Electrochemical Impedance Spectroscopy
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Lecture – 34
Warburg Impedance (3 of 3)

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Previous class

- Assignments

Mass Transfer Effects

- Polarization Curve

Today

- Mass Transfer Effects
  - Impedance

We will continue where we left on the derivation of impedance.

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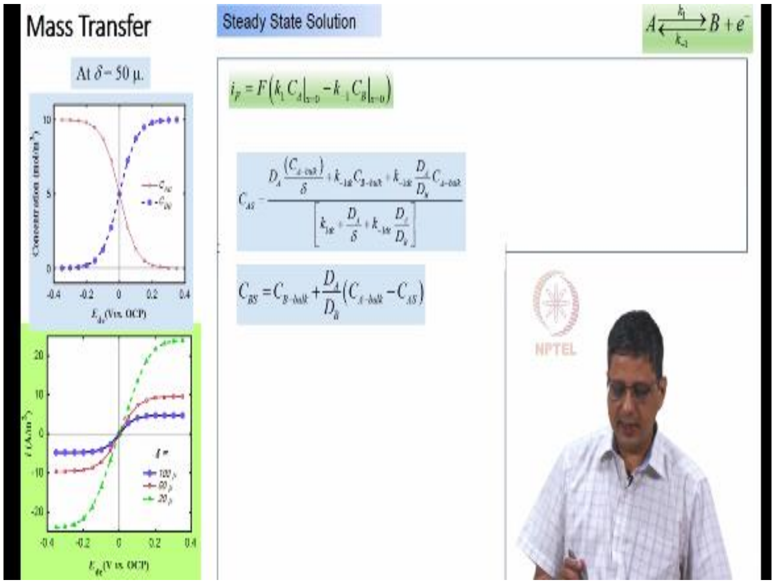

Mass Transfer

At $\delta = 50\ \mu$.

Steady State Solution

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + e^-$

$i_F = F\left(k_1 C_A\big|_{x=0} - k_{-1} C_B\big|_{x=0}\right)$

$$C_{AS} = \frac{D_A \frac{(C_{A\text{-bulk}})}{\delta} + k_{-1E} C_{B\text{-bulk}} + k_{-1E} \frac{D_A}{D_B} C_{A\text{-bulk}}}{\left[k_{1E} + \frac{D_A}{\delta} + k_{-1E} \frac{D_A}{D_B}\right]}$$

$$C_{BS} = C_{B\text{-bulk}} + \frac{D_A}{D_B}\left(C_{A\text{-bulk}} - C_{AS}\right)$$

To refresh your memory; Earlier, we have seen that you have to write the ficks equation, and you have to write the current equation, and under steady state conditions you can solve them and get the concentration profile. Concentration on the surface as a function of potential and at a given potential, you can also find the concentration profile. It is going to be linear and you can also find how the current varies as the rotational speed of electrode changes. As the rotational speed changes, you have different boundary layer thickness and you have different current profiles here.

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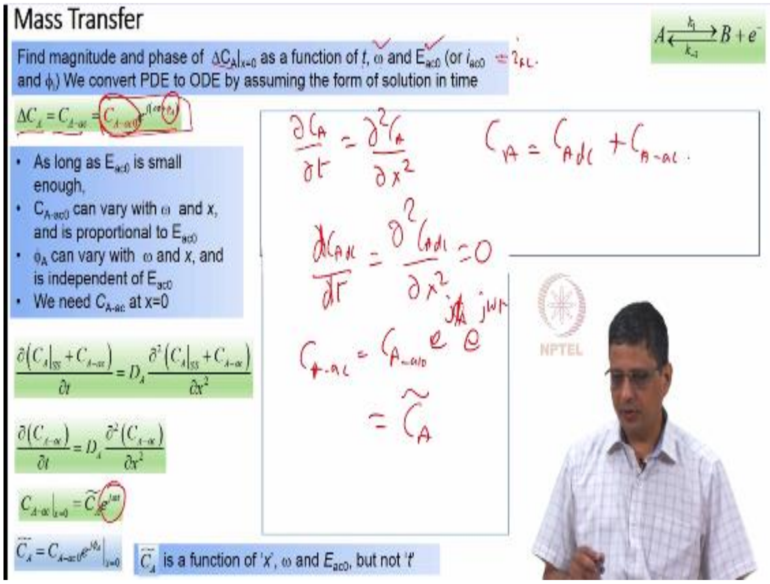

Mass Transfer

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + e^-$

Find magnitude and phase of $\Delta C_A|_{x=0}$ as a function of t, ω and E_{ac0} (or i_{ac0} $= i_{FL}$ and ϕ_i) We convert PDE to ODE by assuming the form of solution in time

$\Delta C_A = C_{A-ac} = C_{A-ac0} e^{j(\omega t + \phi_A)}$

- As long as E_{ac0} is small enough,
- C_{A-ac0} can vary with ω and x, and is proportional to E_{ac0}
- ϕ_A can vary with ω and x, and is independent of E_{ac0}
- We need C_{A-ac} at x=0

$$\frac{\partial\left(C_A|_{SS} + C_{A-ac}\right)}{\partial t} = D_A \frac{\partial^2\left(C_A|_{SS} + C_{A-ac}\right)}{\partial x^2}$$

$$\frac{\partial(C_{A-ac})}{\partial t} = D_A \frac{\partial^2(C_{A-ac})}{\partial x^2}$$

$$C_{A-ac}|_{x=0} = \tilde{C}_A e^{j\omega t}$$

$$\tilde{C}_A = C_{A-ac0} e^{j\phi_A}\Big|_{x=0}$$

$\tilde{C}_A$ is a function of 'x', ω and E_{ac0}, but not 't'

$$\frac{\partial C_A}{\partial t} = \frac{\partial^2 C_A}{\partial x^2} \qquad C_A = C_{Adc} + C_{A-ac}$$

$$\frac{\partial C_{Adc}}{\partial t} = \frac{\partial^2 C_{Adc}}{\partial x^2} = 0$$

$$C_{A-ac} = C_{A-ac0}\, e^{j\phi_A} e^{j\omega t} = \tilde{C}_A$$

Then we started deriving the equation for impedance, so we want to get an expression of i_{Fac} in terms of E_{ac} and other values. Instead of expanding in terms of E_{ac} on the right side, we expand it in the terms of ΔE, ΔC_A and ΔC_B and in order to get the ΔC_A and ΔC_B, we were solving the ficks equation. If you write this ficks equation for ΔC_A, we can write it in terms of amplitude or magnitude and phase at a given ωt.

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When we do this, we get an ordinary differential equation in terms of the location for C_A tilde where C_A tilde is $C_{AC0}e^{j\Phi_A}$. It is a phase and magnitude of the amplitude. If I have to draw it outside;

This is the electrode surface, this is the boundary layer and beyond this, the concentration is fixed here and if there is no DC bias concentration throughout, this is going to be straight.

When we apply an AC, concentration on this surface is going to fluctuate with respect to time. If there is a DC bias, it may look like this and if I apply a small AC on top of it, it is going to fluctuate around this. Out here, it is going to fluctuate, meaning it is going to oscillate and in general it will not have a phase in sync with the AC potential. It will have a phase off set and it depends on the ω value and it depends on where that is. We are interested in finding the concentration here and the fluctuations in the concentration on the surface because we want to know how the current is going to be affected. Reason is, we can measure only the current. We will not be able to measure the concentration fluctuation at any location, so we want to estimate how this is going to be.

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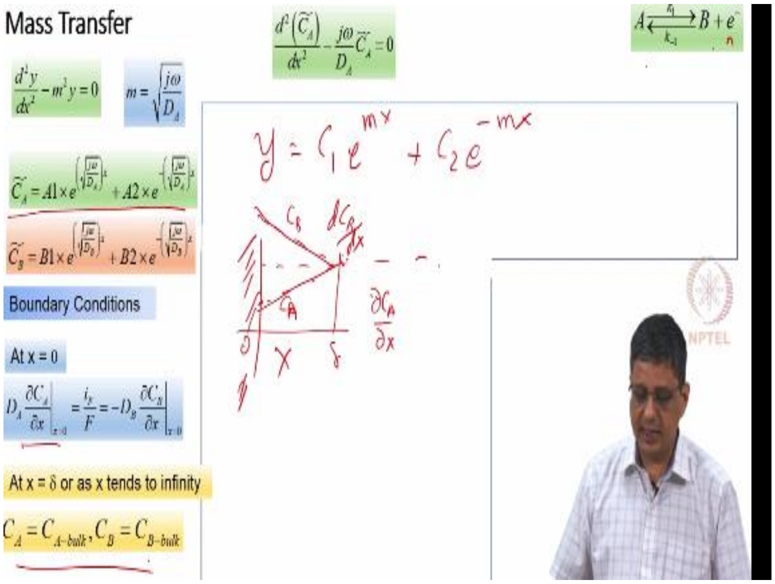

Mass Transfer

$$\frac{d^2y}{dx^2} - m^2 y = 0 \qquad m = \sqrt{\frac{j\omega}{D_A}}$$

$$\frac{d^2(\tilde{C}_A)}{dx^2} - \frac{j\omega}{D_A}\tilde{C}_A = 0$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + e^-$$

$$\tilde{C}_A = A1 \times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)x} + A2 \times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$$

$$\tilde{C}_B = B1 \times e^{\left(\sqrt{\frac{j\omega}{D_B}}\right)x} + B2 \times e^{-\left(\sqrt{\frac{j\omega}{D_B}}\right)x}$$

Boundary Conditions

At x = 0

$$D_A \left.\frac{\partial C_A}{\partial x}\right|_{x=0} = \frac{i_F}{F} = -D_B \left.\frac{\partial C_B}{\partial x}\right|_{x=0}$$

At x = δ or as x tends to infinity

$$C_A = C_{A-bulk}, C_B = C_{B-bulk}$$

$$y = C_1 e^{mx} + C_2 e^{-mx}$$

What we get is an equation ODE and it is a simple ordinary differential equation, second order ordinary differential equation. We can write auxiliary equation so we know how to solve this. We are going to write, this has 2 roots, + or – m. Since we use C for concentration, we are going to use A_1 and A_2 as the integration constants for the oscillations in species A. For oscillations in species B, we are going to write it as B_1 and B_2 and we are going to write it as e^{mx}, e^{-mx} because + or – m are the roots of this equation. Now we want to get the integration constants A_1 A_2 and likewise we will solve it for the B_1 B_2. Actually we would not solve it. I will just tell you this is the solution. If you know how to solve it for species A, you can solve it for species B also.

We have ficks equation we have boundary conditions. We are looking only at the surface, we want to get the concentration on the surface. In general this equation is valid throughout this boundary layer. Now we will get it for 2 cases. 1 is a finite boundary layer thickness and the other is infinite. It is called semi infinite because it goes from 0 to infinity where the solution is not at all steered and that dimension is large enough for us to consolidate to be semi infinite.

We have 2 boundary conditions at x =δ in case of finite boundary condition and when x tends to infinity is a semi-infinite case. In those cases, we say, at that location concentration of A is going to be fixed value. It is going to be C_A bulk and concentration of B is also going to be C_B bulk. It is not changing. On the surface, we can relate the faradaic current to the flux of species A and B.

In this case, we are going to say anodic current is positive. This is reaction A going to B with an electron. When you apply positive or anodic potential, more A will get converted to B and we are going to say that current is a positive current. Imagine this is location 0, this is location δ or infinity wherever that is and this is electrode here. If A is getting consumed, originally let us say this is the concentration of A throughout the solution. If I give positive potential, A is going to be consumed which means concentration of A here is going to be less than the concentration in bulk and concentration of B is going to be more than the concentration in bulk. If I apply an anodic potential this is how it is going to look like and when this is the case what happens to $\partial CA/\partial x$. That is a positive value because it has a positive slope. Increasing x gives us increasing concentration of A.

dC_A/dx is positive, diffusivity is a positive number and that is going to be equal to i_F/F. In general, it is going to be i_F/N_F where n is the number of electrons. In this particular example, we are keeping n=1. If you know how much current is coming, we can also say what is the flux of species A because 1 mol of A will give us 1 mol of electron and 1 mol of electron when you use the factor F here faraday constant, t it tells us how much current is coming.

We are able to relate the current to the flux of A and we can also relate to the flux of B because 1 mol of A gives us 1 mol of B here and concentration of B is decreasing here. That means dC_B/ dx is negative because we chose the convention that anodic current is positive. When we solve for species A, we are going to use this condition at x= 0 when we solve for species B we are going to use this. Now you have an expression for C_A tilde. This is in terms of C_A and this is also in terms of C_A.

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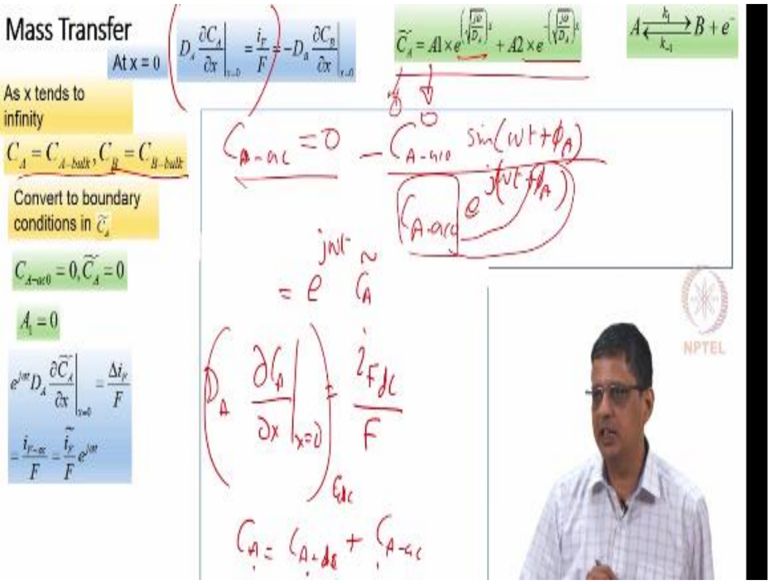

Mass Transfer

At x = 0 $\left(D_A \frac{\partial C_A}{\partial x}\Big|_{x=0} = \frac{i_F}{F} = -D_B \frac{\partial C_B}{\partial x}\Big|_{x=0} \right)$

$\tilde{C}_A = A1 \times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)x} + A2 \times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + e^-$

As x tends to infinity

$C_A = C_{A-bulk}, C_B = C_{B-bulk}$

Convert to boundary conditions in $\tilde{C}_A$

$C_{A-ac0} = 0, \tilde{C}_A = 0$

$A_1 = 0$

$e^{j\omega t} D_A \frac{\partial \tilde{C}_A}{\partial x}\Big|_{x=0} = \frac{\Delta i_F}{F} = \frac{i_{F-ac}}{F} = \frac{\tilde{i}_F}{F} e^{j\omega t}$

$C_{A-ac} = 0 \quad C_{A-ac0} \sin(\omega t + \phi_A)$

$\boxed{C_{A-ac0}}\, e^{j(\omega t + \phi_A)}$

$= e^{j\omega t} \tilde{C}_A$

$\left(D_A \frac{\partial C_A}{\partial x}\Big|_{x=0} \right)_{dc} = \frac{i_{F\,dc}}{F}$

$C_A = C_{A-dc} + C_{A-ac}$

No problem, we want to convert this boundary conditions in terms of C_A tilde. At x tends to infinity we are going to first look at semi infinite boundary conditions and solve for that. Later we will look at finite boundary condition and solve for that. At x = infinity C_A is $C_{A\text{-bulk}}$ and CB is $C_{B\text{-bulk}}$. That means there is no fluctuation there in $C_{A\text{-ac}}$. This is one way of expressing it, this is another way of expressing $C_{A\text{-ac}}$, and this is another way of expressing $C_{A\text{-ac}}$. Fluctuation is 0. We can write in terms of sine, we can write in terms of $e^{j(\omega t+\Phi A)}$. We also know we have grouped this and $e^{j(\omega t+\Phi A)}$ as C_A tilde. In the bulk, there is no fluctuation. That means C_{Aac} is 0 and C_A tilde is 0. The expression here if x = infinity, what happens? This goes to 0, this goes to infinity and yet if I want to say C_A tilde is 0, which means A_1 has to be 0.

We want to find A_1 and A_2 and we have 2 boundary conditions. One of them is at x = infinity another is at x =0. We get the constant A_1 as 0. Only then we can satisfy the boundary condition that as x tends to infinity, concentration is a fixed value. Second, we want to write $\partial CA/\partial x = i_F/F$ divided by diffusivity D_A. We want to use the second boundary condition. Under steady state condition $C_{A\text{-dc}}$ or C_A steady state (refer video).

Under fixed DC potential, we know this is valid, so C_A in general, we can write it as CA steady state + C_{A-ac} or C_{A-dc} +C_{A-ac} and we can write i_F as i_{F-dc}+ i_{F-ac}. Whatever we have written here, we can write it for AC component only and when we write for AC component we are going to write (…refer video)

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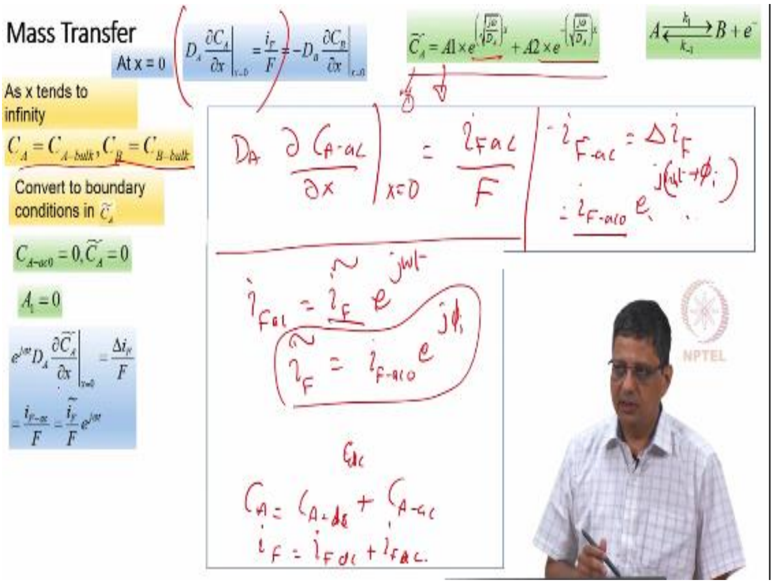

Mass Transfer

At x = 0 $D_A \frac{\partial C_A}{\partial x}\Big|_{x=0} = \frac{i_F}{F} = -D_B \frac{\partial C_B}{\partial x}\Big|_{x=0}$

$\tilde{C}_A = A1\times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)x} + A2\times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + e^-$

As x tends to infinity

$C_A = C_{A-bulk}, C_B = C_{B-bulk}$

Convert to boundary conditions in $\tilde{C}_A$

$C_{A-ac0} = 0, \tilde{C}_A = 0$

$A_1 = 0$

$e^{j\omega t} D_A \frac{\partial \tilde{C}_A}{\partial x}\Big|_{x=0} = \frac{\Delta i_F}{F} = \frac{i_{F-ac}}{F} = \frac{\tilde{i}_F}{F} e^{j\omega t}$

$D_A \frac{\partial C_{A-ac}}{\partial x}\Big|_{x=0} = \frac{i_{Fac}}{F}$

$i_{F-ac} = \Delta i_F = i_{F-ac0}\, e^{j(\omega t + \phi_i)}$

$i_{Fac} = \tilde{i}_F e^{j\omega t}$

$\tilde{i}_F = i_{F-ac0}\, e^{j\phi_i}$

C_{dc}

$C_A = C_{A-dc} + C_{A-ac}$

$i_F = i_{Fdc} + i_{Fac}$

i_{Fac}, another notation is Δi_F and in general, it is going to be i_{F-ac0} $e^{j(\omega t+\Phi i)}$ where Φ_i indicates the phase difference between the current and the potential, and that is going to depend on what the ω is. Like we have done it for C_A, we can also say that i_{F-ac} can be written as… where i_F tilde… [it just makes it a little easier for us to do the calculation].

We can get rid of the time factor from this. In Δi_F/ F, we will write it as i_{Fac} /F and that is going to be i_F tilde $e^{j\omega t/F}$, $e^{j\omega t}$ goes away. It gets canceled from this equation. Then $j\Phi_A$ only remains. $j\omega t$ comes out. I have taken this equation and write it as $i_{F-ac0}e^{j\omega t}$ multiplied by $e^{j\Phi i}$ leaving out the $e^{j\omega t}$, the remaining terms are collected and kept as i_F tilde because on the left hand side of this boundary condition you have $e^{j\omega t}$. I do not need to do that. This is just one way of expressing it. I can write it as $i_{Fac0}e^{j\omega t}$ $e^{j\Phi i}$ and leave it as it is and just cancel the things. Then every time I have to write a lengthy expression. I had to write i_{Fac0} $e^{j\omega t+\Phi A}$. Instead I just write a little shorthand for that.

You have an expression for C_A tilde take the derivative of this. Here we have the expression for C_A tilde and take the derivative with respect to x. We already know A_1 is 0. Therefore we do not have to keep this. [If you take the derivative here what do we get?] We would get A_2 multiplied by – square root of jω/ D_A multiplied by e power whatever that is there. If you take the derivative of e^{mx} with respect to x, you will get m multiply by e^{mx}. I want to take the derivative and substitute there.

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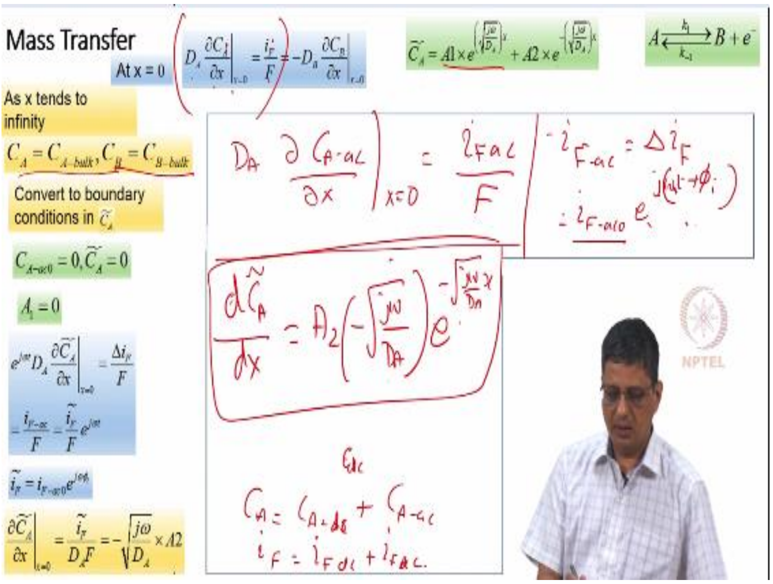

Mass Transfer

At x = 0 $D_A \frac{\partial C_A}{\partial x}\Big|_{x=0} = \frac{i_F}{F} = -D_B \frac{\partial C_B}{\partial x}\Big|_{x=0}$

$\tilde{C}_A = A1\times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)x} + A2\times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + e^-$

As x tends to infinity

$C_A = C_{A-bulk}, C_B = C_{B-bulk}$

Convert to boundary conditions in $\tilde{C}_A$

$C_{A-ac0} = 0, \tilde{C}_A = 0$

$A_1 = 0$

$e^{j\omega t} D_A \frac{\partial \tilde{C}_A}{\partial x}\Big|_{x=0} = \frac{\Delta i_F}{F}$

$= \frac{i_{F-ac}}{F} = \frac{\tilde{i}_F}{F} e^{j\omega t}$

$\tilde{i}_F = i_{F-ac0} e^{j\phi_i}$

$\frac{\partial \tilde{C}_A}{\partial x}\Big|_{x=0} = \frac{\tilde{i}_F}{D_A F} = -\sqrt{\frac{j\omega}{D_A}} \times A2$

$D_A \frac{\partial C_{A-ac}}{\partial x}\Big|_{x=0} = \frac{i_{Fac}}{F}$

$i_{F-ac} = \Delta i_F$

$= i_{F-ac0} e^{j(\omega t + \phi_i)}$

$$\boxed{\frac{d\tilde{C}_A}{dx} = A_2\left(-\sqrt{\frac{j\omega}{D_A}}\right)e^{-\sqrt{\frac{j\omega}{D_A}}x}}$$

E_{ac}

$C_A = C_{A-dc} + C_{A-ac}$

$i_F = i_{Fdc} + i_{Fac}$

We would say $\frac{dC_A}{dx} = A_2(-\sqrt{\frac{jw}{D_A}})e^{-\sqrt{\frac{jw}{D_A}}x}$. Now I want to evaluate this at x = 0, then the e^{mx} or e^{-mx} becomes unity. I would write $A_2(-\sqrt{\frac{jw}{D_A}})$ is going to be given i_F/D_AF. I just moved the D_A to the right hand side of the boundary condition. Essentially we want to find the value of A_2 and substitute it there. It will be nice if A_2 comes in terms of E_{ac} or i_{ac}.

Likewise, we have to calculate B_1 B_2. I can tell you B_1 is going to be 0 and B_2 is going to look like this except because the boundary condition says negative. In terms of the boundary condition at x = 0, we have $D_A\partial C_A/\partial x$ at x =0 = i_F/F and that is equal to - D_B. You would get the constant B_2 just like A_2 with a negative sign. [so you are able to get up to this].

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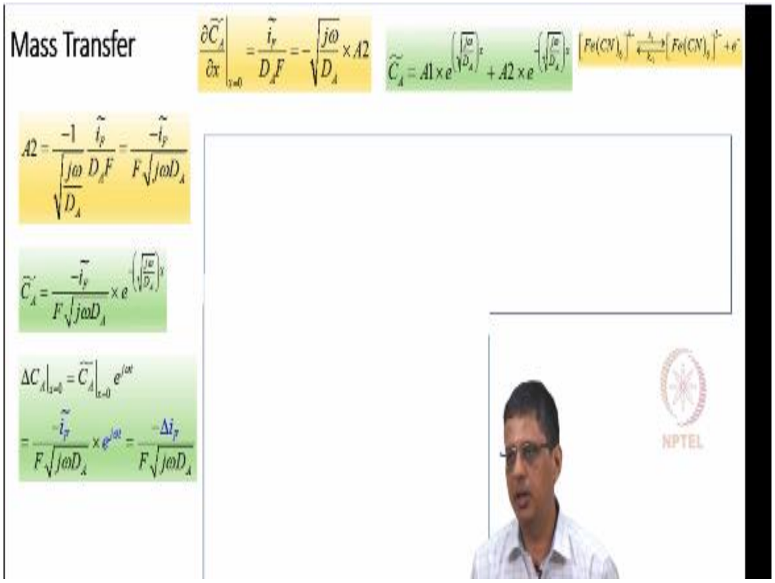

Mass Transfer

$$\left.\frac{\partial \tilde{C}_A'}{\partial x}\right|_{x=0} = \frac{\tilde{i}_F}{D_A F} = -\sqrt{\frac{j\omega}{D_A}} \times A2$$

$$\tilde{C}_A' = A1 \times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)x} + A2 \times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$$

$$\left[Fe(CN)_6\right]^{4-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \left[Fe(CN)_6\right]^{3-} + e^-$$

$$A2 = \frac{-1}{\sqrt{\frac{j\omega}{D_A}}} \frac{\tilde{i}_F}{D_A F} = \frac{-\tilde{i}_F}{F\sqrt{j\omega D_A}}$$

$$\tilde{C}_A' = \frac{-\tilde{i}_F}{F\sqrt{j\omega D_A}} \times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)x}$$

$$\left.\Delta C_A\right|_{x=0} = \left.\tilde{C}_A\right|_{x=0} e^{j\omega t}$$

$$= \frac{-\tilde{i}_F}{F\sqrt{j\omega D_A}} \times e^{j\omega t} = \frac{-\Delta i_F}{F\sqrt{j\omega D_A}}$$

We will rearrange it and we write A_2 as - i_F tilde / faraday constant. We have one factor of D_A and another factor within square root and after rearranging, you would get $j\omega D_A$. It is just an algebraic arrangement of that. Therefore we would write C_A as substituting for A_2. We would write C_A tilde in general it is going to look like this and C_A tilde at x =0 is going to look like the first factor because the second factor is going to become unity.

Once we know, C_A tilde we can write ΔC_A. All that we need is to multiply by $e^{j\omega t}$ and now that i_F tilde combined with $e^{j\omega t}$, you would get it as Δi_F or $i_{F\text{-ac}}$.

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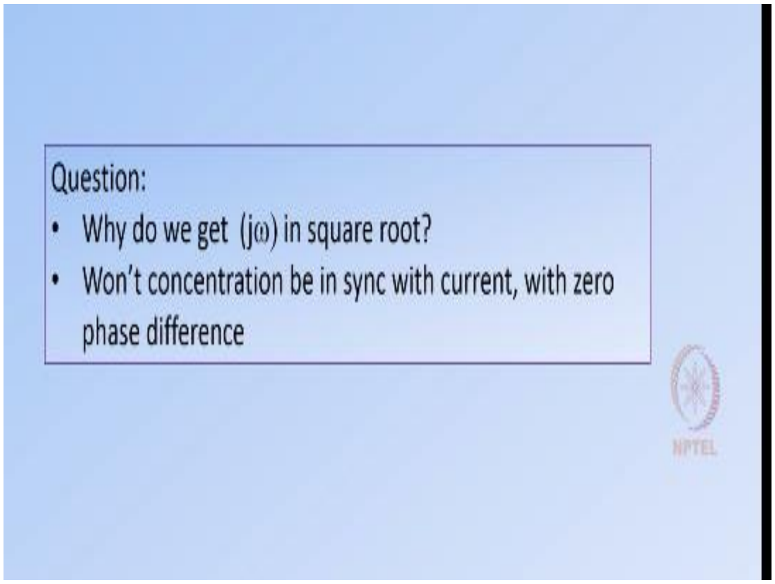

Question:

- Why do we get (jω) in square root?
- Won't concentration be in sync with current, with zero phase difference

This is how it works. The boundary condition says current is related to the derivative of concentration because derivative of concentration gives us the flux. Concentration; it is a concentration gradient, derivative of concentration with respect to space. It is not derivative of concentration with respect to time. Therefore concentration gradient is going to tell us how much material is coming, and how much A is coming tells us how much electrons are being produced. How much A is consumed tells us how much electrons are being produced. Now potential is sinusoidal with respect to time. Current is also going to be sinusoidal with some phase difference. [Let us not worry about it]. Let us just restart it and say when current is going like this we will say, when the current starts as 0, we will call that as origin just for now. Current is going to be sinusoidal with 0 phase now. If current is sinusoidal with 0 phase, concentration is not going to be sinusoidal with 0 phase. Concentration will be sinusoidal, but actually the derivative of concentration with respect to x, that only is going to be in phase with current. What we end up getting is because of that and this is going to be $e^{-\sqrt{jwx}}$, we get the derivative and we get the jω term within he square root here.

Concentration will have an offset with current. Concentration gradient will be in sync with current and current is going to be in general out of phase with potential. Therefore all these 3 with respect to potential current and concentration of A, concentration of B, they will in general have a phase difference. Even if current and potential are in sync, concentration will have a difference. As the concentration gradient is related because it is mass transfer limited or mass transfer plays a role, we have a little more complex expression here. ΔC_B is going to look like same as ΔC_A except that it has a negative sign because the boundary condition says i_F/ N_F or $i_F/F = -D_B\ \partial C_B/\partial x$ x at x =0. If you go through the derivation, it will look the same except that the sign is different. We would not derive it, we will say that this is the correct expression.

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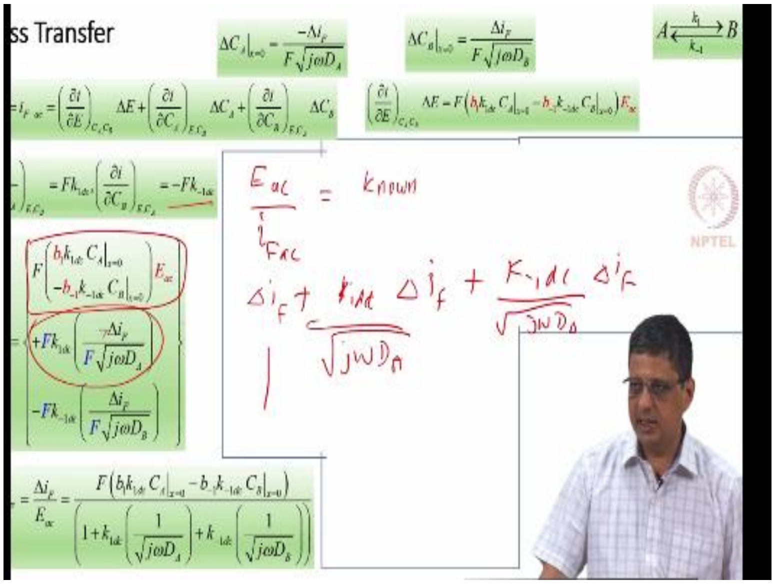

ss Transfer

$$\Delta C_A\big|_{x=0} = \frac{-\Delta i_F}{F\sqrt{j\omega D_A}} \qquad \Delta C_B\big|_{x=0} = \frac{\Delta i_F}{F\sqrt{j\omega D_B}} \qquad A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$= i_{F\,ac} = \left(\frac{\partial i}{\partial E}\right)_{C_A C_B} \Delta E + \left(\frac{\partial i}{\partial C_A}\right)_{E,C_B} \Delta C_A + \left(\frac{\partial i}{\partial C_B}\right)_{E,C_A} \Delta C_B \qquad \left(\frac{\partial i}{\partial E}\right)_{C_A C_B} \Delta E = F\left(b_1 k_{1dc} C_A\big|_{x=0} - b_{-1} k_{-1dc} C_B\big|_{x=0}\right) E_{ac}$$

$$= Fk_{1dc}; \left(\frac{\partial i}{\partial C_B}\right)_{E,C_A} = -Fk_{-1dc}$$

$$= \begin{Bmatrix} \boxed{F\begin{pmatrix} b_1 k_{1dc} C_A\big|_{x=0} \\ -b_{-1} k_{-1dc} C_B\big|_{x=0} \end{pmatrix} E_{ac}} \\ +Fk_{1dc}\left(\dfrac{-\Delta i_F}{F\sqrt{j\omega D_A}}\right) \\ -Fk_{-1dc}\left(\dfrac{\Delta i_F}{F\sqrt{j\omega D_B}}\right) \end{Bmatrix}$$

$$= \frac{\Delta i_F}{E_{ac}} = \frac{F\left(b_1 k_{1dc} C_A\big|_{x=0} - b_{-1} k_{-1dc} C_B\big|_{x=0}\right)}{\left(1 + k_{1dc}\left(\dfrac{1}{\sqrt{j\omega D_A}}\right) + k_{-1dc}\left(\dfrac{1}{\sqrt{j\omega D_B}}\right)\right)}$$

$$\frac{E_{ac}}{i_{Fac}} = \text{known}$$

$$\Delta i_F + \frac{k_{1dc}}{\sqrt{j\omega D_A}} \Delta i_F + \frac{k_{-1dc}}{\sqrt{j\omega D_A}} \Delta i_F$$

ΔE is E_{ac}, ΔC_A written in terms of Δi_F, ΔC_B is also written in terms of Δi_F and everything else is known to us. We will go back to the expression where we write $\Delta i_{F\ ac}$ $\partial i/\partial E$ multiply by ΔE $\partial i/\partial C_A$ multiply by ΔC_A $\partial i/\partial C_B$ multiply by ΔC_B and we already know that $\partial i/\partial E$ multiply by ΔE is given in terms of E_{ac} and other known factors.

We have done this before, derivative of current with respect to concentration of A and B are also known to us. We are going to substitute and rearrange. What we want to get is …. or the inverse of this. And on the right hand side everything else should be known to us. What we used to get previously was Δi_F on the left side or i_{Fac} on the left side, all the things on the right side will be grouped together and you will get E_{ac}.

In this mass transfer based derivation, on the right hand side 1 of the expression has E_{ac} and other expression is brought in terms of $i_{F\text{-}ac}$ or Δi_F and we are going to rearrange it and finally still get the expression for E_{ac}/i_{ac}. This part, ΔC_A is negative i_F. For the second part it is – Fk_{1dc} multiply by + i_F. These 2 actually will have negative sign when you arrange everything and then you bring it to the left side, you are going to get Δi_F on the left side and when you bring this term to the left side, it is going to like + Fk_{1dc}/F, F will cancel out and that is why I have marked them in blue. And on the right hand side we are just left with this. Then take the ratio of $\Delta i_F/E_{ac}$ you are going to get 1 here plus k_{1dc}/ square root of $j\omega D_A$ $k_{-1\ dc}$/ square root of $j\omega D_B$.

This is the expression for semi infinite boundary layer thickness and this will simplify when you have $E_{dc} = 0$. That is when there is no bias in the DC potential whatever is at open circuit potential we are going to leave it at that.

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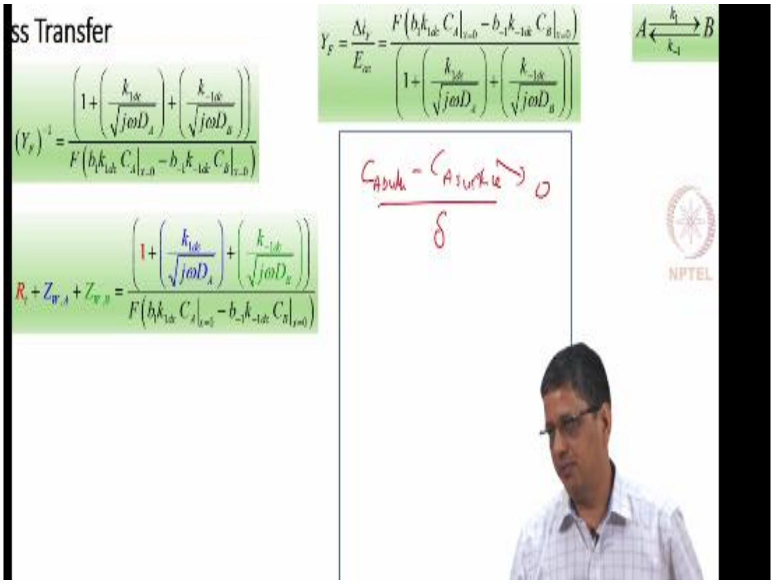

ss Transfer

$$Y_F = \frac{\Delta i_F}{E_{ac}} = \frac{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right)}{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$(Y_F)^{-1} = \frac{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right)}$$

$$R_t + Z_{W,A} + Z_{W,B} = \frac{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right)}$$

$$\frac{C_{A bulk} - C_{A surface}}{\delta} \to 0$$

The admittance form is written here. Impedance is going to be the inverse of that. This is written separated into 3 components. One is written as R_t. There is no ω in it and ω dependence in it. Second is written as Warburg impedance for species A, 3rd is written as Warburg impedance for species B. It is not that well separated, but if you look at the numerator yes, one of them is dependent on the diffusivity of A and one of them dependent on the diffusivity of B, but the denominator you have concentration of A at x = 0 and concentration of B at x = 0 and they will depend on the diffusivity of A and B. Leaving that aside, you can separate this into 3 components. One called as charge transfer resistance; charge transfer resistance is basically faradaic impedance at infinite frequency. At infinity frequency, the terms colored in blue and green will go away.

Therefore, what is left is charge transfer resistance. Numerator red color, denominator is common for all these 3 and often we will write diffusivity of A is roughly equal to diffusivity of B. Right now we are not going to do that. We will just keep it as it is. I want you to notice the following when you have semi-infinite approximation, you cannot say that you have steady state with a DC bias. From the moment you apply a DC bias, E_{dc} is not 0. It will never reach steady state because you have to find concentration at x =0 and concentration at x =infinity is bulk. Concentration gradient is never going to be non-zero because you are going to write concentration gradient as …..(refer video) δ is going to be infinity and this will become… .

As you increase the E_{dc} or as you increase the δ even in finite boundary layer thickness, this is going to become lower and lower value. The lowest it can go to is 0. Concentration of A cannot go below 0 and concentration of any species cannot go below 0. You will never be able to get us non-zero value under steady state condition and if concentration is really 0, you will not have any forward reaction.

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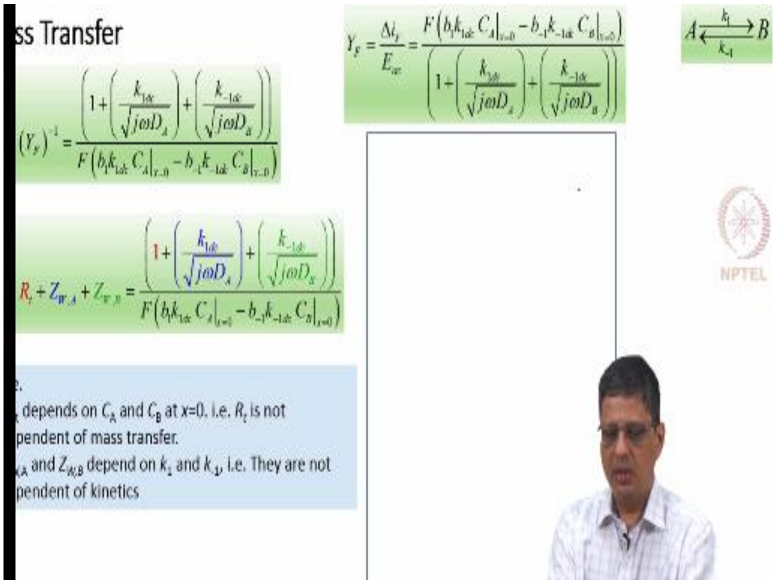


ss Transfer

$$Y_F = \frac{\Delta i_f}{E_{ac}} = \frac{F\left(b_1 k_{1dc} C_A\big|_{x=0} - b_{-1} k_{-1dc} C_B\big|_{x=0}\right)}{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$(Y_F)^{-1} = \frac{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A\big|_{x=0} - b_{-1} k_{-1dc} C_B\big|_{x=0}\right)}$$

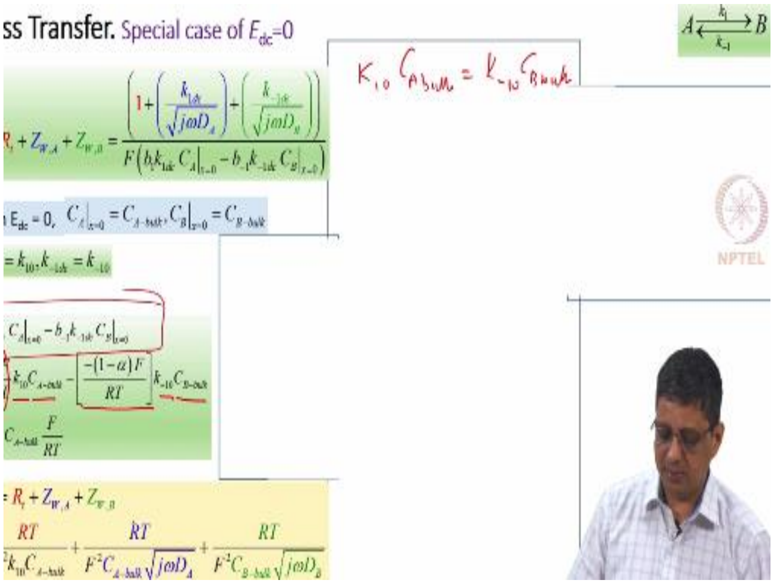
$$R_t + Z_{W,A} + Z_{W,B} = \frac{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A\big|_{x=0} - b_{-1} k_{-1dc} C_B\big|_{x=0}\right)}$$

depends on C_A and C_B at x=0. i.e. R_t is not pendent of mass transfer.

and $Z_{W,B}$ depend on k_1 and k_{-1}, i.e. They are not pendent of kinetics

When you say that the boundary layer thicknesses is really infinity, then you cannot have any potential that is other than [...] It cannot have any DC potential that is other than 0 and expect a steady state concentration profile. You can have unsteady state concentration profile, no problem. You can have a sinusoidal fluctuation and expect steady periodic variation that is still okay. What you cannot say is I will go to point 1 voltage with respect to OCP and maintain that and wait for some time. I will get steady state. You will not get that. In this case, we are going to restrict ourselves to finding the impedance only at E_{dc} = 0. Rt depends on the concentration of the C_A and C_B at the surface. It is not completely independent of mass transfer. Concentration in general, when we come to finite boundary layer thickness it becomes important and likewise if we look here $Z_{W,A}$ and $Z_{W,B}$ depend on k_1 and k_{-1}. And they are not exactly independent of kinetics.

(Refer Slide Time: 27:41)



ss Transfer. Special case of E_{dc}=0

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

$$R_t + Z_{W,A} + Z_{W,B} = \frac{\left(1 + \left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right) + \left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right)}$$

$E_{dc} = 0, \; C_A|_{x=0} = C_{A\text{-bulk}}, C_B|_{x=0} = C_{B\text{-bulk}}$

$= k_{10}, k_{-1dc} = k_{-10}$

$$C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}$$

$$k_{10} C_{A\text{-bulk}} - \boxed{\frac{-(1-\alpha)F}{RT}} k_{-10} C_{B\text{-bulk}}$$

$$C_{A\text{-bulk}} \frac{F}{RT}$$

$K_{10} C_{A\,bulk} = k_{-10} C_{B\,bulk}$

$$= R_t + Z_{W,A} + Z_{W,B}$$

$$\frac{RT}{k_{10} C_{A\text{-bulk}}} + \frac{RT}{F^2 C_{A\text{-bulk}} \sqrt{j\omega D_A}} + \frac{RT}{F^2 C_{B\text{-bulk}} \sqrt{j\omega D_B}}$$

However, if you look at the special case of $E_{dc} = 0$, concentration of A on the surface is going to be same as concentration in the bulk. Concentration of B on the surface is same as concentration in the bulk because we are not applying any DC bias. k_{1dc} is going to be k_{10}. k_{-1dc} is going to be $k_{-1} = 0$ because E_{dc} is 0 here.

"Professor – student conversation starts" if we do not apply bias, there will be a reaction happening?

There will be reaction happening, net reaction is 0. Net reaction rate is zero. Both reactions will happen at the equal rate. Both may happen at fast rate and both may happen at slow rate, but net reaction rate is 0.

If we have an irreversible reaction then…

You cannot have an irreversible reaction and expect equilibrium.

"Professor – student conversation ends"

This open circuit potential here is the equilibrium potential because there is no other reaction. You can have two different reaction. A going to B and C going to D and still one of them may give positive current and another may give negative current and you may get net reaction, net current to be 0. That is a different case. Here we are considering A going to B and B becoming A. We can say that we are going to apply a positive potential or negative potential when you go to shift away from the equilibrium here. We can get steady state condition as long as the boundary layer thickness is restricted. Finite boundary layer thickness, I have a large reservoir of A and B where I am maintaining concentration of A and B. Here I can have steady state and not equilibrium. When I apply a DC potential I will continuously consume A and produce B and they are going to go away. Once it comes here, beyond that boundary layer it is all completely well mixed and there is no change in the bulk concentration because it is a very large reservoir. That is a possibility. In fact if you take a normal cell, put say 200-300 ml of solution, put a small electrode and control the rotational speed. It will give a finite boundary layer thickness. You can have a reaction of A going to B. In fact the counter electrode is typically B going to A. Therefore whatever small amount you consume here will be produced on the other side. [Leave that aside]. If you are consuming small amount here and producing small amounts of B, but you have a large reservoir. In 5 minutes or 10 minutes you are not going to really change the concentration of the bulk.

When you look at this, we can write the expression b_1 k_{1dc} – b_{-1} k_{-1dc} multiply by C_{Bx} = 0. This B_1 is actually alpha F/RT. This is k_{1dc}. This is C_A at x = 0 and this is going to be b_{-1} k_{-1dc} and C_B at x = 0 and after rearranging…(refer video)

k_{10} and k_{-10} are not completely independent. They are related. The moment your specify CA $_{bulk}$, C_{Bbulk} and k_{10} and then say I am going to take equilibrium potential as the reference potential, 0 potential. Then these are related. I can write $k_{10}C_{A\text{-}bulk}$ and I can write k-… [it is ok, it does not like if I write here]. I can write it as $k_{-10}C_{Bbulk}$. Both are equal actually. I do not need to make assumption $C_{A\ bulk} = C_{B\ bulk}$. I will still get that expression.

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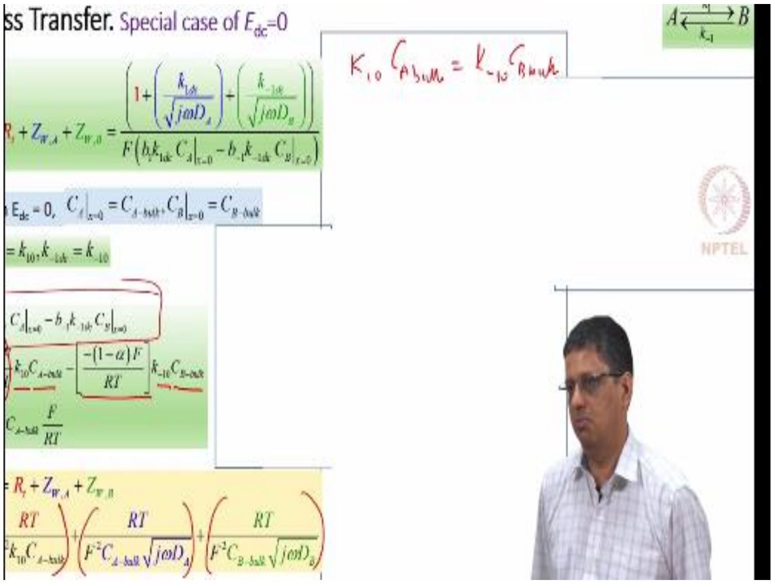

ss Transfer. Special case of E_{dc}=0

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

$$R_t + Z_{W,A} + Z_{W,B} = \frac{\left(1+\left(\frac{k_{1dc}}{\sqrt{j\omega D_A}}\right)+\left(\frac{k_{-1dc}}{\sqrt{j\omega D_B}}\right)\right)}{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right)}$$

$E_{dc}=0$, $C_A|_{x=0} = C_{A\text{-bulk}}, C_B|_{x=0} = C_{B\text{-bulk}}$

$= k_{10}, k_{-1dc} = k_{-10}$

$C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}$

$k_{10} C_{A\text{-bulk}} - \left[\frac{-(1-\alpha)F}{RT}\right] k_{-10} C_{B\text{-bulk}}$

$C_{A\text{-bulk}} \frac{F}{RT}$

$= R_t + Z_{W,A} + Z_{W,B}$

$$\left(\frac{RT}{F^2 k_{10} C_{A\text{-bulk}}}\right) + \left(\frac{RT}{F^2 C_{A\text{-bulk}} \sqrt{j\omega D_A}}\right) + \left(\frac{RT}{F^2 C_{B\text{-bulk}} \sqrt{j\omega D_B}}\right)$$

$K_{10} C_{A\,bulk} = k_{-10} C_{B\,bulk}$

Under this condition, it looks like this part does not have any diffusivity component here. This part does not have any kinetic component k or k_{-1} or k_1. This part does not have any kinetic component. You would get the feeling that R_t is independent of diffusion, $Z_{W,A}$ and $Z_{W,B}$ are independent of kinetics. It is not always going to be clean separation. It is valid only at equilibrium.

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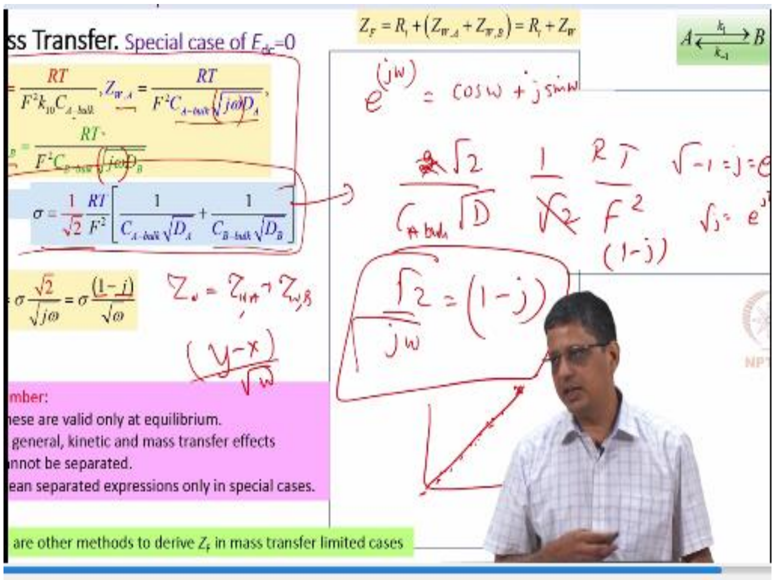

ss Transfer. Special case of E_{dc}=0

$Z_F = R_t + (Z_{W,A} + Z_{W,B}) = R_t + Z_W$

$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

$= \frac{RT}{F^2 k_{10} C_{A\text{-bulk}}}, Z_{W,A} = \frac{RT}{F^2 C_{A\text{-bulk}} \sqrt{j\omega D_A}},$

$= \frac{RT}{F^2 C_{B\text{-bulk}} \sqrt{j\omega D_B}}$

$$\sigma = \frac{1}{\sqrt{2}} \frac{RT}{F^2} \left[\frac{1}{C_{A\text{-bulk}} \sqrt{D_A}} + \frac{1}{C_{B\text{-bulk}} \sqrt{D_B}}\right]$$

$\sigma \frac{\sqrt{2}}{\sqrt{j\omega}} = \sigma \frac{(1-j)}{\sqrt{\omega}}$

$Z_w = Z_{W,A} + Z_{W,B}$

$\frac{(y-x)}{\sqrt{w}}$

mber:

hese are valid only at equilibrium.

general, kinetic and mass transfer effects

nnot be separated.

ean separated expressions only in special cases.

are other methods to derive Z_F in mass transfer limited cases

$e^{(jw)} = \cos w + j \sin w$

$\frac{\sqrt{2}}{C_{A\,bulk} \sqrt{D}}$ $\frac{1}{\sqrt{2}}$ $\frac{RT}{F^2}$ $(1-j)$ $\sqrt{-1} = j = e$ $\sqrt{j} = e$

$\frac{\sqrt{2}}{\sqrt{jw}} = (1-j)$

This can be written in a little more elegant form. It is commonly written in textbooks in this form where you write a parameter σ as 1/ square root of 2RT/ F^2. If RT/ x^2 comes, $C_{A\text{-bulk}}$ square root of D_A, $C_{B\text{-bulk}}$ square root of D_B and you would combine $Z_{W,A}$ and $Z_{W,B}$ and write it as…. and many times diffusivity are not different. People would write DA =DB… becomes a lot simpler.

It will become if $C_{A\text{-bulk}}$ and $C_{B\text{-bulk}}$ are equal D_A and D_B are equal, you are going to just write this expression as diffusivity (refer video) which is A or B does not matter. We will get simplified form. We will end up getting square root of 2/jω as the remaining factor here, square root of 2 is introduced here, so that the numerator gets square root of 2 and when you do this, you can write it as 1 – j. j is actually written as $e^{j\pi/2}$ and you can get the square root or 1/ square root by looking at this. Square root of j is going to be $e^{j\pi/4}$. It is going to be cos π/4+j sin π/4. Similarly we can find 1/ square root of j. It is going to be cos – π/4 +j sin – π/4. You will get 1 – j except that you have got square root of 2 as the factor, cos π/4 is going to be 1/ square root of 2.

This expression gives you a feel for how it will look like in a complex plane. σ is a constant for a given condition, at a given temperature, at a given diffusivity given concentration. ω is what we vary. It is going to look like a 45 degree line. 1 – j with a difference. 1 here is the real part and j is the imaginary part. Therefore it is like writing $\frac{y-x}{\sqrt{\omega}}$.

When I decrease the frequency, this number becomes a larger number. When I increase frequency it becomes a smaller factor. However, the ratio is always 1- j and it is always a 45 degree line. This is going to look like a 45 degree line with decreasing frequencies going towards larger value. The total faradaic impedance is given by R_t, charge transit resistance assistance + Warburg impedance. And we are able to write in this clean separate form only under special condition. It is a simple electron transfer reaction and we are at $E_{dc} = 0$ and I just want to mention there are other methods using Laplace transform. There are probably few other methods where you can get the same expression. [You should get the same expression at the end]. But typically you will get expressions like this for finite as well as semi-infinite boundary conditions. You get expressions like this given in the book. Some books give you also the previous expression which is a little more general. However, do not assume that R_t will not vary if you change the DC potential. This gives you the feeling that R_t will be dependent only on k_{10} and $C_{A\text{-bulk}}$ and temperature, and that is valid only at equilibrium. When you change the potential, R_t will change and not only that, it does depend on diffusivity.

In this special case you can rearrange and get certain equations substituted here and then you can get this value here.

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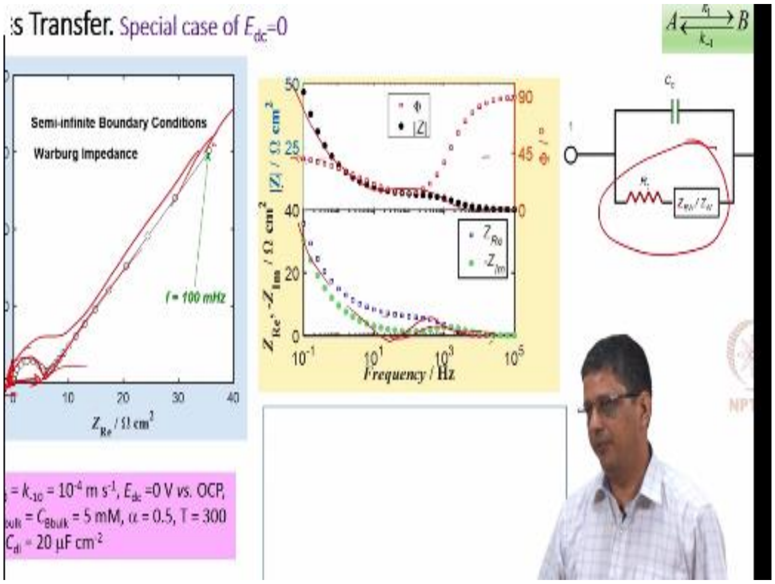

s Transfer. Special case of E_{dc}=0

$= k_{-10} = 10^{-4}$ m s^{-1}, E_{dc} =0 V vs. OCP,
$_{bulk} = C_{Bbulk}$ = 5 mM, α = 0.5, T = 300
C_{dl} = 20 µF cm^{-2}

And when you look at the R_t, when you look at the C_{dl}, solution resistance is 0. I have made up some numbers here. k_{10} k_{-10} has some numbers. E_{dc} is of course 0. I set C_A and $C_{B\ bulk}$ as 5 millimolar. Charge transfer coefficient is half. Temperature is at 300 kelvin. Double layer capacitance is 20 µF/cm^2. This is how it will look like and I have denoted Z_ω as a Warburg impedance. I can also represent bounded Warburg impedance when δ = finite value. I can set it as B_W. This is a 45 degree line only if you do not have anything else. [Here you have solution resistance. Solution resistance is not here, it is 0]. Double layer capacitance is there and charge transfer resistance is there. From here onwards it looks like a 45 degree line and depending on the values, it may look like this. At very low frequencies, it will look like a 45 degree line. Here it is not a 45 degree line shifted origin, shifted by $R_{solution}$ and R_{ct} or R_t. When you plot it in bode plot, you should also have a feel for how it will look like. Magnitude at low frequencies keep increasing. You have 1 loop and then the 2nd loop. Phase value starts at 90 here. This is not 45. It goes to little less than 45 here because its origin is shifted.

If you go to larger value of impedance or lower frequency, this will tell that it will be approaching 45. If this is very low, it will again approach 45 and if you look at Z_{real} and $Z_{imaginary}$, you get 1 loop in $Z_{imaginary}$ and it goes up, comes down and then it increases, goes up, comes down and then it increases as the frequency decreases. Real part moves up and then somewhat settles and then moves again. Real part increases, remain somewhat constant and then increases again. This is signature for you to look at either in complex plane plot or in the bode plot.

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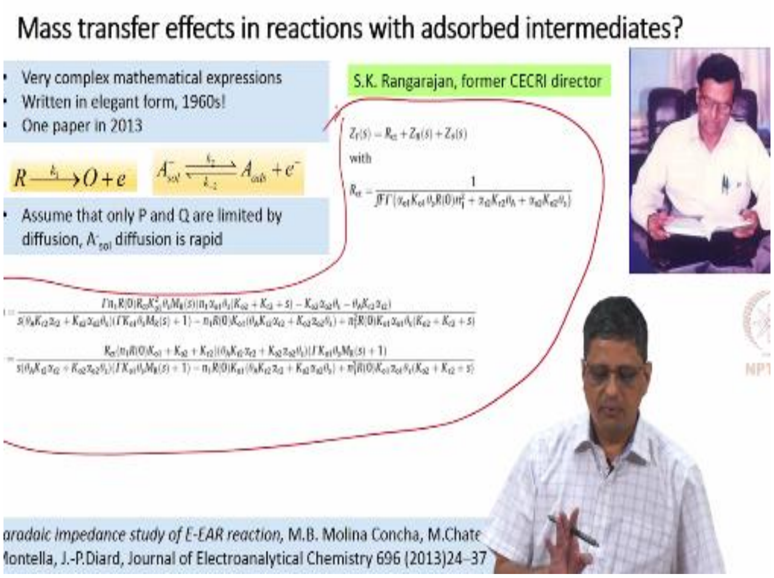

Mass transfer effects in reactions with adsorbed intermediates?

- Very complex mathematical expressions
- Written in elegant form, 1960s!
- One paper in 2013

S.K. Rangarajan, former CECRI director

$R \xrightarrow{k_1} O + e$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

- Assume that only P and Q are limited by diffusion, A^-_{sol} diffusion is rapid

$Z_T(s) = R_{ct} + Z_\theta(s) + Z_s(s)$

with

aradaic impedance study of E-EAR reaction, M.B. Molina Concha, M.Chate
ontella, J.-P.Diard, Journal of Electroanalytical Chemistry 696 (2013)24–37

"Professor – student conversation starts"

All this is for semi finite delta, right?

Yes, semi-infinite delta. We have not solved it for finite condition yet [and we will probably have to postpone it for next class]. All this is done for simple electron transfer reaction. When you have 1 adsorbed intermediate, when you have 2 adsorbed intermediate, none of this formula will work and you cannot just take the expression for Faradaic impedance and then add Warburg impedance there [although some people sometimes tend to do that].

It is possible to derive the expression. It is very complex. [I will just tell you a brief story and then leave you].

"Professor – student conversation ends"

[In 1960, S. K. Rangarajan, who was a former director of CECRI, derived some expressions for small amplitude, large amplitude conditions for general, not for 1 reaction. He was actually BSc mathematics person. He was not PhD and he was not in electrochemistry and at that time the CECRI director contacted him. In the beginning he started his career as a movie critic. Then went to academia and he was given a problem thinking it will probably take a year and he solved it in a day.

It is like a Ramanujam who solved very high level mathematics with very simple elegant expressions. To actually derive that and solve, you will have to spend a lot of time. Normal people will have to spend a lot of time to do. After 50 years an example paper came to say it take this reaction of E-EAR where we have 1 electron transfer reaction and one adsorption reaction which we have seen. We can derive the expression for kinetic limited case without any problem. It gives you a negative differential impedance. If you use the metrics form that he has given you will get expression like this. Each one of these again, what is this and what is this etc. goes with many expressions. What it means is it is possible to derive, but it is extremely complicated and lengthy and to tell you I have not derived it yet. I am aware that it is possible].

If you can understand what is done for electron transfer reaction that is good. I am not expecting that you will be able to derive for more complex cases but you should be aware that it is not as simple as writing the kinetic limited faradaic expression and then putting 1 more term there. These are interrelated. Basically the boundary condition where it says this concentration flux is equal to the current in 1 of the terms. Species that is coming here may not directly give you electron transfer. It may adsorb and after adsorption it may give you electron transfer reaction in the next step. The current may not be directly related to this. Current may be related to an adsorbed species and then the adsorbed species concentration may be related to the flux. They are coupled, and you cannot normally separate them out. [We will stop here and what we will do next is to derive the expression for bounded Warburg impedance and after that we will go to what is called CPE. Constant phase element].