Corrosion – Part I
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Lecture – 37
Summary of concentration polarization (CP) and introduction to mixed potential theory-I

Hello everyone, today we will have lecture 37. Since now, we have been talking on several aspects of thermodynamics and kinetics of electrochemistry. In thermodynamics, we have looked at phoebe diagram and in the kinetics part, we actually looked at polarization, which is the manifestation of current flow during electrochemical reactions on a metal surface. And, when we have looked at the polarization part, we saw that it actually relates kinetics of rate of transformation of metal into ions or ions into metal with the voltage.

So, the voltage part is talking about thermodynamics and the current is actually looking at the kinetics. So, it is a basically relation between kinetics and thermodynamics and then now today, actually will step into the aspect, which is called mixed potential theory. In the mixed potential theory, which is basically a very modern theory to understand corrosion and here you would be able to see that, yes it can allow us to understand why that different kinetic factors like exchange current density, like one is exchange current density of course, if it increases as a function of galvanic coupling between active metal with the noble metal.

And the exchange current density of hydrogen evolution reaction, if it increases on those active components, we would see that the metal dissolution increases to a great extent that active component dissolves quickly. Even in case of zinc, we have seen 3 examples that, if we have pure HCl without any oxygen in it then we have some rate. If we have oxygen in it we see that the rate increases and if we have one more that impurity in the form of ferric ion, we see that the corrosion rate of zinc increases enormously.

So, we this particular theory can explain it better that why those changes in corrosion rate of zinc happens due to those kinetic factors as well as the environmental factors coming into the picture coming into consideration, while considering the corrosion of a particular metal.

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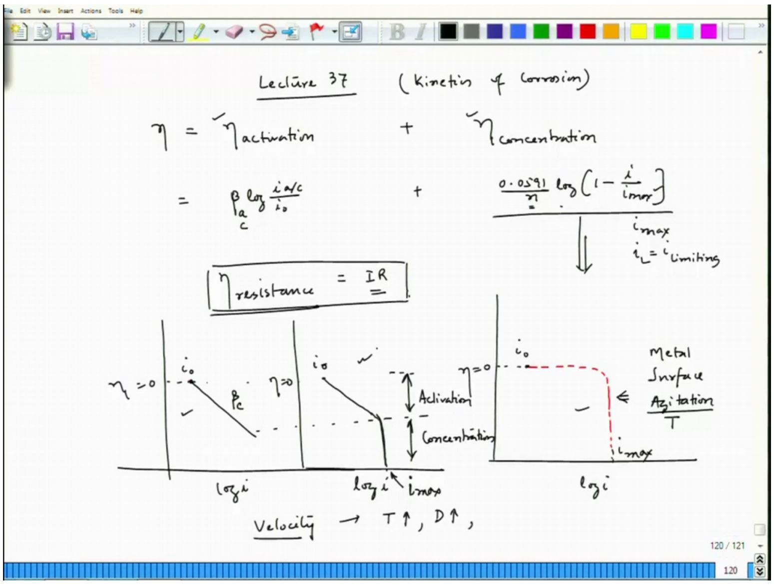

Lecture 37 (Kinetics of Corrosion)

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

$$= \beta_{a/c} \log \frac{i_{a/c}}{i_0} + \frac{0.0591}{n} \log\left(1 - \frac{i}{i_{max}}\right)$$

i_{max}

$i_L = i_{Limiting}$

$$\boxed{\eta_{resistance} = IR}$$

Velocity → T ↑, D ↑,

So today, we have lecture 37, and we will still continue on kinetics of corrosion and eventually, we will get to the modern theory of mixed potential theory. Now as we have seen that the polarization has 2 components activation plus concentration.

And the activation part is can be related with beta log i i 0 and this one can be related as 0591 n log 1 minus i by i max and this i max in different books, it is sometimes it is written as i max or sometime it is written as i l which is nothing, but i limiting current density. Now apart from that there is one more polarization, because of that the potential can shift from equilibrium potential to other potential or the stable potentials to other potential that particular polarization, we call it resistance polarization which is a eta, over voltage resistance is basically nothing, but IR drop that resistance of the circuit, which will lead to some drop in voltage in the form of IR, I is the current and that polarization is called resistance polarization.

But in case of corrosive environment, when we see that the metal is put up put in or immersed in a in an electrolyte, which is sufficiently very high conductivity. And that is what that IR drop in kind of conducting electrolyte is very small and that is what we will not be able to consider, this IR drop in our common corrosion processes, but definitely, we will talk about over voltage duty activation and over voltage due to concentration affect on the corrosion of a particular metal.

And now if I try to plot these 2 particular polarization remember this, beta i by i 0, I can write either a which is activation or c which is a is anodic c is cathodic and here also accordingly, we can write a or c i 0 is nothing, but the exchange current density and here n is the number of electrons participating in that redox reaction. Now if I try to plot, the plot nature as we have seen before would be like this, if I try to plot this one, this is over voltage, this is log i. And, if this is the point, where over voltage is 0 and corresponding to i 0 of that particular metal and if I try to plot this plot will look like this is the plot pattern.

Now, if I try to plot this one same eta here is equal to 0 eta over voltage is 0 corresponding to i is 0 and this plot would look like this corresponding to beta c since, we are considering cathodic over voltage, now if I try to see the total over voltage. So, we have to just combine these 2. So, the combination of these 2 would be so, this is the point eta equal to 0 i i 0 equal to this is the point, which corresponding to log i 0 and this axis is log i, this axis is also log i.

Now, once we combine the combination curve will look like. So, if I combination curve will look like this. So, this part is activation and this part is concentration polarization and we have also seen that this concentration polarization actually depends on several factors of course, the metal type of metal, metal surface, agitation, temperature, all those will have affect on this i max, this particular current is i max.

Since once, i max is reached you see that this over voltage becomes infinitely large. So, that is what the act when it reaches i max it actually, drops vertically with reference to the log i axis; that means, this point is also i max ok. Now, if I try to see one factor let us say, agitation let us say I increase the velocity. If I increase the velocity because of the churning it could lead to temperature increase and once temperature increases diffusivity increases.

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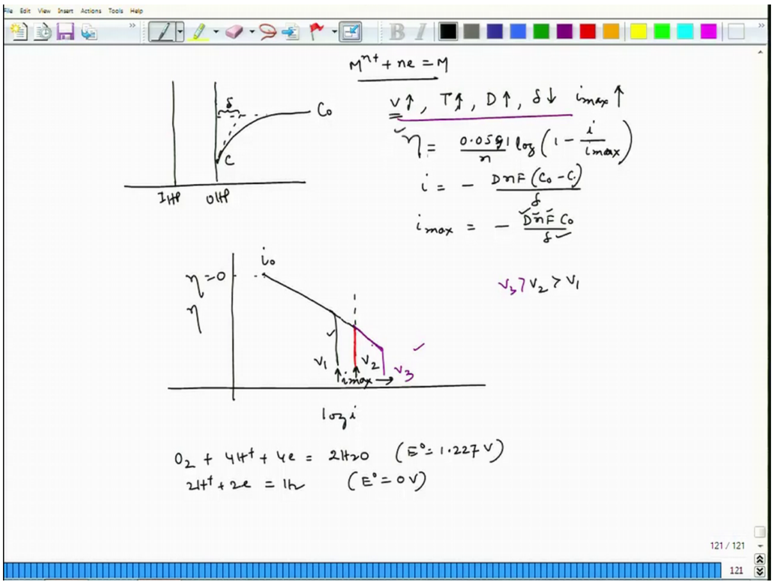

$M^{n+} + ne = M$

$v\uparrow,\ T\uparrow,\ D\uparrow,\ \delta\downarrow\ \ i_{max}\uparrow$

$$\eta = \frac{0.0591}{n}\log\left(1 - \frac{i}{i_{max}}\right)$$

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

$$i_{max} = -\frac{DnFC_0}{\delta}$$

$v_3 > v_2 > v_1$

$O_2 + 4H^+ + 4e = 2H_2O \quad (E^\circ = 1.227\,V)$

$2H^+ + 2e = H_2 \quad (E^\circ = 0\,V)$

Now, and once I increase the velocity, if I try to look at the boundary layer as well as the way concentration is changing so, this is the IHP OHP and we have seen the concentration is changing like this is the bulk concentration and if this is the c. So, then this is my diffusion distance delta or boundary layer thickness and then if I increase velocity of course, I am seeing temperature increases and if temperature increases diffusivity increases. Now if agitation increases then or the velocity increases delta decreases and interestingly concentration polarization, the cathodic current side 0.0591 by n log 1 minus i by i max, you could see that this i also related to minus D n F C 0 minus c divided by delta and i max is equal to minus D n F C 0 by delta.

Now for a particular process reduction process n and f are constant now because of this velocity increases I am increasing this I am increasing temperature and due to this D is increasing delta is decreasing. So, i max also. So, if I try to write here. So, i max increases now interestingly, if i max increases then I would have also corresponding change in the polarization response. Now you could see that combination of those 2 situations, one is activation and another one is concentration and this is the combination of these 2.

Now, here if I try to see the combination first it will go like this, which is activation part and then concentration part would increase this particular polarization, which is cathodic side this is i 0 and corresponding to (Refer Time: 11:40) equal to 0, now as the i max is increasing that suggests that this i max would go to the right direction. So now, i max would appear at new position. So now, if this is my i max. So, then this activation polarization would still extend till i max is reached in the second case.

So, now this case it is velocity 1 and this case it is velocity 2 and V 2 greater than velocity one. So, i max increases and that is what this curve is switching to the new position which is this one now if your velocity increases farther. So, i max will again switch to the right. So, then we will have another new position of i max let us say, this is my i max when V 3 and V 3 greater than V 1 as well as V 2. So, this activation polarization part would still increase further.

Now interestingly, you could see that as we are increasing velocity, because of these factors, we are increasing i max and that is what that polarization curve is switching to shifting towards right; that means, the i max appearance of i max is shifting towards right, this situation will be explained will have strong effect on corrosion of metal. We will see later that actually after certain time, after certain velocity in some metal corrosion, we see that the corrosion of metal initially increases and then it becomes stable or constant corrosion rate.

So, that will be explained with the help of mixed potential theory. So, this is one factor, the second factor sometimes, we have combination more than 1 cathodic reactions. For example, if a system has got dissolved oxygen then and if that system is acidic. So, we can have this reaction, this cathodic reaction as well as since it is acidic. So, we can have this reaction also. Now here, the standard reduction potential is E 0 equal to 0 and here E 0 equal to 1.227volt, if I try to see the response of cathodic polarization as well as what happens in the concentration as well as activation polarization regime, we can have a response like this.

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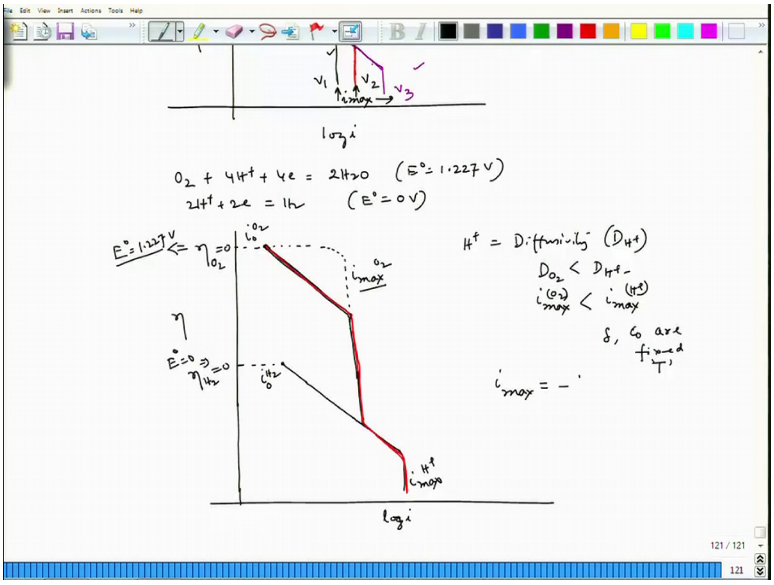

$O_2 + 4H^+ + 4e = 2H_2O \quad (E^\circ = 1.227\,V)$

$2H^+ + 2e = H_2 \quad (E^\circ = 0\,V)$

H^+ = Diffusivity (D_{H^+})

$D_{O_2} < D_{H^+}$

$i_{max}^{(O_2)} < i_{max}^{(H^+)}$

δ, C_0 are fixed 'T'

$i_{max} = -$

This is log i this is over voltage. Now, if this is eta for oxygen reaction is equal to 0 at this point and corresponding to the potential, which is E 0 equal to 1.227 volt, remember this is the equilibrium voltage and an at equilibrium voltage, we have over voltage to be 0 for that oxygen reduction and if I try to see if E is equal to 0 here then it corresponds to eta H 2 evolution to be 0 at this point and let us say, this is the i shift switch, this particular plot little down. So, then only we will be able to see the variation, this is log I, this is i 0 for hydrogen reaction, this is i 0 for oxygen reaction.

Now, for oxygen it will have it is own activation polarization. Let us say this is my activation polarization of oxygen reduction, now let us say, this is my i max for oxygen reduction so; that means, it cannot go, it can come to this point up to this point and then it will take this particular path. So, this part is out as per our understanding. Now for once, it is going towards cathodic polarization regime and it is polarized over voltage is increasing gradually.

Now, this hydrogen reaction also has got it is own activation polarization, if that one moves like this. So, then if it comes like this, because once I max is reached for option reduction, it will fall rapidly almost perpendicular to the log i axis and then it will experience the activation polarization of hydrogen reduction and hydrogen ion, if I consider H plus ion diffusivity D H plus let us say and if i consider D O 2. So, D O 2 is actually less than D H plus then correspondingly i max O 2 O 2 should be should be less than i max H plus i.

Considering that fact that delta and C 0 are fixed of course, temperature is also fixed, I am just saying the size of those particular molecules. Since, it is a very small size that is why it is diffusivity would be very fast. So, that case i max should be high for H plus i so; that means, if I try to without considering this oxygen polarization part, if I try to look at only the hydrogen polarization part, it will have it is own polarization and then finally, it will reach it is i max H plus.

So, the curve pattern would be since, it is polarization is starting from higher potential from oxygen reduction. So, it will fall like this, if I try to draw it in a different color. So, this particular fall would be like this, it will follow this pattern and then it will switch to this pattern and then follow like this. So, this red kalama lines would be the actual polarization line for both the reactions, if I can go up to a very very high over voltage or very very great bit of polarization occurs in the cathodic side.

So, this also has got relation with the non the diffusivity part and finally, it is basically, this equation which is governing, this kind of i max variation, which is minus D n F C 0 by delta.

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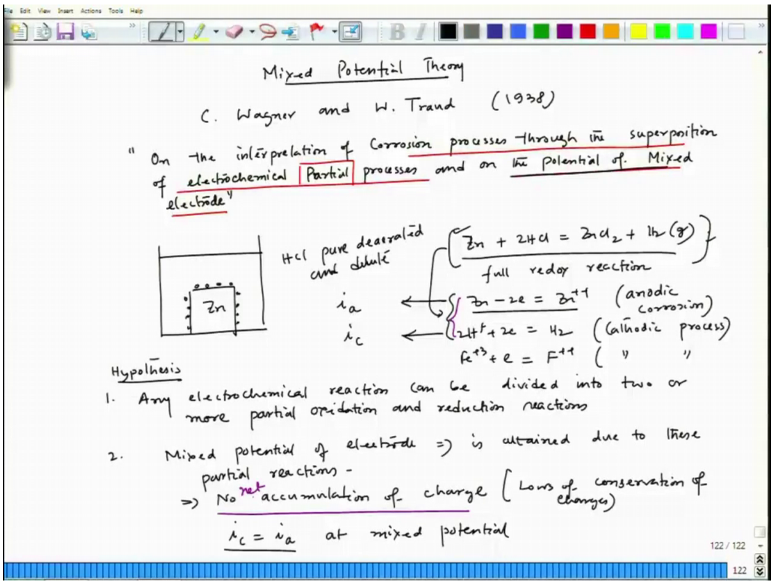

Mixed Potential Theory

C. Wagner and W. Traud (1938)

" On the interpretation of Corrosion processes through the superposition of electrochemical Partial processes and on the potential of Mixed electrode"

HCl pure deaerated and dilute

$Zn + 2HCl = ZnCl_2 + H_2(g)$

full redox reaction

i_a ← $Zn - 2e = Zn^{++}$ (anodic corrosion)

i_c ← $2H^+ + 2e = H_2$ (Cathodic process)

$Fe^{+3} + e = F^{++}$ (" ")

Hypothesis

1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions

2. Mixed potential of electrode ⇒ is attained due to these partial reactions -

⇒ No net accumulation of charge (Laws of conservation of charges)

$i_c = i_a$ at mixed potential

So, this is about concentration polarization as well as activation polarization and how in combination, how do you look? Now, let us get to the fundamental of mixed potential theory, whatever understanding we have on kinetics of corrosion that part will be now used for understanding corrosion events. And, then you will see that yes whatever understanding, we have we have whatever fundamentals, we are going through they will be really useful in corrosion events.

This mixed potential theory is as we have mentioned that it is a very modern theory and it starts it actually, it was known way back in 1990 in 1900 and, but it was proposed and formalized by 2 scientist, C Wagner and W Traud in 1938. This was formally formulated, I would say and they had a famous paper in journal of electro (Refer Time: 20:58) it is 1938 publication. This is on the interpretation of corrosion process through, the superposition of electrochemical partial processes and on the potential of mix electrons.

So, if I try to see the paper name it is says on the interpretation of corrosion process processes through the superposition of electrochemical partial processes. And, on the potential of mixed electrode interestingly, if you see this corrosion processes through superposition of electrochemical partial processes, this is very important partial and also on the potential of mix electrode.

Now, if I could get back to the corrosion of zinc in pure deaerated dilute HCL solution. So, this is a beaker and where I have put HCl, which is pure deaerated and dilute solution. In that case, I have put a zinc piece and immediately I could see that hydrogen bubble will form on the metal surface. Now if I analyze this, I will see that the actual processes, this is the actual reaction that takes place interestingly, this is a full redox reaction and here.

So, this full redox reaction in case of instead of processes, I could see that this is a single process, this redox reaction can be broken into 1 oxidation and 1 reduction process. So, the oxidation is this is the oxidation or anodic process or I could say corrosion process and the second part is H plus plus 2 e equal to H 2. So, this is cathodic process so; that means, the first statement, which says the corrosion process through the superposition of electrochemical partial processes.

Now, you see that this one full redox reaction has been broken into 2 redox reaction 2 2 of reactions partial reactions002C one is oxidation and other one is reduction. Now instead of that if we have ferric ions then of course, there could be one more red or a reduction process, which is plus 3 plus 1 electron, it go to plus 2. So, this is another cathodic process so; that means, whenever an actually the anodic processes this one, which is the corrosion event, the corrosion event is single corrosion event, but you have that entire process has been divided into 3 partial reactions 1 anodic and 2 cathodic.

So, from there the first hypothesis has been drawn. So, this says that any electrochemical reaction can be divided into 2 or more partial oxidation and reduction reaction. Now the second, this is the first hypothesis by from C Wagner and W Traud in 1938, this is the hypothesis of mixed potential theory and the second hypothesis they are saying that the, what they are saying in the title is potential of mixed electrode. In fact, that potential of mixed electrode or the mixed potential of electrode will be achieved due to this reactions due to these partial reactions.

And when this mixed potential of electrode is attained, due to these reactions partial reactions, it says that the there will be no accumulation of charge or in other words it says that laws of conservation of charges. So now, we see that there is 1 cathode, there are 2 for example, if I consider this particular reactions I could see that there are 1 cathodic and 1 anodic reactions.

So, if there is no accumulation of charge net accumulation rather, I would say this net part net accumulation. So; that means, that all the charges are balanced that case I must say this for example, for this reaction there could be a current called i a, because this is the anodic current density for anodic process and this for this reaction there should be i c, which is the cathodic current or current density I would say. So, that case i c should be equal to i a at mixed potential. So, this is the second hypothesis. So, on these 2 hypothesis, we will start looking at the understanding of corrosion events in our next lecture, let us stop here.

Thank you very much.