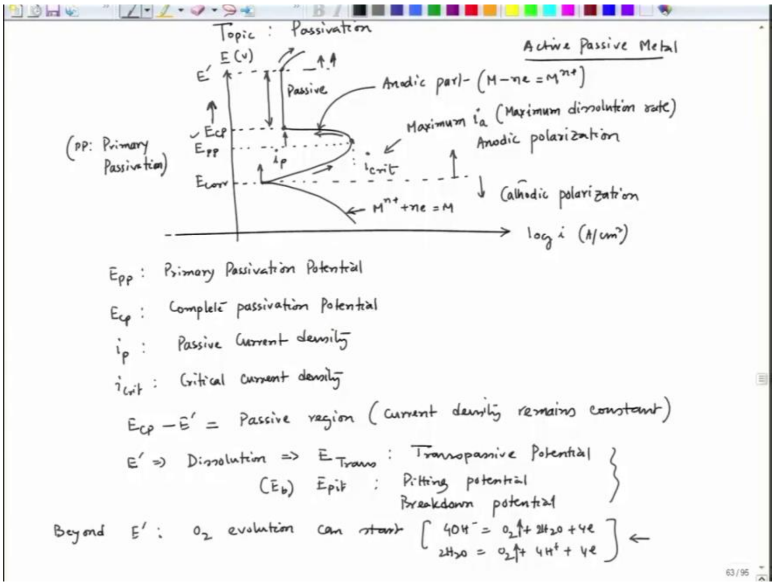
Corrosion – Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology – Kanpur

Lecture – 24
Interaction between Passivation and Pourbaix Diagram: I

Hello everyone let's start the lecture 24. We will continue our discussion on passivation. If we see a polarization plot for an Active Passive metal; so, that time the plot.

(Refer Slide Time: 00:33)



E_{pp} : Primary Passivation Potential

E_{cp} : Complete passivation Potential

i_p : Passive Current density

i_{crit} : Critical current density

$E_{cp} - E' =$ Passive region (current density remains constant)

$E' \Rightarrow$ Dissolution $\Rightarrow$ E_{Trans} : Transpassive Potential
(E_b) E_{pit} : Pitting potential
Breakdown potential

Beyond E' : O_2 evolution can start $\left[\begin{array}{l} 4OH^- = O_2\uparrow + 2H_2O + 4e \\ 2H_2O = O_2\uparrow + 4H^+ + 4e \end{array} \right] \leftarrow$

Looks like this; the plot is this kind of plot one can experience. Now here, this segment of course, this is the cathodic part and this segment and if we see the Ecorr this is Ecorr and if we draw that line this way, we are getting anodic polarization and this part is cathodic polarization. Now, when you go to anodic polarization, so, there are some critical points in this particular Active Passive plot.

So, this is a typical plot for Active Passive metal now here, if we see this, this is of course, E corr then in this direction, we are getting higher and higher corrosion rate or the metal dissolution rate as we are going towards the anodic polarization side. Since, this part is

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

So ions are forming. Now, it reaches to a maximum which is maximum i value this is in the log i plot with a small i current density.

I can say ampere per centimetre square. So, this particular position which is the maximum position we can say that this is i critical. So it is simply mentioned as i critical i crit, okay. So, this is i critical position and corresponding potential we call it Epp and its pp means primary passivation is pp Super square subscript pp is nothing but the primary passivation and this is called Epp is nothing but primary passivation potential.

And once this is reached, this is basically, the maximum ia that can be possible or this is maximum dissolution rate when we go from E corr towards positive side. Now, once we reach this if we further increase the potential this potential is increasing, we would see that the graph is taking a left turn. So, that means graph is moving this way and it reaches some point which is corresponding to this, these point is also a critical another important point.

Which we call it as Ecp, so the Ecp means complete passive potential or complete passivation potential and corresponding i value we call it ip or we can call it as ip or i passive. So, there are several names, so I will just put it as ip. So ip is nothing but passive current density and of course i critical is critical current density, fine. And then as the potential is increasing we will see that the potential is maintained.

Constant potential is this current value which is ip is maintained in this particular segment. So, these segment we call it a passive region. So, from and let’s say this potential, we put some name E prime. So, Ecp to E prime we can say this is passive region where current density remains constant almost constant. Now, beyond E prime if we increase the potential further, I could see that the plot is moving, rightwards again.

So, this particular zone beyond E prime that can be due to several factors. It can be due to our dissolution of that metal, it can be due to an oxygen evolution reaction, it can be due to pitting related phenomena. It can be due to complex ion formation of the metal oxide that has formed on the metal surface and then further dissolution. So, if it is dissolution related phenomena above Ep.

If it is related to dissolution, then this particular potential can be termed as E trans. So, it is name as trans-passive potential or it can be Epit, it can be pitting potential. So, they are several names or it can be either it can be pitting potential or Eb which is nothing but breakdown potential. So, breakdown of the passive layer, so, this particular term this particular part or this beyond E prime.

The metal surface the oxide layer the passive layer will not have any influence. But rather it can reach to a potential where oxygen evolution can start. Now, interestingly the oxygen evolution can start so, and if we check those reactions that is possible beyond E prime it can be either

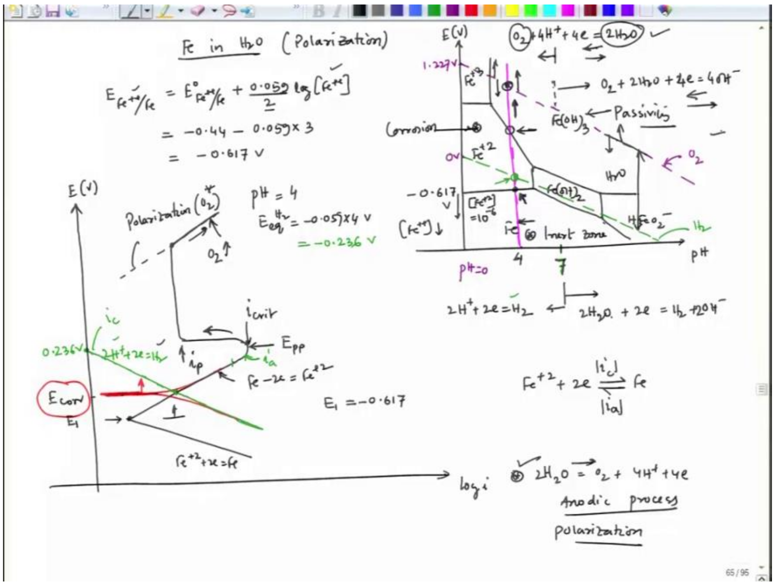
$$4OH^- = O_2 + 2H_2O + 4e$$

$$2H_2O = O_2 + 4H^+ + 4e$$

If, I could see this oxygen gas evolution starts. So, from here we could see that oxygen gas can evolve at a higher potential.

But, remember that time it may not be the trans-passive potential, because that time the metal oxide layer the passive layer may not dissolve. So, oxide layer remains but the surface acts as a substrate for the oxygen evolution reactions. Now, these critical values will talk gradually one by one. But first address this part, okay. Why we come across this oxygen evolution at a higher potential. Now, in order to find that.

(Refer Slide Time: 11:00)



We have to now get back to pourbaix diagram. So, if we draw a pourbaix diagram of iron on the, we are considering consideration of iron in H2O if we consider and then we are talking about polarization of iron in H2O with a different pH. So, if we draw the diagram pourbaix diagram this is pH, this is potential voltage. Now, these are the boundaries and this is iron region, this is HFeO2 -, this is OFeOH whole two and these are the positions of different phases.

We have already talked detail on this particular for a diagram in phase one. So, there are two more point lines one is hydrogen evolution line this is hydrogen evolution line and there is one more line which corresponds to the oxygen evolution line. So, which is parallel to the hydrogen evolution line, so, it starts arbitrarily and choosing some values. So, of course, it is not arbitrary this value is 1.227 volt.

So, if we went pH = 0 so, and this voltage is 0 volt. So, if we draw that parallel line so, this is another line. So, this is oxygen line this line is hydrogen line and if we take a pH of 7 so, this is pH 7, right side of it will have water reduction and left side we have hydrogen ion reduction and here also if we consider 7, right side will have this particular reaction. And the left side of this pH will have again water reaction in but is oxygen reduction.

But, it is in acidic medium, fine. Now, if we consider some pH let's say if we arbitrarily take any pH that said this is the pH I consider So, accordingly I need to find out what will be the behaviour of polarization plot. Let's assume that we are taking a condition. Where iron concentration is concentration of iron is iron Fe+2 ion or Fe+3 ion is Fe+2 = 10^{-6} molar.

And this potential if you calculate you will say that this is becoming like this - volt, how come we can get to this value. I can find out $E_{Fe+/Fe} = E^{o}_{Fe+/Fe} + (0.059/2) \log Fe^{++}$ ion concentration. So, this is - 0.44. And this becomes 0.059 into 3, because this 10^{-6}. So, there is a 2 here, so then it becomes - 0.617 volt. So if we try to increase the potential from let's say, this particular position.

From here, I take the potential to positive side, and the anodic as well as cathodic line will have its own existence. See if we see that plot of course log i and potential voltage. Now, if we start from this, until unless it reaches to this, I will not have I will have very low iron and concentration lower than 10^{-6}. Because as we go down from this point iron ion concentration produces.

So, that means as we go up the dissolution rate will increase little bit. So, that is the deposition rate would reduce also. So, that since the deposition rate reduces the plot would look like this. If we try to see the only the plot related to iron metal deposition and metal dissolution the plot would be, fine. So, now here this is cathodic side. And this is the point where I will start having intersection of this point where I could have, I can have.

So, actually we have this reaction, so this is cathodic ic this is ia, so this point corresponds to the point here. So this is the potential corresponding to this point quite why because at this point, iron is going from inert to corrosive zone, because we have already seen that this is the zone where corrosion happens because it forms ions, this is the zone which is inert zone, fine.

So, this is the potential let's say this potential is E1 and E1 is nothing but 0.617 as per this way, because from at this particular point we are having transition from inert to corrosion. So, that is what beyond this point dissolution rate increases. Now, when we go up, it is intersecting the Hydrogen evolution line at this point. So, this point would appear due to the intersection of metal dissolution and hydrogen evolution line.

So, if we try to draw the; and hydrogen evolution has its own polarization line in this plot, so, if we try to see. So, that means here pH we have maintained the pH to be let's say it is - it is 4 let's say. So, pH is 4. So, E equilibrium hydrogen would be - 0.059 into 4 this much would be the voltage considering the factor the hydrogen gas pressure is maintained as one atmosphere. So, somewhere it will cut, okay. So, this cut point, corresponds to this point.

So, that means, when metal is dissolving and this is at a lower potential, this is the point where hydrogen evolution happens. So, that was the cathodic polarization for the hydrogen evolution reaction will cut it. So, it will have its own hydrogen evolution polarization line. So, let's say this is my hydrogen evolution polarization line. So, this is $2H^+ + 2e = H_2$. And this potential is nothing but volt.

And this potential is appearing at pH 4 when the polarization line of hydrogen evolution and below 7 this reaction happens. So, we are talking about these reactions. So, this becomes intersection point of cathodic as well as and anodic portions of 2 separate reactions. One reaction is metal dissolution and another reaction is this one. So, now, as per our mix potential theory.

These becomes our E corr and polarization line if I want to draw up to this let's say up to this potential if I draw polarization line will be like this. Now, as we go beyond this, so, this becomes my steady state potential, fine. So, beyond this if we go ahead and we go ahead going to go ahead we could see that we are already considering ia because current density corresponding to ic is very low compared to ia.

This is basically nothing but ia, okay. So, now, it is reaching to i critical. Now, i critical is the point where maximum dissolution takes place and beyond i critical that means if we increase the potential further, my ia is reducing to a great extent. Now, this reduction in ia happens when we have already mentioned we have already seen that this reduction in ia happens when there is a conversion from active to passive state.

And this passive state happens when we have oxide layer or hydro oxide layer formation on the metal surface and this particular maximum point corresponds to Epp that means primary passivation potential. And that corresponds to this point where the polarization cuts the line between Fe+2 and FeOH whole 3. And FeOH whole 3 forms on the metal surface, that makes it passive.

So, that is what once it covers of the metal surface, then the surface the electrolyte is seen FeOH whole 3 rather than Fe and FeOH whole 3 is a very, is a, is an hydroxide with a very low solubility product. So, that means, the solubility product is very low means the iron Fe+3 concentration in the solution would be extremely low. So, the dissolution will be decided by the solubility product of that FeOH whole 3.

So, the corrosion rate or the dissolution rate or the ia should reduce and that’s what the reduction happens rapidly. And then it appears ip because, that this ip corresponds to the dissolution rate as decided by the solubility product of FeOH whole 3 or other way around the ion movement from the metal surface to the electrolyte surface and now as we increase the potential further.

So, we are increasing the potential further in case of if we consider pourbaix diagram. So, then it is still in the FeOH whole 3 region that is the passive layer is still there, but we could see that there is a cut point and that cut point is cutting the line the point corresponding to oxygen evolution or oxygen reduction line. So, below this we have already seen below this particular potential and above this particular potential.

So, below this potential we have water to be stable phase and beyond this potential oxygen should evolve. So, that means beyond this potential reaction beyond this particular line this particular line beyond this line, reaction will move this way. And below this line, this is beyond this line and below this line reaction would move this way. So, that is what this particular between this 2 lines, we have H2O stable zone.

So, once it cuts at this particular point and if we go beyond that, we have to consider this reaction because this is in acidic media. So, we will start happening we will start getting $2H_2O = O_2 + 4H^+ + 4e$. So, this reaction happens. So that is this is anodic process, and this anodic process would have its own polarization as decided by the tafel slope for that particular reaction.

So, will come across this is the polarization oxygen of this reaction. So, we are talking about this reaction. So, beyond this point though it is still in the passive zone and we have already know that this particular phase lead to passivity in the metal. So, beyond that passive zone the passive zone does not change, but we will see that the polarization plot takes a right turn and here oxygen starts evolving.

So, that is what, in the previous plot, we could see that oxygen evolution can start depending on the situation what we have just now seen the interaction between polarization and Pourbaix diagram. So, will stop now. We will continue our discussion in our next lecture. Thank you.