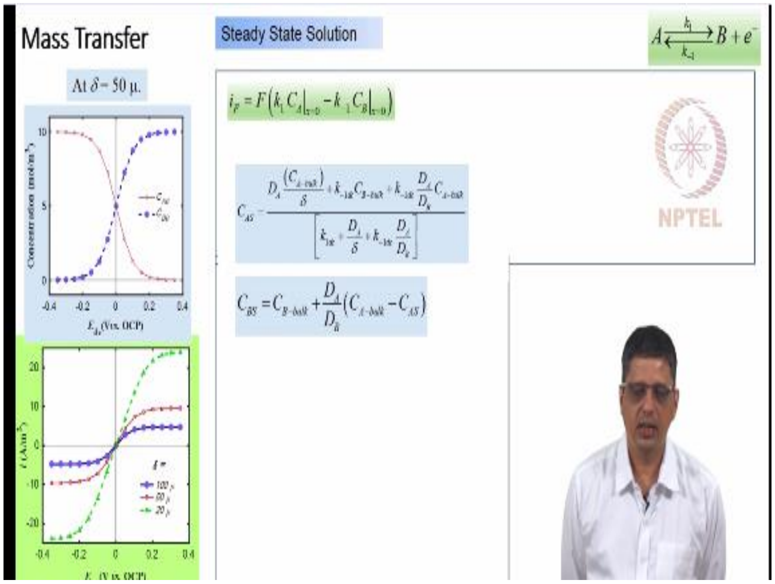
Electrochemical Impedance Spectroscopy
Prof. S. Ramanathan
Department of Chemical Engineering
Indian Institute of Technology- Madras

Lecture – 33
Warburg Impedance (2 of 3)

(Refer Slide Time: 00:15)


Mass Transfer

At $\delta = 50\ \mu$

Steady State Solution

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

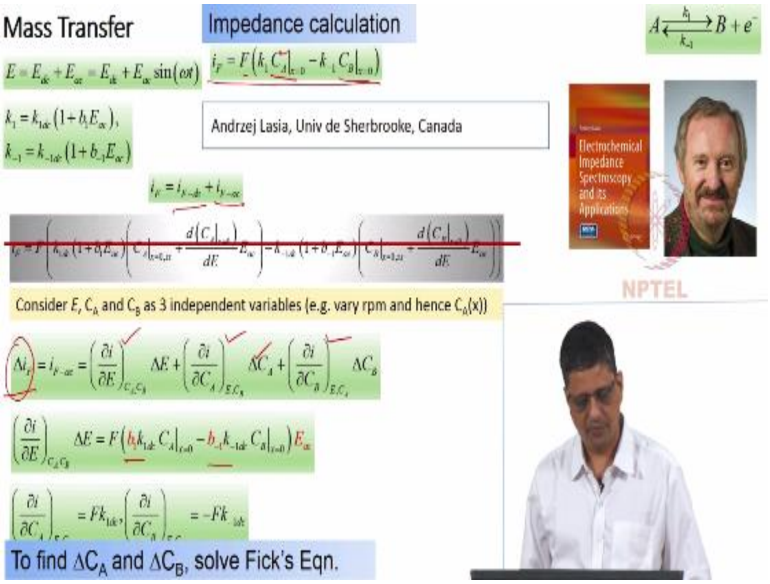
$i_F = F\left(k_1 C_A\big|_{x=0} - k_{-1} C_B\big|_{x=0}\right)$

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

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

So, going back to the problem, where we started looking at electron transfer reaction with deficient also playing a role and diffusion is also not very fast. Yes, all this Fick's equation for study state state condition, we have got the electro chemical current faradic current and we have predicted the concentration as a function of dc potential, we have predicted the current as a function of dc potential at different rotational speeds. We have got the expression for the faradic current, concentrations of A and B and from this only we have got this plots.

(Refer Slide Time: 00:58)



Mass Transfer

Impedance calculation

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

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac}\sin(\omega t)$

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

$k_1 = k_{1dc}\left(1 + b_1 E_{ac}\right),$

$k_{-1} = k_{-1dc}\left(1 + b_{-1} E_{ac}\right)$

Andrzej Lasia, Univ de Sherbrooke, Canada

Electrochemical Impedance Spectroscopy and its Applications

$i_F = i_{F-dc} + i_{F-ac}$

$$\cancel{i_F = F\left(k_{1dc}\left(1+b_1E_{ac}\right)\left(C_A\big|_{x=0,dc} + \frac{d\left(C_A\big|_{x=0}\right)}{dE}E_{ac}\right) - k_{-1dc}\left(1+b_{-1}E_{ac}\right)\left(C_B\big|_{x=0,dc} + \frac{d\left(C_B\big|_{x=0}\right)}{dE}E_{ac}\right)\right)}$$

Consider E, C_A and C_B as 3 independent variables (e.g. vary rpm and hence $C_A(x)$)

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

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

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

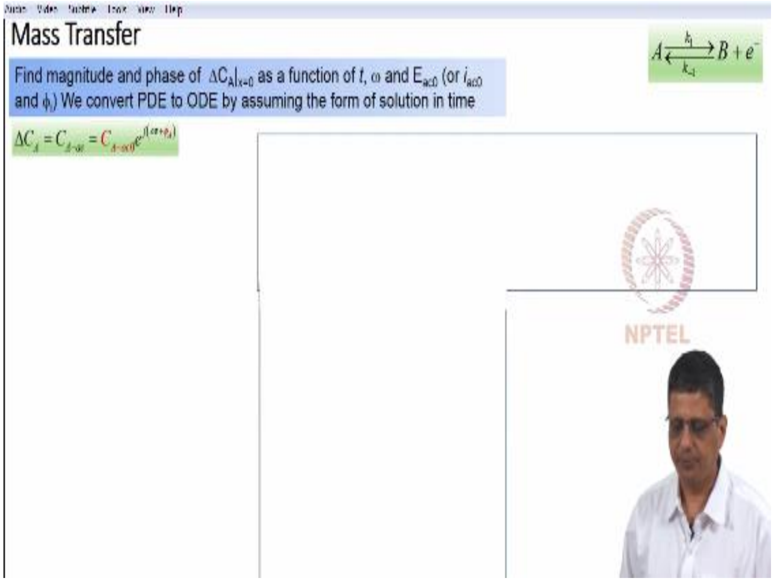
To find ΔC_A and ΔC_B, solve Fick's Eqn.

Then we started working on calculation of impedance, right, we applied dc potential and on top of dc potential we are applying ac potential that is a general case. Rate constants of course we know how to approximate them k_1 is written as k_{1dc} $(1+b_1E_{ac})$, k_{-1} in the same way and they are multiple ways of deriving it. We are using the methodology that is given in book by Lasia.

Instead of looking at the concentrations so if we look here, the concentration here as a function of ac oscillating around dc we looked at it differently we write potential C_A and C_B as three independent variables, so we take Δi_F so Δi_F represents the fluctuating part of the current i_{dc} + i_{ac} is what we normally write and $i_{F\text{-}ac}$ here is represented by $\Delta i_{F.}$ We can write it as partial derivative with respect to E the partial derivative of i. with respect to C_A C_B and then multiply by the corresponding fluctuating style.

These three terms are easy to get we know that function i current as a function of k_1 C_A k_1 C_B k_1 and k_{-1} when we take the derivative it is going to give you b_1, b_{-1}, So the first part i di/dE is easy to get, di/dC_A is easy to get and k_1 is going to remain. C_A when you take derivative becomes unity right side goes away for C_B it is going to be left with -F k_{-1dc}. I think up to this we have seen in the last class. So, what we want to do next is to find how the concentration oscillation is going to be related to the potential oscillation.

(Refer Slide Time: 02:59)



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} and ϕ_i) We convert PDE to ODE by assuming the form of solution in time

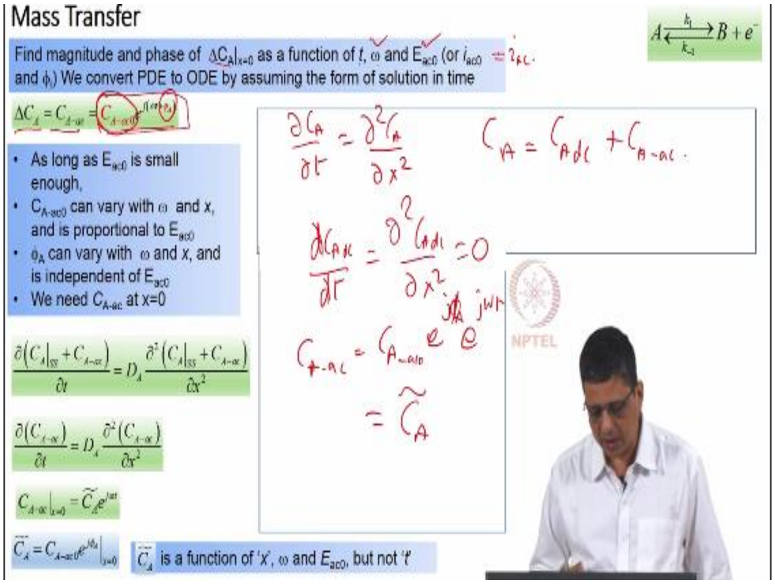
$\Delta C_A = C_{A-ac} = C_{A-ac0} e^{j(\omega t+\phi_A)}$

In order to find this, we need to solve fix equation we write the concentration oscillation as $C_{A\text{-}ac0}$ and that in the complex notation is written as $C_{A\text{-}ac0}$ exp(jωt + φ_A) so that means we are assuming after we apply a potential wait for some time you get to study periodic response. Concentration of A and B on the surface will show fluctuation with a frequency of ω. Now concentration oscillation can be written as just like we write E_{ac0} sin(ωt + 0 phase). Current will be i_{ac0}sin(ωt+ some phase), possibly 0 possibly non 0. Concentration also we will write it as C_{Ac0} or $C_{A\text{-}ac0}$, $C_{B\text{-}ac0}$ concentration of species A and B, sin(ωt + φ_A and φ_B). Complex notation, it is easier to solve, so we will write it as exp(jωt + φ_A). Now as long as E_{ac0} is small we can linearize the equation only after linearization we got k1 as k_{1dc}(1+ b_{1ac}) we neglected the higher order terms under those conditions.

We can write concentration will also show as sinusoidal fluctuation because we assume ΔC_A has particular form. It is given as C_{A0} exp(jωt+φ_A) and likewise for C_B. We can use this in the fix equation $\partial C_A/\partial T$ you can actually get an expression and the PDE partial differential equation which is basically two independent variables of time and x, two dependent variables C_A and C_B will convert in to set a of ODE’s, Because we are assuming a form of solution for this C_A and C_B in terms of time location wise we will find what it is but we are mainly interested in finding the concentration fluctuation on the surface, because only that is going to impact the current calculation although concentration fluctuation and other places will indirectly impact here but direct calculation ultimately under stable periodic result.

We want to know what is the concentration fluctuation on the surface, because the current year is proportional or related to the concentration of the surface now $C_{A\text{-}ac0}$ is going to related to E_{ac} it is going to be dependent on ω. φ here will not vary with E_{ac0}. If I increase the perturbation amplitude, the phase will not change concentration fluctuation the magnitude will change. Now the thing is this, if you go back to the previous expression, here I want to take this equation this is replaced by E_{ac} this of course I know I know this. I know this here if I can write this in terms of E_{ac} then I can group all the E_{ac} terms all the other terms can be grouped and then I read E_{ac}/i_{ac} $E_{F\text{-}ac}/I_{F\text{-}ac}$, that is going to be impedance, or I will write $I_{F\text{-}ac}$ /E_{ac}, that going to be admittance that is what we have done so far and what we are going to do now is instead of writing in terms of E_{ac}. We will find that it is easier to write in terms of $i_{F\text{-}ac}$ then we will group all the $i_{F\text{-}ac}$ on 1 side we will group all the E_{ac} on another side it would not be all the E_{ac} there is only one E_{ac} and still we will be able to get the expression for impedance just that do not expect that we are going to write ΔC_A, ΔC_B in terms of potential. It is easier to write in terms of the current that is because the boundary condition for the fix equation comes in terms of current. So, the derivation is little different than what we have seen before.

(Refer Slide Time: 07:08)



Mass Transfer

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

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

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

- As long as E_{ac0} is small enough,
- $C_{A\text{-}ac0}$ 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 $C_{A\text{-}ac}$ at x=0

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

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

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

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

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

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

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

$$C_{A\text{-}ac} = C_{A\text{-}ac0} e^{j\phi_A} e^{j\omega t}$$

$$= \tilde{C}_A$$

So, that is why I write, we want to find the magnitude and phase of ΔC_A at x = 0 as a function of t, ω and E_{ac0} or it can be a function of i_{ac0} and φ_i here meaning phase of the current i_{ac0}, φ_i is actually going to be equal to i_{ac}. We will convert PDE to ODE by assuming that solution is in this form. Now this is true as long as ac 0 is small concentration of A, magnitude of the fluctuation can vary with ω, vary with location and as long as ac0 is small it is proportionate to E_{ac0} just like current i_{ac0} is going to be proportionate to E_{ac0} as long as $E_{ac\ 0}$ is small now the phase can vary with this. It will be independent of E_{ac0} and we need to calculate concentration of A, the ac part at x = 0 so we take the Fick's equation. [Please refer to video 8.50] Now dc is in fact obtained by taking this and setting this to 0, $\partial C_{Adc}/\partial T$, this is obviously valid when you do not have ac either, ac also right.

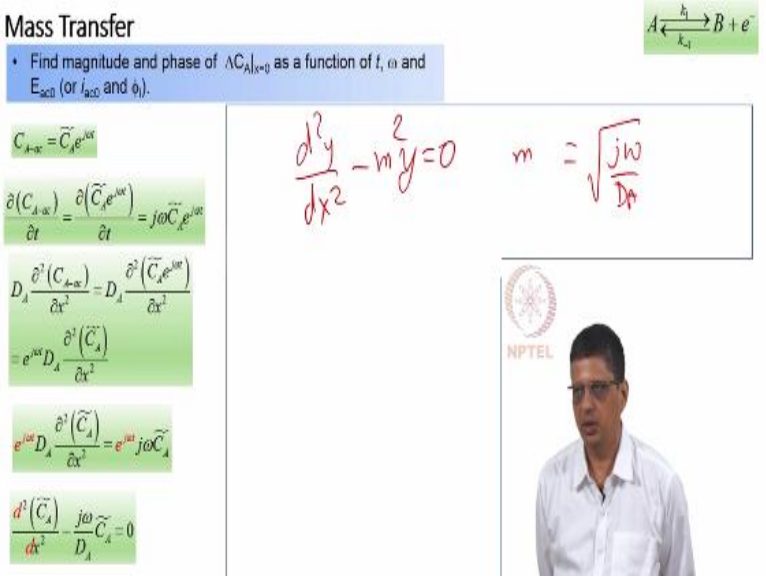
So, I can take this and write for ac component this equation can be written like this. Now C_{Aac}, I will not write it here, I will write it this side $C_{A\text{-}ac}$, I am going to write it as $C_{Aac0}\exp(j\varphi_A)$ $\exp(j\omega t)$. **"Student-Professor conversation starts"** You can assume it to be sinusoidal if you assume it to be something else it will not work jωt will make it easier for us expjωt, but you can assume it to be $C_{AC0}\sin(\omega t + \varphi_A)$.

You would expect the concentration to change with potential. Imagine this is a dc, imagine you are changing the dc very slowly, so what will happen is dc potential will increase come back to old potential decrease and come back to the old potential. I am giving a sinusoidal dc, but with a very low frequency let us assume we are going step by step it is slow enough that when it goes from here to here. I am drawing from here time zero, and so if you have to draw from your side time zero here dc potential is 0.2 it becomes 0.21, 0.22 very slowly, so current also more or less dc current it is changing, but very slowly it is coming to steady state very quickly concentration will also change. When I go to higher potential concentration of A will decrease, concentration of B will increase that will also change sinusoidally. As long as I am in the linear regime, means very little change in dc potential, it is sinusoidal from 0.2, I am not going to 0.3 and 0.1. I am going from .2, 0.205 at the max 0.195 at the minimum so 5 mV amplitude, it is going to go like this concentration will also change and if you go very slowly enough concentration will be at the dc level current will be at the dc level more or less at the dc level therefore I will be as zero phase difference.

Current has to be sinusoidal, when E_{ac0} is small frequency can be large or small or medium but that will correspond to a non zero phase it is easy for us to visualize what happens when frequencies is very low. But why would I expect it to be non-sinusoidal when E_{ac0} is small it has to be sinusoidal. **“Student-Professor conversation ends”**

Now I have taken it in this form, I am going to write it as C_A which corresponds to C_{ac0} and φ_A. So, I am taking the magnitude and phase and call it as C_A tilde, and I am taking the omega t and keep as it is so instead of writing C_{ac} at x = 0, I write it as C_A-tilde because all that I need is they as a function of ω, tell me the value of C_{Aac0} and φA agree with me. We will derive this for C_A we would not derive it for C_B we will say it is going to be similar. So our aim is to find whatever is shown here in the red for any ω what are the values for any E_{ac0} as long as it is small enough what are the values? So, we use fix equation. Now C_A tilde is a function of location although we want to look at it only when x = 0. It is a function of ω, E_{ac0} but not a function of t, the function of t is isolated and brought here.

(Refer Slide Time:13:08)



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} and ϕ_I).

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

$$\frac{\partial(C_{A-ac})}{\partial t} = \frac{\partial\left(\tilde{C}_A e^{j\omega t}\right)}{\partial t} = j\omega\tilde{C}_A e^{j\omega t}$$

$$D_A\frac{\partial^2(C_{A-ac})}{\partial x^2} = D_A\frac{\partial^2\left(\tilde{C}_A e^{j\omega t}\right)}{\partial x^2} = e^{j\omega t} D_A \frac{\partial^2\left(\tilde{C}_A\right)}{\partial x^2}$$

$$e^{j\omega t} D_A \frac{\partial^2\left(\tilde{C}_A\right)}{\partial x^2} = e^{j\omega t} j\omega\tilde{C}_A$$

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

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

Now substitute into the equation on the left hand side when you take the derivative exp(jωt) you are going to get jω multiplied by exp(jωt), on the right hand side you have the second order derivative with respect to the location x and we know C_A tilde can be a function of x, but exp(jωt) can be pulled out. It is an independent variable ω is something that we decide t is anyways independent of location.

So, what that means is you can cancel out the exp(jωt) and you will get an ordinary differential equation, not a partial differential equation and as far as the location x is concerned, independent variable is x, jωD_A then nothing to do with x, they are not functions of x, which means it is very easy to solve this equation you have an equation which is like $d^2y / dx^2 - m^2y = 0$. [Please refer to 14.22]. Where you have taken this and you have done what is called auxiliary equation and so on. We will stop it today.