Corrosion-Part II
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Lecture-02
Recap of Electrochemical Polarization-Activation and Concentration Polarization

Let us start lecture 2.

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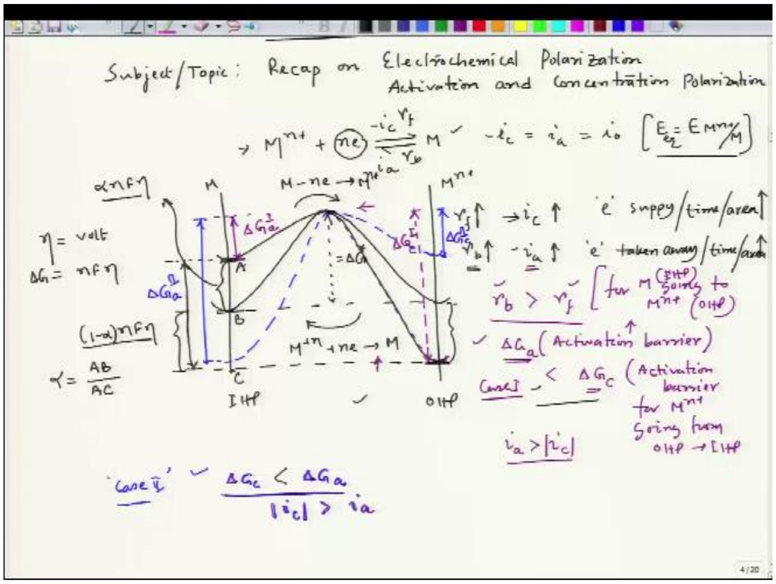

Subject/Topic: Recap on Electrochemical Polarization Activation and Concentration Polarization

And the subject of letter 2 will be same as subject the lecture 1 is basically a topic is recap on electrochemical polarization and will consider 2 aspects activation and concentration polarization. Now we have already seen that energy distribution across double layer for an electrochemical reaction in the reversible situation

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

where ic ia, ic = ia = i0 when $E_{eq} = E_{Mn+/M}$.

And this is generalized condition E = E0 when concentration of metal ions in the solution is 1, otherwise it can have different other values depending on last equation what we have expressed in our previous lecture. Now energy distribution wise we saw that they are on the same level and this is OHP M+ and this is n and we have an energy barrier equal to delta G star and for the thermally activated jump of metal ion as well as metal from one plane to another plane.

This is OHP and this is IHP is in the same barrier and that what the rate of forward as well as backward reactions are similar or same. Now we need to see what happens if there is any disturbance and this is equal to specifically anodic reaction and this is cathodic reaction, now if there is any disturbance and disturbance I mean to say that by many chance if there is an excess flow of electrons, this excess flow of electron would break that equilibrium.

This equilibrium will be broken. Now this excess flow of electron can be either a situation where electrons are supplied to the system and for example in this reaction if more electron is supplied that means this increases then of course in order to balance that particular charge more metal ion would try to reduce. Similarly, if I take away electron from the system then this take away electron means metal has to send more electrons into that.

So how can it sent, it can send by oxidation, so if the charge flow into the system in the form of electron per unit time per unit time area, if that increases means what means I am increasing ic. So that means electron supply per unit time per unit time area increases, that is ic I am increasing, so the value of ic increasing, I'm increasing. So that means in other words I am sending negative currents into the system.

Similarly, ia would increase if electron taken away per unit time per unit time area, so that increases then ia would increase, that is in this case r_f, so this is r_f, this is r_b, r_f increases in this case rb increases and that situation I would have changed in this particular pattern, particular energy distribution. Now let us say I considered r_b that is increasing, if r_b increases that means the rate of forward reaction is more than the rate of backward reaction.

Sorry in this case definitely rate of backward reaction is more than the rate of forward reaction. So that means this reaction is taking place faster than this, so r_b greater than r_f and as for Arrhenius theory if this rate is more than this that time delta G which is the activation barrier for the backward process mass decrease as compared to the forward process. So backward process is nothing but anodic process I can mention a here which indicates the free energy barrier for the backward process or the anodic process.

Must be lower than delta G of c which is the forward process of cathodic process this is the activation energy felt by the metal ion for the jump from OHP to IHP. So this is activation barrier again for metal ion going from OHP to IHP and in this case this is nothing but activation barrier for metal going to metal ion or OHP this is IHP. Fine. So that means this particular activation energy should be lower than the activation energy felt by metal ion for its own jump from OHP to IHP.

So then energy distribution would be interestingly it will go up and then this should go down**.** Now interestingly you say the activation energy felt by metal for the jump from IHP to OHP is this much which is nothing but delta G a and what would be then activation energy felt by metal ion for its movement from OHP to IHP is this much. So this is delta Gc. So that means we could see that in this situation which is basically the colored line that case my activation energy for the anodic process is less than activation energy for the cathodic process.

So that time ia is actually more than in this case ia is more than ic, now I will put a mode sign just to indicate that I am comparing the value, but still even at this condition ic is flowing opposite to value, now there could be the another situation where delta Gc can be less than delta Ga. So that time I will see that ic would be greater than ia, and what will be my energy distribution, if I put in different color, if I put in blue color.

So that time this will go up and this will go down, this side will go down. Fine. So now when this situation or let me put it in blue color, so that time the activation energy which is Ga is this much for case 2 this is case 1 and activation energy which is felt by metal ion two. So now interestingly you could see the forward rate which is the cathodic reaction rate is more than the anodic reaction rate or the magnitude of ic is more than the magnitude of ia that can be possible if case 2 is satisfied.

Similarly, ia can be more than the magnitude of ic for the case 1 this is case 1. Now when we have such situation that case will experience that the potential shifts from this equilibrium potential. Fine. So this equilibrium potential shift.

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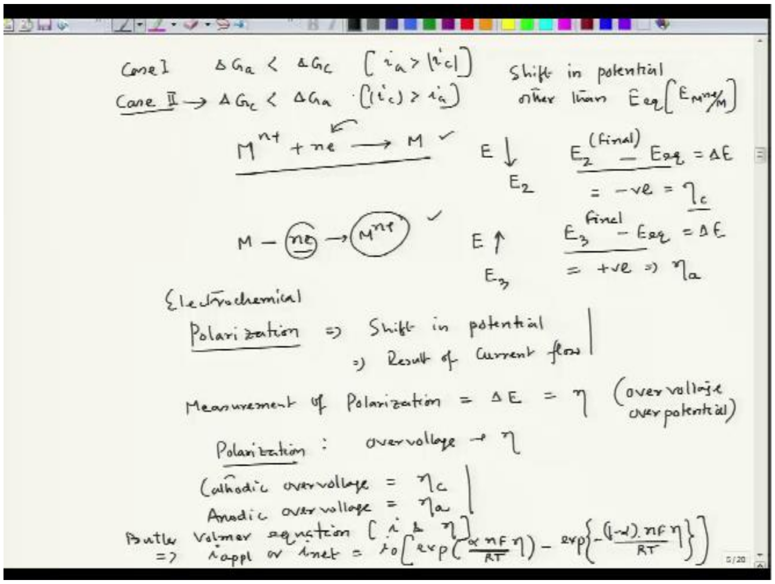

Case I $\Delta G_a < \Delta G_c$ $[i_a > |i_c|]$ Shift in potential other than $E_{eq}[E_{M^{n+}/M}]$

Case II $\rightarrow \Delta G_c < \Delta G_a$ $(|i_c| > i_a)$

$M^{n+} + ne \longrightarrow M$ ✓ $E \downarrow E_2$ $E_2^{(final)} - E_{eq} = \Delta E = -ve = \eta_c$

$M - \boxed{ne} \rightarrow \boxed{M^{n+}}$ ✓ $E \uparrow E_3$ $E_3^{final} - E_{eq} = \Delta E = +ve \Rightarrow \eta_a$

{Electrochemical

Polarization ⇒ Shift in potential
⇒ Result of Current flow

Measurement of Polarization $= \Delta E = \eta$ (overvoltage overpotential)

Polarization : overvoltage → η

Cathodic overvoltage $= \eta_c$

Anodic overvoltage $= \eta_a$

Butler Volmer equation $[i \;\&\; \eta]$

$$\Rightarrow i_{appl} \text{ or } i_{net} = i_0\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left\{-\frac{(1-\alpha).nF\eta}{RT}\right\}\right]$$

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So that means whenever I have situation like a less than delta Gc or ia greater than ic. On another hand delta Gc less than delta Ga or ic greater than ia those such cases I will have shift in potential which is other than equilibrium and in this case we have considered $E_{Mn+/M}$. Now let us consider the case 2. So in the case 2 I am sending more electron in to the system is not because I am increasing the negative current or ic.

So if I send negative charge to a system its potential decreases, so that means in this case potential decreases, that means if I see that this potential goes after some current flow E potential goes to E2 that time E2 which is the final potential, this is final - E equilibrium should be negative. Now when we take out for example in case of case 1 I am taking out electrons that is I am reducing the negative charge.

In other way I can say that I am increasing the positive charge relatively that case

$$M - ne = Mn^{+}$$

that is I am taking out this and so I am increasing this number, so the positive charge increases so the potential goes up. So if I consider this potential goes to E3, so E3 which is final potential after some current flow - E equilibrium should be positive. Now this change from the equilibrium non corroding situation is taking place because of either the relative increase of negative current of cathodic current as compared to the positive current or the ia.

And vice versa like ia is increasing with reference to ic magnitude wise that time my potential shifts from the equilibrium non-coding situation which was corresponding to i0 the exchange current density. So this particular phenomenon we call it polarization and this polarization is taking place because of this electrochemical reaction. Fine. So that what we called electrochemical polarization.

Now if we understand this electrochemical polarization is nothing but a shift in potential from the equilibrium value and this shift in potential can be measured ok and this is basically due to the manifestation of current flow. So this is nothing but shift in potential or this is a result of current flow and this measurement of polarization is nothing but del E and del E here it is del E and here it is also del E. Fine. Now this del E which is basically measure of polarization. We termed it as η or over voltage or over potential. Fine.

So now in this case over potential is negative and in case where anodic current density is more than cathodic current density over voltage is positive and just to indicate that whether it is a negative change or positive change we can also term it as cathodic because the cathodic polarization over voltage is negative and we can put a subscript a which indicates anodic. So now we could see that the polarization can be expressed in the form of overvoltage or meter.

And cathodic voltage equal to nCη_c, anodic equal to η_a, now this η_a and η_c can have relation with the current density and in this case we can have a relation and we have also proven it in our one in one of the lectures in corrosion part 1 you can go to that those lectures and find out the proof but for our convenience we can also write down that particular expression final expression and the final expression we can mention in the form of an equation with that equation is called as butler volmer equation.

So the butler volmer equation which is the relation between I and overvoltage. So that can be written as i I can mention

$$i_{applied} = i_{net} = i_o \left[exp\ exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\ exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

So this is the Butler volmer equation for a situation where the concentration change at the interface is not there. So that means we are considering only thermally activated process that is metal is going to metal ion or metal ion is going to metal layer.

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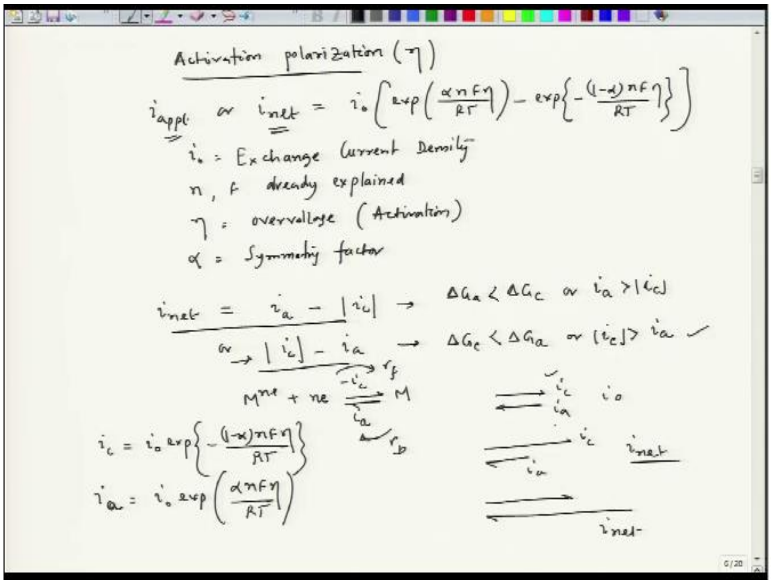

Activation polarization (η)

i_{appl} or $i_{net} = i_o \left[exp\left(\frac{\alpha n F \eta}{RT}\right) - exp\left\{-\frac{(1-\alpha) n F}{RT}\eta\right\}\right]$

i_o = Exchange Current Density

n, F already explained

η = overvoltage (Activation)

α = Symmetry factor

$i_{net} = i_a - |i_c| \rightarrow \Delta G_a < \Delta G_c$ or $i_a > |i_c|$

or $\rightarrow |i_c| - i_a \rightarrow \Delta G_c < \Delta G_a$ or $|i_c| > i_a$ ✓

$M^{n+} + ne \underset{i_a}{\overset{-i_c}{\rightleftharpoons}} M$

$i_c = i_o \exp\left\{-\frac{(1-\alpha) n F \eta}{RT}\right\}$

$i_a = i_o \exp\left(\frac{\alpha n F \eta}{RT}\right)$

So that is basically in the activation side, so we call it activation polarization which is η in terms of overvoltage and that time i applied on i net can be expressed in the form of this equation. Now interestingly we need to know all the terms. Fine. So in this equation the terms are let me write it again

$$i_{applied} = i_{net} = i_o \left[exp\ exp \left(\frac{\alpha n F \eta}{RT}\right) - exp\ exp \left(-\frac{(1-\alpha) n F \eta}{RT}\right)\right]$$

Here i0 of course is exchange current density, n and F we have already explained, η is overvoltage and in this case activation, alpha is nothing but symmetry factor. We have to just understand what is alpha that is symmetry factor as well as overvoltage. Now if I consider the condition for case 1 this is the condition where ia is more than ic that time this particular line is this line is applicable.

Now in that case if η to be my overvoltage this is in volte this can be converted into free energy with this expression nFη this is delta G. I'm just considering delta G that is the value that is the change in value change in that particular energy distribution. So in the energy access this particular distance that means difference between this and this is nothing but nFη.

And if I give notation A, B and C. This point is C. So alpha is nothing but AB divided by AC, hence the change in free energy for the anodic side is this much which can be given as alpha nFη and change in cathodic side which is nothing but this much or same as this value is nothing but 1 - alpha this. So now we understand that symmetry factor is nothing but the contribution of the total over voltage towards the change in free energy on the IHP as well as OHP.

And in this case on the IHP the change is alpha nFη and on the cathodic side is (1-αnFη). Now coming back to this so this is my expression. Now what is i net, i net is nothing but ia - ic or ic - ia. Now this case delta G a less than delta Gc or ia greater than ic and in this case delta Gc less than delta Ga or ic greater than ia. So now whenever we have this forward reaction more than the rate of forward reaction is more than the rate of backward reaction.

So this is rf this is rb that time this situation will prevail, you go back and then see those energy distributions. So that time in the system there will be net current and this net current is nothing but the difference between these 2 currents why because these 2 current flows in opposite direction. So this is ic this is ia. In case of I zero these 2 are same length, but whenever I have ic more that time ia should be this one.

So that case there will be net flow of current i net which is nothing but this and if ic is less ia is more that time i net will be there which is nothing but this. So that is expressed in this form, now we can separately write

$$i_c = i_o \left[exp\ exp \left(-\frac{(1-\alpha)nF\eta}{RT} \right) \right]$$

$$i_a = i_o \left[exp\ exp \left(\frac{\alpha nF\eta}{RT} \right) \right]$$

And I net you can see this is a i net or i applied which is the net flow of current into the system.

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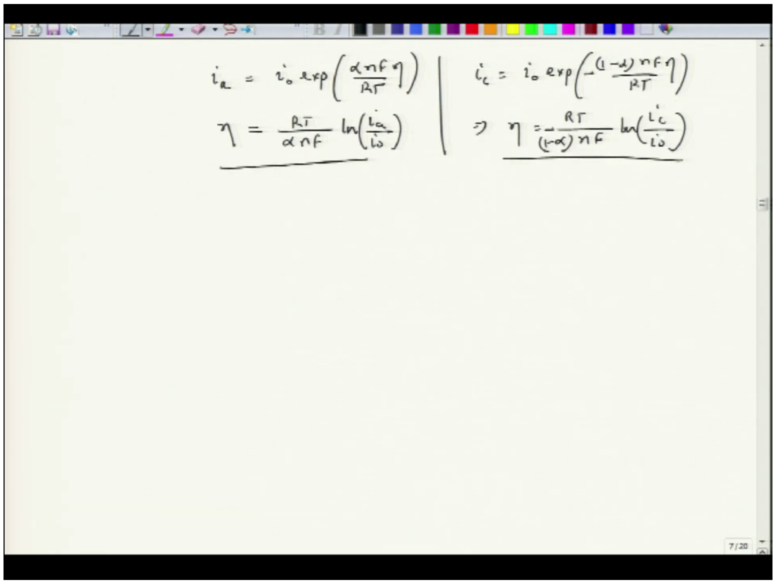

$$i_a = i_o \exp\left(\frac{\alpha n F}{RT}\eta\right) \qquad i_c = i_o \exp\left(-\frac{(1-\alpha) n F}{RT}\eta\right)$$

$$\eta = \frac{RT}{\alpha n F}\ln\left(\frac{i_a}{i_o}\right) \qquad \Rightarrow \eta = -\frac{RT}{(1-\alpha) n F}\ln\left(\frac{i_c}{i_o}\right)$$

Now interesting part is this 2 equations, these 2 equations leads us to one interesting equation for example if I consider

$$i_a = i_o\left[exp\ exp\ \left(\frac{\alpha nF\eta}{RT}\right)\right]$$

If we convert it into log scale so that time I can write

$$\eta = \frac{RT}{\alpha nF}\left[ln\ ln\ \left(\frac{i_a}{i_o}\right)\right]$$

I can write this and where similarly I can write

$$i_c = i_o\left[exp\ exp\ \left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

$$\eta = \frac{RT}{(1-\alpha)nF}\left[ln\ ln\ \left(\frac{i_a}{i_o}\right)\right]$$

So these 2 equations are very critical for our next few classes.

So let me stop here, will continue our lecture on these 2 equations in our subsequent lectures, so thank you very much will continue our discussion in next lectures.