Corrosion – Part II
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Lecture – 25
Interaction between Passivation and Pourbaix Diagram: II

Hello everyone, today will have lecture 25 we have been talking on passivation. Today also will continue our discussion on passivation and in last few lectures we could find that in certain metals and alloys for in the metal is taken to anodic side that means anodically polarized its corrosion rate reduces to a great extent. And we could also see that the corrosion rate becomes constant over a range of potential.

And also there could be spontaneous passivation there could be Active Passive transmission, where the material can go to active state to the passive state. And then we started looking at another segment in the polarization graph, where the current density again starts increasing from the constant current density in a range of potential that means, in the passive range, if we continue increasing the potential towards positive side at certain point.

It starts increasing again and there we could find that there could be a possibility of oxygen evolution and we tried to connect this oxygen evolution with reference to with respect to fore bay diagram and we have given 1 example of iron system where depending on the PH 1 can have in oxygen evolution in all the PH, but if the PH is less than 7, the oxygen evolution is from a reaction where water breaks down.

And then forms oxygen and H plus ion with electron liberation. Whereas, as if it is a basic medium that will basic or neutral, that oxygen evolution still would happen, but here, which minus would did would form oxygen and H2O along with electron liberations. That means, both a cases it will be anodic polarization of oxygen evolution reaction. And we could see that yes, the current value will again further start increasing.

Now, there could be other reasons for the increasing current density after reaching to a potential where constant current density is maintained that means after the passive range, the current density can again increase and those increase in current density can relate to differ other phenomenal. So, we will try to understand those phenomenal, why it happens at the same time in case of Active Passive transition.

Why the graph reaches to a maximum that means i critical and then it reduces and reaching reaches to a constant current density of our range of potential. So would try to understand those kind of that 2 situations also why it happens. Now, if we try to see

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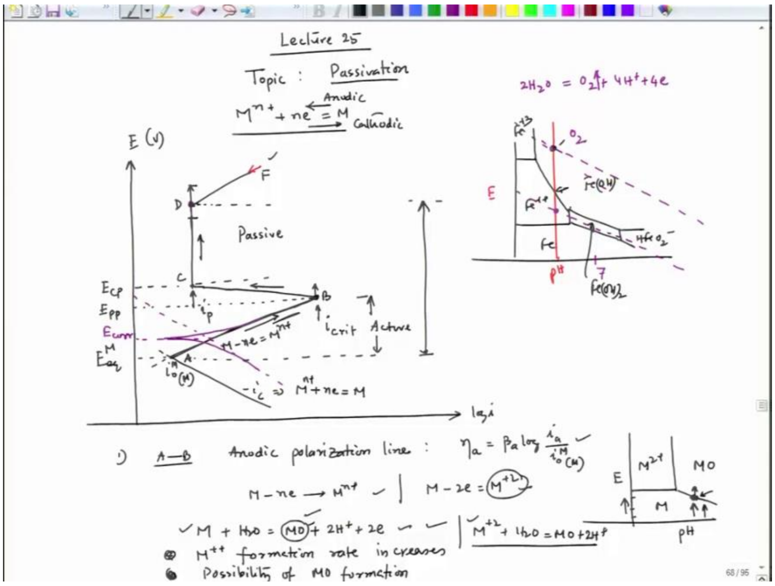

i) A—B Anodic polarization line : $\eta_a = \beta_a \log \frac{i_a}{i_0^M(M)}$ ✓

$M - ne \rightarrow M^{n+}$ ✓ | $M - 2e = \boxed{M^{+2}}$

✓ $M + H_2O = \boxed{MO} + 2H^+ + 2e$ ✓ ✓ | ✓ $M^{+2} + H_2O = MO + 2H^+$

- M^{++} formation rate increases
- Possibility of MO formation

A typical polarization plot for the anodic process. So if we consider this reaction of course, this is part is anodic and this is cathodic. Now, if we try to plot the anodic and cathodic both sides that said this is my ic corresponds to

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

This is a cathodic process, then we would have anodic process and it reaches to a maximum point. This is let us say the maximum point.

And then we have found out that the it starts decreasing and then it reaches to a very low value and then constant value is maintained and then from here you can have a graph like this. So, this is the segment, this is I zero, this is E equilibrium of that metal all those specific points are ic or i critical. This is Ecp or complete passivation this point is Epp is called primary passivation.

And then of course, this region, we call it passive. And then this particular region active region. Now, in one instance we could see that when the polarization curve let say if this is my fore bay diagram of iron. This is the fore bay diagram of iron here it is FeOH whole 3, this segment is FeOH whole 2, this is Fe+, this is a Fe+3 and this is HFeO2 minus in that case, we have understood why this particular line appears.

If we have a situation, if we take if we increase the polarize potential at a particular PH value fine. So, this is E vs PH and there we could see that it interact intersects with 2 reaction. So, this particular point corresponds to this where oxygen evolution happens and in this case since this PH is if it is this is 7, PH is less than 7. So, reaction would be H2O O2 + 4H + 4E.

So this oxygen gas will evolve and here we can have hydrogen evolution reaction. So, this particular there could be another plot corresponding to this. So, this is nothing but Ecorr and then we can have corrosion plot like this, we have understood that. Now, if we try to see the polarization line corresponding to this line, and let me put some mark let say this is A this is A, this is C, this is D and this is and I am not putting any values.

This is let say F or DE since we have putting E as potential, so, let me put F now If we go from A to B along the anodic polarization line we are following a duffel equation, which is Nita anodic equal to beta a log of ia by i0 of metal on metal surface. This is the i0 of metal on metal surface. Now, when it goes there, so we are having this reaction. Now, if we take a simple reaction like

$$M - 2e = M^{2+}$$

And if we take this particular M+/M can also Have a reaction like H2O I can have this reaction also. Now, if you go back to let is say in case of nickel, we have seen that in case of nickel, our polarization plot looks like this Ni+, Ni, NiO instead of Ni I can put it as M. M2+, MO. Now, this particular line corresponds to this line this particular equation which is potential as well as pH dependent.

So, MO is there is a possibility for the formation of metal oxide and this metal oxide is forming as we are going iron and so, because we are taking the potential in the positive direction, because we are going in anodic side. So, if we take the potential in the anodic side, so, actually we are increasing the potential. We are increasing this reaction at the same time there is a possibility for the formation of MO.

So, we are 2 situation increasing situation case this is two cases M++ formation rate increases because as we go along the potential access towards positive direction, I have to increase the amount of metal line formation because that those potentials are decided by the metal ion concentration in equilibrium with the metal like this here. So, as we go positive side metal and concentration has to increase.

And since, we are considering the plot between log i and E, so that means, the i indicates the rate of the process, so, the rate of metal and formation increases. Now, second part, since, we are going towards positive direction towards positive side, I am also having and an a situation of formation of having this particular reaction. So, when this reactions happens, again, there is a possibility of this is and this is possibility of metal oxide formation. Now

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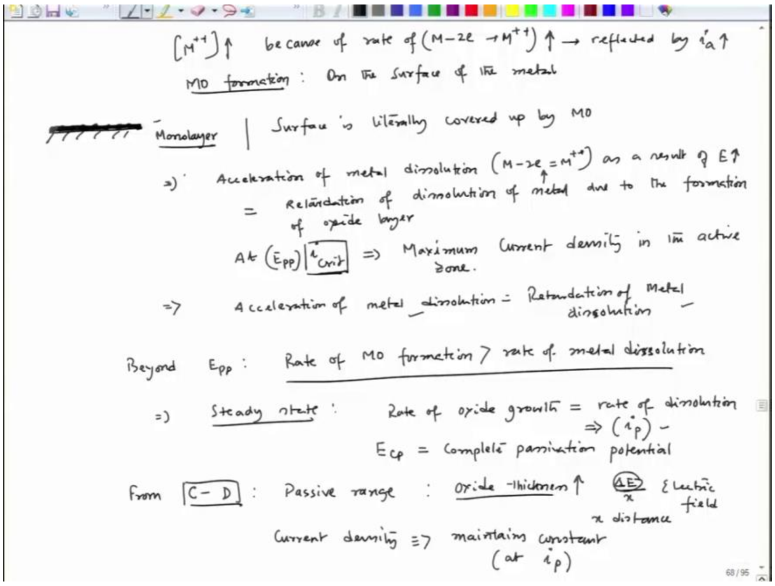

$[M^{++}]\uparrow$ because of rate of $(M - 2e \rightarrow M^{++})\uparrow \rightarrow$ reflected by $i_a\uparrow$

MO formation : On the surface of the metal

Monolayer | Surface is literally covered up by MO

$\Rightarrow$ Acceleration of metal dissolution $(M - 2e = M^{++})$ as a result of $E\uparrow$

= Retardation of dissolution of metal due to the formation of oxide layer

At (E_{pp}) $\boxed{i_{crit}}$ $\Rightarrow$ Maximum current density in the active zone.

$\Rightarrow$ Acceleration of metal dissolution = Retardation of Metal dissolution

Beyond E_{pp} : Rate of MO formation > rate of metal dissolution

$\Rightarrow$ Steady state : Rate of oxide growth = rate of dissolution $\Rightarrow (i_p)$

E_{cp} = Complete passivation potential

From $\boxed{C - D}$: Passive range : Oxide thickness $\uparrow$ $\frac{\Delta E}{x}$ Electric field

x distance

Current density $\Rightarrow$ maintains constant (at i_p)

If we compare the metal oxide formations that means, MN+ increases, concentration increases because of the rate of sorry here we are not considering N plus N we have already assumed to be 2. So, here it is 2e they should be 2 plus the rate of this particular reaction increases. Now, these increase is reflected by ia increment. So, if we see this as we go towards positive side, ia is gradually increasing along this line.

And governed by this equation taffel equation. Now, at the same time if we have MO formation and if MO form on the surface of the metal. So, we have a metal surface and these MO is are forming like this locally those are nucleating and forming now, as we are going higher and higher polarization side So, I am seeing that MO formation MO amount should also increase because it is crossing this line it is still further going up.

So, if MO formation increases. So, far the nucleation of MO would happen and at some point of time, there could be a mono layer of MO that will form okay. So, this mono layer will cover up the metal surface. So, when it is in the beginning of formation, I can assume that along at a fairly large potential we can start forming this one to be higher amount at the same time this metal oxide formation.

There could be metal oxide formation because of another reaction. So, this reaction is also possible. So, metal oxide is also forming so, that means, when it is start building up at fairly large potential around this region, I can have a kind of coverage of the surface of that metal by the metal oxide. Now at certain points so, when it reaches to this, so, that means, this point indicates the boundary between this boundary we have talked about.

In this case this was the boundary we talked about in the last lecture. So, at that point I can have a complete coverage of the surface by a kind of mono layer or di layer bi layer of metal oxide on the surface. So, we can have when this mono layer or bi layers are forming that is the surface is literally covered off by memo and that will be the point where I could have this particular situation.

Where acceleration of metal dissolution due to the anodic polarization is equal to the by of course, by this reaction as a result of increasing E would be equal to the retardation of dissolution of metal by the same reaction due to the formation of oxide layer. Know once we have this situation this particular situation which appears at i critical and i critical is nothing but maximum current density in the active zone.

So, after that since I have already reached to the, because I have crossed this particular boundary point I can if the process goes on, I will only have the situation of more and more formation of metal oxide. So, this particular thing can be stated as acceleration of metal dissolution equal to retardation of metal dissolution. But, both the cases the situation this is happening because of formation of oxide layer.

And this is happening because of the anodic polarization. Now, once we increase the potential beyond this i critical or corresponding to Epp beyond Epp if the potential increase, I could have a situation like rate of metal oxide formation exceeds the rate of metal dissolution. Now, when we have this particular situation, then I Will see that after reaching this once we increase potential little bit.

Since the metal layer is completely covered up by metal oxide and metal oxide is also amount of metal oxide is also increasing. So, it will cover up the metal surface completely and the current density start dropping because Now, the dissolution of metal will be decided by the ion diffusion from inner surface that means metal and metal oxide interface to the outer surface which is metal oxide and electrolyte.

And at certain location I will have a situation like steady state I will have a steady state situation where the rate of oxide growth would be exactly equal to the rate of dissolution which is nothing but ip and this ip is this is ip or i passive. So, after crossing i critical current density reduces because more and more oxides are forming on the surface and at certain location the rate of oxide growth will be just equal to the rate of dissolution.

And that point I will experience ip and that point potential point will be called us Ecp or complete passivation potential. So, this is the steady state. Now, what happens so, at i critical the retardation of metal dissolution due to the metal oxide formation is equal to the acceleration of metal dissolution due to the anodic polarization now, after that, since we have already covered up the surface metal oxide amount is increasing.

So, it is covering up completely. So, actually metal oxide is growing and when it grows at certain location, the growth of metal oxide because of that reaction of metal line with the environment or because of this 2 reactions, this is 1 reaction this is another reaction these 2 reactions. So, we will have continuous growth of metal oxide and this continuous growth of metal oxide also this little oxide is also allowing.

This metal line to move out from the inner surface to the outer surface that means, metal oxide interface to the metal and oxide and electrolyte interface and then it is dissolving that means it also have got influence on the solubility of that metal oxide. So, metal oxide is soluving as per the solubility of that metal oxide at that particular temperature it is dissolving at the same time it is growing.

And that growth rate will be just equal to current density at ip. And that passivation starts now beyond this passivation, actually, I could see that beyond this passivation, my IP does not change, it is a constant current density, which is the dissolution rate of that particular metal over a range of potential, now, what happens here so, from if I try to see indicate those points from C to D.

It is called passive range and there the oxide thickness increases, why oxide thickness increases, because it has to maintain this excess the distance and daily is the potential change. This is basically the electric field and this electric field has to be maintained constant over the entire passive range, this potential range and that is what the thickness has to increase and oxide thickness increases.

When it is increases at the same time this increase in potential tries to pull out metal oxide to the outside surface, but this increase in oxide thickness will maintain the rate of the metal dissolution constant. So, that is what the current density maintains constant at ip. So, we could understand why what happens in this particular range, we could understand now. At this point if it intersects this, then of course, oxygen evolution happens.

But if it stills if we go far the positive side an or it can happen below this oxygen evolution also at this point or at this point, where oxygen evolution is not coming across because of this cutting cross section of the oxygen line in the fore bay diagram, then there could be a possibility of trans passivity.

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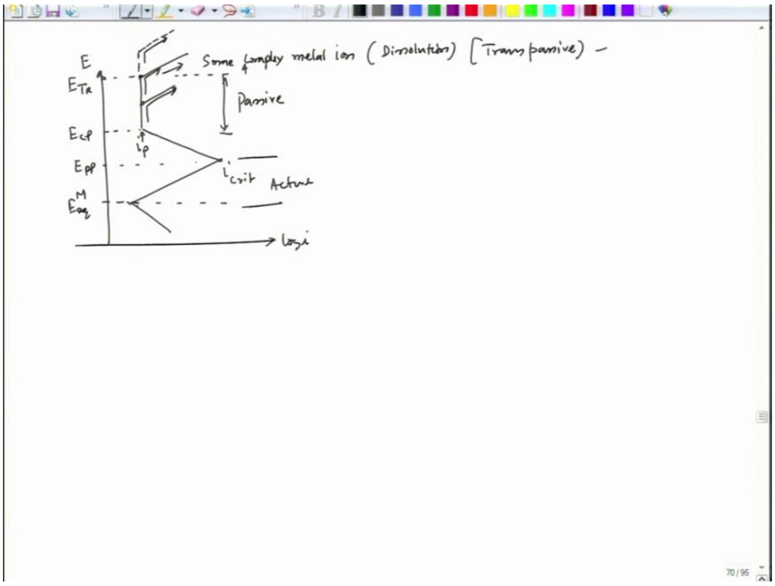

How trans passivity appears let us see that. So, that means, the graph if we see logi and potential, so, I have this plot fine. So, these are the plots I am not indices this is i critical. This is i passive. And now, instead of having oxygen evolution reaction this there could be possibility of formation of some complex metal line and there could be possibility of dissolution.

Now, when it happens like that, time this particular zone is called passive this particular zone is called active and then beyond this zone, we call it Trans Passive. So, this I can write it as ETR okay which is Trans passive so this is Ecp this is Epp this is E equilibrium of M. So, now why Trans passive appears and this breakdown there could be possibility of breakdown of that passive layer.

And by before reaching to a higher potential, the surface oxide layer can dissolve and the line can move this way, it can move this way. So, this is a breakdown, there could be possibility of it can go to very high potential, and there could be possibility of formation of a porous passive layer. Would happens at a very high potential in case of aluminium or titanium. So, we will try to analyse these in our next lecture.

So, let us stop here. Will talk will continue our discussion on this Trans Passivity breakdown of Passive layer or the formation of anodic formation of a porous layer at a higher potential. Will talk more on this in the next lecture. Let us stop here. Thank you very much.