Corrosion - Part II
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Lecture - 5
Concentration Polarization and Mixed Potential Theory

Let us start lecture 5.

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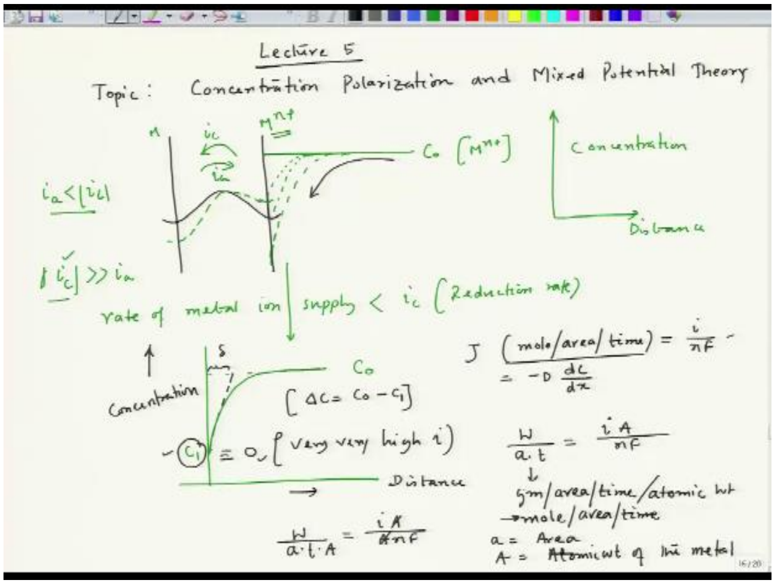

Lecture 5

Topic: Concentration Polarization and Mixed Potential Theory

$i_a < |i_c|$

$|i_c| >> i_a$

rate of metal ion supply < i_c (Reduction rate)

$[\Delta C = C_0 - C_1]$

$C_1 = 0$ [very very high i)

J (mole/area/time) $= \frac{i}{nF}$ $= -D\frac{dC}{dx}$

$\frac{W}{a \cdot t} = \frac{iA}{nF}$

↓

gm/area/time/atomic wt

→ mole/area/time

$\frac{W}{a \cdot t \cdot A} = \frac{i\cancel{A}}{\cancel{A}nF}$

a = Area

A = Atomic wt of the metal

And topic will now get to gradually to concentration polarization and mixed potential theory. Till now we have got the situation that activation polarization happens when there is activated jump of metal ion or metal atom across the double layer over an activation barrier. Now we have also seen that there could be situation of equilibrium and that time we will come across exchange current density and when polarization happens this is the manifestation of current flow or other net current flow into the circuit.

And that time either ia can go up as compared to ic or ic can go up as compared to ia and that would lead to anodic polarization and cathodic polarization and you can measure the polarization by over voltage which is neeta. Now again we have also seen that activation polarization happens at lower current density when the concentration across the metal surface does not change, the bulk concentration or as well as the interface composition of the metal species other reducing species would not change.

But if we go to a higher current density that reducing species can change is concentration at the interface of the metal. Now that time will come across concentration polarization. So if we see the concentration evolution of concentration polarization, so if we have double layer, so here we have situation like let say if I consider a situation where ic is greater than ia so in this case Mn+. So this current ic and this current ia and ia less than ic.

And the energy distribution plot will be the dotted green line, this happens, now that time if I see the concentration C zero let's say metal ion concentration C zero in the bulk that concentration remains same as C zero at the interface, but once ic becomes greater than greater than ia then the rate at which this jump happen, the rate at which the metal ion is supplied by the bulk these 2 rates becomes different.

So the rate this current density other reducing current density for the ic is so high that there will be a depleted iron layer across the interface. So now gradually the concentration will go down will keep going down across the interface because if this access is concentration and this access is distance**.** So then the rate the reduction rate is so high that the metal ion depletion happens across the interface.

And the rate at which this happens and if I consider rate of metal ion supply is then lower than ic for the reduction rate. So that time I will have a depleted layer. So if I try to draw this one in the concentration profile mode so I will see that this is C1 and this is the bulb consideration C zero then I will have a plot like this. So when we have a plot like this then I will have a diffusion distance which is delta is the boundary layer thickness.

Now the entire reduction process will be decided by how quickly the metal ion is supplied from bulk to the interface and then that metal ion will get reduced. From this, this is of course this line is distance, this is concentration, from this we can have one more polarization, let us see how we get to that, now I can see that J which is the flux nothing but mole per unit area per unit time I can write a simple Fick's first law - D (dC/dx) and C is the concentration.

Now this is nothing but I by nF. Why? Because W by area let us says a capital A area and time is t that is I into let's say let me mention it as small a which is area, this is A which is the atomic weight nF for that. We have seen it before, so this unit is gram per unit area per unit time. So now if I want to convert into mole so that time this is to be divided by atomic weight. So now W by at divided by A which becomes the unit like this. So then ia AnF.

So these 2 cancels out and here small a is area and capital A is molecule atomic weight of the metal. Right. So now if I try to see the polarization situation when if you see this particular C1 if the current density is extremely high that time the C1 can have the extreme value which is zero, so this is very high very very high i. Ok. So that time it can have the limiting value which is zero, that means whatever ions are coming from the bulk to the interface so the ions are immediately getting reduced.

So now in one case I will have C1 and in one case I will have extreme situation the concentration and interface goes to zero. Let us see that what will be the equation at this 2 boundary conditions.

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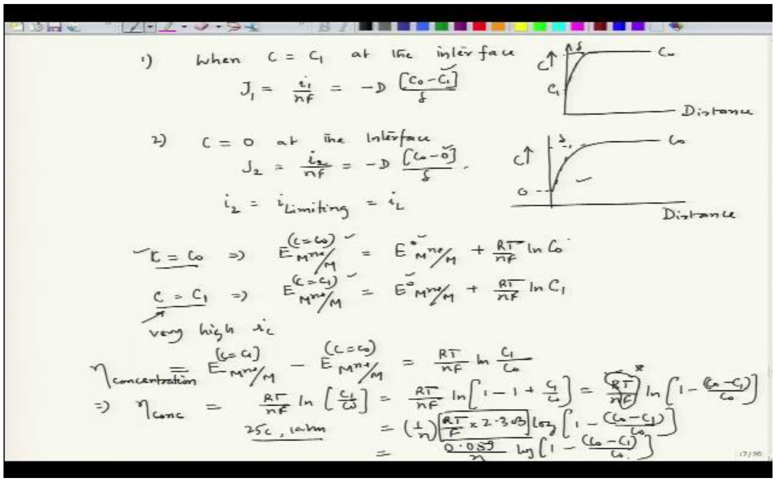

1) When $C = C_1$ at the interface

$J_1 = \frac{i_1}{nF} = -D\frac{[C_0 - C_1]}{\delta}$

2) $C = 0$ at the interface

$J_2 = \frac{i_2}{nF} = -D\frac{[C_0 - 0]}{\delta}$

$i_2 = i_{Limiting} = i_L$

$C = C_0 \Rightarrow E^{(C=C_0)}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\ln C_0$

$C = C_1 \Rightarrow E^{(C=C_1)}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\ln C_1$

very high i_L

$\eta_{concentration} = E^{(C=C_1)}_{M^{n+}/M} - E^{(C=C_0)}_{M^{n+}/M} = \frac{RT}{nF}\ln\frac{C_1}{C_0}$

$\Rightarrow \eta_{conc} = \frac{RT}{nF}\ln\left[\frac{C_1}{C_0}\right] = \frac{RT}{nF}\ln\left[1 - 1 + \frac{C_1}{C_0}\right] = \frac{RT}{nF}\ln\left[1 - \frac{(C_0 - C_1)}{C_0}\right]$

25C, 1atm

$= \left(\frac{1}{n}\right)\boxed{\frac{RT}{F}\times 2.303}\log\left[1 - \frac{(C_0 - C_1)}{C_0}\right]$

$= \frac{0.059}{n}\log\left[1 - \frac{(C_0 - C_1)}{C_0}\right]$

So the one boundary condition is when C = C1 at the interface. So that time J = i/nF = $-D ((C_o - C_1)/\delta)$ and let me put it as J1 or let me put it as i1 corresponding to the condition C1 the interface condition. So that means here the situation is if I consider this is to be interface and this is the bulk concentration I am having a situation like this. This is distance, this is concentration and this concentration is C1.

Now for a boundary condition when C = C zero sorry C = zero at the interface that time

$$J_2 = \frac{i_2}{nF}$$

this i is nothing but the current density = -D $((C_o - C_1)/\delta)$. So this situation is like this, if this is the zero value, so now this is C zero, this delta here it is delta. So this is C concentration, this is distance. Right. So that condition I will have this equation like this. Now I could immediately make out this is i2 is the limiting value.

Because I am reaching the limiting value of zero at the end, so i2 is right is considered as i limiting or iL. So we see that i limiting is appearing when I am having this situation. Now let us considered the potential that is being developed at the interface. So in a situation like when C equal to C zero at interface that time potential

$$E^{C=c_o}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF} lnC_o$$

I can mention C zero since it is a pure metal and we have already seen then the concentration of metal ion is nothing but C zero, so I am putting C zero.

Similarly, when C = C or 1 that time C so let say this C = C zero and here C = C1, so

$$E^{C=c_1}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF} lnC_1$$

So these are the 2 potential when the concentration at the interface are this, so if we see this particular situation, now when we are having activation polarization that time the concentration at the interface is maintained C zero all the time, so this is that time we already get activation polarization.

And that we can express in the form of tafel equation, but once we have a very high current density that means reduction current density ic that time the concentration will start reducing at the interface so will get up depleted zone and then these 2 potential values must be different and this is the condition we are getting when we are having very high ic. Fine. So this condition is getting. So now if I try to see what is the polarization due to this concentration change is nothing but

$$E^{C=C_o}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF} ln\ ln\ C_o$$

So these 2 values are same because the standard potential, so this is I can write it as nF ln (C_1/C_o). This is nothing but concentration, we shortly write as concentration is equal to then RT by nF ln. I can see C1 by C zero. I can do little bit of juggling here (RT/nF) ln (1-1 + (C_1/C_o)) we can write it as (RT/nF) ln (1 - (C_o - C_1)/C_o). I can write this. I can convert into log and if I consider 25 degree Celsius 1 atmosphere pressure that time this factor will become factor multiplied by. So that means (1/n)(RT/F)(2.303) log (1 - (C_o - C_1)/C_o), this factor would become (0.059/n) log (1 - (C_o - C_1)/C_o) ok.

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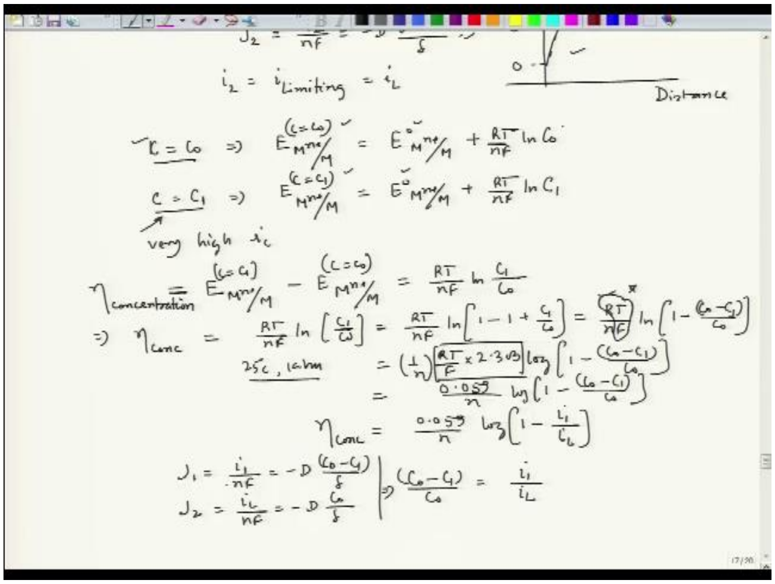

$$i_2 = i_{Limiting} = i_L$$

$$C = C_o \Rightarrow E^{(C=C_o)}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\ln C_o$$

$$C = C_1 \Rightarrow E^{(C=C_1)}_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\ln C_1$$

very high i_c

$$\eta_{concentration} = E^{(C=C_1)}_{M^{n+}/M} - E^{(C=C_o)}_{M^{n+}/M} = \frac{RT}{nF}\ln\frac{C_1}{C_o}$$

$$\Rightarrow \eta_{conc} = \frac{RT}{nF}\ln\left[\frac{C_1}{C_o}\right] = \frac{RT}{nF}\ln\left[1-1+\frac{C_1}{C_o}\right] = \frac{RT}{nF}\ln\left[1-\frac{(C_o-C_1)}{C_o}\right]$$

25c, 1atm

$$= \left(\frac{1}{n}\right)\boxed{\frac{RT}{F}\times 2.303}\log\left[1-\frac{(C_o-C_1)}{C_o}\right]$$

$$= \frac{0.059}{n}\log\left[1-\frac{(C_o-C_1)}{C_o}\right]$$

$$\eta_{conc} = \frac{0.059}{n}\log\left[1-\frac{i_1}{i_L}\right]$$

$$J_1 = \frac{i_1}{nF} = -D\frac{(C_o-C_1)}{\delta}$$

$$J_2 = \frac{i_L}{nF} = -D\frac{C_o}{\delta}$$

$$\Rightarrow \frac{(C_o-C_1)}{C_o} = \frac{i_1}{i_L}$$

So I can for that write 0.059 by n log of now get to this particular 2 situations this and this, so I tried to write

$$J_1 = \frac{i_1}{nF} = -D\frac{C_o - C_1}{\delta}$$

$$J_2 = \frac{i_l}{nF} = -D\frac{C_o}{\delta}$$

So then I can see that

$$\frac{C_o - C_1}{C_o}\frac{i_1}{i_L}$$

We can get to this. In both the cases D would be same because it is at a particular temperature n and F for both the cases are same. So this ratio we are getting so I can write it as $1 - (i_1/ i_L)$.

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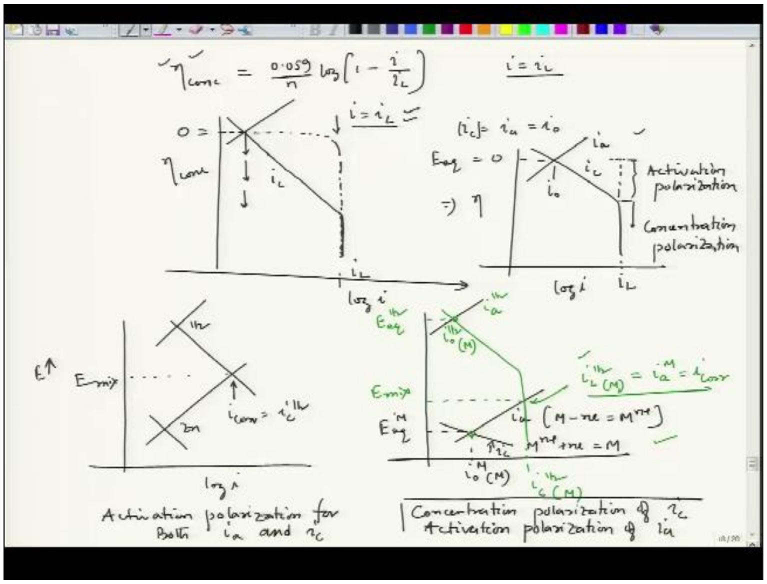

So this is concentration polarization, if I would like to plot it**,** so this is n concentration equal to $(0.059 /n) \log (1 - (i_1/ i_L))$. Now here instead of 1 I just put i because the generalized equation then this step it is valid for any other compositions. This C1 could be anything other than C zero and once I reaches to iL that time this quantity becomes infinite. So if I try to plot it, the plot nature would be.

So this is the situation if you see this the situation this is the value zero overvoltage zero and this is log i, so when it can go to zero when ic = ia = i zero. So that means I will have situation like this. These are the activation region and now at this point I = iL, so that was concentration polarization becomes infinite, so it goes down directly straight. So this value corresponds to iL, i limiting.

Now you could see that before I achieve this situation the concentration polarization or the change in concentration change in potential due to concentration effect is not that significant, but there is a change in potential due to activation. Now the activation will take the potential down but the concentration affect will not allow the potential to be down significantly, it will be in significant.

So initially at the lower current level the activation current will try to take activation polarization leading to the ic that will take the potential down and finally when the ic reaches this particular criteria it will merge with this. Fine. So the final plot would be so this is for ia, this is for ic, this is i zero, this is zero voltage corresponding to E equilibrium, this is the corresponding iL. So this combines. So, up to this we are having activation polarization and after this we are getting concentration polarization. Fine.

So this is the significance of this is the in the log scale is the significance of concentration polarization and this plot shows the combination of both activation and concentration. Now if I try to see the mixed potential theory here also, now in case of zinc and hydrogen these 2 reactions you could see that the plots were like this. So this is the and these point I am not indicating you just go back and see that what are those points.

This is for hydrogen, this is for zinc and now this point is nothing but i corr = ic hydrogen and this is E mix, and this is the potential axis. This is the situation what we had in case of activation site activation, when the polarization is control polarization is nothing but activation polarization. Now if we have a situation like this let say 1 metal which is having its own activation polarization in the cathodic side this is ia for M - ne = M^{n+}.

And this is ic for that metal. Fine. And this is i zero of that metal on the metal surface, this is E equilibrium of that particular metal. Fine. Now if I consider the hydrogen evolution on that particular metal and if we consider the hydrogen reaction is taking place like this and before it reaches the mix potential I will have achieved if I achieve concentration polarization in case of hydrogen. This is the concentration polarization line.

This is ic hydrogen on that metal surface, if we have a situation like this, this is ia for hydrogen, this is i zero hydrogen on that metal surface and this is E equilibrium hydrogen. So that time the mix potential be this one. Fine. And at this point i limiting hydrogen on that metal surface is equal to ia of that metal or i corrosion. Fine. This is the situation. this is the mixed potential theory for in the situation when we have interaction of concentration polarization with activation part of that metal.

And these 2 extreme points they try to reach a mix potential where total cathodic current density is equal to total anodic current density. We will have interaction like this. So this is the interaction of activation polarization for both ia and ic and this is interaction of concentration polarization of ic and activation polarization of ia.

So these 2 situation we have just now explained. So let us stop here, now we have understood a kind of we will basically this is the recap, now will get to understand lot of corrosion phenomena with the help of mixed potential theory one after another, thank you.