Corrosion – Part I
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Lecture – 32
Correlation between Current Density and Overvoltage

Let us start lecture 32.

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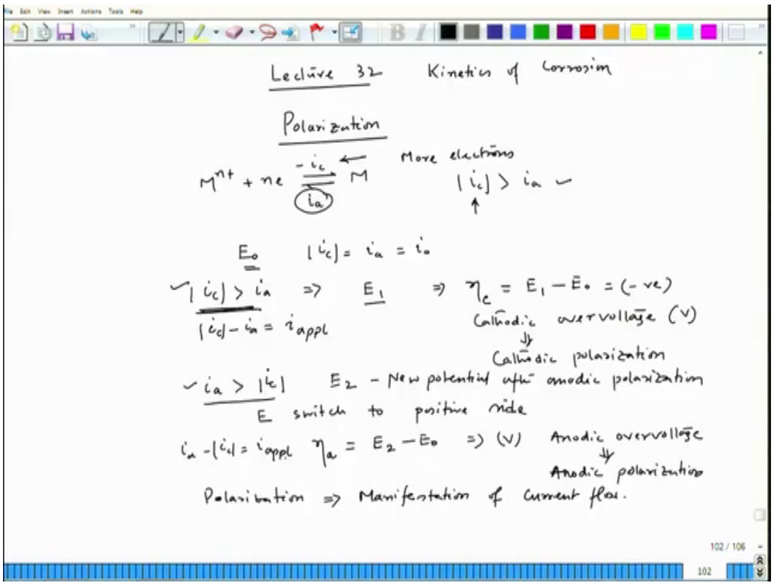

Lecture 32 Kinetics of Corrosion

Polarization

$M^{n+} + ne \underset{\textcircled{i_a}}{\overset{-i_c}{\rightleftharpoons}} M$ ← More electrons

$|i_c| > i_a$ ✓

E_0 $|i_c| = i_a = i_0$

✓ $|i_c| > i_a$ ⇒ E_1 ⇒ $\eta_c = E_1 - E_0 = (-ve)$

$|i_c| - i_a = i_{appl}$

Cathodic overvoltage (V)

⇓

Cathodic polarization

✓ $i_a > |i_c|$ E_2 - New potential after anodic polarization

E switch to positive side

$i_a - |i_c| = i_{appl}$ $\eta_a = E_2 - E_0$ ⇒ (V) Anodic overvoltage

⇓

Anodic polarization

Polarization ⇒ Manifestation of current flow.

And, we will continue our discussion on kinetics of corrosion. In the last class we started discussing on polarization and there we have noticed that for this particular reaction. We have negative current which is minus i c or at a current density which indicates the rate at which cathodic reaction takes place and we have anodic current density which is the rate at which the metal ion forms from metal.

And now then we notice that if we supply negative current to this; that means, if we supply more and more electrons then I can increase the i c value if we see the board value of i c; that means, we are not considering the negative term which is actually the direction of the flow of current is greater than i a then the rate of forward reaction increases because it indicates the rate nothing, but the rate of forward reaction.

So, if the rate of forward reaction increases the potential shifts to the negative side, that what we have noticed. We have said in the last lecture and then if we had the equilibrium potential before having this condition or when i c equal to i a equal to i 0; that means, the reversible condition, non-corroding situation we have E 0 potential. Now, once we have this i c greater than i a; that means, we more and more electrons supply or more and more negative current, then it leads to the potential a new potential which is the manifestation of this current flow and the new potential let us say E 1. Then my the polarization then we say that the electrode has polarized and then the polarization quantity of polarization will indicate by n eta and the c means the superscript c means the cathodic equal to final potential which is E 1 minus initial potential.

This is the value of polarization and you see this is a negative and we are also seeing if we send negative current then definitely the potential would go to the negative side. So, this is called cathodic over voltage and it is unit is in v and this is due to cathodic polarization.

Similarly, if we have a situation i a greater than i c then actually I am increasing the rate of backward reaction or the rate of metal ion formation reaction and that case the potential would switch to positive side in comparison to this equilibrium potential. And that time we also say that the material has that electrode has polarized and that polarization we call it as anodic polarization and the measure of that polarization is n eta anode equal to E 2 minus E 0, where E 2 is the potential, the new potential after anodic polarization and this is you see that this is also unit volt and this is also anodic over voltage this is due to anodic polarization.

Now, interestingly this potential change in the case of cathodic polarization the potential drops from the equilibrium potential or in case of anodic polarization the potential goes up from the equilibrium potential this is due to the excess current flow. This is interesting, when this excess current flow is taking place in this case preferentially cathodic current density is increasing and in this case anodic current density is increasing. In case of anodic polarization and in case of cathodic polarization i c is more than i a; that means, this polarization is the manifestation of current flow or manifestation of net current flow.

Since, once we have this situation then I would say that i c minus i a is basically i applied or the i external. Similarly, here i a minus i c is equal to i applied, which is basically the external current what we are providing or we are sending, this is the difference between these two current densities.

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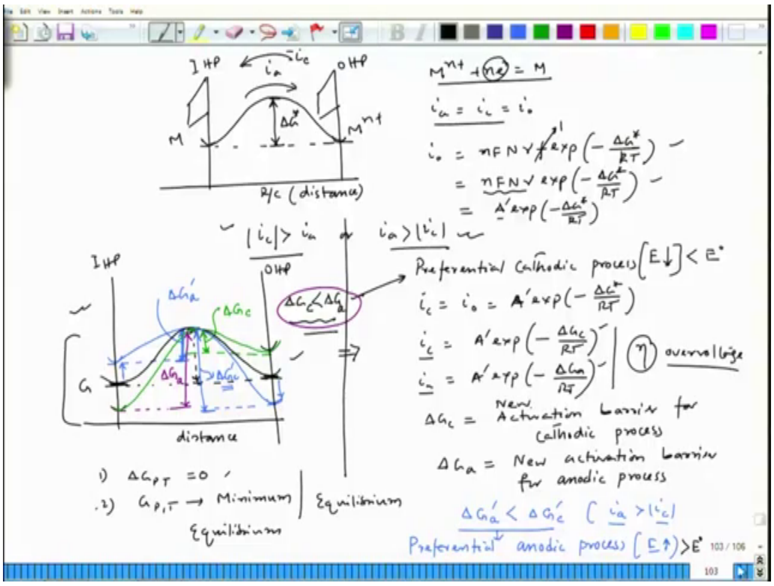

$M^{n+} + ne = M$

$i_a = i_c = i_0$

$i_0 = nFN\nu \cancel{f} \exp\left(-\frac{\Delta G^*}{RT}\right)$

$= nFN\nu \exp\left(-\frac{\Delta G^*}{RT}\right)$

$= A' \exp\left(-\frac{\Delta G^*}{RT}\right)$

$|i_c| > i_a$

$i_a > |i_c|$

Preferential Cathodic process $[E\downarrow] < E^\circ$

$i_c = i_0 = A' \exp\left(-\frac{\Delta G^*}{RT}\right)$

$i_c = A' \exp\left(-\frac{\Delta G_c}{RT}\right)$

$i_a = A' \exp\left(-\frac{\Delta G_a}{RT}\right)$

η overvoltage

ΔG_c = New Activation barrier for cathodic process

ΔG_a = New activation barrier for anodic process

$\Delta G_a' < \Delta G_c'$ ($i_a > |i_c|$

Preferential anodic process ($E\uparrow$) $> E^\circ$

1) $\Delta G_{P,T} = 0$

2) $G_{P,T} \rightarrow$ Minimum | Equilibrium

Equilibrium

Now, if we try to look at the evolution of i 0 the way we have looked at it is basically we have considered IHP and OHP and this is the metal side and this is the metal ion side and both are at the same level energy level and we have high energy barrier and this barrier is delta G star. And, then we have noticed that this particular flow of metal to metal line is i a and then the backward current is i c with a negative sign. Then at condition of equilibrium when i a equal to i c equal to i 0 and we have found out an expression for i 0 which is n F N nu f exponential minus delta G star by RT. This we have noticed and we have said that if f is equal to one this can be brought down to n F N nu exponential minus delta G star by RT. We can write this one or this one anyone would be ok.

In this case f is 1; that means, whatever metal ions are coming from the OHP to IHP they are all getting accommodated after reduction and whatever metal atom is going to the OHP from IHP they are also accommodated on OHP surface. N is the number of moles per unit area and this area we are considering this area and this area and both are if we have a cathodic reaction on top of it and then anodic reaction is also taking place on the same area because this is a reversible reaction. It is happening on the same area F is 1 faraday n is the number of electrons participating in this redox reaction or half cell reaction.

Now, interestingly when we are saying that i c is greater than i a or i a greater than i c; that means, rate of forward and backward reactions are also changing. In this case both i a and i c they are experiencing the same barrier, activation barrier. Now, once we have this two situation the activation barrier would change. How would be the change? Now, in case of condition like this let us see what happens. In this case we have IHP and OHP and interestingly this is reaction coordinate in this case I can considered as distance. Now, here also distance between the double layer.

Now, in the beginning it was on the same level because we are having i 0; that means, they are on they are equilibrium their free energies are also similar and equilibrium concept is says that when a system reaches equilibrium first condition del G PT equal to 0, second condition G PT goes to minimum. This is equilibrium and that is what you see these two regions are these two energy tropes are basically the minimum point and they are at the same plane, so, that means, they are also same. So, both the conditions are meeting. So, this is the condition of equilibrium.

Now, if I send extra negative current or i c; that means, the rate at which this particular backward reaction happens in this case would be faster than the forward reaction and that means, definitely in this case delta G which is let us see the new delta G c. That means, the jump activation barrier for metal ion to metal should be lesser than the jump activation barrier to be less than jump activation barrier for anodic process. The cathodic process then would be faster. Why? Because if we try to see that or i c equal to n F.

Now, this one I can simplify simply I put exponential minus delta G star by RT a is basically the part considered here now i c equal to i 0 equal to a prime exponential minus delta G star by RT in this situation. Now, in second situation when we have this particular condition, so that the rate at which backward reaction happens is faster than the forward reaction then this would become a prime exponential minus delta G c by RT and i a should be a prime exponential minus delta G a by RT.

Now, delta G c is equal to activation barrier, new activation barrier for cathodic process and delta G a equal to new activation barrier for anodic process. So, now, in order to have this situation where delta G a equal to delta G c is less than delta G a then this should move up, this plane and this should go down.

Now, let us see if we have some situation here. Let us say we put a different color green color. So, if you have a situation like this, let us see how the activation barriers are changing. So, in this case now this is the nu delta G c and this is the nu delta G a and in this situation I could see that this particular condition is met. So, the rate since the activation barrier height has gone down in case of cathodic reaction the rate at which cathodic reaction would take place as compared to the anodic reaction would be faster than anodic reaction. So, in this case we have higher rate of cathodic reaction.

Now, what happens a situation when we have this that case the equation pattern would be same, but only change would be if we put it in a blue color only change would be that case delta G a be greater than would be less than delta G c when i a greater than i c. How the situation changes let us see that is it that case this one will move up and this one will go down. So, this go down this will go down and this will go up. So, how it would look like? So, you see now what is the new barrier for anodic reaction? This is my new barrier for anodic reaction which is delta G a let us say prime and new barrier for cathodic reaction would be delta G c prime let us say.

Now, you see the length of this activation area or the height of this activation barrier has decreased even compared to i 0 and the height of this delta G c which is the new activation for barrier for cathodic reaction has increased enormously as compared to even i 0 and if you see the height difference between delta G a prime and delta G c prime this condition is met. So, i a is greater than i c. So, that case anodic process would be faster. So, in this case this is the situation; this is the situation when I will have preferential cathodic process and in this case we would have preferential anodic process.

Now, we can also indicate this that in this case it will be potential E would go down or cathodic polarization in this case we will have E goes up. So, the new potential would be higher than the equilibrium potential sorry, we made a mistake here it should be standard is E 0 make a make an amendment this would be E superscript 0, this is also E superscript 0. Now, here also this will be less than E 0 and this should be more than E 0.

So, now, you could see that how the energy barriers are changing and accordingly we have preferential cathodic and preferential anodic reactions. Now, once we know this situation, this particular situation energy barrier situation. Since it is a thermally activated process we can have a correlation between this current density of a cathodic and anodic with activation barrier and finally, we can have a correlation between over voltage. We can have the correlations let us look at that correlation.

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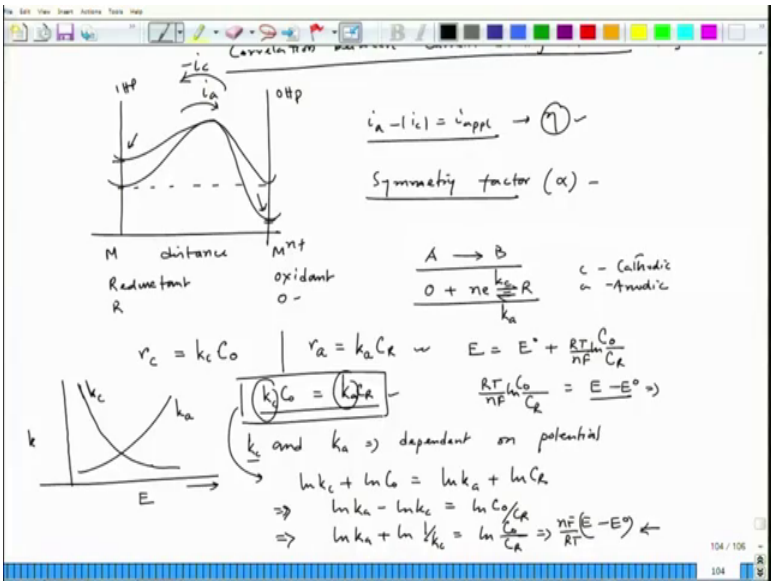

$i_a - |i_c| = i_{appl} \rightarrow \eta$ -

Symmetry factor (α) -

$A \longrightarrow B$

$O + ne \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$

c - Cathodic
a - Anodic

$r_c = k_c C_O$ | $r_a = k_a C_R$

$E = E^\circ + \frac{RT}{nF} \ln \frac{C_O}{C_R}$

$\frac{RT}{nF} \ln \frac{C_O}{C_R} = E - E^\circ \Rightarrow$

$\boxed{k_c C_O = k_a C_R}$ -

k_c and $k_a \Rightarrow$ dependent on potential

$\ln k_c + \ln C_O = \ln k_a + \ln C_R$

$\Rightarrow \ln k_a - \ln k_c = \ln C_O / C_R$

$\Rightarrow \ln k_a + \ln 1/k_c = \ln \frac{C_O}{C_R} \Rightarrow \frac{nF}{RT}(E - E^\circ) \leftarrow$

So, now our intention is to find out the correlation between this basically current and overvoltage. So, our intention would be to find out this particular correlation and then we would see that; that would enable us to understand mix potential theory. So, that is what I am trying to concentrate more on this correlation.

Now, when we see this particular this is M surface, this is M n surface initially it was on the same plane because it was equilibrium and then we are switching from because in this case we are assuming that i a is higher than i c we can have this kind of situation.

Now, we have to understand that whenever we have this; that means, we have a net current flow i a minus i c I applied this net current flow would lead to an over voltage which is neta. Now, we have to understand that out of this neta how much would be required to change this energy barrier for this side and how much would be required to change this barrier to this side. And in order to know this we have to understand a particular concept which is called symmetry factor and this is termed as alpha.

Now, in order to know symmetry factor which decides that how much fraction of this neta will be used up for changing the activation barrier on the anodic side and how much will be used up to change the activation barrier on the cathodic side. Now, we can also put it in this fashion, this is reductant, this is oxidant or we can simply put it as R and O. These are some notation this is reductant this is oxidant or we simply put as capital O and capital R. Now, in order to understand symmetry factor we have to look at the rate constant. Now when we have a kind of reaction like this A goes to B or in the same in this case O plus ne equal to R that time the forward reaction rate I can put it as k c and the backward is k a and c and a is basically cathodic and this is anodic.

So, k c into the concentration of ox oxidant, so, I can put it as C o equal to r c; r c is nothing, but the rate of the forward reaction. Similarly, r a which is the rate of backward reaction is nothing like nothing, but k a which is the rate constant and concentration of R. Now, at equilibrium both these rates are equal k c C 0 equal to k a C r. Since this is an electrochemical process and this is going for equilibrium and this is reaching equilibrium and this is the condition for equilibrium then I would have a potential developed which is E equal to E 0 plus RT by nF concentration of O ln and concentration of R concentration of oxidant and concentration of reductant.

So, RT by nF C 0 ln c 0 by C R equal to E minus E 0 and interestingly these two constants are also dependent on potential and the dependency looks like this. This is let us say E it is increasing, now this is k; when k c which is the rate constant for the forward reaction or the reduction reaction, when it increases that time the potential drops from the standard reduction potential. So, it should have opposite reaction with respect to the potential increase.

So, the reaction this is if this is k c, so, as the k c increases then potential goes to the left side. Similarly, in case of k a as the k increases; that means, the oxidation process increases the potential goes to the positive side as per the polarization concept. So, we have positive direction variation of k a. Now, at this condition both are equal. So, we have this equilibrium situation and then we can take logarithm on both sides. So, ln k c plus ln C 0 equal to ln k a plus ln C R, we can simplify this is ln k a minus ln k c equal to ln C 0 by C R. Or we can simply write it as ln k a plus ln 1 by k c equal to ln C 0 by C R and interestingly ln C 0 and C R I can write in the form of potential which is E minus E 0 nF by RT.

So, this is one important formula what we have derived by seeing looking at the equilibrium condition. Now, this will be our starting point for the next lecture where we will try to see the symmetry factor. Let us stop here. We will continue our discussion on this symmetry factor from this equation onwards.

Thank you.