xi^2} = S^2 \Phi \qquad [S^2 = R_{ion} Q s$$

$$\Phi = c_1 \cosh[S \xi] + c_2 \sinh[S \xi]$$

(B) $\because \left. \frac{d\Phi}{d\xi} \right|_{\xi = 0} = 0 \Rightarrow \boxed{c_2 = 0}$

$\Phi = 1$ @ $\xi = 1$

$$\therefore 1 = c_1 \cosh[S]$$

$$\boxed{c_1 = \frac{1}{\cosh[S]}}$$

$$\therefore \boxed{\Phi = \frac{\cosh[S \xi]}{\cosh[S]}} \longrightarrow \Phi \text{ in Laplace domain}$$

current in laplace domain,

$$\boxed{I = \frac{A K_{eff}}{L} \frac{d\Phi}{d\xi}}$$

(e) $$Z = \left.\frac{\Phi}{I}\right|_{\xi=1}$$ (in laplace domain)

(f) $$Z = \left.\frac{\frac{\cosh[S\xi]}{\cosh[S]}}{\frac{A K_{eff}}{L}\frac{d\Phi}{d\xi}}\right|_{\xi=1}$$

$$\cancel{Z = \frac{R_{ion}}{S} \cosh}$$

$$\therefore \frac{A K_{eff}}{L}\frac{d\Phi}{d\xi} = \frac{S . A K_{eff}}{L}\frac{\sinh[S\xi]}{\cosh[S]}$$

$$\boxed{\therefore Z = \frac{R_{ion}}{S} \coth[S]}$$

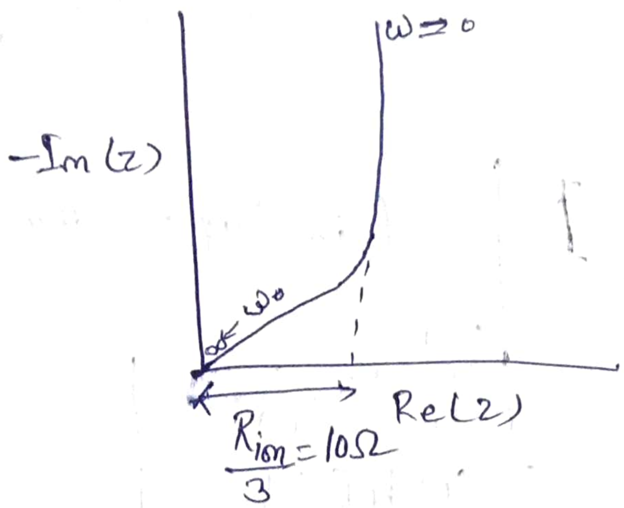
$$\left\{ \because \frac{L}{A K_{eff}} = R \right.$$

$$\because S = \sqrt{R_{ion} Q s} \quad \& \quad s = i\omega$$

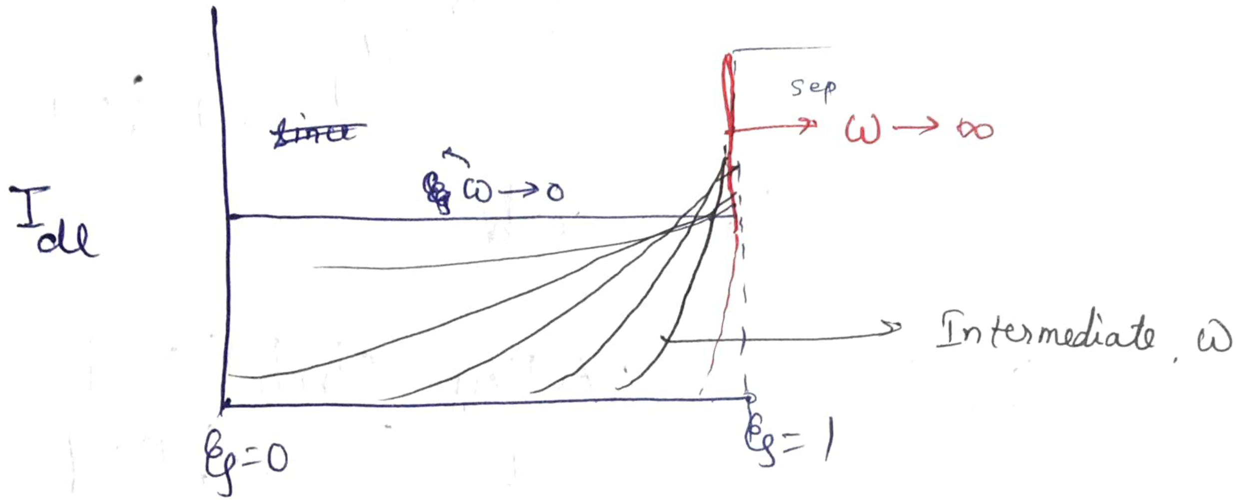
$$S = \sqrt{R_{ion} Q . i\omega}$$

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

(g) $R_{ion} = 30\,\Omega$, $Q_{dl} = 1\text{ mF}$



h)



Since At $\omega \to 0$, current will flow equally from all the branches, therefore a flat line at $\omega \to 0$.

At $\omega \to \infty$, current will flow through the branch near separator only. Therefore huge current ~~at~~ near separator side at $\omega \to \infty$

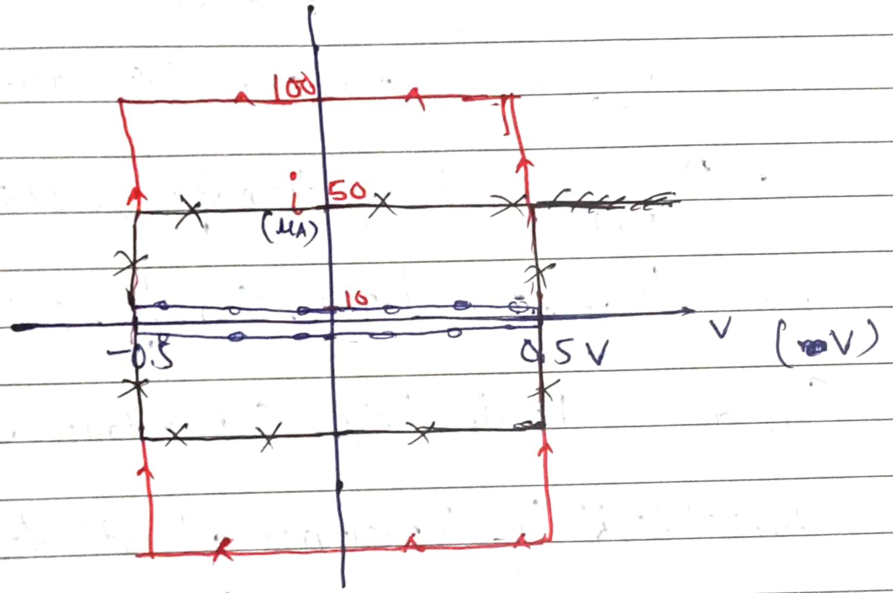
As ω decreases from ∞, current will utilize more and more electrode part from separator side.

② $i = C\frac{dV}{dt} = C\nu$, $C = 10\,mF$

At $\nu = 10\,\frac{mV}{s}$, $i = 100\,\frac{\mu A}{s}$

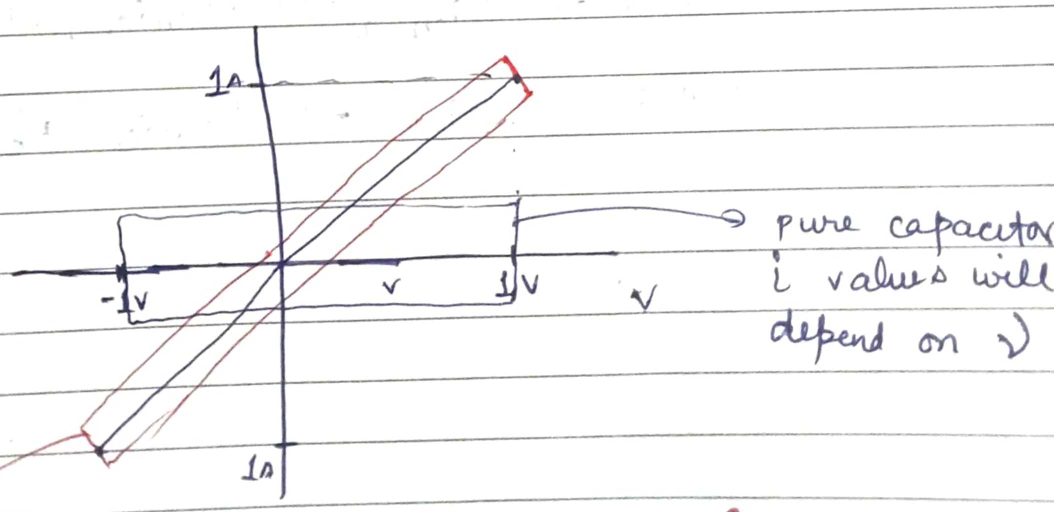
At $\nu = 50\,\frac{mV}{s}$, $i = 500\,\mu A$

At $\nu = 100\,\frac{mV}{s}$, $i = 1000\,\frac{\mu A}{s}$



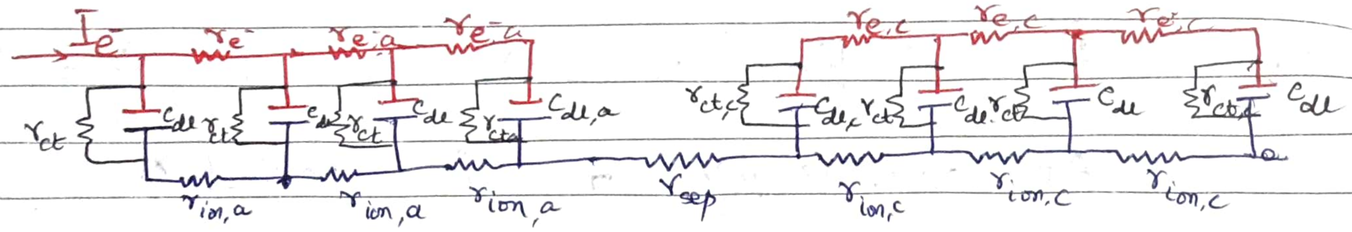
③ $i_R = \frac{V}{R} = 1$

$i_c = C\nu$
↓
1 mF



Resultant, R & C in parallel.

(4).



$R_{e^-,a} = \sum r_{e^-,a} \rightarrow$ electronic resistance through Anode

$R_{e^-,c} = \sum r_{e^-,c} \rightarrow$ electrode resistance in Cathode

$r_{sep} \rightarrow$ separator Resistance

$\sum r_{ct,a} = R_{ct,a} \rightarrow$ Charge transfer resistance of Anode

$\sum r_{ct,c} = R_{ct,c} \rightarrow$ Charge Transfer resistance of Cathode

$C_{dl,a} \rightarrow$ Double layer Capacitance at Anode-electrolyte Interface

$C_{dl,c} \rightarrow$ Double layer capacitance at Cathode electrolyte interface

$\sum r_{ion,a} = R_{ion,a} \rightarrow$ Ionic Resistance of Anode

$\sum r_{ion,c} = R_{ion,c} \rightarrow$ Ionic Resistance of Cathode

(5) Single Particle ~~Ass~~ Model Assumption →

(a) NO concⁿ gradient in electrolyte

(b). All the particles are assumed to be spherical and particle size is same.

(c) Uniform current distribution throughout the electrode.

(d) Each electrode can be represented as single particle.

(e) Uniform flux on the surface of particle.

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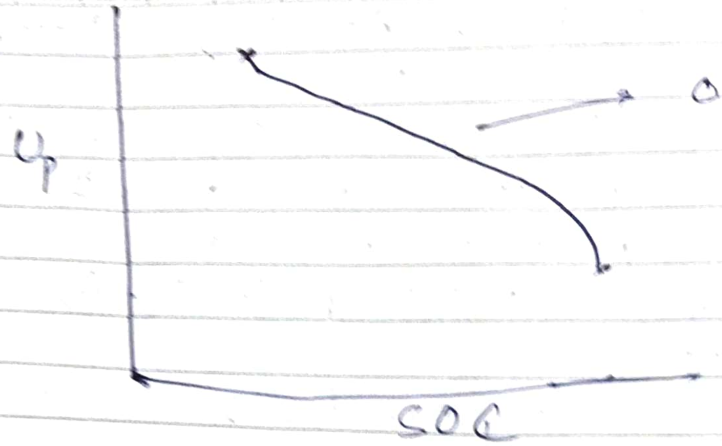
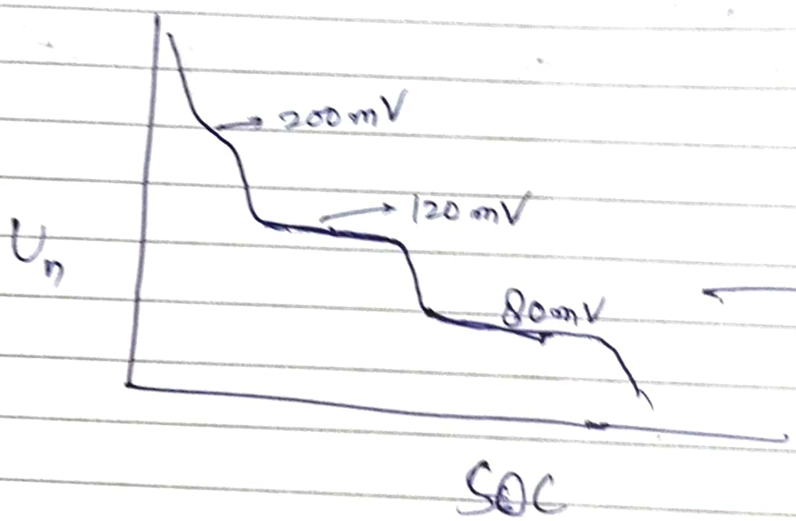


OCV of Li_xMO_2



OCV of graphite