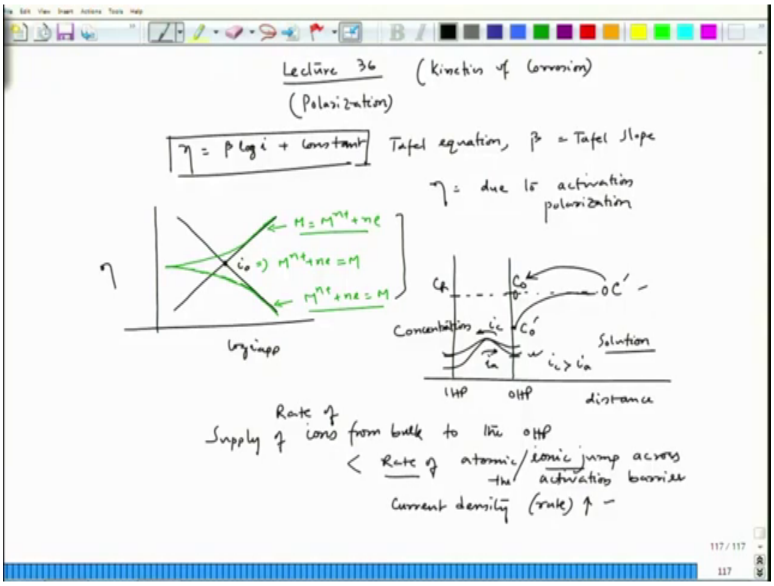
Corrosion – Part I
Prof. Kallol Mondal
Department of Materials Science Engineering
Indian Institute of Technology, Kanpur

Lecture – 36
Activation polarization, concentration polarization and total polarization

So, let us begin lecture 36.

(Refer Slide Time: 00:17)



Lecture 36 (Kinetics of Corrosion)
(Polarization)

$\boxed{\eta = \beta \log i + \text{constant}}$ Tafel equation, β = Tafel slope

η = due to activation polarization

Rate of Supply of ions from bulk to the OHP < Rate of atomic/ionic jump across the activation barrier

Current density (rate) ↑ –

We will continue our discussion on polarization, which is part of Kinetics of Corrosion. Now, there we have seen that, this particular equation is a Tafel equation. Beta is Tafel slope and there also we have seen that how this experimental log I applied varies with over voltage. This is the point with i 0 and it varies like this, fine. And at this point I see M n plus plus n e equal to M and on this side I have preferential anodic reaction and this side we have preferential cathodic reaction, fine.

So, these were our concept that we have seen in the last lecture. And this Nita C is nothing but, Nita C or Nita a either it could be cathodic over voltage or anodic over voltage, which is due to cathodic as well as anodic polarization; respectively is due to activation polarization. Since, we could see that if I have a bulk medium, this is IHP, this is OHP and the concentration of C R and C O and then bulk concentration C let us say prime, they are on the same plane and this is distance.

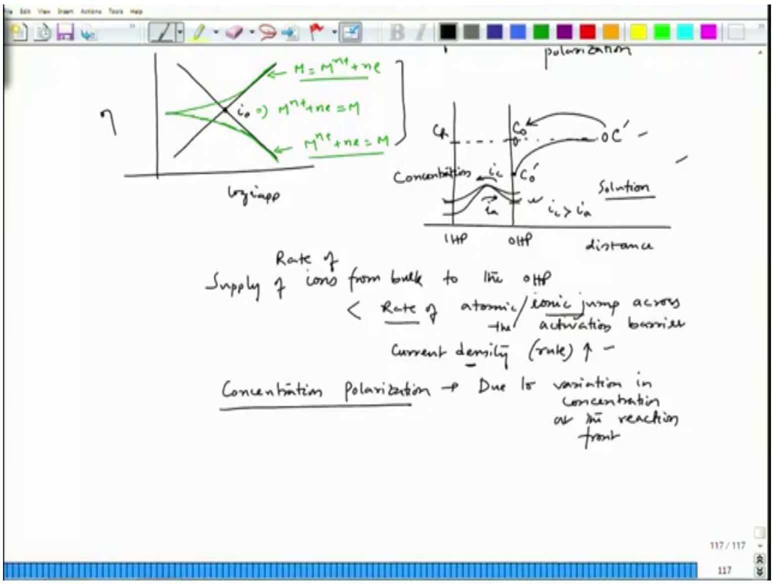
And we are saying that reaction or this particular process is taking place, because of the interface jump of ions or atoms over the energy barrier. This energy barrier could be depending on whether it is a anodic current density or cathodic current density, which one is more compared to as compared to the other, then this particular plot will rearrange itself. So, then this would be in this case this is the situation where we have i c to be more than i a.

So, when there is enough supply of cations to this particular plane. So, that concentration is flat in the solution side, this is solution side. Then the rate at which these interface jump is taking place that will control the overall potential drop or potential increase, or cathodic polarization or anodic polarization. And that would lead to over voltage; either it could be cathodic or anodic polarization anodic over voltage. Now, let us say this at certain point the supply of ions from bulk to the interface to the OHP and if I say that rate of supply is less than the rate of atomic or ionic jump across the activation barrier, then there would definitely be a lag of metal ion supply to the bulk to the interface.

So, there would be a lag from this section to this section. And that lag could be generated because since this rate is increasing. So, that suggest that the current density which is nothing but a rate is very high, at a very high current density, there could be a situation there is a lag of ion supply to the interface OHP for the ionic jump from OHP to the high IHP; because when we have this kind of modification in the energy distribution, then we have more of i c, in this case i c is greater than i a, so there would be a lag.

So now, there could be concentration profile with decreasing concentration as we come from the bulk concentration to the interface. So, this concentration would have a distribution like this. So, here it would become then C O prime. So, this is the interface concentration due to this very high activation, this very high rate of current flow because of this higher rate of ionic jump across the activation barrier.

(Refer Slide Time: 06:45)



Rate of Supply of ions from bulk to the OHP < Rate of atomic/ionic jump across the activation barrier

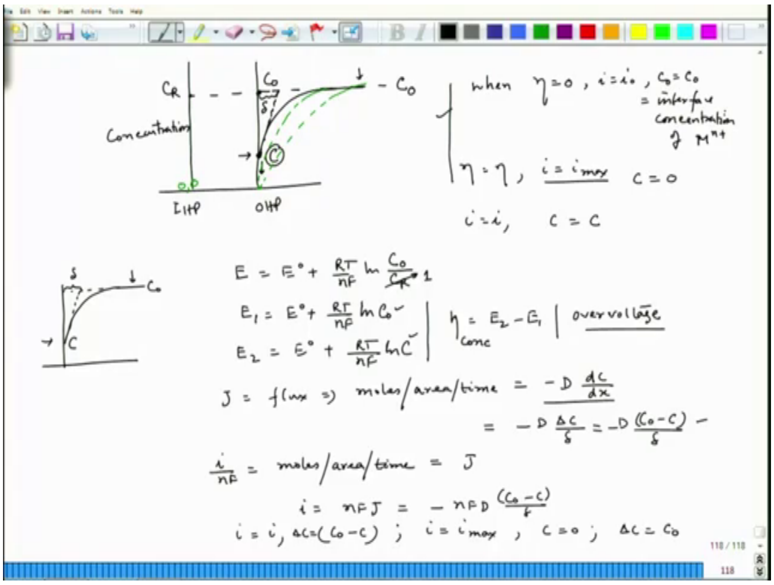
Current density (rate) ↑ –

Concentration Polarization → Due to variation in concentration at the reaction front

So, that situation we would come across the another type of polarization which is called concentration polarization. This is due to variation in concentration at the reaction front. And that happens at a very high activation current density, at a very high current density because, if it is a low current density, the rate of atomic jump is little low. So, it can be possible that the rate of ions supply from the bulk would be equal to the rate of ionic jump.

So, there should not be any a lag of concentration from bulk to the interface. Now, in this situation, let us look at this concentration polarization in a little depth.

(Refer Slide Time: 07:56)



when $\eta = 0$, $i = i_0$, $C_0 = C_0$ = interface concentration of M^{n+}

$\eta = \eta$, $\underline{i = i_{max}}$ $C = 0$

$i = i$, $C = C$

$$E = E^\circ + \frac{RT}{nF} \ln \frac{C_0}{\cancel{C_R}} 1$$

$$E_1 = E^\circ + \frac{RT}{nF} \ln C_0$$

$$E_2 = E^\circ + \frac{RT}{nF} \ln C$$

$\eta_{conc} = E_2 - E_1$ | $\underline{\text{overvoltage}}$

$$J = f(\text{ux} \Rightarrow) \text{ moles/area/time} = \underline{-D \frac{dc}{dx}}$$

$$= -D \frac{\Delta C}{\delta} = -D \frac{(C_0 - C)}{\delta} -$$

$$\frac{i}{nF} = \text{moles/area/time} = J$$

$$i = nFJ = -nFD \frac{(C_0 - C)}{\delta}$$

$i = i$, $\Delta C = (C_0 - C)$; $i = i_{max}$, $C = 0$; $\Delta C = C_0$

So, let us talk about concentration polarization. So, as we have saying that, there could be so this is IHP, this is OHP and this is the initial concentration, this is the concentration in the bulk, which is similar to C O let us say. Because, the bulk concentration is similar to the interface concentration, in the beginning when there was no current supply or the over voltage is 0. And after supply after the current flow and let us say it is a little bit higher current density, so then there could be a concentration profile, this is the concentration profile and this axis is concentration. This is C R this is similar to C O; because the bulk concentration I am considering C O.

And let us say this concentration is C, which is the interface concentration; now when Nita equal to 0, or i equal to i 0 I would get C equal to C 0. The concentration or C 0 equal to I would say equal to 0 or interface concentration; concentration of metal ion n plus. Now, when Nita equal to Nita and i equal to i max let us say; that means, the if as the current density is increasing, I am getting over voltage, as well as the over voltage is increasing, I am seeing that this particular concentration is going down gradually.

So, this concentration profile will keep changing as we increase the current density. And finally, it will reach to 0 value, this is 0 0 axis let us say so, it will reach to 0 value. So that means, when i equal to i max, I should get concentration should be 0 at the interface ok so, these 2 are boundary conditions. Now, I know that when i equal to i, so then concentration would be C at the interface and that time I would get sum over voltage.

Now, when this concentration is changing from this point to this point, I can apply equilibrium condition and find out potential developed at the electrode; because of this concentration change via by applying Nernst equation.

So, then E equal to E 0 plus RT nF ln concentration of O divided by concentration of R. Now, if I consider the concentration of R is or in terms of activity, if it is concentration is considered to be 1, so then I can write it is only dependent on the concentration of ln C 0 and that time that potential I consider to be E 1 and E 2 would be E 0 plus RT nF, when concentration is C.

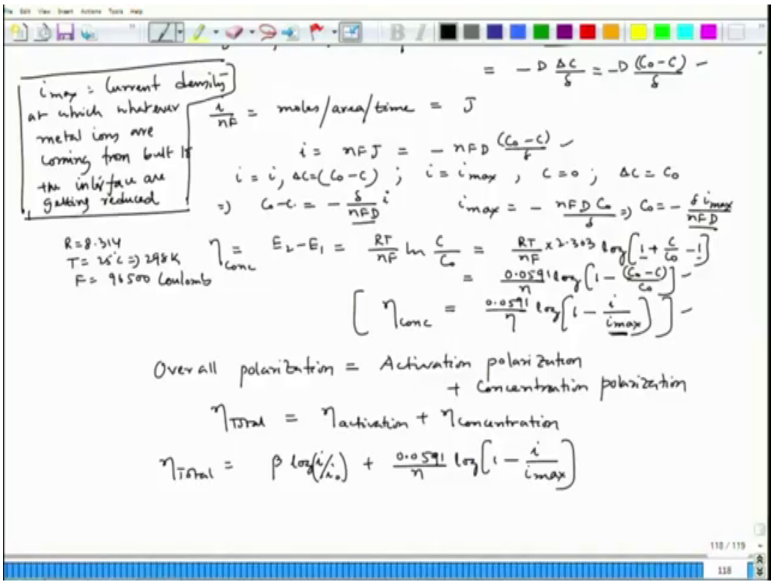
So, this I am getting these 2 equations. So, the over voltage would be is equal to E 2 minus E 1. And this over voltage is due to this concentration change of this metal line, so I can put it as concentration or in short I can mention it as concentration. And this is concentration polarization or over voltage. Now, whenever I have this diffusion or concentration profile, I have a boundary layer thickness which let us say I consider to be dell which is the boundary layer thickness. This is the dell which is the boundary layer thickness.

Now, I can use Fick's first law here. J which is the flux I can write in these form moles per unit area per unit time equal to minus D dc dx, I am considering steady state situation here. And this can be when the situation is; situation is this and this is C, then the flow of metal ion from this bulk to the interface or bulk to the interface that rate would be decided by this particular equation, which is the Fick's first law and we are considering steady state flow. This can be approximated as minus D dc can be written as del C and x can be written as del; which is minus D C 0 minus C divided by delta.

Now, I know i by nF equal to moles per unit area per unit time if you go back if you check you will see that this is the rate of flow of metal ions per unit area per unit time, which should be equal to J. Then I can write i equal to nF J so, I put this particular situation minus nF D C 0 by minus C delta. Now, I use these 2 conditions; when i equal to i, so that time the concentration difference is C 0 minus C.

And when i equal to i max, so that means, that maximum current density where the whatever metaline is coming from the bulk to the interface that meta line is immediately getting reduced and going to the IHP the or inner Helmholtz plane, at that situation the concentration at OHP should be 0. So, then C equal to 0 or del C would be then equal to C 0.

(Refer Slide Time: 15:47)



$= -D\frac{\Delta C}{\delta} = -D\frac{(C_0 - C)}{\delta}$

i_{max} : Current density at which whatever metal ions are coming from bulk to the interface are getting reduced

$\frac{i}{nF}$ = moles/area/time = J

$i = nFJ = -nFD\frac{(C_0 - C)}{\delta}$

$i = i, \Delta C = (C_0 - C)$; $i = i_{max}$, $C = 0$; $\Delta C = C_0$

$\Rightarrow C_0 - C = -\frac{\delta}{nFD} i$ $\quad i_{max} = -\frac{nFDC_0}{\delta} \Rightarrow C_0 = -\frac{\delta i_{max}}{nFD}$

R = 8.314
T = 25°C ⇒ 298 K
F = 96500 Coulomb

$\eta_{conc} = E_2 - E_1 = \frac{RT}{nF}\ln\frac{C}{C_0} = \frac{RT}{nF} \times 2.303\log\left[1 + \frac{C}{C_0} - 1\right]$

$= \frac{0.0591}{n}\log\left(1 - \frac{(C_0 - C)}{C_0}\right]$

$\left[\eta_{conc} = \frac{0.0591}{\eta}\log\left[1 - \frac{i}{i_{max}}\right)\right]$

Overall polarization = Activation polarization + Concentration polarization

$\eta_{Total} = \eta_{activation} + \eta_{concentration}$

$\eta_{Total} = \beta\log(i/i_0) + \frac{0.0591}{n}\log\left[1 - \frac{i}{i_{max}}\right)$

So, in those situation, I let us continue from here, now then I can write i max equal to minus nF D C 0 by delta. Therefore, Nita equal to or concentration E 2 minus E 1 equal to E 0 E 0 they both will get cancelled.

So, that means, we are left with nF ln C by C 0. And remember whenever we try to understand over voltage, we have to always differentiate between initial final to initial. So, the over voltage should be E final minus E initial. Here this one is initial potential when the concentration of metal ion at the interface is C 0 and this particular is the final. So, that is what the over voltage is E 2 minus E 1. So, this I can write in terms of nF into 2.303 log I can have C minus C 0 plus 1. And if I take R to be 8.314 t equal to 25 degree Celsius; that means, 298 Kelvin. And F equal to 9 6 5 0 0 coulomb, then I can get 0.059 by n log 1 minus C 0 minus C by C 0. Here I have sorry; this should be minus I have just made some modification here. Here it is I am just adding 1 and then also subtracting 1 from that.

So, that is what I am getting this equation. And then this I can write 0.059 Nita log 1 minus I will put this expression. So, in this case C 0 minus C equal to minus delta by nF D i and here I can put C 0 equal to minus delta i max divided by nF D. So, if we put them, so delta delta as well as this nF D part would get cancelled, so we would be left with this equation.

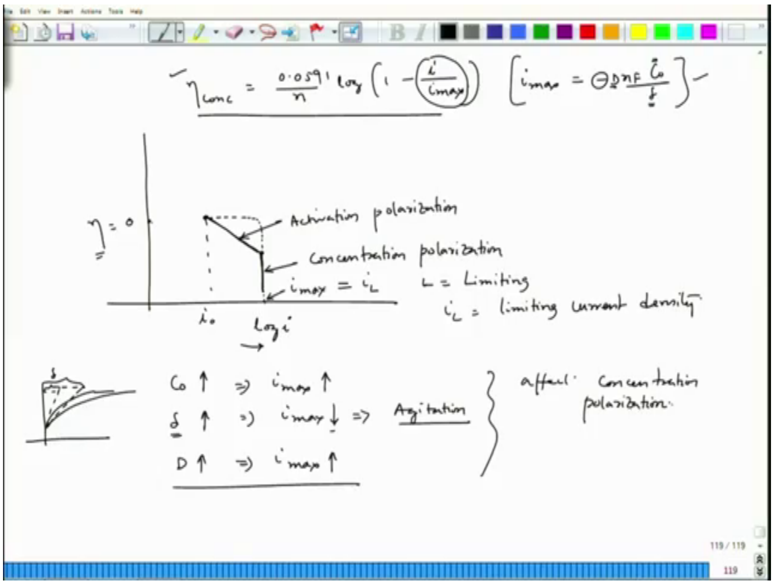
So, this is concentration. So, this is the expression for concentration polarized over voltage. And as we have said that what is i max? I max is basically the current; current density we have explained also, at which whatever metal ions are coming from bulk to the interface are getting reduced are reduce.

So, that means, my interface concentration should be 0 when i reaches i max so, this is another equation. Now, if I try to connect this both this concentration, so this means this is concentration polarization. So, overall polarization should be equal to activation polarization plus concentration polarization. So, I can write total equal to n activation plus n concentration.

So, then I can put it as plus, so there should be 1 n log 1 minus I by i max. Because, when we have overall polarization if we try to reach to the concentration polarization end, we should go first to activation part and then the concentration part will come up. Because, when we have activation part, when we have activation control polarization, then I have enough supply of metal ions from the bulk to the interface. So, there is no compentation concentration depletion in that interface.

But, as we go higher and higher activation polarization; that means, we as we are going for higher and higher current density, we could see that there will be depletion of metal ions, at this OHP as we have seen in the present case. And then we will get to the concentration polarization regime. So, there if we have concentration polarization, then there should be it should start with the activation polarization, then we will reach to the concentration polarization.

(Refer Slide Time: 22:29)



$$\eta_{conc} = \frac{0.0591}{n} \log\left(1 - \boxed{\frac{i}{i_{max}}}\right) \quad \left[i_{max} = -\frac{DnF\,C_0}{\delta}\right]$$

$C_0 \uparrow \Rightarrow i_{max} \uparrow$

$\delta \uparrow \Rightarrow i_{max} \downarrow \Rightarrow$ Agitation

$D \uparrow \Rightarrow i_{max} \uparrow$

So now, if I try to plot concentration polarization which is n is equal to 0.0591 n log of i minus i by i max; where i max equal to minus D nF C 0 by delta. So, this plot would look like this so, this is log i again, this is polarization. Now, when we have 0 over voltage, this is my i equal to 0 i 0, this is fairly basically i 0 value, where the polarization is nil or over voltage is 0. Then first concentration polarization will start. And then immediately once we reach to the i max, because I am seeing that the current density is gradually increasing, I would get immediate because when I reach i max, so this becomes 1, this becomes 1.

So, this Nita concentration would be infinite, the over voltage have been infinite. So, it would be a flat parallel line, parallel to the over voltage axis. Until this particular current i max if I try to plot this particular equation, I would see a plot like this ok. So, this is activation polarization and this part is concentration polarization. And this particular current density for that particular reaction is i max. This is also termed as i L which is L is nothing but limiting so, this is i L is equal to limiting current density.

Now, here couple of interesting facts is this term, this term as well as this term. Now, if C 0 increases, let us say I increase the C 0 and I am not changing other things are remaining same. So, that situation I would get i max should increase. If we do not change D which is function of temperature, n and F for this particular redox reaction (Refer

Time: 25:30) reaction should be same, delta if we do not change the boundary layer thickness, so I should have this particular consequence.

Now, if I change delta let us say delta increases; that means, delta increase means if we have the concentration profile like this. So, then this is my delta; delta, if it increases let us say if it becomes like this so; that means, it increases to this much. So, then as per this equation if you concentration is not changing, D is not changing the consequence should be i max should decrease.

And how can we change this delta? Delta can be changed if we incorporate agitation. Agitation means, if we chant the solution we would lead to have this kind of situation. Now, if D increases; that means, diffusivity increases as per this formula, this minus sign remember this minus sign is indicating of indicative of flow of ions against the concentration profile. Concentration this minus sign is basically indicative of cative of flow of ions from higher to lower concentration and this D increases i max also increases.

So, these are some factors which affects this affect concentration polarization, fine. So, let us stop here, we will continue our discussion in the next lecture onward. We would try to connect this activation as well as concentration polarization and get to a concept called mixed potential theory; which will enable as to understand corrosion mechanism in a much better way, rather than going through a very analytical path ok. So, let us stop it stop here and we will continue our discussion in the next lecture.

Thank you.