Electrochemical Impedance Spectroscopy
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Lecture – 35
Bounded Warburg

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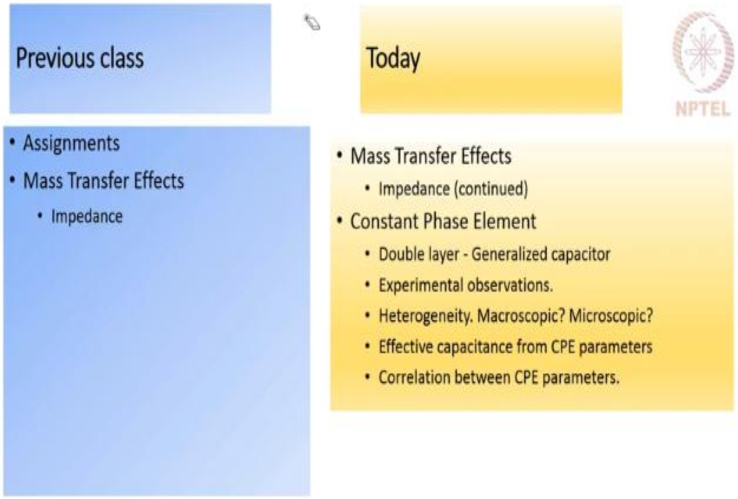

Previous class

- Assignments
- Mass Transfer Effects
  - Impedance

Today

- Mass Transfer Effects
  - Impedance (continued)
- Constant Phase Element
  - Double layer - Generalized capacitor
  - Experimental observations.
  - Heterogeneity. Macroscopic? Microscopic?
  - Effective capacitance from CPE parameters
  - Correlation between CPE parameters.

The equation for impedance we have seen it for impedance under what is called semi-infinite boundary conditions.

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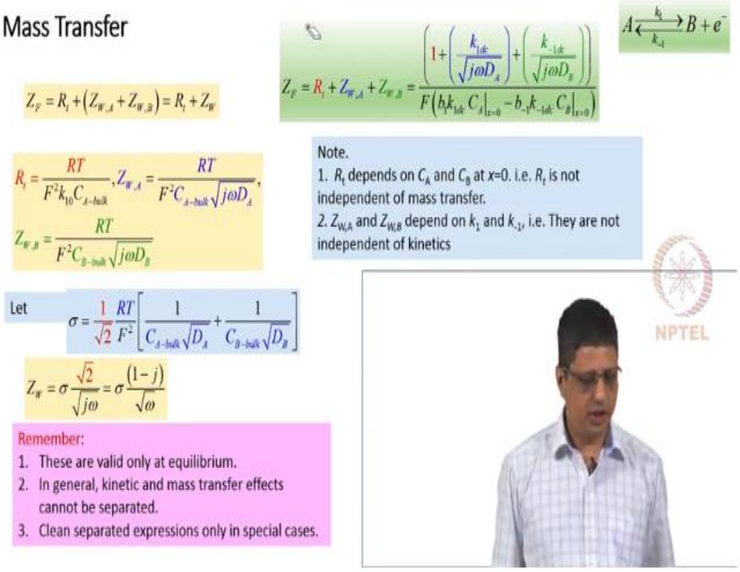

Mass Transfer

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

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

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

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

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

Note.
1. R_t depends on C_A and C_B at x=0. i.e. R_t is not independent of mass transfer.
2. $Z_{W,A}$ and $Z_{W,B}$ depend on k_1 and k_{-1}, i.e. They are not independent of kinetics

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

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

Remember:
1. These are valid only at equilibrium.
2. In general, kinetic and mass transfer effects cannot be separated.
3. Clean separated expressions only in special cases.

Just to refresh your memory, we had taken the Fick's second law equation with the appropriate boundary conditions. We had derived the equation for steady state current values at different rotational speed, and as a function of dc potential. We have also derived the equation for impedance assuming that the boundary condition is at $\delta=\infty$, that is semi-infinite boundary condition. We saw that you can write it in the faraday impedance in three different terms; one corresponds to charge transfer resistance, another corresponds to Warburg impedance for species A and another for species B under certain conditions that when we say dc potential is 0. You can simplify this and split it into these three component such that the charge transfer resistance does not have any diffusion term and the diffusion term does not have any kinetic term.

And of course if you have a semi-infinite boundary condition, only $E_{dc}=0$ is the steady state condition you would not get steady state condition for any non-zero value of E_{dc}.

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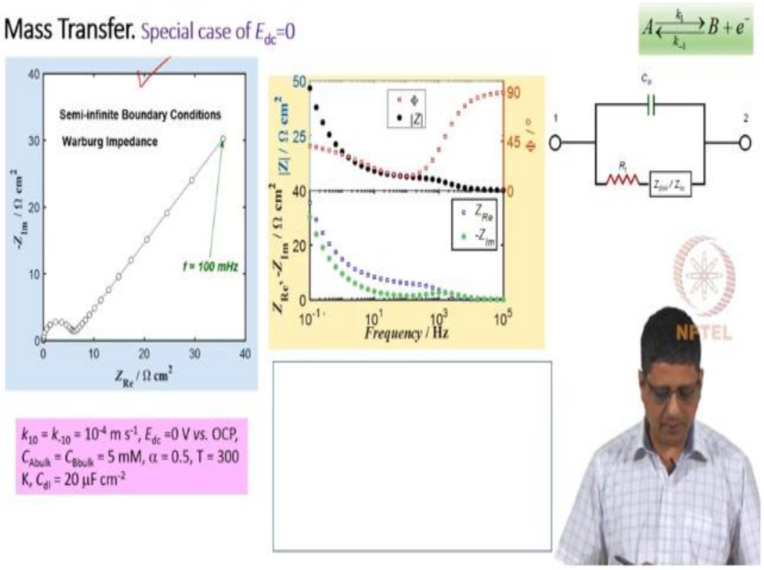

Mass Transfer. Special case of $E_{dc}=0$

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

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

We have seen that the complex plane plot would look like the one that shown here that is a 45° line with an offset of course to the origin and you have the bode plot represented here for certain values of kinetic parameters and the diffusivities.

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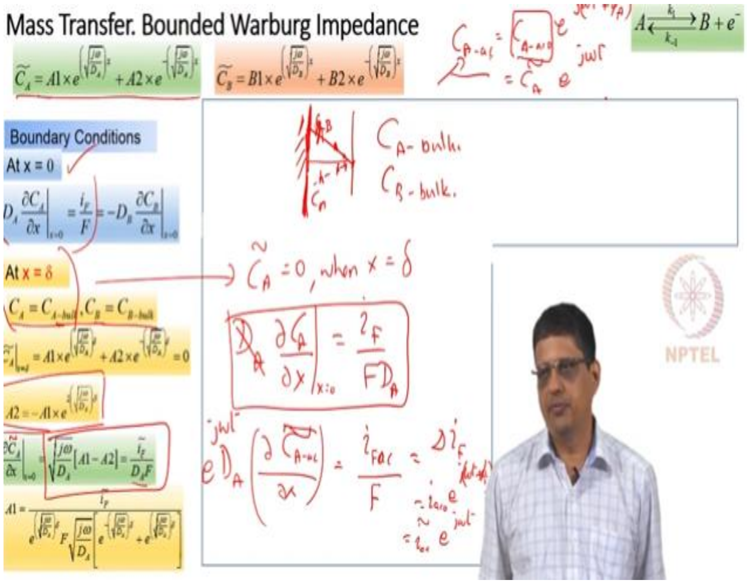

Mass Transfer. Bounded Warburg Impedance

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

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

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

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

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

$$\left.\widetilde{C_A}\right|_{x=\delta} = A1 \times e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} + A2 \times e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} = 0$$

$$A2 = -A1 \times e^{2\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta}$$

$$\left.\frac{\partial \widetilde{C_A}}{\partial x}\right|_{x=0} = \sqrt{\frac{j\omega}{D_A}}[A1 - A2] = \frac{\widetilde{i_F}}{D_A F}$$

$$A1 = \frac{\widetilde{i_F}}{e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} F \sqrt{\frac{j\omega}{D_A}} \left[e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} + e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta}\right]}$$

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

$C_{A\text{-bulk}}$

$C_{B\text{-bulk}}$

$\tilde{C}_A = 0$, when $x = \delta$

$$\boxed{\cancel{D_A} \left.\frac{\partial \tilde{C}_A}{\partial x}\right|_{x=0} = \frac{i_F}{F D_A}}$$

$$e^{j\omega t} D_A \left(\frac{\partial \tilde{C}_{A-ac}}{\partial x}\right) = \frac{i_{Fac}}{F} = \Delta i_F = i_{ac0}\, e^{j\omega t} = \tilde{i}_{ac}\, e^{j\omega t}$$

What we want to do is to derive the equations for a finite boundary condition that means the boundary layer thicknesses is finite. So, the basic equation is going to be the same. The general solution is also going to be the same. We are going to apply a different boundary condition. Previously we would have said, at extending to ∞ this is the result. Whereas, here we are going to say x= δ. It is going to be like this.

So, the general solution is going to be $_A$ $_B$ Φ and again to refresh your memory, see ac was written as C_{Aac} was written as C_{Aac0} e power j ω t+ $_A$ and then we wrote it as $_A$ e power j ω t. That is to say $_A$ is defined like this. And similarly we have $_{B.}$ And our original equations were unlike those dC_A/dt then we said C_A can be split as $C_{Adc}+C_{Aac}$.

And therefore these equation we wrote in terms of C_{Aac}. And then we said C_A ac can be returned to this form that is our assumption and with that assumption this pde became ode. That means, we have a form for this, therefore, we are supposed to find how C_{Aac} depends on x. Then this became equation in $_A$ and that is how we got the solutions. Now we want to say at x = 0 the boundary condition is the same that is the flux of this A species tells us how much current is coming through, how much faraday current is there. And that is also related to the flux of the species B. Just as sign is opposite because A comes in it gets converted to B. Therefore, B goes out at the anodic potential. Second boundary condition is instead of saying x = ∞ we say x= δ concentration is C_A bulk and C_B bulk. Which means if this is the electrode, this is the boundary layer. Beyond this concentration remains the same. Here, when I apply only dc potential it is possible this is C_B and this is C_A, a straight line, linear line and if I apply a sinusoidal potential on top of this concentration here will fluctuate with time. Concentration here will also fluctuate with time concentration here will fluctuate here also will fluctuate. And you can imagine that amplitude of fluctuation will go down as you go further towards the boundary. At the boundary, we say it is not changing. C_A is C_A bulk, C_B is C_B bulk, which means ${}_{A}$ is going to be 0, ${}_{B}$ is going to be 0. That is because the ac component magnitude is 0. Only the dc component remains there. We are going to solve it for C_A and then I am going to say if you solve for C_B you are going to get similar thing except the negative sign.

So, we want to calculate A1 A2 using these two boundary conditions. Can you try this? Earlier case when $x = \infty$ we could say A1 has to be 0 because otherwise it goes to ∞. Here you have to solve these equations by solving them simultaneously. So, we take this equation we take this boundary condition, and the second boundary condition which is written as ${}_{A} = 0$ when $x = \delta$ and then use this to find value of A1 and A2. When $x = \delta$, concentration is constant. It is C_A bulk. That means fluctuations are 0 since the amplitude of the concentration oscillation is 0. It will take you a few minutes but it is not that difficult. First part you can show that A2 is related to A1 with the factor of e power 2 square root of j ω/D_A δ. We can rearrange the first equation and write A2 instead of A1. Second is little more complex but we have seen the procedure at x=0, this is what we know. This means when I write in terms of ${}_{A}$, I can write in terms of ac+dc. I would get C_{Aac} δ/δ x diffusivity= i_{Fac} and that is Φ the same as Δi_F. That is one way of writing. And other way of writing it is, iac0 e power j ω t+ i. Another way of writing ac e power j ω t. ${}_{A}$ e power j ω t. That means I should write δ C_A/ δx δ ${}_{A}$ /δx at x=0 is same as i_F /diffusivity of A and F faraday constant, F and the numerator.

So, instead of writing like this I can of course bring this D_A below the denominator here instead of writing δC_A/ δx at x=0 = i_F/D_A F, I can write δ ${}_{A}$ /δx at ${}_{F}$ /F D_A. And of course I can take the derivative of C_A with respect to x and then at x = 0 I can find the value. Now using this equation and this equation I can write A1 and A2 in terms of known parameters.

I would actually like you to try that and get this. A lot of times in the books, you would see that this is the equation. But how do you get it? And when you derive, you would also see under what conditions they are valid. So for example, you should not take the equation for semi-infinite boundary condition and apply it when E_{dc} is not 0. If you are going to use a dc offset, dc bias, you should always take at least if you are going to compare with analytical solution, take the finite boundary layer condition. In case the boundary layer thickness is large, estimated to be large, used that large value. And when boundary layer thickness is large, that finite boundary layer thickness equation should approach this semi-infinite boundary thickness equation. That is. But, you should be aware of what are the limitations of the formula that we derived.

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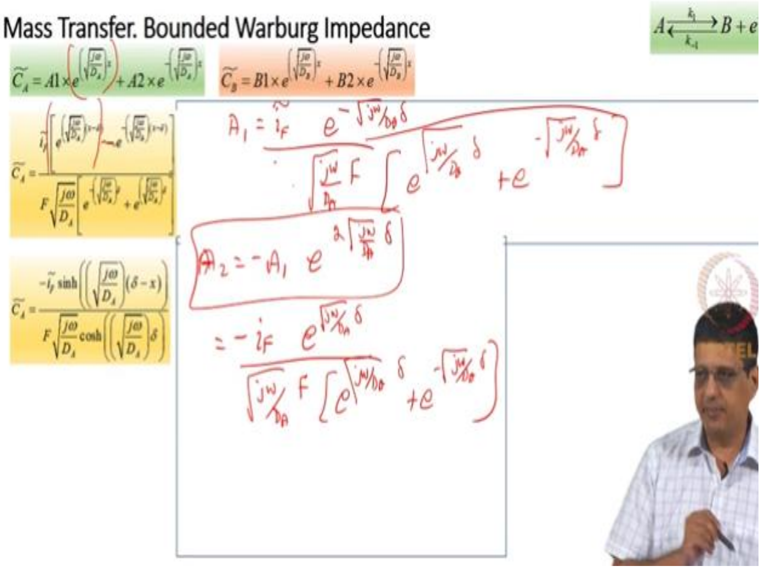

Mass Transfer. Bounded Warburg Impedance

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

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

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

$$\widetilde{C}_A = \frac{\widetilde{i}_F\left[e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)(x-\delta)} - e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)(x-\delta)}\right]}{F\sqrt{\frac{j\omega}{D_A}}\left[e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} + e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta}\right]}$$

$$\widetilde{C}_A = \frac{-\widetilde{i}_F \sinh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)(\delta - x)\right)}{F\sqrt{\frac{j\omega}{D_A}} \cosh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}$$

$$A_1 = \frac{\widetilde{i}_F\, e^{-\sqrt{j\omega/D_A}\,\delta}}{\sqrt{\frac{j\omega}{D_A}}\, F\left[e^{\sqrt{j\omega/D_A}\,\delta} + e^{-\sqrt{j\omega/D_A}\,\delta}\right]}$$

$$\boxed{A_2 = -A_1\, e^{2\sqrt{\frac{j\omega}{D_A}}\,\delta}}$$

$$= \frac{-i_F\, e^{\sqrt{j\omega/D_A}\,\delta}}{\sqrt{j\omega/D_A}\, F\left[e^{\sqrt{j\omega/D_A}\,\delta} + e^{-\sqrt{j\omega/D_A}\,\delta}\right]}$$

So, if you get the value of A1 and A2 do you get an equation like this? So concentration fluctuation, the magnitude and phase depend on the location x. We really want to know the concentration fluctuation at x=0. But here you can see if x = δ you get 0 fluctuation so that equation at least appears to be. I mean x=δ that you will get e power 0- e power 0 therefore the numerator goes to 0 fluctuation goes to 0.

At x=0, fluctuations are maximum. This is basically substituting for A1 and A2. So I have skipped one or two minor re arrangements here. Maybe I should not. What is the value of A1? $_F$ / (you got this before). And A2 is going to be -A1. We got this from the first boundary condition. And therefore it is going to be $-i_F$. If I multiply by e power 2 square root of j ω/D_A, I am going to get correct? So it is going to look like this. A1 I can write like this or I can write in the numerator as… now A1 x e power square root of j ω/D_A x is going to be e power j ω/D_A square root x-δ. So, this first part comes from the A1 component. This -sign comes here, denominator remains the same. A2 is going to be e power j ω/D_A δ –x. Instead of writing it as δ – x, I write it as – of (x-δ), so that it can be written in a little more compact form. This numerator is actually two times hyperbolic sine written as sin h, and the denominator is two times hyperbolic cosine. So, the factor of two cancel out. So, ${}_F$ sin h, the numerator has δ-x denominators cos sin h with the δ factor and then of course 1/j ω D_A for the concentration of A. So, it needs careful algebraic rearrangements but that is enough.

Similarly ${}_B$ it is going to be same that except instead of the diffusivity of A you would have the diffusivity of B involved in it; instead of +sign you will have – sign there. Because the boundary conditions, the second boundary condition is the same at δ x=δ, you will have C_B fluctuations at 0. First boundary condition it would say i_F/F is – of D_B δC/δx. So, because of that the factors will have interchanged in the sign. So, it will look similar to ${}_A$ but with the negative sign or the negative sign is gone here and instead of D_A you will have diffusivity D_B there. **“Professor - student conversation starts”** But sir x=δ we got both C_A and CB=0, but at some boundary they must be some one component. We do not get C_A and C_B to be 0. We get fluctuation in C_A, ${}_A$ ${}_B$ to be 0. C_A is actually C_A bulk. C_B is C_B bulk.

(Sir can you go to the previous slide sure yes) here we are solving that δ ${}_A$/δx right, at x=0? Yes. So if you substitute A1, A2 as in the form of A1, ${}_F$ / D_A*F right to solve A1 from that equation, that square equation, δ ${}_A$ /δx, at x=0, from that equation if we substitute A2 in terms of A1 and solve for A1 right? In that case F/D_A*F right? F/D_A*F divided by some j, root j ω*1+something. Now, look at this. I am still keeping it. This is there. Now if I want to find the value of A2 or A1, what do I do? I take this equation and substitute it here. What do I get?

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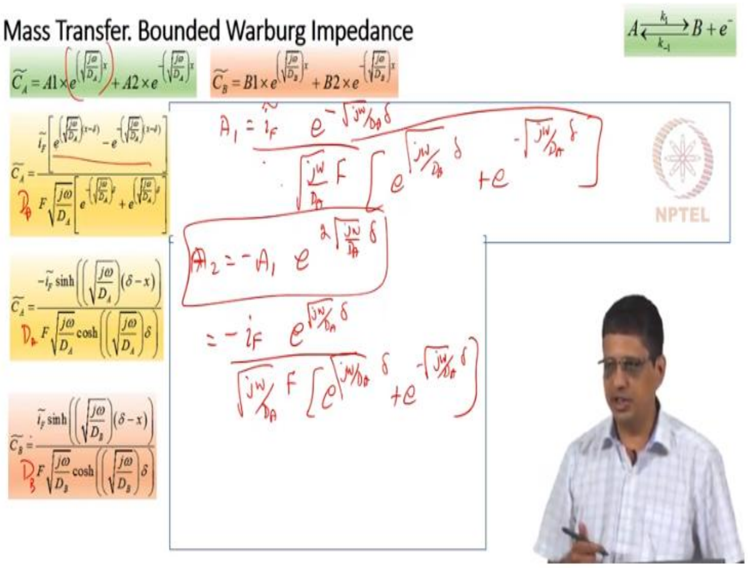

Mass Transfer. Bounded Warburg Impedance

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

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

$$\widetilde{C_A} = \frac{\widetilde{i_F}\left[e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)(x-\delta)} - e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)(x-\delta)}\right]}{D_A F\sqrt{\frac{j\omega}{D_A}}\left[e^{-\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta} + e^{\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta}\right]}$$

$$\widetilde{C_A} = \frac{-\widetilde{i_F}\sinh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)(\delta - x)\right)}{D_A F\sqrt{\frac{j\omega}{D_A}}\cosh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}$$

$$\widetilde{C_B} = \frac{\widetilde{i_F}\sinh\left(\left(\sqrt{\frac{j\omega}{D_B}}\right)(\delta - x)\right)}{D_B F\sqrt{\frac{j\omega}{D_B}}\cosh\left(\left(\sqrt{\frac{j\omega}{D_B}}\right)\delta\right)}$$

$$A_1 = \frac{\tilde{i}_F\, e^{-\sqrt{j\omega/D_A}\,\delta}}{\sqrt{\frac{j\omega}{D_A}}\,F\left[e^{\sqrt{j\omega/D_A}\,\delta} + e^{-\sqrt{j\omega/D_A}\,\delta}\right]}$$

$$\boxed{A_2 = -A_1\, e^{2\sqrt{\frac{j\omega}{D_A}}\,\delta}}$$

$$= \frac{-i_F\, e^{\sqrt{j\omega/D_A}\,\delta}}{\sqrt{j\omega/D_A}\,F\left[e^{\sqrt{j\omega/D_A}\,\delta} + e^{-\sqrt{j\omega/D_A}\,\delta}\right]}$$

NPTEL

I am going to write square root of j ω/D_A A1 – I will write it little more neatly this is correct because instead of -A2 I would write it as A1 e power 2 square root of j ω/D_A δ? T F

/DAF. Now I can pull A1 out of this, so it I going to loo F

/DAF. I divide by j ω/D_A. I have missed the DA. Have I? And then instead of writing it as 1+epower that is one way of writing it. Another way is to pull out I can multiply and divide by (()) (17:53) δ and then I will get yes I have missed the F factor is there. I have missed the D_A. That is one way or I can write it as I can bring it in and then cancel. Right now it is easier to write like this and that means is it correct? Can we say that C_A+C_B will be C_T always? [can we consider a function like overall function will not change, so, instead of no no no no not overall function overall concentration at a given location]. Not exactly, not always. If D_A=D_B, you can do that. But according to this equation for 1 mole we are getting 1 mole of B this is… 1 mole of A will get 1 mole of B. If we take the entire volume on the boundary layer you can say that but not at one location because the concentration of A can build up or B can build up because B may not diffuse that fast].

Concentration of A may decrease up to some level so when the diffusivity of A and B are equal, A will get consumed concentration will go down it would not go to 0 because it is coming at a particular rate. Let us take a steady state condition, concentration of B will also build up but if B diffusivity is slow it will build up more. Net 1 mole of A will give you 1 mole of B there is no doubt about that. But the concentration of A + B need not be a constant regardless of any irrespective of the location and space you cannot always say that. But for a binary system, we say that D_{AB}=D_{BA} that is what we have proved in mass transfer, if we have a binary system the diffusion of diffusivity of A in B (()) you are talking about two gases so it is just diffusivity of A in this mixture, diffusivity of B in this mixture.

And if we takes for example ferro-ferri example they would not be the same in fact it is more or less diffusivity of A in water and B in water although it is a mixture. Then it will be different it is different but if we have two mixtures we have a binary mixture here we have A and B and we do not have any other substance. In that case even here sometime people will approximate and say D_A is roughly = D_B and simplify it makes it a little easier to look at this equation because it will have fewer terms. But for binary system we have proved the J_A=-J_B. If 1 is dC_A/dx is decreasing in that case if even if we considered that D_A is not =D_B. So one is increasing the other component of that is decreasing. That is why we write the boundary condition as when it is positive here it is negative there. Then the flux we do consider it as the amount of either that is coming in is going to= the amount of B that is going out. J of A an J of B with the opposite sign and they are equal, but unless D_A and D_B are equal you cannot say that C_A and C_B the sum of them is going to be the same. But if it will not happen, then at one point the overall composition will keep changing. It would not keep changing you get to be a higher value, but under steady state condition that higher concentration gradient with lower diffusivity is allowing it to go at the steady rate.

Amount of A that is coming in should be equal to amount of B that is going out. So, if diffusivity of A is a much much larger than the diffusivity of B, that means to B diffuses slowly. Now, a small concentration gradient will allow A to come at a particular rate. Same rate if B has to go it needs a larger concentration gradient.

So, concentration of B will be higher. A would have gone down. For example, initially A is at 5 mM B is also at 5 mM. A would have gone down to 4 mM because of reaction, it is consumed. B will not be at 6 mM it may need to be at 7 mM to go at the same rate. So, under steady state condition, it will build up to a different value but it would not keep increasing. Because the diffusivity is for example in this case we assumed it is less or smaller. So, when you apply a sinusoidal also, A will come at a particular rate or fluctuate at a particular rate, B will fluctuate at a different rate and it will fluctuate around the different mean value. But it would still be sinusoidal with a different amplitude. You cannot assume that the amplitude of A and B will be the same. Based on the diffusivity values, the amplitude values will change. Phase value will also change. But if the diffusivity happened to be equal then they can say they are fluctuations will be mirroring each other exactly. Here the sign is changing so when C increases A will decrease that is expected, amplitude will be comparable because typically D_A and D_B are in similar range. But you cannot assume that they are going to be equal “**Professor - student conversation ends”**.

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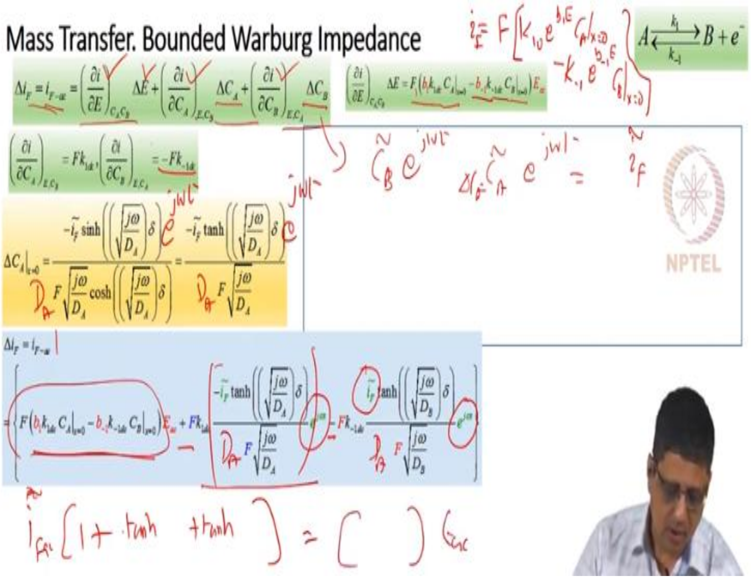

Mass Transfer. Bounded Warburg Impedance

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

$$\Delta i_F = i_{F-ac} = \left(\frac{\partial i}{\partial E}\right)_{C_A,C_B} \Delta E + \left(\frac{\partial i}{\partial C_A}\right)_{E,C_B} \Delta C_A + \left(\frac{\partial i}{\partial C_B}\right)_{E,C_A} \Delta C_B$$

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

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

$$\Delta C_A|_{x=0} = \frac{-\tilde{i}_F \sinh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{D_A F\sqrt{\frac{j\omega}{D_A}} \cosh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)} e^{j\omega t} = \frac{-\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{D_A F\sqrt{\frac{j\omega}{D_A}}} e^{j\omega t}$$

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

$$= \left\{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right) E_{ac} + Fk_{1dc}\left(\frac{-\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{D_A F\sqrt{\frac{j\omega}{D_A}}}\right) e^{j\omega t} - Fk_{-1dc}\frac{\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_B}}\right)\delta\right)}{D_B F\sqrt{\frac{j\omega}{D_B}}} e^{j\omega t}\right\}$$

$$i_F = F\left[k_{1,0} e^{b_1 E} C_A|_{x=0} - k_{-1} e^{b_{-1} E} C_B|_{x=0}\right]$$

$$\tilde{C}_B e^{j\omega t} \quad \Delta i_F \tilde{C}_A e^{j\omega t} = \tilde{i}_F$$

$$\tilde{i}_{Fac}[1 + \tanh + \tanh] = [\quad] E_{ac}$$

Now, we go back to the original equation where we write current fluctuation as a function of change in potential, change in concentration of A and concentration of B, and this we have written it as $_B$ e power j ω t, $_A$ e power j ω t, for ΔC_A. Now we have written it in ter $_F$. So what would happen is $\delta i/\delta C_A$ and $\delta i/\delta C_B$ we have the values. And this is based on the equation i = faraday current is = the net rate of production of electrons. So, from this we saw that i_F can be written as $i_{Fdc} + i_{Fac}$ and iF_{ac} can be written as δi/δE when you take the δi/δE you get Fb_1k_{1dc} C_A at x=0, $b_{-1}k_{-1dc}$. Because when we take the partial derivative action concentration of A and B are fixed. Here we assume concentration of B and the potential are fixed. Potential is fixed and concentration of A is fixed. You get three terms. We got expression for this is of course E_{ac}, we got expression for this got this. Now we derive the expression for ΔC_A. So ΔC_A is basically going to be $_A$ = e power j ω t and ΔC_A at x = 0 we substitute x=0 there and you would get sin h/cos h which is going to give you hyperbolic tangent and I am also adding the diffusivity D_A.

Previously it was (δ- x) but since we substitute for x as 0, we would get this simplified expression. And if it is ΔC_A we should write e power j ω t $_A$ I will leave it e power j ω t out. Now if you substitute to the entire thing. We can write for the first expression *ac* it comes in terms of E_{ac}, $_F$ and e power j ω t, $_F$ and e power j ω t which is basically Δi_F. So, we can rearrange and get an expression for i_{Fac}/E_{ac}. So, you can see that this is going to give you 1+ whatever is here + whatever it is here you got a negative sign because it is going to be -F k_{-1dc} for the partial derivative with respect to C_B. Here you have got the negative sign because $_A$ is with a negative sign. So when you bring them to the left side, this will also become positive this will also become positive. So, you would get $_F$ or i_{Fac} 1+tan h something+tan h something and that is going to be = a factor multiplied by E_{ac}. So, you can rearrange and get i_{Fac}/ E_{ac} or E_{ac}/i_{Fac}.

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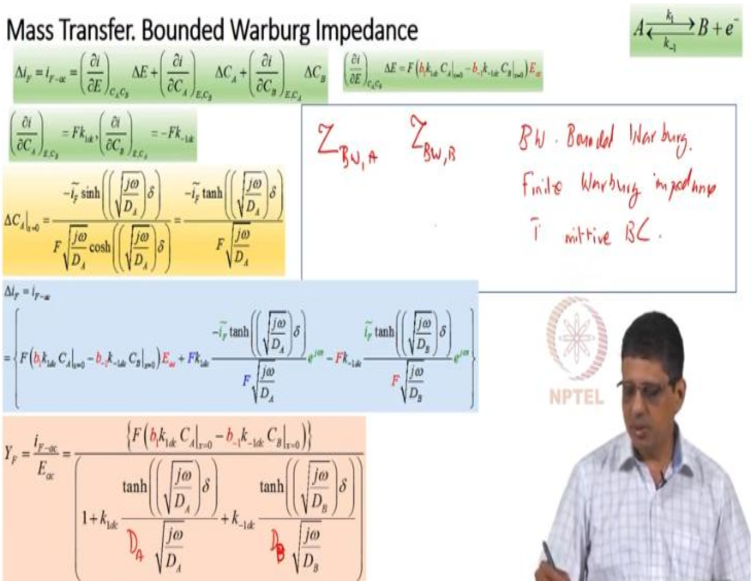

Mass Transfer. Bounded Warburg Impedance

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

$$\Delta i_F = i_{F-ac} = \left(\frac{\partial i}{\partial E}\right)_{C_A C_B} \Delta E + \left(\frac{\partial i}{\partial C_A}\right)_{E,C_B} \Delta C_A + \left(\frac{\partial i}{\partial C_B}\right)_{E,C_A} \Delta C_B$$

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

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

$$\Delta C_A|_{x=0} = \frac{-\tilde{i}_F \sinh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{F\sqrt{\frac{j\omega}{D_A}} \cosh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)} = \frac{-\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{F\sqrt{\frac{j\omega}{D_A}}}$$

$$\Delta i_F = i_{F-ac}$$
$$= \left\{F\left(b_1 k_{1dc} C_A|_{x=0} - b_{-1} k_{-1dc} C_B|_{x=0}\right) E_{ac} + F k_{1dc} \frac{-\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_A}}\right)\delta\right)}{F\sqrt{\frac{j\omega}{D_A}}} e^{j\omega t} - F k_{-1dc} \frac{\tilde{i}_F \tanh\left(\left(\sqrt{\frac{j\omega}{D_B}}\right)\delta\right)}{F\sqrt{\frac{j\omega}{D_B}}} e^{j\omega t}\right\}$$

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

$Z_{BW,A}$ $Z_{BW,B}$

BW . Bounded Warburg.

Finite Warburg impedance

T mittive BC.

So, fairly large expression but I think D_A and D_B has to be there. You can invert it and write this in three terms again as Rt Z ω Z_{WA} Z_{WB}. Sometimes it is written as BW to say bounded Warburg impedance. Sometimes it is called a transmittive boundary condition to say that there is a film, diffusion occurs there and at the end of this, A can come in or go out B can come in or go it transmits.

Sometimes they would derive the expression for the impedance in the film where at the end of the film nothing moves in or out. That would be called as blocked boundary condition. There you would say the derivative of this concentration is going to be 0, because the flux is going to be 0 that means that dC_A/dx and dC_B/dx acts at the boundary is going to be 0. So, you may have a film it will may diffuse in and out but in and out. Diffuse in the sense it may be produced or consumed in this boundary and it can diffuse in and out but at the other boundary it is not taken. So, it will have a slightly different expression of course and the way it looks a bit different. But the equations to going to be same except when you finally get the value of A1 and A2 you need to use a slightly different boundary condition.

So, compared to that this will be called as transmittive boundary condition, open finite link diffusion, no, different groups would use different acronyms for this. But we normally say it is bounded Warburg or finite Warburg impedance.

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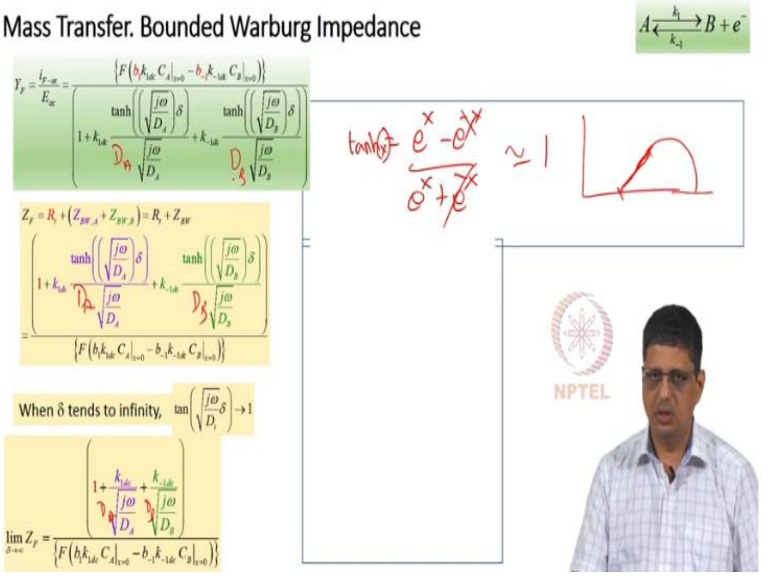

Mass Transfer. Bounded Warburg Impedance

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

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

$$\tanh(x) = \frac{e^x - \cancel{e^{-x}}}{e^x + \cancel{e^{-x}}} \simeq 1$$

$$Z_F = R_t + \left(Z_{BW,A} + Z_{BW,B}\right) = R_t + Z_{BW}$$

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

When δ tends to infinity, $\tan\left(\sqrt{\frac{j\omega}{D_i}}\delta\right) \to 1$

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

So, if I invert it i would get it as 3 terms. Thing is, when δ tends to ∞ when I put large value of δ what happens to tan h? x tends to ∞ this goes out it is going to go towards 1. x tends to ∞ or here it is δ tending to ∞. Even when δ is not ∞, ω is relatively large it is going to look like tan h is going to be 1. So, what you would expect to see is, it should look like the Warburg impedance. maybe this is not nice but look like a 45° line with offset at this frequency range later it is actually going to come down and settle. At limit δ tends to ∞ it is going to look like what you have seen before. Of course here too, right? So far we have not assumed that the DC potential is 0 in this example. When δ is finite value when ω becomes 0 what do we see.

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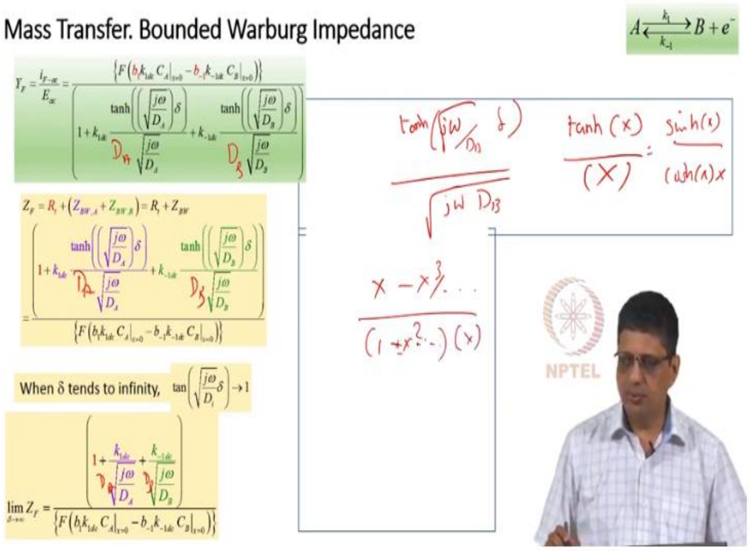

Mass Transfer. Bounded Warburg Impedance

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

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

$$Z_F = R_t + \left(Z_{BW,A} + Z_{BW,B}\right) = R_t + Z_{BW}$$

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

When δ tends to infinity, $\tan\left(\sqrt{\frac{j\omega}{D_i}}\delta\right) \to 1$

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

$$\frac{\tanh\left(\sqrt{\frac{jw}{D_B}}\,\delta\right)}{\sqrt{jw\,D_B}}$$

$$\frac{\tanh(x)}{(x)} = \frac{\sinh(x)}{\cosh(x)\,x}$$

$$\frac{x - x^3/\ldots}{(1 \pm x^2\ldots)(x)}$$

You are going to get tan h square root of j ω D_B, D_A it does not matter. So it is going to look like 0/0 and you can apply L'Hospital's Rule and get up expression for this it will settle at a finite value. Sin h of x is going to be x this is going to be $1 \pm x^2$ etc. So, if you do this you would get 1 here for tan x tan hx/x but then you have other factors so when you take this you would find it will come to finite value.

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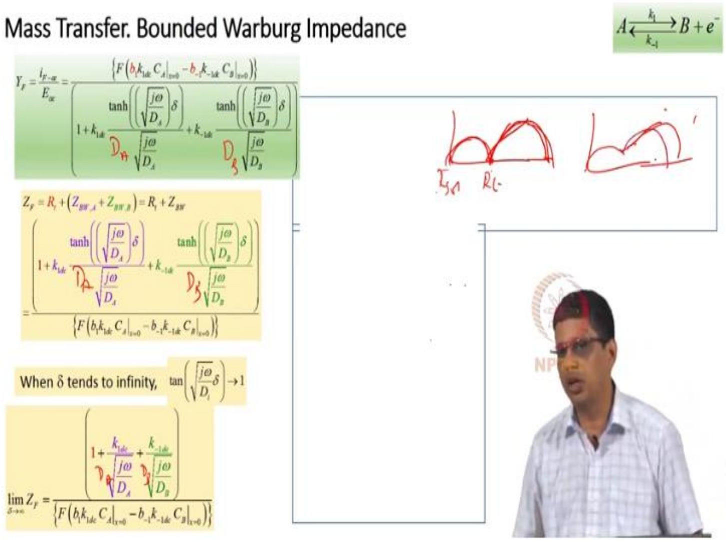

Mass Transfer. Bounded Warburg Impedance

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

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

$$Z_F = R_t + \left(Z_{BW,A} + Z_{BW,B}\right) = R_t + Z_{BW}$$

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

When δ tends to infinity, $\tan\left(\sqrt{\frac{j\omega}{D_i}}\delta\right) \to 1$

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

Which means, this will settle on the real access. It is not going to be a complex number. It is going to be a real number and it is not 0. So, it is going to be R_t + some value so this is the R_t value at high frequency it is going to look like the 45° line because it is similar to at low frequencies it is going to settle here and that settling function is given by tan h of this terms within bracket divide by this term within bracket.

Sir the first loop corresponds to Cdl right Cdl and R_t this is our solution which is we are taking it as 0, this is going to be R_t and this would not look like a loop it will look like a 45° line, I mean it would not look like a semi-circle it look like a 45° line to some level and then a 45° line and then with an offset of course and it may not even come nicely all the way here and go. It may come like this and go here but it is going to be different from a capacitive loop which you have seen for one absorbed intermediate. But in order to clearly see that, we should always plot it in the equal scale. Plot it in non-equals scale it can stretch and it is not easy for us to see

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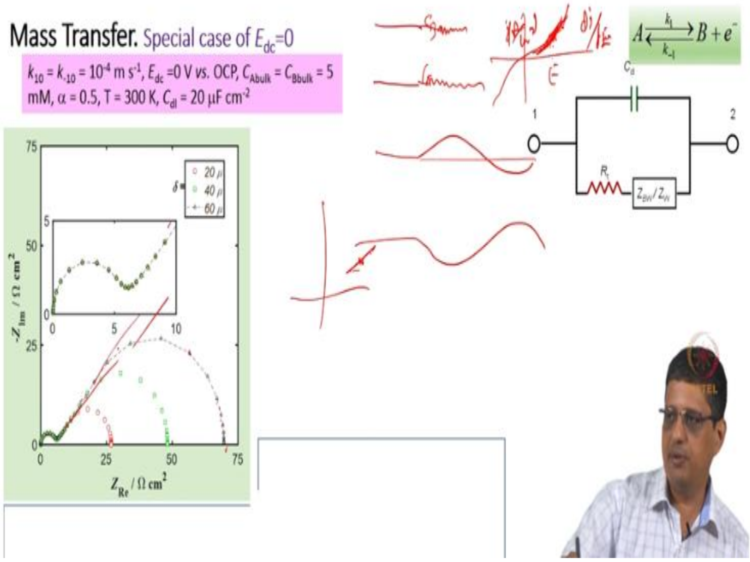

Mass Transfer. Special case of E_{dc}=0

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

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

So, taken certain values I just use the formula and predict that impedance for variety of frequencies and plot it for different boundary layer thicknesses. If we look here it looks like a semicircle not completely touching the real access of course and then it looks like a 45° line to some level and then it settles at a real axis when you go to high frequencies you will not see any difference when the boundary layer thickness is varying.

When you go to low frequency you would see a difference. So here in the inside all the points are overlapping only at the latest stages they are separating out. You can see this is not a semi-circle right. It is a sort of distorted semicircle. It looks like a nice semicircle or on the right side arc is neat on the left side but medium frequencies the arc is definitely not a part of a circle. Now when the boundary layer thickness is large why do the impedance values go higher or larger at low enough frequency? At high frequency why does it look similar for all this boundary layer thickness values? Basically at high frequencies, fluctuation in concentration is not that high. At high frequencies, you have potential varying because of it the concentration of the surface concentration of A and B will change but it cannot keep up that easily the diffusion cannot keep up that easily.

If you give very high change very high frequency very fast change the rapid change in the potential rate constant will still keep up with that at least that is our assumption k will keep fluctuating as quickly as the potential fluctuates. But the concentration of A and B will not fluctuate that much. So the magnitude of the concentration change C_A is at this level C_B is at this level if I apply a dc potential if i apply very fast ac it is going to look like this.

If I apply a slow frequency potential changes to the same maximum extent but it increases slowly and decreases slowly that means this can also change concentration fluctuation can change means it will go like this of course B increases A will decrease. But it can keep up so when I go to low enough frequency as the potential changes you can almost look at the DC curve and then say from here I very slowly increase the potential to this and slowly decrease the potential to this. I can say this is how the current will also increase and decrease. In fact in potentiodynamic polarization we go to a potential measure the current, we go to another potential and measure the current and practically we end up doing it at a scan rate, slow scan rate. Which means we are thinking it is more or less at steady state. So, from this potential dynamic polarization curve you can estimate how the low frequency impedance will come.

This tells if I start at dc potential and give a sinusoidal potential fluctuating at a very slow rate, low frequency, current will also going to go like this. I am not giving a large sinusoidal potential. I am giving a small 5 mV 10 mV amplitude. So, I can estimate the polarization resistance from the potentiodynmaic polarization curve. I can look at the slope of that curve and I will get the value experimentally when you compare the polarization resistance from the impedance data and from the potentiodynamic polarization curve you should get within the experimental error you should get the same value. Of course here it is going to be the inverse of this because what you get is di/dE and polarization resistance is dE/di. So, get the slope take the inverse of it and then compare with the here it is going to be ohm centimetre square. Here of course this means it is going to be amp per centimetre square do not take the raw data of amp. Other than that precaution you should get more or less same value polarization resistance is just the impedance right? Or we are talking about something else polarization resistance is the if you look at the impedance data is that the impedance is at the low frequency limit which is basically we expect it to be 0 frequency limit but whatever low frequency you can get if you get somewhere here you should extrapolate and get it. It should be a real value and phase should be 0. So here if I give more and more frequencies that means lower and lower frequencies it is not going to go like this it is just going to settle here. Points are packed more and more closely here and of course because I have the equation, I can substitute there $\omega=0$ and find the value.

But in general if you are measuring experimentally and then you are finding it settling there you will take that as a polarization resistance. That is one way of experimentally measuring it. Another way is to measure this around this value, go at, actually you do not have to even go you go here settle there measure the dc current, then go to another point wait for sufficient time measure the dc current, go to another point wait for sufficient time measure the DC current that is one way of doing it or go at a very slow rate and measure the dc current, find the slope of that fit it to a straight line if it is a curved line treat it to a quadratic equation and find the slope of it. That inverse of the slope would give you a polarization resistance. Basically it tells if I want to change the potential by little bit what is the resistance offered by the system? If the current is large you can change the potential a little bit, the change in current is large, then you have a low polarization resistance. If it does not change that much you have a large current does not change that much you have large polarization resistance. That is to say I have certain charge here in the interface, I have certain potential and certain charge how easy or difficult is it for me to change it? Change it if it is a 0 it is a change of polarity you can also measure it at any dc bias. Current is very low, resistance is very high. Now if I have a large δ versus small δ if you have a large δ it is harder for the diffusion. Large δ is one assumption I mean one way of looking at it low D_A diffusivity D_A and D_B that is also going to be equivalent. So instead of doing this of course this is practically easier to say I have one system I will change the rotational speed or change the δ. You can compare different systems with different diffusivity and you will get similar results. Lower diffusivity will end up giving you a larger polarization resistance. But our here I am just comparing different δ values, different boundary layer thicknesses you will end up getting larger boundary layer larger polarization resistance.

And of course you can visualize, when δ becomes ∞ it is going to look like this and settle at ∞ which is basically a 45° line. We are not really going to see where it settles but you can visualize that as you increase the δ it is going to approach more and more the 45° line for a large number of frequencies before it comes down and settles.

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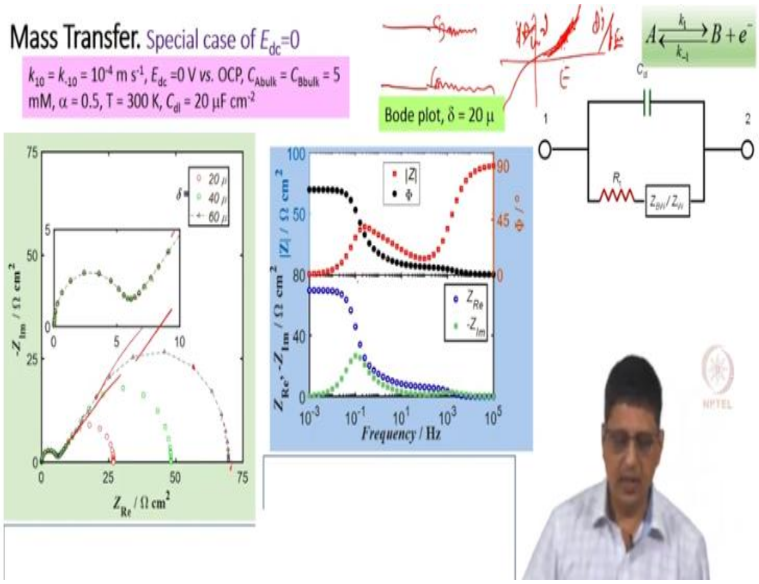

Mass Transfer. Special case of E_{dc}=0

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

Bode plot, δ = 20 μ

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

And if I really look at the bode plot, there is a small maximum here it is not easy to see in this scale. And then imaginary part, imaginary part goes through them maximum here and then another maximum correct real part of course goes settles goes and settles again that means it increases settles increases settles again. Magnitude and phase of course here you do not see it is a starting at 90 degree because it starts like a vertical line. Practical cases when you have a solution resistance it actually starts at 0, it will go up in the phase come down go up and come down. But it is not a clean symmetric peak because it is not really a semi-circle. But this is a signature that you would see in boundary plot.

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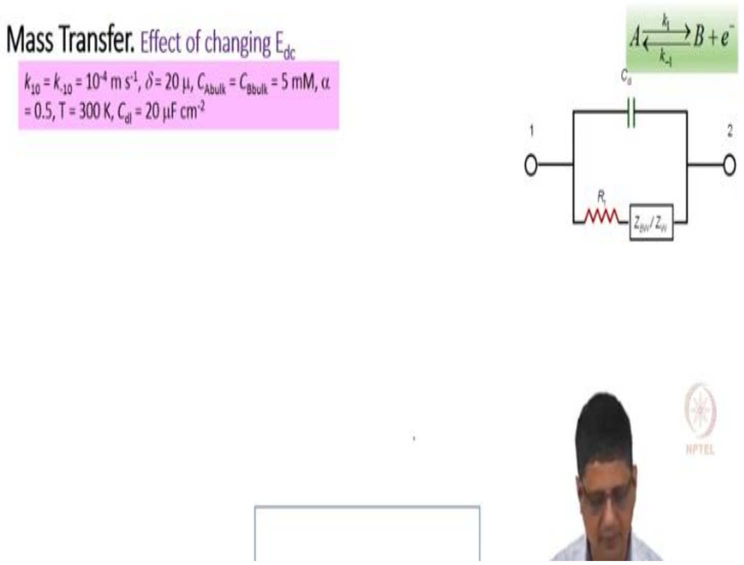

Mass Transfer. Effect of changing E_{dc}

$k_{10} = k_{-10} = 10^{-4}$ m s^{-1}, $\delta = 20$ μ, $C_{Abulk} = C_{Bbulk} = 5$ mM, $\alpha = 0.5$, T = 300 K, $C_{dl} = 20$ μF cm^{-2}

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

I think I will continue it tomorrow with the one more part of it that is the effect of dc potential and then we will move on to a phenomena called CPE constant phase element we will stop here today.

So, we will just continue with where we left yesterday which is to wrap up the part on mass transfer effects on the impedance and then we will start with what is known as constant phase element. If time permits, we will also go to the porous electrodes.

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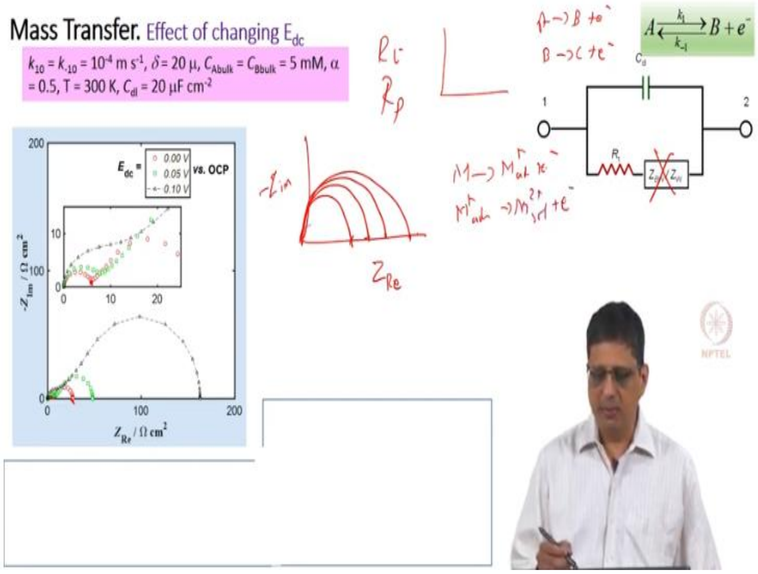

Mass Transfer. Effect of changing E_{dc}

$k_{10} = k_{-10} = 10^{-4}$ m s^{-1}, $\delta = 20$ µ, $C_{Abulk} = C_{Bbulk} = 5$ mM, $\alpha = 0.5$, T = 300 K, $C_{dl} = 20$ µF cm^{-2}

So, we were looking at the electron transfer reaction A → B and we got a complex expression for impedance. We can simplify this to a more familiar expression if you assume that DC potential is 0 that is at OCP. Right now the way I have written is valid for any DC potential with or without DC bias that is valid and if we say that the DC potential is at 0. At many times people use this for corrosion experiment or other experiments at OCP in which case you could get a simpler expression where charge transfer resistance will come only in terms of kinetic parameters. The Warburg impedance or bounded Warburg impedance will come only in terms of the diffusion parameters. but that is not in general going to be true or correct. We have seen an example where different δ values affect the impedance especially at the lower frequency.

What I want to show you is if you use this expression and calculate for a given δ value, for a given mass transfer limitation for a given δ value boundary layer thickness if you change the dc potential here the red colour, red colour rounds circles are the dc potential at 0. The green squares correspond to the impedance when dc potential is 50 mV, and the triangles correspond to the case where DC potential is 100 mV.

So, notice the following when dc potential is 0 the first loop which is shown in the insert here comes dips down and then it starts increase and then comes and touches the real axis. This corresponds to charge transfer resistance, and this value corresponds to polarization resistance this value meaning we are assuming of course solution resistance is 0. Earlier, for a reaction like this if you assume that mass transfer is not a limiting factor if you assume that it is very rapid mass transfer at dc potential of 0 you might get a spectrum like this in the complex plane. When you increase the dc potential, it is going to go down. 100 mV, 150 mV, the charge transfer resistance and polarization resistance both were the same in that case. Because you would represent that by just one resistance which case polarization resistance charge transfer resistance they are the same. And both of them decrease with respect to potential. We also saw other examples where is A → B, B → C we would have used a slightly different notation, we might have said $M \rightarrow M^{+}_{ads} + e^{-}$, $M^{+}_{ads} \rightarrow M^{2+}_{sol} + e^{-}$. In those cases generally charge transfer resistance tended to decrease with increasing potential.

However, when you have mass transfer limitation, when you increase the potential, the charge transfer resistance actually increases. So, if you look here the red circle will tend to touch the real axis earlier, green will probably touch somewhere here, black if it were extrapolated and touching it it is going to touch here. This of course corresponds to the Z_W or Z_{BW}, BW_A and BW_B for both A and B species bounded Warburg impedance right.

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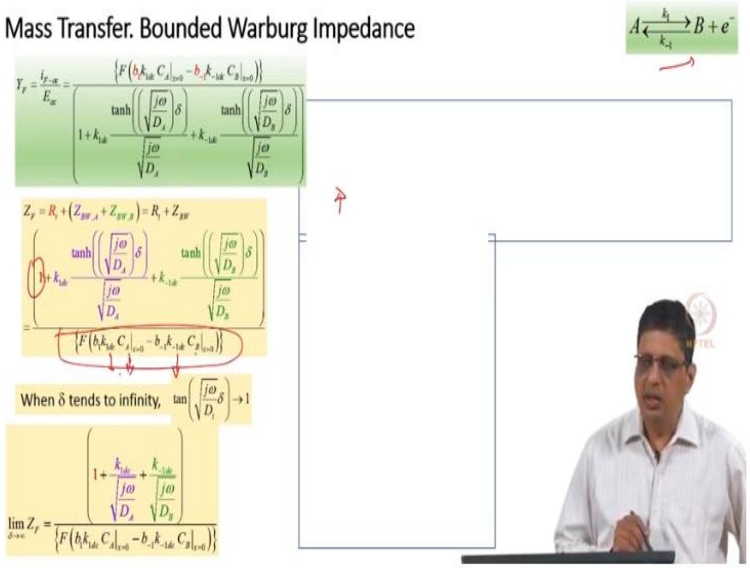

Mass Transfer. Bounded Warburg Impedance

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

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

$$Z_F = R_t + \left(Z_{BW,A} + Z_{BW,B}\right) = R_t + Z_{BW}$$

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

When δ tends to infinity, $\tan\left(\sqrt{\frac{j\omega}{D_i}}\delta\right) \rightarrow 1$

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

Now why does it behave that way? When you increase the potential you expect the reaction to happen at a faster rate. At least one of the reactions should happen at a faster rate. Faster rate means more electron transfer and we would say less resistance. So, if you go back to the expression, the red colour part in the numerator with the black colour part in their denominator corresponds to R_t. When I change the potential, when I increased the potential, k_{1dc} will increase k_{-1dc} will decrease concentration of B will increase because I am producing more B when I increase the potential I am producing more B I am driving the forward reaction more concentration of A will decrease. Earlier when we assume mass transfer was very rapid we said C_A is fixed C_B is fixed. Then when I increase the potential k_{1dc} will increase k_{-1dc} will decrease.

In general, the denominator will increase and therefore we would say the charge transfer resistance will decrease. Now, although the effect on k_1 and k_{-1} effect on change in potential k_1 and k_{-1} they are the same but concentration of A will decrease and concentration of B will increase and that has the effect that net effect is that are t is larger that means denominator is the smaller number.

So, whatever learning we had that pattern recognition, that if I increase the potential it decreases, that is valid only when the mass transfer is very rapid. When mass transfer plays a role you cannot extrapolate whatever you have learnt there and use that here.

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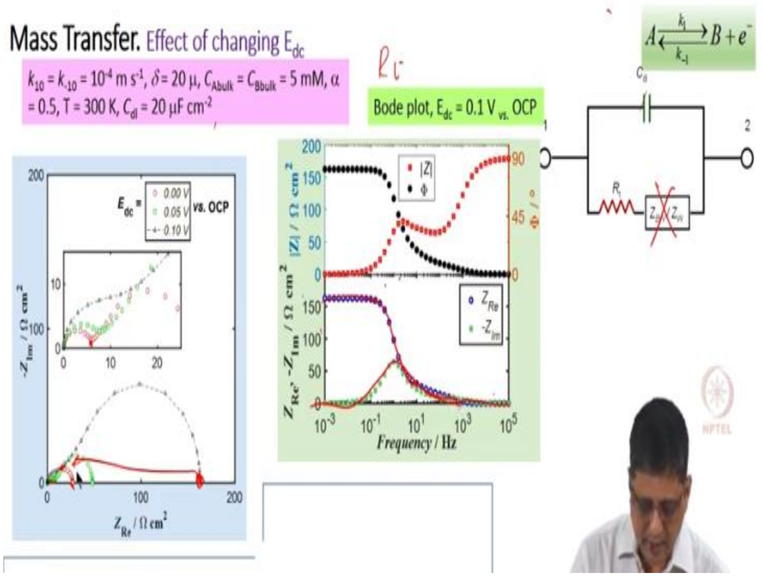

Mass Transfer. Effect of changing E_{dc}

$k_{10} = k_{-10} = 10^{-4}$ m s^{-1}, $\delta = 20\ \mu$, $C_{Abulk} = C_{Bbulk} = 5$ mM, $\alpha = 0.5$, T = 300 K, $C_{dl} = 20\ \mu F\ cm^{-2}$

Bode plot, $E_{dc} = 0.1$ V vs. OCP

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

Same with polarization resistance. We get the larger polarization resistance when the dc bias is changed. When it is 0 dc bias you get minimum resistance for R_t and R_p. If I go to -50 mV or -100 mV it is going to be similar to this which means if this is 0 resistance, 50 mV may come here, of course diffusivities are the same – 50 mV will also give me the same thing. I cannot differentiate between these two if they are slightly off then these numbers will be slightly off. So, when they go to a larger potential or a more negative potential both cases the impedance will increase impedance at mid and low frequencies to increase high frequency of course it is determined by the capacitance value as long as the capacitance value is assumed to be the same you will get similar results. But + 50 mV, + 100 mV will go like this – 50 mV will also go in the same way. 50 will show up -100 will also come in the same way. A spectrum for + 100 reversal show up. And when I represent that in a bode plot imaginary part of course there is a slight increase and decrease and then a significant increase and decrease. Real part is going to be flat at low frequency meaning it is not changing that much here. It decreases there is some sort of flat area here and then it decreases again. You may not see it very clearly here. But that is asymptotically going towards it. This again it is starting at 90 degree that means it is going vertically up. So, it is the phase is at 90 although when you have a resistance when you have a solution resistance, it will start close to 0 and then it will go to 90 come down, this again shows the second peak corresponding to the mass transfer resistance here.