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

Lecture – 32
Warburg

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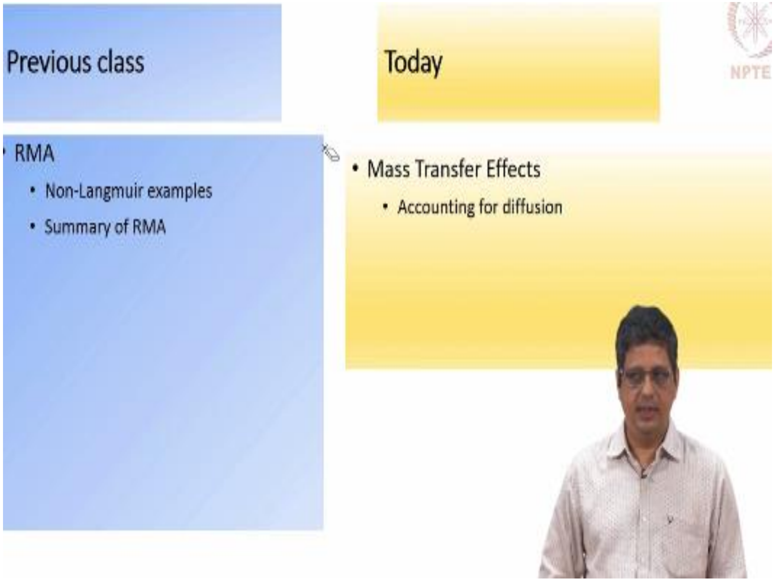

Previous class

- RMA
  - Non-Langmuir examples
  - Summary of RMA

Today

- Mass Transfer Effects
  - Accounting for diffusion

~~So~~ Until now we have assumed that mass transfer is not significant in terms of it is not going to increase the impedance it is rapid, diffusion is fast and kinetics are the rate limiting step. So what happens when you also have mass transfer?

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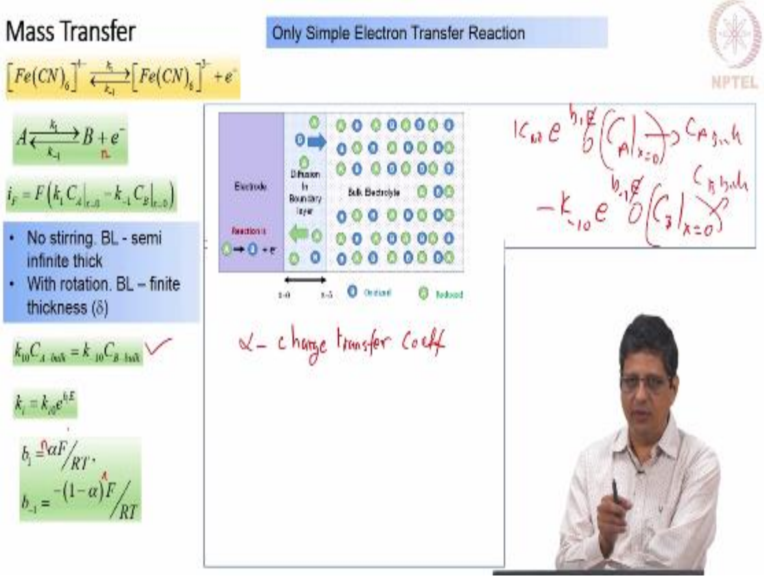

Mass Transfer

Only Simple Electron Transfer Reaction

$[Fe(CN)_6]^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Fe(CN)_6]^{3-} + e^-$

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

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

- No stirring. BL - semi infinite thick
- With rotation. BL – finite thickness (δ)

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

$k_i = k_{i0} e^{b_i E}$

$b_1 = n\alpha F/RT$,

$b_{-1} = -(1-\alpha)nF/RT$

$k_{10} e^{b_1 E} \delta (C_A|_{x=0}) \to C_{A\,bulk}$

$-k_{-10} e^{b_{-1} E} \delta (C_B|_{x=0}) \to C_{B\,bulk}$

α – charge transfer coeff

Meaning what happens when you also have slow mass transfer? When you have diffusion playing a role or when the concentration changes, you can derive the equation for impedance while accounting for mass transfer and normally all that shown in the textbooks are for simple electron transfer reaction. We do not usually find expressions for impedance accounting for kinetics as well as mass transfer for any reaction which is complex which is for example with absorbed intermediate and even this is fairly long derivation.

So I want to go through it, I want you to understand the implications of this. So the reaction we take is ferrocyanide, ferricyanide redox couple. So it is Fe2, Fe3 but it is not just simple Fe ion, but surrounded by 6 cyanide groups. [Please refer to video 1.44] This pictorial here gives an idea of what we are looking at. So I have shown the reaction as 'A' going to 'B' it is reversible I have not shown the reverse arrow here, but you can imagine 'A' is a one entity, 'B' is the other entity. So it charged Fe^{4-} is 'A' $Fe(CN)_6^{3-}$ is 'B'. 'A' can lose an electron and become 'B' and 'B' can gain an electron and come as 'A', 'A' and 'B' are in solution and in the bulk solution we assume they are completely well mixed and there is uniform concentration. Near the surface there is a formation of bound layer. On the surface the velocity of fluid is the same as velocity of the surface.

So you can consider 2 different scenarios, one where the bulk of fluid is stationary just the surface is moving and the thin layer along with the surface is dragged, that is one possibility. Other possibility surface is stationary fluid is moving and the fluid is considered as a bulk here, it has a completely well mixed condition and close to the surface there is a boundary layer formation and velocity on the surface is 0, velocity at the bulk is same as the bulk velocity.

Typically, we use what is called rotating disk electrode. So there is an electrode where you have an electrode like a cylinder, but all the sides are surrounded by insulator, only that bottom surface is exposed and when this is rotated fluid is pulled towards this and by centrifugal force it is pushed out or thrown out. So it forms something like a vortex like fluid motion, but this can be approximated as a boundary layer of certain thickness.

You can control the thickness of the boundary layer by changing the rotational speed. The boundary layer thickness depends on viscosity, density etc, but if you are taking a particular fluid during operation what easy for us to change is the rotational speed. So we are going to say that boundary layer has a thickness of δ. So we can assume if we take the reference here meaning for the movement if the electrode is taken as reference then we will say on the electrode this velocity is zero outside the electrode the velocity is relative to the surface is some number. We do not even need to worry about the velocity we just need to know the boundary layer thickness. So we say boundary layer thickness is δ and δ we can relate to the rotational speed and other parameters. Within the boundary layer we are going to say that the mass transfer is by diffusion alone there is no convective mass transfer.

So we are going to assume boundary layer is stationary and mass transfer occurs from higher concentration to lower concentration. If we are generating lot of B here by going to the positive potential, then B will move away because on the surface you will get more of B generator and A will be consumed and therefore A will come from bulk to the surface and B will go from surface to the bulk.

The current here is going to be written as usual k_1 multiplied by concentration of A, previously we would have said concentration of A is constant now we will say concentration of A on the surface and likewise minus k_{-1} concentration of B on the surface and this will be different from the bulk in general if we say that there is no stirring at all it is stationary electrode.

Then the boundary layer thickness will go to infinity, meaning if the electrode is stationary the fluid is stationary nothing is moving. Then when you convert A to B concentration of A near the surface will keep increasing and diffusion will happen and there is no end to that practically the distance from the electrode to the vessel wall will be the boundary layer thickness.

In general, you can say if it is large it is going to be considered as ∞. So we will call that as semi infinite because one side it is electrode it is going from zero to ∞ it is not going from $-\infty$ to ∞ so it is called as semi infinite boundary layer, and if you have rotation it has a finite thickness that is one. Second the rate constant k_{10} k_{-10} they are not arbitrary in the sense they cannot be varied arbitrarily.

Because we take the reference as the open circuit potential, at open circuit potential current will be zero and at open circuit potential there is no net reaction, A going to B and B going to A they happen at the equal rate they may happen at a fast rate or slow rate, but both will happen at the same rate. So you would write it as k_{10} exp(b1E) $C_A|_{x=0}$ - $k_{-10}\exp(b_{-1}E)C_{B|x=0}$

and if there is no net reaction there would not be any consumption, net consumption of A or net production of A. Therefore, they would not be any need for net diffusion from one location to another. So everywhere concentration will be uniform. At open circuit potential, in this particular case you would not have any net reaction, therefore concentration will be uniform even within the boundary layer. Concentration everywhere will be same as C_A bulk and C_B bulk. Therefore, I can replace $C_A|_{x=0}$ with C_A bulk $C_{B|x=0}$ with C_B bulk.

Potential is zero here because it is at OCP, so I have a relationship which says k_{10} and k_{-10} are related, so if I tell this is the bulk concentration and this is k_{10}, I cannot give you k_{-10}, I have already specified it. I cannot give you arbitrary number for that. So not just in this reaction, in general when you consider all the reactions reversible reactions you will have to say at equilibrium the net rate is zero and therefore you will find that you cannot fix all the rate constant and pre exponents arbitrarily they have a relationship. If you are far away from an equilibrium you probably will throw away some of them therefore you can specify the others and once which are thrown away are neglected, you can see they can be calculated or they are not relevant here. So both k_1 and k_{-1} we will write in this standard form k_{10} exp(b1E) - k_{-10} exp (b_{-1}E), that we know.

We will also say that these are elementary reactions therefore b_1 and b_{-1} are related. We relate b_1 as α F/RT, F is a faradaic constant R is the universal gas constant T is the temperature. α is what is what is known as charge transfer coefficient. So here there is one electron transfer, sometimes you can write this as n electron transfer 2, 3 etc in which case this is going to be multiplied by n.

But right now by and large we are going to have single electron transfer reaction for this simple electron transfer reaction, therefore we will keep it as one and the reverse reaction will have 1-α so alpha will vary between 0 to 1 and if we do not know any specific value for that if we do not have any reason to specify we will just take it as half, 0.5.

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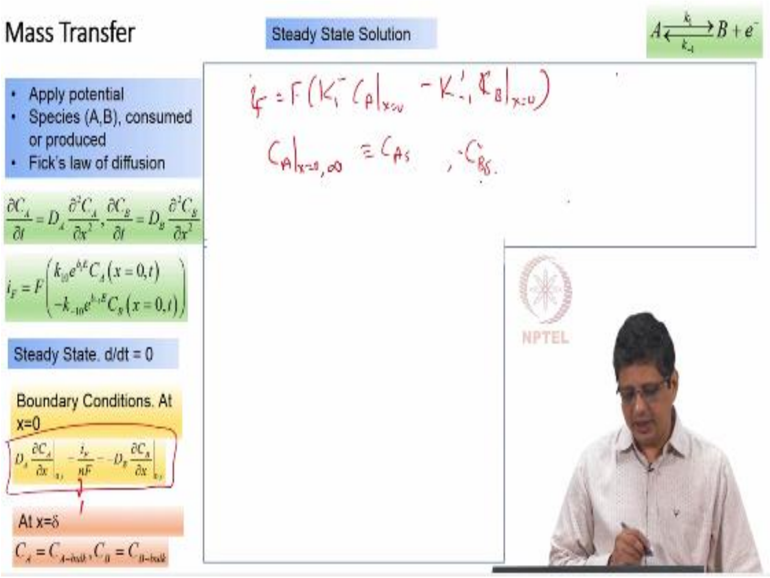

Mass Transfer

Steady State Solution

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

- Apply potential
- Species (A,B), consumed or produced
- Fick's law of diffusion

$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}, \frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$

$i_F = F\begin{pmatrix} k_{10} e^{b_1 E} C_A(x=0,t) \\ -k_{-10} e^{b_{-1} E} C_B(x=0,t) \end{pmatrix}$

Steady State. d/dt = 0

Boundary Conditions. At x=0

$D_A \frac{\partial C_A}{\partial x}\Big|_{x,t} = \frac{i_F}{nF} = -D_B \frac{\partial C_B}{\partial x}\Big|_{x,t}$

At x=δ

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

$i_F = F(K_1 C_A|_{x=0} - K'_{-1} C_B|_{x=0})$

$C_A|_{x=0,\infty} = C_{As}, C_{Bs}.$

Now I want to find first steady state solution earlier we have seen this right, we write the mass balance equation, charge balance equation, but that is with absorbed intermediate with no absorbed intermediate we just write the charge balance equation. We can find the steady state current, we will write the expression for current main potential is dc plus small amount of ac and then we will see if we can write it as del i/del E which will become faradaic.

Here we are going to go in similar path, but we will take some detour. When we come there I will mention that right now first we want to see how the current will vary when potential is varying. Earlier it was very straight forward we will write it as i faraday is F×k_1×$C_{A\text{-bulk}}$ because we assume throughout the regime it is C_{Abulk} and it is a constant, minus k_{-1} $C_{B\text{-bulk}}$ and this was k_{10} exp(b1E).

This was k_{-10}expb_{-1}E. If we say this is E and this is i you can say when it is far away in the positive direction k_1 is large number k_{-1} is negligible therefore it is going to look like an exponential curve. When it is large negative value it is going to go look like this in between both are important so it is going to go through 0 and it will look somewhat like this. When we have mass transfer effect present here, I mean mass transfer is also going to impact the result this $C_A|_{x=0}$ and $C_B|_{x=0}$ they are depended on the potential.

So we will have to account for this and get the result and this is actually fairly straight forward and it is not that difficult. So we apply potential and we realize A will be consumed or A will be produced depending on whether you apply positive or negative potential. We need to use Fick's law of diffusion to get the concentration at the surface. And the law that we use here is Fick's second law for each species we write partial derivatives ∂ $C_A/\partial t$ is diffusivity of A multiplied by $\partial^2 C_A/\partial x^2$.

I think people in chemical engineering would have seen if you are in other field you can still you might have seen this. So I am just expanding the current value, I have not specified whether it is dc or ac yet. So I will say k1 is written as k_{10} exp(b_1E), C_A we want to look at $C_A|_{x=0}$ and in general at any time t. If it is steady state that means it is not time varying E will become E_{dc} and $C_A|_{x=0}$ will be some finite number.

So that means steady state condition will take the derivative with respect to time as zero. We have two boundary conditions one at x=0, how much A is consumed that tells us how much current is produced, it also tells us B is produced. So the rate of consumption of A, rate of production of B they are going to be given by this flux. $D_A \partial C_A/\partial x|_{x=0}$ should be equal to $D_B \partial C_B/\partial x|_{x=0}$ except that the signs are opposite.

If we say the amount of A that is coming here per second per unit area is one mole per square centimeter per second. Then you can say amount of B coming here for that area it is not going to be amount of B coming here it is going to be going away because A is decreasing in concentration B is going to increase in concentration, so I have sign change and the equation here tells one mole of A consumes gives you one mole of e, electron.

So that is given by i_F is the faradaic current divided by faraday constant and n here is number of electrons as per the reaction it is going to be one here. So this is one boundary condition at x=0 we relate the faradaic current to the flux. Second boundary condition is easy, at x= δ concentration of A is same as bulk concentration of B is same as bulk. So second boundary condition is given in a simple expression, first boundary condition basically relates the flex of A and B at the electrode surface to the faradaic current that is measured.

Now let us say the concentration of A at the surface under steady state condition meaning time = ∞, I give $E=E_{dc}$ and then wait for long time. I can call it as C_{AS} similarly C_{BS} this is mainly for steady state condition.

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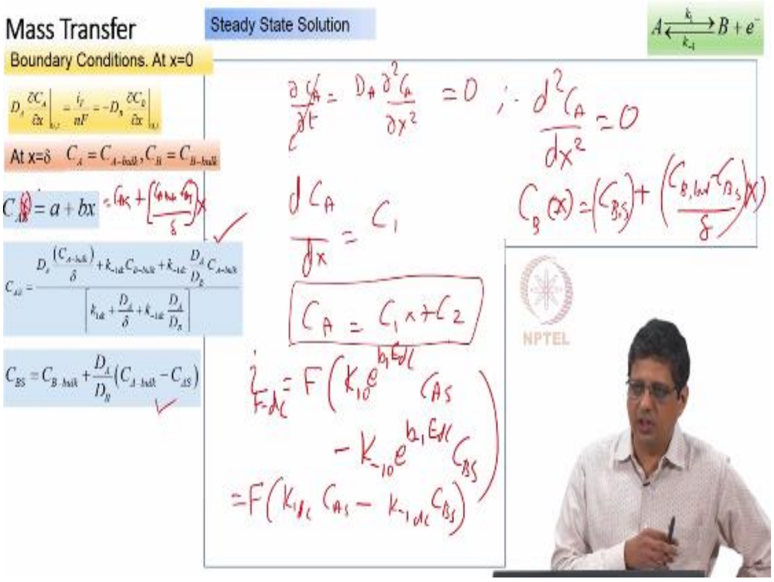

Mass Transfer

Steady State Solution

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

Boundary Conditions. At x=0

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

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

$$C_{AB} = a + bx = C_{AS} + \left[\frac{C_{A\,bulk} - C_{AS}}{\delta}\right]x \checkmark$$

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

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

$$\frac{\partial C_A}{\partial t} = D_A\frac{\partial^2 C_A}{\partial x^2} = 0 \;;\therefore \frac{d^2 C_A}{dx^2} = 0$$

$$C_B(x) = (C_{BS}) + \left(\frac{C_{B,bulk} - C_{BS}}{\delta}\right)x$$

$$\frac{dC_A}{dx} = C_1$$

$$\boxed{C_A = C_1 x + C_2}$$

$$i_{F\text{-}dc} = F\left(k_{10}e^{b_1 E_{dc}}C_{AS} - k_{-10}e^{b_{-1} E_{dc}}C_{BS}\right)$$

$$= F\left(k_{1dc}C_{AS} - k_{-1dc}C_{BS}\right)$$

At steady state condition this is going to go to zero so it is going to tell you this is time invariant therefore you can write this as within the boundary layer, some integration constant I am calling it as C1+C2 or A and B does not matter within the boundary layer, concentration of both species A and B will vary linearly. Of course slope value constant they will be different that is, but it is going to be linear function within the boundary layer.

Given dc potential, can you estimate the concentration of A and B on the surface using these two boundary conditions? It is fairly lengthy, but I would like you to try that. [Please refer to video 16.00] Under steady state condition at a given dc I will write i_{Fdc}, faradaic dc current is faraday constant multiplied by the net rate and I can write this as k_{1dc} which means k_1 at E_{dc} C_{AS} - ($k_{-1dc}C_{BS}$).

If you assume D_A and D_B are equal it will become lot simpler to do, but it is not necessary. So you have C_A on the surface, sorry C_A not on the surface this is C_A within the boundary layer, so it is a function of x varies like this C_A on the surface is at x=0, C_B again varies as C_B of x is going to be ((C_B on the surface + C_B bulk - C_B surface) / δ)×x so I can tell you this is going to be the slope, this is going to be the constant.

But we need to find the value here. C_A on the surface is going to be given by sorry C_A on the boundary line is going to be given by $C_{A\text{ on the surface}}$ + $C_{A\text{ bulk}}$ - $C_{A\text{ surface}}/\delta$ multiplied by x because at x = δ it is going to be $C_{A\text{ bulk}}$ at x=0 it is going to be CA surface and anywhere in between it is a linear interpolation between these two this derivation. So if you give you C_A at x can you find dC_A/dx.

dC_A/dx is going to be actually constant here therefore dC_A/dx at $x=0$ you can also find that.

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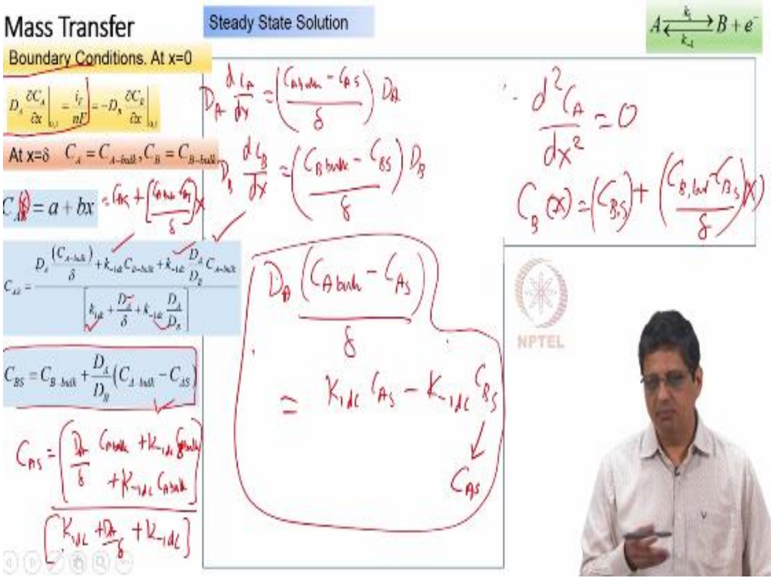

Mass Transfer

Steady State Solution

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

Boundary Conditions. At x=0

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

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

$$C_A(x) = a + bx = C_{AS} + \left[\frac{C_{A\,bulk} - C_{AS}}{\delta}\right]x$$

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

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

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

$$D_A\frac{dC_A}{dx} = \left(\frac{C_{A\,bulk} - C_{AS}}{\delta}\right)D_A$$

$$D_B\frac{dC_B}{dx} = \left(\frac{C_{B\,bulk} - C_{BS}}{\delta}\right)D_B$$

$$\therefore \frac{d^2C_A}{dx^2} = 0$$

$$C_B(x) = (C_{BS}) + \left(\frac{C_{B,bulk} - C_{BS}}{\delta}x\right)$$

$$D_A\frac{(C_{A\,bulk} - C_{AS})}{\delta} = k_{1dc}C_{AS} - k_{-1dc}C_{BS}$$

C_{AS}

So you can find dC_A/dx, dC_B/dx you can say D_A multiplied by this must be equal to D_B multiplied by this with a negative sign. Therefore, we can find a relationship between C_{AS} and C_{BS} that is what I have given here, that is correct. See we want to find both C_{BS} and C_{AS} it is easy to find the relationship between C_{AS} and C_{BS} and it is a linear relationship. You can get it and then substitute in the other conditions which is $D_A\partial C_A/\partial x$ at $x=0$ that is equal to i_F/F. i_F/F contains k_{1dc}, C_{AS}, k_{-1dc}, C_{BS}.

We can write the C_{BS} in terms of C_{AS} we can leave k_{1dc} and k_{2dc} as they are that means if you tell me the δ, and you tell me the dc potential at a given RPM given rotational speed if I vary the dc potential meaning at one time, I will wait at this dc potential wait for sufficient time I want to know the current. Next I want to move the dc potential to another value I want to know the current.

In order to do this, we need to know C_A at the surface for that dc potential C_B at the surface of that dc potential and that is what we are doing here. Once you know this can you relate i_F and the flux. So the first part of this equation tells us $(D_A\ C_{A\ bulk} - C_{A\ surface})/\delta$ is going to be $(k_{1dc}\ C_{AS}) - (k_{-1dc}\ C_{BS})$ and since we already know how C_{AS} and C_{BS} are related so we can substitute for this in terms of C_{AS} and other known values.

Known values meaning we know the diffusivity we know the bulk concentration and then rearrange to bring C_{AS} on the left side. It is a linear equation so it is pretty straight forward. So please do that and check whether the expression that I have given here is correct or not. Normally diffusivity will not vary that much operation of the cell will be at room temperature may be little bit higher little bit lower.

So 20 °, 30 ° maybe 40 ° diffusivity will not vary that much, δ can be varied to some level. If you estimate the delta if you are keeping it stationary of course it is a large number otherwise it will be may be 100 micron, 50 micron somewhere in that range meaning you can vary it by one order of magnitude, k_1 and k_{-1} on the other hand you can really vary a lot.

So potential can be varied and with that the rate constant can be varied very much. The rotational speed can be varied to some level and you will vary the boundary layer thickness diffusivity usually does not change that much. It will change with temperature, but not like 10 times higher, 10 times lower. You can also see whether it makes sense when you look at the expression if I increase the potential what happens to k_1 what happens to k_{-1}.

k_1 will become a large number k_{-1} will become negligible for simplicity let us just imagine or let us just say that $D_A = D_B$ therefore some of the terms will cancel out and become simpler. On the numerator this will become negligible this will become negligible k_1 is a large number this is a constant this is negligible.

Therefore, it is going to become C_A D_A and δ are constants by k_{1dc} when k_1 is a large number that means at large potential concentration on the surface will tends towards zero it would not go to zero and likewise if potential is left at zero, at OCP you should get the bulk concentration here. When potential is left with OCP, k_1 and k_{-1} are related and if you say that C_{Abulk} and $C_{B\text{-}bulk}$ are the same and diffusivities also are the same.

Then you would see that it would reduce to the similar expression. **“Professor - student conversation starts”** So numerator second term will come negative, $k_{-1\ dc}$ $C_{B\ bulk}$ if we are putting that and C_{BS} value directly in that one so we will get $-k_{-1\ dc}$. **“Professor - student conversation ends.”** We are just imagining do the calculation and then show me I will give you an alternate suggestion.

Let us say D_A=D_B $C_{A\ bulk}$=$C_{B\ bulk}$ let us say E_{dc} is 0 then what do you have in the denominator

($k_{1\,dc}$+ D_A/δ + $k_{-1\,dc}$) D_A/D_B is unity. k_{1dc} and $k_{-1\,dc}$ are also some, but you will say retain it as k_{10} and k_{-10}. On the numerator you should get $C_{A\,bulk}$ because concentration on the surface must be equal to $C_{A\,bulk}$. That means you should be able to $C_{A\,bulk}$ and C_B are same you can take it out D_A/B will become unity.

You should have k_1+ k_{-1}+ D_A/δ, see it takes little time to do this, but it is worth your effort to do this. If it is really lengthy take $D_A=D_B$ and see whether you get an expression that you would get if you simplify this. So if $D_A=D_B$, I would write, [Please refer to video 25.01] then I am going to move further saying that in that given time you might be able to complete it and this expression hopefully is correct.

Now that we have the expression for C_{AS} so whenever we vary dc potentials we know the $k_{1\,dc}$, $k_{-1\,dc}$ and then we can tell this is going to be C_{AS} this is going to be C_{BS} and we can write the faradaic current. I am not going to substitute it and give you a large expression, I will just say that if you are if you have given a Matlab or any other programming environment you will be able to calculate.

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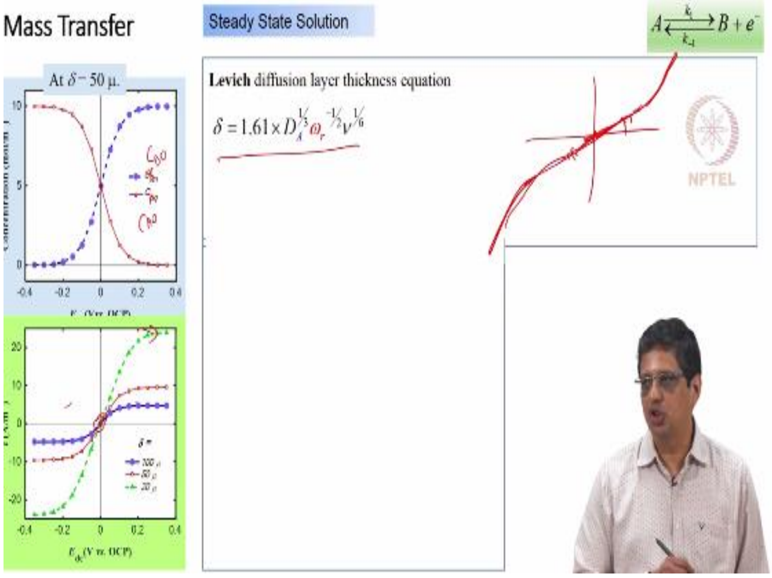

Mass Transfer

Steady State Solution

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

At δ ~ 50 µ.

Levich diffusion layer thickness equation

$$\delta = 1.61 \times D_A^{1/3} \omega_r^{-1/2} \nu^{1/6}$$

Now there is an equation which relates the rotational speed this is angular rotational speed ω_r here is the rotational speed of the electrode. This ν is the kinetic viscosity and D_A is of course diffusivity. Typically D_A D_B they are all in similar order and this you can use it to estimate the boundary line thickness. I do not expect you to memorize it you can find it any of the standard books.

Levich, there are few equations one of the equations relates the angular speed to the boundary layer thickness. So I have given I think I have made a mistake here if I go to positive potential A will decrease and B will increase. So I think this maybe, but it will saturate. This will go towards zero and the other species will go towards the $C_{A\ bulk}+ C_{B\ bulk}$ maximum. If you go to very negative value B is getting consumed, and A is getting produced therefore the concentration profile will just flip over.

Once you know the concentration you can also get the current values and this is how it will look. So I have estimated it for different delta value obviously I have assumed some diffusivity, I have assumed some k_{10}, α is probably as 0.5, I do not remember now and if I change the boundary layer thickness by changing the rotational speed, I will get different current values. If the boundary layer thickness is 100 micron that means it is slow rotation.

Then current will increase and then saturates it is not 100% flat, but it is almost flat. If you look at the actual values, they will keep on increasing very slightly. If I go to higher RPM I will get thinner boundary layer, even higher RPM even thinner boundary layer. So current originally, if there is no mass transfer limitations it is going to become somewhat exponential here, exponential here and in between it is going to be like a curve that connects these two.

You see if you do the simulation while accounting for mass transfer effect, here mass transfer effect is not felt that much it is not going to be very different here, but you never get to see the exponential curve. You would see it is saturating because of mass transfer effect. So people would call this regime as mass transfer limited regime, this regime as kinetic limited regime and somewhere in between as mixed control regime where both mass transfer and kinetic play a role.

Here of course kinetic do play a role, but mass transfer is the dominant effect and out here mass transfer does play a role, kinetic is the dominant effect. What it means is mass transfer limited current is going to be like this, kinetic current is going to be like this. If I assume that the mass transfer is not slow it is rapid, then the curve here that I get, and if I compare with the curve that I get including mass transfer effect they will be more or less same.

So if I change it here for various δ somewhere here all the curves are more or less similar. I move little away I see the difference and even right here if I do impedance spectroscopy I will find the mass transfer effect are seen. So when both are significant we would call it as mix control regime. In the potential dynamic polarization curve you would get curves like this and experimentally when you do you will get curves like this. You do not get the exponential curve that you see for the ferro, ferri cyanide.

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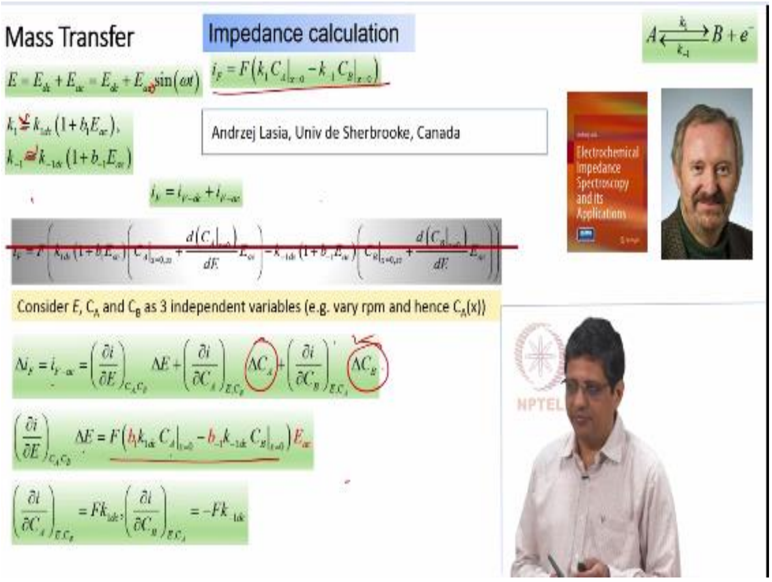

Mass Transfer

Impedance calculation

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

$$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$$

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

$$k_1 \cong k_{1dc}(1+b_1E_{ac}),$$
$$k_{-1} \cong k_{-1dc}(1+b_{-1}E_{ac})$$

Andrzej Lasia, Univ de Sherbrooke, Canada

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

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

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

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

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

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

If you want to do impedance calculation it is going to be lengthy. So I will tell you that right now. So we will probably go through one more class and if necessary little more than that, but I want to start with that, and this derivation follows the derivation given by Lasia. He has written a book he has also given I think extensive introduction that is available in the web.

There are different ways of doing this. One way is to Laplace transform another way is to expand in Taylor series, truncate and proceed that is what we are going to do here because that is what we have been following so far so we will continue with that. We are going to say we give a potential E_{dc}+ E_{ac} where E_{ac} is given as E_{ac0} sin(ωt)

Now we know that standard process, we expand in Taylor series, truncate the higher order terms and we say approximately as long as E_{ac} is small or E_{ac0} is small, k_1 can be approximated as k_{1dc}+ (b_1 E_{ac}). k_{-1} can be approximated and when we substitute here concentration of A will also show fluctuation concentration of B at the surface within the boundary layer everywhere it will show fluctuation.

Only at the delta we are going to say let us fix this concentration with the bulk. We do not know how it is going to fluctuate we are going to derive that, but we are going to say that current can also be written as dc current + ac current because the E_{ac} is small it will have steady current + a fluctuation, that means if I draw like this if I apply only dc current will be like this. At time t=0 we are going to apply an ac, so potential will look like this potential will be like this E and then it is going to be sinusoidal on top of dc. Current will look like this of course it will take some time to stabilize and right now do not worry about it, but we do know that it will actually oscillate and stabilize at a slightly different location, but very slightly so let us not worry about it.

We will say it will oscillate and after sometime it will give what is called steady periodic motion. This is the current I am going to say it has a dc part and then ac part and I want to calculate the ac pot so that I can calculate admittance corresponding to the faradaic reaction under the condition that mass transfer also plays a significant role. So normally what we would have done is the following.

We would have written k_1 as k_{1dc}+ linear term. We would have written concentration of A as steady state + concentration of A variation with respect to potential multiplied by E_{ac}. We ignore the other Taylor series expansion terms that is C_A square E_{ac} square E_{ac} cube etc. And likewise we would have done that for k_{-1} and C_B, but we are not going to do that way.

We are going to consider C_A, C_B and potential three as independent variables and it is possible to actually do that way. We can vary the concentration on the surface, by changing the rotational speed. Let us say I go to some E_{dc} so A is getting reacted produces B, A is consumed B is produced and it depends on the boundary layer thickness.

If I give 600 RPM it will have certain thickness if I give 700 RPM it will have a different thickness. It is possible for us to vary the RPM and make it sinusoidal meaning it will go from 600 to 700 to 500 at a particular speed. So I can give a sinusoidal oscillation, the RPM will be something like this 600 + 100 sin(ωt) or sin 2 πf(t) where f maybe 0.01 that means every 100 second it will come to 600. So it will increase RPM will increase go to 700 come down to 600 come to 500 come back to 600 and so on.

That way what will happen is boundary layer thickness will also change, concentration on the surface will also change although E_{dc} is not changing or E is not changing because this enables us to derive the expression we are going to follow that method where we say the current changes because the potential changes, current can change because the concentration of the surface changes. Current can change because concentration of B on the surface changes, and in our case next line we are going to say concentration of A and B on the surface changes because potential changes. But in general I can account for change in current arising due to change in potential, change in concentration of A, change in concentration of B. So that means I will write it as partial derivatives $\partial i/\partial E$ at constant C_A, C_B multiplied by ΔE. $\partial i/\partial C_A$ constant potential and constant B multiplied by ΔC_A that tells how much is the variation in C_A.

And the third term tells is the variation in C_B. **"Professor - student conversation starts"** Is there assumption in assuming such a situation that the deltas are very small. No we are not going to assume delta is very small you mean this delta not the boundary layer thickness, delta. Yes, basically this is also Taylor series expanded chopped off. **"Professor - student conversation ends".**

This Δi_F is basically we are expanding this in Taylor series not just around Edc it is around E_{dc}, C_{Ass}, C_{Bss} and you will cross product terms. So you will have terms like $\partial^2 i/\partial E^2$. We will have terms like $\partial^2 i/\partial E\ \partial C_A$ $\partial^2 i/\partial\ C_A\ \partial C_B$ because we are saying linear terms we are happily removing all these things and we are left with this term here.

Yes, we are assuming that this ΔE, ΔC_A, and ΔC_B are very small. Now Δ is very easy is it right we know it is a sinusoidal perturbation so we will write it as E_{ac0} sinωt. $\partial i/\partial E$ I take the expression for this and when I fix concentration of A and concentration of B only rate constant changes. Therefore, I take this, F is retained here derivatives of k_1 with respect to E gives me b_1, derivatives of k_{-1} with respect to potential gives me b_{-1}.

And this is left as it is and ΔE is given as E_{ac}. So the first time we it is easy to do, second and third terms are also easy to do as far as the derivatives are concerned. Take this expression, take a derivative with respect to C_A k_1 of course is independent C_B is independent therefore you are left with only F k_{1dc}. Take this expression at a fixed dc potential and fixed C_A if I take derivative with respect to C_B, I will get –F $k_{-1\ dc}$.

So we have got everything except these two and these two will take quite some time to do. So we will stop here today.