Corrosion-Part II
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Lecture-01
Recap of Electrochemical Polarization

Welcome to the course corrosion part II.

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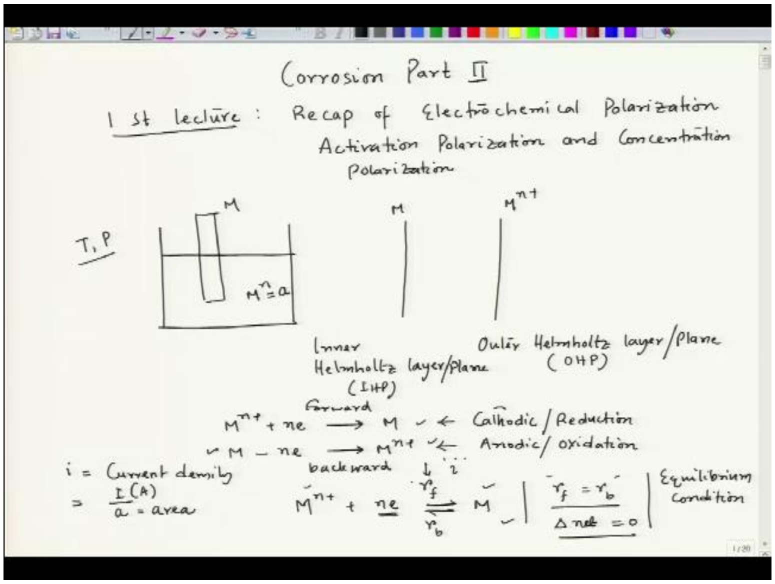

Corrosion Part II

1 st lecture : Recap of Electrochemical Polarization
Activation Polarization and Concentration Polarization

$M^{n+} + ne \xrightarrow{\text{Forward}} M$ ← Cathodic / Reduction

$M - ne \xrightarrow{\text{backward}} M^{n+}$ ← Anodic / oxidation

i = Current density = $\frac{I(A)}{a}$, a = area

$M^{n+} + ne \underset{r_b}{\overset{r_f}{\rightleftharpoons}} M$ | $r_f = r_b$, Δ net = 0 | Equilibrium Condition

And today we will just recap what we have discussed in part 1 are important aspects of electrochemical polarization, activation and concentration polarization. So the first lecture will be on the recap of electrochemical polarization and we have understood in the first lecture which is this part 1 that there are 2 kinds of polarization we will talk about activation polarization and concentration polarization.

Now when we talked we start a discussion corrosion in part 1 we got into the fundamentals and the fundamentals are based on thermodynamics of electrochemical reactions as well as kinetic of electrochemical reactions. Now later we got to know from polarization aspect that polarization actually connects thermodynamics aspect which is basically the potential and kinetic aspects which is basically the current density.

So we will just briefly talk about electrochemical polarization, so that our consecutive lectures become easy to understand and I would request you to go back to the lectures in part I. So that it becomes easy. Now we have understood that if we allow 1 metal to be dipped into on an electrolyte containing that particular metal ion. For example, if I have if you see that if this is a beaker and there is an electrolyte which is aqueous electrolyte.

And here you have metal ion concentration of let say some activity if we mention in the form an activity, so some activities there in the solution of that particular metal ion and if we dip the same metal in then immediately some potential will be developed, and at the same time at the interface of the metal there will be double layer formation and those double layers you have understood that the double layers are called Helmholtz double layer.

And there could be outer double layer outer Helmholtz layer or plane and there could be inner Helmholtz layer or plane, in short we call it OHP and this one we call it IHP. IHP is forming on the metal stuff on the on the metal and just in front of that particular metal surface in the electrolyte we have OHP and in this case this forms OHP and this forms IHP. Now once we introduce this metal into that electrolyte containing metal ion you will experience 2 reactions.

One reaction is in

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

at the same time opposite reaction would also happen M+ and we should realize that this particular arrangement that metal inserted or dipped in that electrolyte containing metal ion at particular temperature and pressure. So this temperature and pressure both are constant for this particular experimentation. Now we see that one particular reaction is cathodic in nature.

Cathodic or reduction and another reaction is anodic or oxidation, now every reaction would try to reach equilibrium for a particular temperature pressure condition. These 2 reactions would also like to go to equilibrium. Now if they would like to go to equilibrium, so that means the rate of forward reaction if we consider this is to be forward reaction, and if this is to be a backward reaction. So then this rate of forward and backward reaction at a particular temperature pressure condition should be same should be equal.

So that means at equilibrium we will have M so that means forward rate if this is basically rate of forward reaction and this is rate of backward reaction for equilibrium condition r_f equal to r_b. Now interestingly for a steady state that time also we have the situation like the rates are equal. But in this case we will see that we are not having any net reaction, later on we would understand that corrosion event is basically a steady state process.

If there are nothing external agents added, so that time it steady state the rate of reduction reaction is equal to rate of rate of oxidation reactions will see later, but that time there is a constant change in the consent in the amount of a species we will see later, but in this case whenever the situation arises we will see that rate of forward and backward reaction are same. But at the same time there is no net change in product or reactant.

So that means this and this they will not have any net change, so the net change if I consider net should be 0, so this condition we call it as equilibrium condition. Now at the same time interestingly if I consider r_f, r_f is basically reduction process or cathode process. And in the cathodic process we see that electrons are accepted by metal ions and they are actually going to deposit on the metal object.

Whereas in the backward reaction I can see the electrons are taken away from metal atom and they are forming metal ions. So once they form metal ions they will be part of that electrolyte. Hence if we take that rate of electron flow, then that can be consider in the form of current. Because here I could see the charge which is electron in case of cathodic we are introducing electron. So that forward reaction is possible.

And in case of backward reaction we are taking away electron and if we consider time scale, so they can be considered as a current flow. When the forward reaction if we consider the rate of charge flow per unit time there would be current and if we consider the overall area of the surface just to normalize it with respect to area and we know why we normalize from corrosion part 1.

So then that can be considered as current density which is ‘i’. Now this ‘i' which is current density it is basically nothing but ‘i by a’, ‘a’ is basically the area. Now here ‘i' is ampere which is current which is basically the rate of charge flow per unit time. And then per unit area it becomes current density. And if we see the kinetics of corrosion we have realized that rate of any reaction or electrochemical reaction.

Because we have seen that these reaction is electrochemical in nature rate of electrochemical reaction can be expressed in the form of current density and let’s say in this case the forward reaction is deposition, and the backward reaction is ion formation.

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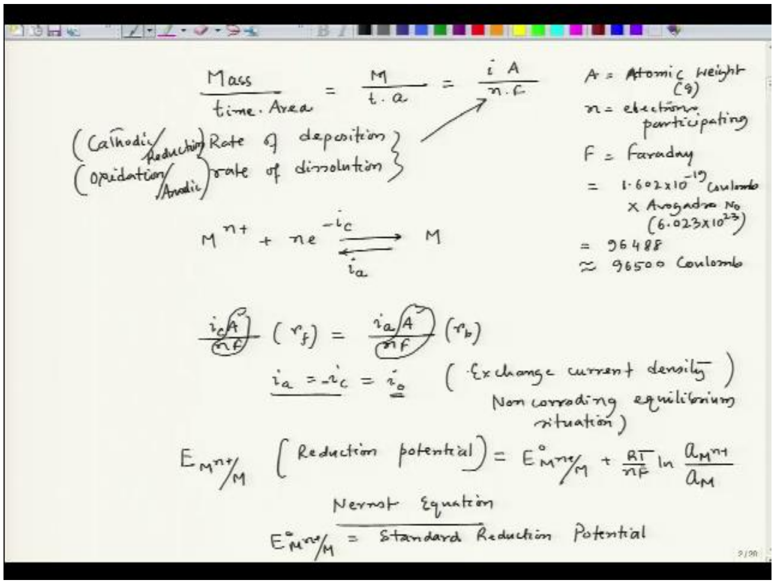

$$\frac{\text{Mass}}{\text{time}\cdot\text{Area}} = \frac{M}{t\cdot a} = \frac{i\,A}{n\cdot F}$$

(Cathodic/Reduction) Rate of deposition

(Oxidation/Anodic) rate of dissolution

A = Atomic weight (g)

n = electrons participating

F = Faraday

$= 1.602\times10^{-19}$ Coulomb × Avogadro No (6.023×10^{23})

$= 96488$

≈ 96500 Coulomb

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

$$\frac{i_c A}{nF}\,(r_f) = \frac{i_a A}{nF}\,(r_b)$$

$$\underline{i_a = -i_c} = \underline{i_0}$$

(Exchange current density)

Non corroding equilibrium situation)

$$E_{M^{n+}/M} \left(\text{Reduction potential}\right) = E^\circ_{M^{n+}/M} + \frac{RT}{nF}\ln\frac{a_{M^{n+}}}{a_M}$$

Nernst Equation

$E^\circ_{M^{n+}/M}$ = Standard Reduction Potential

So then I can express either deposition rate or the dissolution rate in the form of mass per unit time per unit area which is written as M/(ta).

It can be related to i A, A is nothing but the atomic weight n F what are those terms, i of course is the current density A is atomic weight in gram, n is equal to the number of electrons participating in unit reduction process or oxidation process and this n in this case it is easy to understand that this is nothing but oxidation number of that particular metal electrons participating and F equal to 1 Faraday.

And this can be calculated from charge of an electron which is $1.602*10^{-19}$ coulomb into Avogadro number which is nothing but $6.023*10^{23}$ because 1 faraday is nothing but charge of 1 mole of electron. So that becomes 96488 which approximately consider as 96500 coulomb. Now you could see that the rate of deposition or rate of dissolution I can term it as cathodic or reduction and in this case this is oxidation or anodic. Both can be reflected by this reaction by this particular equation. Now, If I consider this particular process that is in this case when I am considering reduction process.

I have to term it to some current density, and since the cathodic process is taking place, I term this particular current density what is flowing into the circuit I can term it as i c and c should subscript is not nothing but the cathodic and whereas the backward reaction which is anodic reaction, the current density I can term it as i a, now interestingly this i c is actually flowing opposite to i a that is the flow of current for the anodic reaction anodic rate rather is from positive to negative whereas in case of i c is negative to positive.

Now in order to indicate the direction convention is we put negative sign in front of i c, so that is it is not a negative current it is basically the direction of that particular current and remember if we do not know explicitly express that its current most of the situations this i small i means current density. Even if I say current for a small i take it as a current density.

Now for this case if they become equal. So that means $(i_c A)/(n F)$ for the forward reaction which is nothing but r_f should be equal to $(i_a A)/(nF)$, because for both the cases A are same because the same area of the metal that is taking part in the reaction n is the number of electron participating in for unit reaction and F is 1 Faraday. So that means this part and here this part both are same for both the rates and this is r_b which is backward reaction.

So that means i a equal to i c, now since we have to indicate the direction so that what we put a negative sign, and when this situation arises we call it as i zero and remember this i zero is with respect to non deposition with respect to the situation where there is no net change in that particular process that reversible reaction we do not have net change. So that means there is no net dissolution there is no net deposition.

So we call it as i zero is exchange current density and with respect to non-corroding equilibrium situation, fine, now at when the system reaches this equilibrium that means the flow of current or the current density for both these backward and forward reactions they are same which is indicated by i zero which is exchange current density area in the under non-corroding equilibrium situation.

That time the system must have attained some equilibrium potential, and that potential we express in the form of n+M. So this is reduction potential and remember our consideration will be all throughout our 40 lectures wherever we consider potential this potential is in the form of reduction potential. Now this can be written in the form of

$$E_{Mn^+/M} = E^o_{Mn^+/M} + \frac{RT}{nF} ln \frac{a_{Mn^+}}{a_M}$$

And here oxidant is M n+ and activity of M, now this is a generalized form for Nernst equation where we have considered in the form of activity of that particular metal ion and here E zero n+ M is nothing but standard reduction potential**.**

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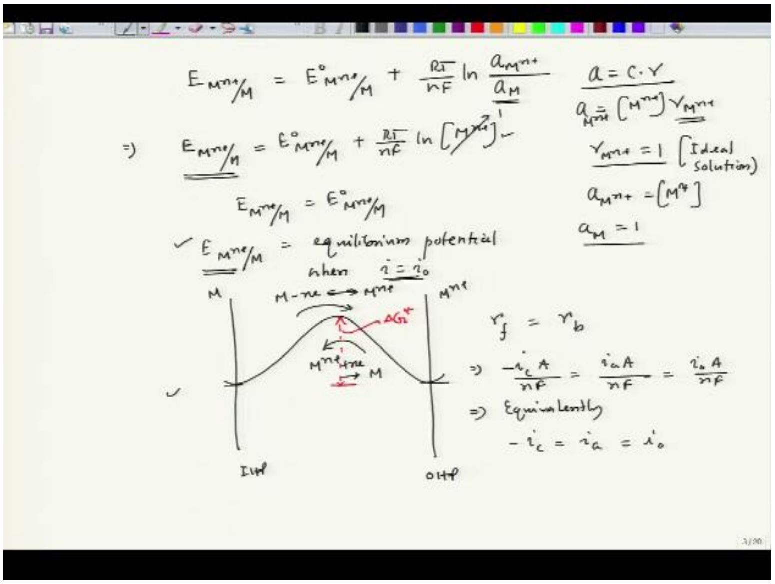

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}$$

$$\Rightarrow E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]$$

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M}$$

✓ $E_{M^{n+}/M}$ = equilibrium potential when $i = i_0$

$a = C \cdot \gamma$

$a_{M^{n+}} = [M^{n+}]\gamma_{M^{n+}}$

$\gamma_{M^{n+}} = 1$ [Ideal solution)

$a_{M^{n+}} = [M^{n+}]$

$a_M = 1$

$r_f = r_b$

$$\Rightarrow \frac{-i_c A}{nF} = \frac{i_a A}{nF} = \frac{i_0 A}{nF}$$

$\Rightarrow$ Equivalently

$$-i_c = i_a = i_0$$

Now if we write it again, so that means

$$E_{Mn^+/M} = E^o_{Mn^+/M} + \frac{RT}{nF} ln \frac{a_{Mn^+}}{a_M}$$

Now this activity as per thermodynamics we can write in the form of concentration with concentration and activity coefficient in the form of concentration and activity coefficient and this concentration we can write in the form of molarity. So M n+ activity coefficient of M n+. I can write this way. Now if the system is not behaving ideally then it must have some finite value which is different than unity.

And when this goes to 1 we can call it as ideal solution, so that means in that case M n+ equal to molarity of that particular metal ion concentration in the solution. Now interestingly most of our situations unless it is specifically mentioned will consider in the form of molarity assuming that this activity coefficient is 1. And now here we are considering a pure metal though we have not mentioned in the beginning.

Let us considered that it is a pure metal that is dipped into the solution so that case activity of M goes to 1. So that means I can write this equation in the form of molarity

$$E_{Mn^+/M} = E^o_{Mn^+/M} + \frac{RT}{nF} ln\, [Mn^+]$$

Fine. So this is my final equation. Now interestingly these value this is the actual potential that is been developed on the surface on the metal. Now if this is 1 then of course

$$E_{Mn^+/M} = E^o_{Mn^+/M}$$

but otherwise if this has got value other than 1 then this would be my equilibrium potential when i equals to i zero in the system that is in the non corroding system.

So we could see that whenever we have a situation of equilibrium setting up between a metal and metal ion in an electrolyte at particular temperature and pressure, we always will develop an equilibrium potential corresponding to that condition. Now if we can express this one in the form of energetics then that energetics will look like this. So that means we have double layers and this is M n+ layer.

This is M and then at this condition that means equilibrium potential and when i equals to i zero reversible condition, if I draw the energetics the energetics will look like this. So that means this is M side, this is metal ion side and if this process is taking place that means

$$M - ne = Mn^+$$

and if this process is taking place

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

So the reduction is the thermally activated jump of metal ion from OHP to IHP crossing the barrier of if I consider this barrier to be this which is del G star.

This much barrier is crossed by metal ion to go to the metals surface from OHP to IHP after taking n number of electrons. Similarly, if metal is planning to go to the other side from IHP to OHP it has to release any number of electrons to form M n+ but that time also it is crossing the same area size area height. So as per the thermally activated jump theory this 2 rates 2 jump situations are actually having the same barrier same barrier height.

If they have same barrier height their rates will be same, so that means r_f equal to r backward or I can write I c equivalently or maybe absolute sense I can write equal to

$$\frac{-i_c A}{nf} = \frac{i_a A}{nf} = \frac{i_o A}{nf}$$

So this energetics is valid for equilibrium condition which is the non corroding situation and when the equilibrium potential is this one and whenever we mention this that means it is not that condition for M n+ equal to 1 the molarity of the particular metal ion is 1 in that system.

In some other conditions and when exchange current density is experienced. So this is energetics for the equilibrium situation. Now we will talk more on this and we will get into the polarization concept and then after that will slowly get into this mix potential theory and understanding of corrosion events via the mix potential theory. So let me stop here and in the next lecture will continue our discussion on this energy distribution in a situation when polarization takes place. Thank you.