

Corrosion - Part 1
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Lecture - 40
Understanding of mixed potential theory through the case studies and events of corrosion-II

So, let us start lecture 40.

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Lecture 40

Case studies on Corrosion event [Mixed Potential Theory]

1) Mixed potential is achieved

2) $\sum i_c = \sum i_a = i_a = i_{corr}$

Case I

- (1) H⁺ evolution
- (2) Metal dissolution

Case II

- (1) H⁺ evolution
- (2) Fe³⁺ reduction
- (3) Metal dissolution

Area of Cathode = Area of Anode

Cu ———— Cu

Effect area ration : Case II

Area of Cathode ↑
Area of Anode ↓
rate of corrosion of active component ↑

And we will continue our discussion on case studies on corrosion event and try to explain with the help of mixed potential theory. In fact, in the last 2 cases we have looked at 2 instances: one is when we have a galvanic coupling of an active metal with a noble metal where, the areas of both the components were same. And the second case we looked at the effect of an oxidant or oxidizer on the corrosion rate of a metal, of a metal active metal.

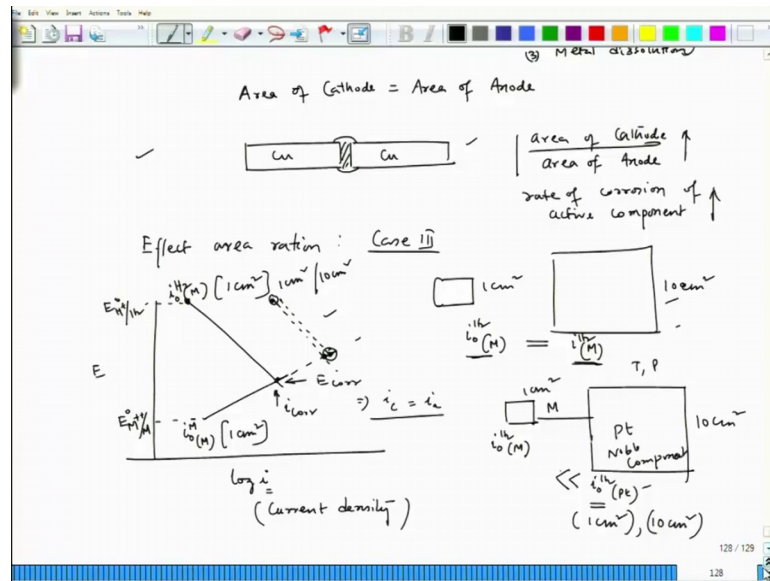
So, in both the cases we could see that concept of mixed potential theories are made; that means, it achieves a mixed potential and then at that potential, the total the net corrosion current densities is equal to the net cathodic current density. So, we could see that first instance mixed potential is achieved and second part i c equal to i a and here i a since, there were in both the cases we considered only one corrosion event which is i a, so is equal to i corr.

And we could see in that case the total reactions are broken into in first case first example, it is broken into hydrogen evolution and second case metal dissolution case I and case II hydrogen evolution, 2 ferric ion reduction and third metal dissolution case II. And case I, we had only 1 cathodic reactions, but this cathodic reaction was taking place on 2 surfaces, one was on zinc surface another one was platinum surface. And in the case of second case, we had 2 cathodic reactions one is hydrogen evolution other one is ferric ion reduction. And, one oxidation reaction in both the cases metal dissolution which is the main oxidation reaction or corrosion reaction happening in both the cases.

Now, if I try to look at case 1 carefully, we had the situation with the area of cathode equal to area of anode. Now we had already explained the situation when we have a situation like let us say copper and in between you have a iron rivet, this is copper, this is copper. And, if this particular component with the iron rivet joint is placed in an electrolyte, we did see that the rate of iron rivet corrosion has gone up enormously. Because, there the cathodic component has got a higher area as compared to the anodic component area and that increase in area ratio which is nothing, but area of cathode divided by area of anode.

So, this area if it goes up, I could see the rate of corrosion of active component goes up enormously. And there we could see that of course, the current density the effective current density on active component has gone up because of larger number of cathodic reactions on the larger area of cathode. So, this particular situation the effect of area ratio this is our case III, the case studies III. So, let us explain this particular situation, in order to do that we have to first look at for the peculiarity in this particular situation.

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As we have seen that the Evans diagrams in first two cases, we explained on the basis of E versus $\log i$. This i is the current density. And we saw that this is my mixed potential, this is E_0 of metal dissolution, this is i_0 metal dissolution on metal surface and this was my hydrogen evolution of i_0 on metal surface and this is E_0 of hydrogen. So, that was the pattern. This particular potential was E_{corr} and this particular current density was i_{corr} and here I could see i_c equal to i_a . This is no problem.

But interestingly that time this was on 1 centimeter square area, this was on 1 centimeter square area. For the time being we consider 1 centimeter square, it can also consider 1 meter square does not matter so; that means, they have the same area. But, when we have let us say this hydrogen evolution reaction is taking place on 1 centimeter square area and it is taking on let us say 10 centimeter square area. Since, it is i_0 and of hydrogen evolution and it is on the same metal surface and if temperature, pressure, the surface condition of that metal if these are not changing, the only thing that is changing is the area.

Then these 2 would be, have would have same values because, they cannot change this is exchange current density which is basically the number of reaction cathodic or anodic reaction per unit area when the system is equilibrium, in equilibrium and reversible condition and that too non corroding situation. So, if I consider in this particular diagram if I need to consider these area effect we will not be able to do it because, if it is 1

centimeter square or 10 centimeter square, it will lie on the same point. And if it is the same metal it is not an issue because, both the cases it will lie on the same point. But, if let us say the situation arises when 1 centimeter square metal is connected to 10 centimeter square platinum or noble component, so then i_0 hydrogen on metal and i_0 hydrogen on platinum surface, they would be a different.

If it is so, this value would be greater than greater than this. Now whether it is on 1 centimeter square platinum surface or 10 centimeter square platinum surface both the cases this value would remain same. So, then if I have this point to be my i_0 of hydrogen evolution on platinum surface. So then whether it is 1 centimeter square or 10 centimeter square, it will lie on the same point and accordingly I have the new mix potential and accordingly new corrosion current density. So, actually it should be here this point.

But as we have understood from this example that if we have a higher area of that noble component then the corrosion rate of the active component increases enormously. But, on this Evans diagram if we consider current density, I could see that whether it is 1 centimeter square or 10 centimeter square it does not matter the corrosion rate remains same. So that means, it is missing something, this Evans diagram is missing something. Now in order to tackle this if we consider current instead of current density, we would see that this can be explained in the same by the same Evans diagram.

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Current density \rightarrow Current

$$i = \frac{I}{A}$$

$i = I$ (Magnitude) $\xrightarrow{1 \text{ cm}^2}$ $I = i \times 10$

$i \neq I$ (magnitude) $\xrightarrow{10 \text{ cm}^2}$

$$\eta = \beta \log \frac{i_{nc}}{i_0}$$

$$\eta = \beta \log \frac{(I/A)}{(I_0/A)}$$

$$= \beta \log \frac{I}{I_0}$$

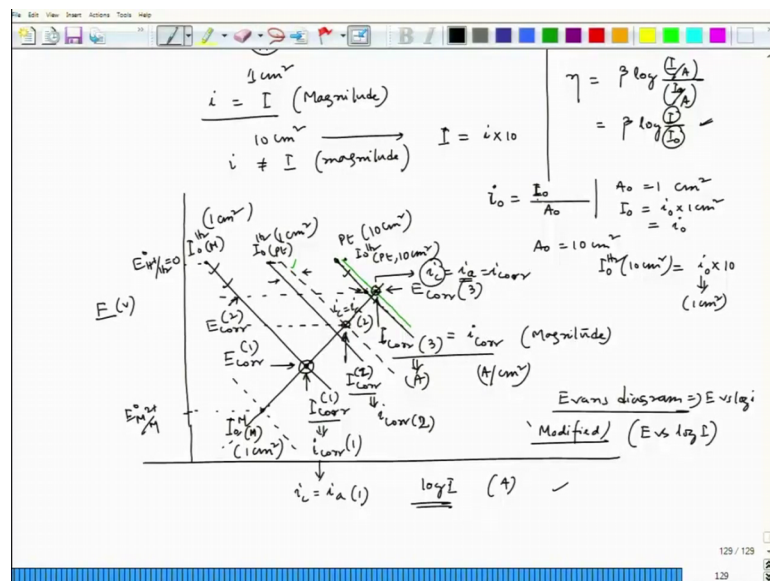
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Only change would be instead of current density, we will consider we will shift to current. Now current density is I by A and current is I . Now, if it is 1 centimeter square, 1 centimeter square, so the i would be same as I by I magnitude wise. But, once it goes to 10 centimeter square, then i will not be equal to I magnitude wise because, i would be always I by A , but i the small i would be I by A capital I by A , which is current by area. But, when we have 10 centimeter then I would be equal to capital I would be equal to i into 10.

So, then I could see that current value is changing. Now if I look at the Tafel equation, this is beta general Tafel equation $\log i$ by i_0 . Now this i could be i_a or i_c , this is i_a i_c i_0 would remain like this and that time this was a or c anodic or cathodic polarization. Now this I can write it as beta $\log I$ by $A I$ by I_0 by A . I can write this. So, this can be converted to $\log I$ by I_0 , capital I by I_0 , which is current. Now if I try to plot the current instead of current density in the Evans diagram, we could see a difference.

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Now, let us say this is $\log I$ which is ampere or this is ampere instead of ampere per centimeter square this is E in volt. This point let us say $E_0 M^2$ plus, let us say 2 plus M is this value this is $i_0 M$ on metal surface, it would have its own cathodic and anodic polarization plot and let us say this is my E_0 hydrogen evolution let us say this is 0 volt. And now this point is i_0 hydrogen on metal surface and here I am writing area, area as

centimeter square or 1 centimeter square area and this is also 1 centimeter square area. Now, instead of i_0 I right now capital I_0 here also it should be capital I_0 .

Now, accordingly because the equation for the cathodic as well as anodic polarization would be same as before only thing is I am converting small i with capital I . So, this will also follow the same track this. So, this is my I_{corr} , this is my E_{corr} . Now if we have platinum of 1 centimeter square area; this would be $I_0 H_2$ on platinum surface and then accordingly I have. So, now this is my new E_{corr} , let us say 2 this is 1, this is 1 and accordingly we have $I_{corr} 1$ sorry 2. Now interestingly if I try to see the relation between these 2, since I am not changing the area of the metal they it would be magnitude wise, it would be equal to $i_{corr} 1$ equal to this is $i_{corr} 1$ magnitude wise. This would be equal to $i_{corr} 2$, since I am not changing the magnitude.

But now if I change the area of the platinum, this is let us say platinum of 10 centimeter square area now i_0 equal to capital I_0 1 centimeter square 0 by A or I would say I_0 by A 0, now if A 0 equal to 1 centimeter square then I_0 equal to capital I_0 equal to 1 centimeter square. So, this is equal to i_0 , but A 0 equal to 10 centimeter square then I_0 10 centimeter square on 10 centimeters here value would be i_0 into 10 centimeter square and this i_0 is on 1 centimeter square area.

So, now, I could see that the I_0 of hydrogen evolution on 10 centimeter square is increasing, that means, the exchange current on 10 centimeter square area on platinum is increasing. So, now this point would be I_0 hydrogen on platinum of 10 centimeter square. So it would have its own polarization and then you have to add this current density because, this particular part is for 1 centimeter square. Now I have replaced this 1 centimeter square platinum area with the 10 centimeter square per platinum area. So, the hydrogen evolution is taking place on 1 centimeter square area of metal and 10 centimeter square area of platinum.

So, this current density and these current densities are to be added for getting the total cathodic current densities. So, I just add them. So, only thing is it will be little bit closer than what we had here because it is in the log scale. So, this is the part. So, now if I extend it this is the new E_{corr} case 3 and this current density is the I_{corr} or capital I_{corr} case 3. And since the area of metal is not changing which is still remaining same 1 centimeter square is equal to i_{corr} since equal to current density magnitude wise.

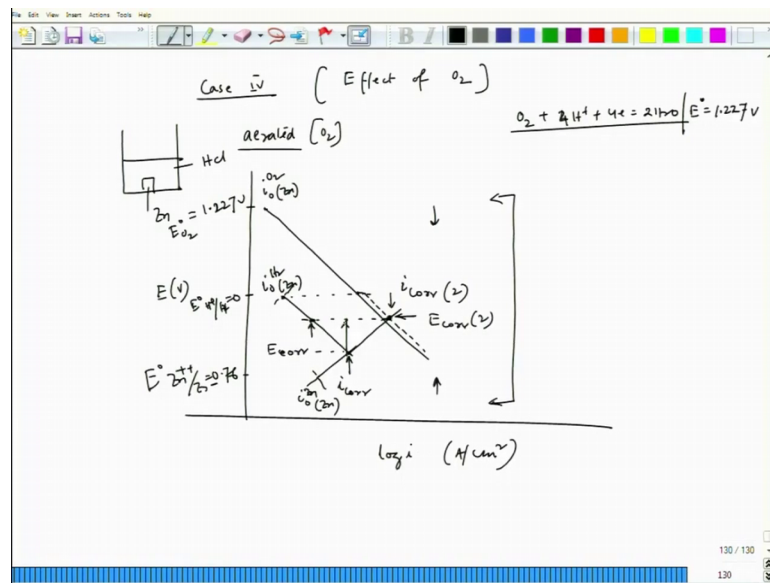
Remember this is magnitude wise, when I am writing this is magnitude. They are, their units are different, in this case it is ampere and in this case it is ampere per centimeter square.

Since, its area is not changing for metals, so that is what this value would be equal to this. Now you see that: what is the change in the current density for anodic reaction. Now in the beginning when there was no connection between active and noble metal my i_a was at this point and at this point I have i_c equal to i_a case 1. This particular region, this particular part here again i_c equal to i_a situation 2 and here also I could see i_c equal to i_a equal to i_{corr} and in this case i_c is basically, this current and this current densities another current. Now here we have to add current because, now we are changing the area.

Now once we could see this i_a , this i_a has gone up enormously, if I see the log scale value. So, the corrosion rate why the corrosion rate of the active component increases, if we increase the area of the noble component that can be explained with the help of Evans diagram. Rather it is modified Evans diagram modified because, Evans diagram is basically E versus $\log i$, but here it is E versus \log capital I.

Now, we could understand why the corrosion rate of that active component increases when it is joined to a metal which is noble and of larger area. And, that explains the effect of iron rivet dissolution, when the copper area is very large and the rivet area is very small. And this particular situation is explained better by this Evans modified Evans diagram. So, this is about case 3. Let us consider another case which is case IV.

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The case IV is about effect of presence of oxygen. Let us say in acid medium let us say HCl, we have zinc piece and if it is aerated, so that means we have oxygen, that case we see that the corrosion rate of zinc increases to a large extent as per our previous understanding. It can be also explained with the help of Evans diagram. This is log i ampere per centimeter square, I just missed 1 point here, the unit is ampere, but if we see here the unit is ampere per centimeter square.

Now, coming to this, this is E , let us say this is zinc plus plus zinc E^0 equal to 0.76 of course, minus sign and this is H let us say this point is $E^0_{H^+/H_2}$ equal to 0 volt is involved. And oxygen in case of acid medium oxygen evolution reaction, oxygen reduction is like this, this is oxygen reduction and the potential E^0 equal to 1.227 volt, so I put it as 1.227 volt equal to $E^0_{O_2}$. So, this is the E_{corr} and this is the i_{corr} when there is no dissolve oxygen.

Now, once we have dissolved oxygen that this is i_0 of dissolve oxygen on zinc and this is i_0 hydrogen evolution on zinc and this particular one is i_0 zinc on zinc surface. So, it would also have its own polarization, so this is my own polarization. It is cathodic polarization and it has to move downwards and this has to move upwards because, the mix potential should lie between these 2 extreme potentials. So, now, once it reaches to this potential it is coming across another cathodic reaction. So, the total cathodic reaction should be added up.

So, we add up and then we extend this, this is my new corrosion rate. So, this is i_{corr} case 2 when we have oxygen presence and this particular potential is E_{corr} case 2 when we have oxygen. And remember when we have this, the hydrogen evolution reaction on zinc surface is decreasing to a great extent because of depolarization effect. So, this is the similar situation when we what we had in case of presence of Fe plus 3 in the acid medium. So, let us stop here, we will continue our discussion.

There will be one more lecture which will be concluding lecture and there we will consider one more major 2 case studies and then we will conclude for the corrosion 1. And then we will see what the more understanding on corrosion in the phase 2, which is the corrosion 2. Let us stop here, we will continue our discussion in the next lecture.

Thank you.