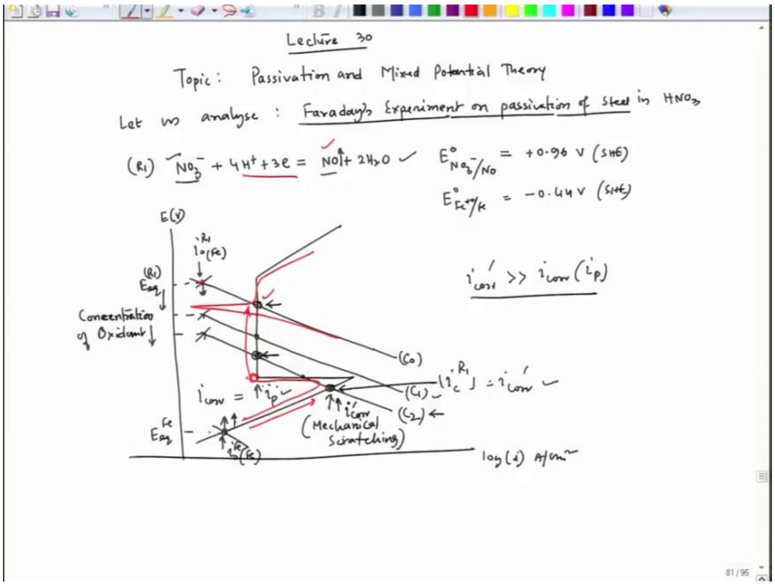
Corrosion – Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology – Kanpur

Lecture – 30
Passivation and Mixed Potential Theory: Case Studies (Cont….)

Let's start lecture 30. And the broad topic of course passivation and mix potential theory, we have considered one case studies like increase in concentration of oxidant and then after reaching to a final high concentration decrease in the concentration gradually in the same path and then also we have seen the influence of mechanical disturbance of the passive film after reaching the region or the concentration.

Where the mixed potentials that particular concentration polarization and this cathodic polarization plot is cutting across the anodic polarization plot at two or three locations. So, there we could see that if we do a mechanical disturbance of the passive film instead of maintenance of activity, we can increase the corrosion rate because of the breakdown of the passive layer. Now, if we recall. So, lecture 30

(Refer Slide Time: 01:30)



Lecture 30

Topic: Passivation and Mixed Potential Theory

Let us analyse : Faraday's Experiment on passivation of Steel in HNO_3

(R1) $NO_3^- + 4H^+ + 3e = NO\uparrow + 2H_2O$ ✓ $E^0_{NO_3^-/NO} = +0.96\ V\ (SHE)$

$E^0_{Fe^{++}/Fe} = -0.44\ V\ (SHE)$

$i'_{corr} >> i_{corr}\ (i_p)$

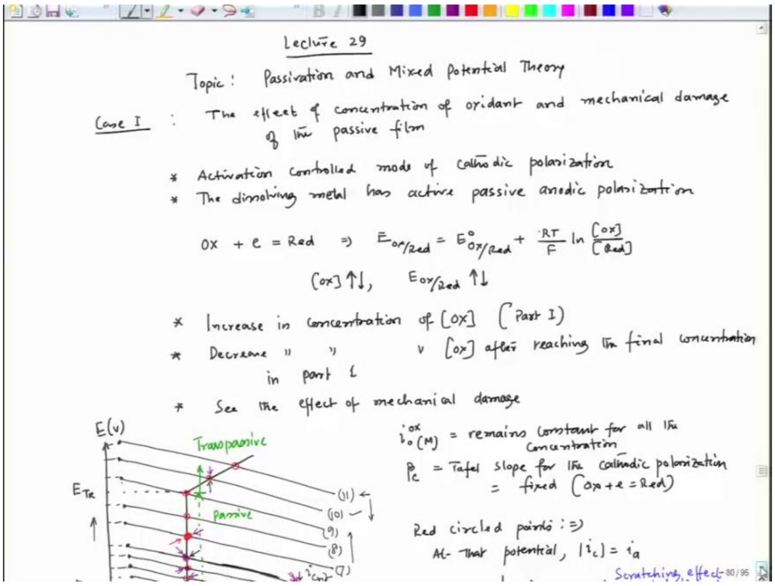
Topic it is same as last one passivation and mix potential theory and here will be now try to see, we will try to see the few more case studies and before we go to the case study second case study let's analyse Faraday's experiment. The Faraday's is experiment on passivation of steel in HNO3. Now, in that experiment, if we go back and see that experiment initially iron block is put in a concentrated HNO3 which is around 70% concentration.

So, there initially there will be a little bit of bubble formation on the iron surface and then immediately the bubble formation vanishes. And then if we see the weight loss due to the corrosion effect, we see that there is negligible weight loss. Now, after that what was done in the same beaker if we add water and then keep diluting the HNO3 solution we see that still there is no noticeable change in our weight loss.

Now, if we go to a very dilute HNO3 solution, the system shows no weight loss. So, that point we say that initially when it was dipped in acid solution concentrated as its solution it went into passivation and then it remains passive when we change the concentration from high to low. Now, after that in the dilute HNO3 solution, if we shake the particular beaker or if we do with a glass slide, if we just scratched the top surface of the Iron object,

We could see that the vigorous bubbling starts and we could see that the weight loss is noticeable now, due to corrosion. So, this is the phenomena which can be solved after seeing after understanding the effect of concentration of oxidant from high concentration to low concentration and addition to that is the mechanical disturbance of the passive player. So, in the last case what happened if I go back to the last one.

(Refer Slide Time: 04:56)



Lecture 29

Topic : Passivation and Mixed Potential Theory

Case I : The effect of concentration of oxidant and mechanical damage of the passive film

* Activation controlled mode of cathodic polarization
* The dissolving metal has active passive anodic polarization

$$Ox + e = Red \Rightarrow E_{Ox/Red} = E^{0}_{Ox/Red} + \frac{RT}{F} \ln \frac{[Ox]}{[Red]}$$

$$[Ox] \uparrow\downarrow, \quad E_{Ox/Red} \uparrow\downarrow$$

* Increase in concentration of [Ox] (Part I)
* Decrease " " " [Ox] after reaching the final concentration in part I
* See the effect of mechanical damage

$i_0^{ox}(M)$ = remains constant for all the concentration

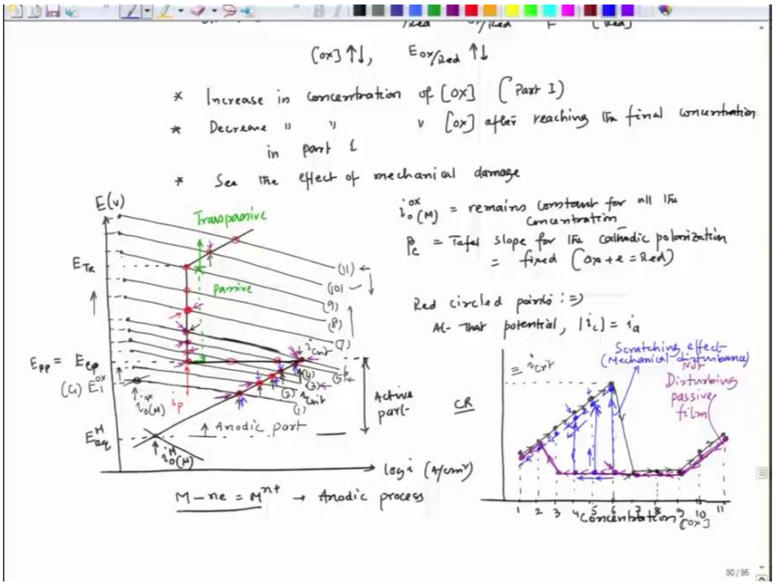
β_c = Tafel slope for the cathodic polarization = fixed (Ox + e = Red)

Red circled points : ⇒
At that potential, $|i_c| = i_a$

80/95

If I try to see that when we see the blue one.

(Refer Slide Time: 04:58)



$[ox]\uparrow\downarrow, \quad E_{ox/Red}\uparrow\downarrow$

- * Increase in concentration of [ox] (Part I)
- * Decrease " " " [ox] after reaching the final concentration in part I
- * See the effect of mechanical damage

$i_o^{ox}(M)$ = remains constant for all the concentration

β_c = Tafel slope for the cathodic polarization = fixed (ox + e = Red)

Red circled points :⇒ At that potential, $|i_c| = i_a$

$M - ne = M^{n+}$ → Anodic process

This blue curve at the 6 point when we reduce the concentration from let’s say concentration 8. Concentration 8 it’s spontaneously passivity, but as we decrease the concentration when it reaches to concentration six. Concentration 6 if we do not disturb the passive current density will be the corrosion rate. But if we disturb the surface with the mechanical effect scratching or other means, then the corrosion rate immediately moves to the point.

Which is this one which is nothing but i critical. So, this exactly happens in case of HNO3. Now in case of HNO3 the reaction the oxidation this reduction reaction we can say that

$$NO_3^- + 4H^+ + 3e = NO + H_2O$$

and that is what when we scratch the iron block when it was taken from a high concentration to low concentrated HNO3. We see the NO gas that will might this nitrogen oxide gas is present there.

So, that bubbling is nothing but the because of this this particular gas this is a gas phase that happens and this E0 E node for this oxidation reaction. So, I can say that NO3$^-$/NO, I can say because here it is. So, this is the value is + 0.96 volt with reference to SHE and if we consider E^o for iron equal to - 0.44 volt with reference to SHE which is standard hydrogen electrode, okay. So, if we see the interaction,

Iron has got its own active passive transition mode. This is the iron plot active passive polarization plot log i which is ampere per centimetre square. Now, when the concentration is very high the cathodic polarization line is cutting at this location. So this is E equilibrium for this reaction. Let’s say r1 is a reaction r1 and this is E equilibrium of iron i zero of iron over iron surface. This is i zero of reaction one over iron surface.

Because that reduction process is also taking place on the iron surface. So, I could see that it is actually being spontaneous passivity and if I see the passive polarization plot, the polarization plot will look like this, okay. Now, if we decrease the concentration, so now, I am changing the concentration or let’s say this particular location that is i zero does not change. So, it goes like this and then it comes here like this. So, okay.

So, if we see those concentration, so, as this potential is decreasing, the concentration of oxidant decreases and here oxidant is of course, this one. So, this oxidant decreases and if it decreases, I could see that when it decreases to let’s say, C1 this is C0 initial concentration, this is C1 this is C2 and C1 and C2 if we do not disturb it will maintain those passivity, okay. Now, at this location at this concentration.

If I scratch the surface, then where will be the point where mix potential should be maintained so, the point will move from this location to this location. So, this location comes when we have mechanical scratching, but if we do not scratch the system would maintain i passive which is nothing but i corr. So, it will maintain passivity i corr is of course very low point when it is equal to the passive current density.

But once we disturb because, when it is C2 that time, it is actually going through a 3 locations where ic = ia, but it will maintain this point if it is not disturbed if it is disturbed, it will come to this is a similar discussion what we had in the previous case where we change the concentration of oxygen from high to low and then coupled with mechanical disturbance. So, we could see that the corrosion rate.

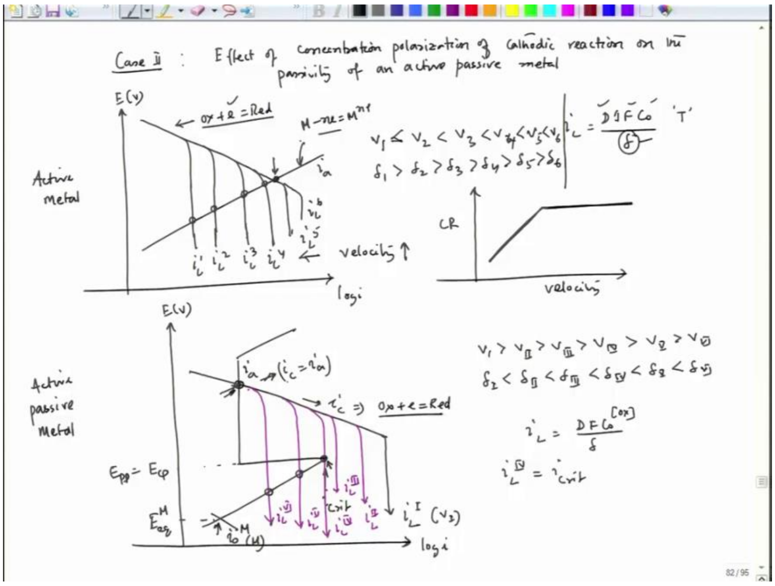
Initially it was here and then it is moving to this particular equation, this is i corrosion prime. So, i corrosion prime is very large compared to i corrosion close to ip. So, we could see this particular reaction would happen at a very high rate, which is equal to this one. So at this location ic, ic of this particular reaction 1 equal to i corr, right. So that was that corrosion rate increases.

If we scratch the iron block in the dilute nitric acid solution after it is passivated, remember after it is passivated if it is not passivated. If we put it in dilute nitric acid then of course it will corrode at this particular rate, okay. And when it reaches to the concentration C1 they not only the passivation happens so, that is what when we put the iron block in the HNO3 solution, the concentrated HNO3 solution.

Initially we do see a little bit of bubbling because that time this particular potential and this potential, they are trying to drag both of them and to a particular mix potential which is nothing but this and then only passivation appears. So, initially when it when this particular potential is dragged to higher location, it will move in this fashion then only it reaches here. So, before that when it moves like this, until unless it reaches to this location.

You will have a little bit of vigorous gas formation which is this that means vigorous this particular reaction rate would be higher because the anodic dissolution rate is also higher. Since it is moving in this location in this particular pattern. So, this will follow this anodic polarization like so, this is the understanding of faradays is experiment on passivation of steel HNO3 with reference to mix potential theory.

(Refer Slide Time: 13:48)



Case II : Effect of concentration polarization of cathodic reaction on the passivity of an active passive metal

$v_1 < v_2 < v_3 < v_4 < v_5 < v_6$

$\delta_1 > \delta_2 > \delta_3 > \delta_4 > \delta_5 > \delta_6$

$i_L = \frac{D\,n\,F\,C_0}{\delta}$ 'T'

$v_I > v_{II} > v_{III} > v_{IV} > v_V > v_{VI}$

$\delta_I < \delta_{II} < \delta_{III} < \delta_{IV} < \delta_V < \delta_{VI}$

$i_L = \frac{D F C_0^{[ox]}}{\delta}$

$i_L^{IV} = i_{crit}$

So, let’s take up case 2. Case 2 let’s see the effect of concentration polarization of cathodic reaction on the passivity of an Active Passive metal. So, we have seen in case of a condition where the cathodic reaction is concentration controlled and anodic reaction is activation control that will dissolving metal is going through activation control mode. We could see that constant corrosion rate at certain point it becomes constant.

But that case if this is voltage, so, if this is my, so this is iL1 iL2 this is iL3 IL4 and it happens when velocity increases, we have seen that, that anodic this ox this is my ox + e = red. This is the reduction process and it is reaching for limiting current density at a different location with increasing velocity. So, 1 velocity let's say velocity 1 is less than velocity 2 like that it moves.

And that case Delta 1 would be greater than delta 2 greater than delta 3 greater than delta 4 and this delta is nothing but $i_L = DnFC_0/\delta$. This is the basic equation and since we are considering e which is 1 electron. So, this will be 1, fine. So, now, this delta which is the boundary layer diffusive layer so that it decreases as we increase the velocity. So, now, in case of active metal if this is the condition,

so, now so, this is iL 5, so, V 5 and then delta 5, so, all other factors are same, if we start with the same concentration every case and if it is at a temperature T which is let's say room temperature, so, this will be the situation and then if we try to see the corrosion rate as a function of velocity. So, these are the points where I could maintain mixed potential theory. But once it crosses V4 velocity.

Once we go to V5 or V6 if we have iL 6, which is delta 6 this is V6 it does not matter that with all other velocities apart from V4 the corrosion rate would be at this point. So, the corrosion rate increases and then it remains constant. Now, this is the situation where active portion of the dissolving metal. So this is $M - ne = M^{n+}$ so, this is polarization ia. So, in case of that corrosion rate initially increases and then it remains constant.

But, what will be the situation if this interaction is with active passive metal. So, in that case the situation would be little it would be a little it the situation would be very different. So, this is log i, this is voltage in this is case where active we are considering active metal and in this case this is active passive metal in that case. Let's see what will be the situation. So, if this is the active passive anodic plot.

And of course, all the points are there. So, this is Ecp = Epp in this particular situation this is i critical. This is E equilibrium of that metal. This is i zero metal over the metal surface. Now, if we see a cathodic plot let's say this is the cathodic plot and now, this is the iL 1, now after the very high current density. This is ic this is ia and this corresponding to ox + e = reduction. This particular reduction process and here it is reaching limiting current density.

So, if we, this corresponding to some V1 speed of the V1 velocity of the solution. So, if we reduce the V1 then of course, the this particular factor will increase. So, if we increase that all other factors are remaining same. So, this will achieve at a lower so this is iL2, iL3, iL4, iL5, iL6. So, this when we, 6 velocities we are considering and accordingly I could see that V1 here in this particular case, V1 has the highest speed.

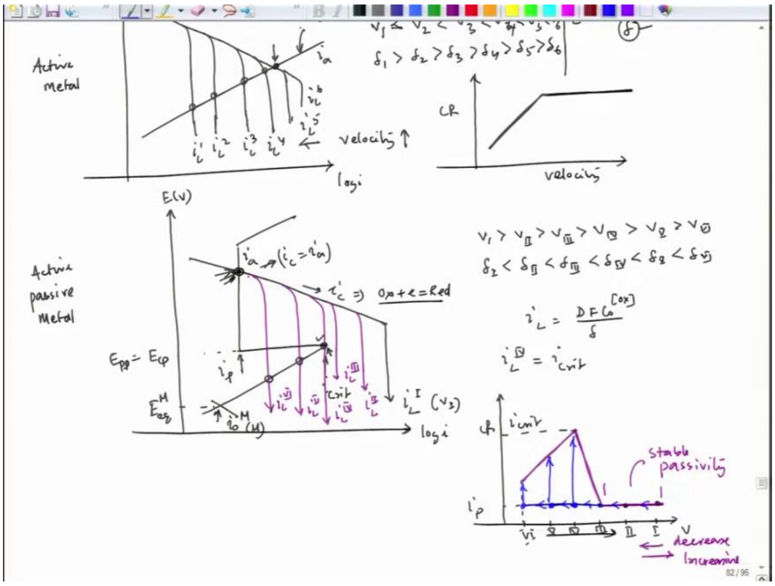
So, V1 = V2 = V3 or since we are taking italics, so, this is Roman we are considering. So, V4 greater than the V5 greater than V6. So, correspondingly Delta 1 would be less than delta 2 less than delta 3 less than delta 4 delta 5 Delta 6. So, this will be the situation. And we are considering $i_L = DnFC_o/\delta$ and C_o is the concentration of oxidant. Now, interestingly iL 4 is exactly equal to i critical.

Now if we start from iL 6, let’s say this concentration is started from iL 6 as we are increasing the concentration to V1. So, then if it is a freshly prepared surface with no oxide surface on the soft on the metal surface oxide layer on the metal surface. So, that case as we have discussed in case of the case one were case study one where concentration of oxidant is increasing.

So, the mix potential point the corrosion rate will be in these locations. Now, once we cross the velocity 4 to velocity 3 that means, the velocity is increased from 4 to 3 immediately the corrosion point will reach here. So, and then after that if we keep increasing the velocity iL does increase. But my passive region would be always at this location.

And remember when we have this kind of situation that the passive film is very strong in nature so that with that increasing velocity the passive film does not break down we can easily at the same time even it breaks down still immediately it starts reforming because all the time I have to maintain this particular point where ic = ia.

(Refer Slide Time: 23:55)



So, the corrosion rate would be with velocity if I see this is corrosion rate, if I try to see the corrosion rate when it was 6 and starting from 6, so, this is 6 so, velocity is increasing like this, okay. So, at this point the corrosion rate would be here then corrosion rate in case of 1, 6, 5 it will be increasing 6, 4 it will be here this point which is nothing but I critical and then once we reach 3, the corrosion rate would drop down to the passive region.

Corresponding to the passive current density. So, this is ip since this is ip and then if we increase the speed the corrosion points would be this point only all the time. So, the distribution or the variation of corrosion rate would be this one. So, I could see that the corrosion rate varies initially it increased initially it increases and then once it crosses i critical i will have the existence of ip which is a very low current density.

Or this particular zone is nothing but stable passivity. So, this is the analysis and now if I try to see the concentration if I if the velocity decreases in this way velocity is increasing. So, if it is this is decreased, now, the pattern would be when it reaches to IV, if the oxide layer does not get dislodged, my corrosion rate point would be when the velocities corresponding to V4 will be here. Now, after that even if we go to 6 which is the lowest velocity.

If the oxide layer is not getting dislodged. I will keep that passive layer. So, the when we return the return point that was the velocity is decreased gradually from 1 to 6, I could say that every place I will get passivity, because the surface is not getting disturbed, but if the surface is disturbed, let’s say at 4 point if it is disturb, this will reach to this or at 3 see 5 point if it is disturbed it will reach to this or 6 point if it disturbs it reached to this.

So, this way we can analyse, the effect of concentration polarization on the Active Passive metal corrosion rate. So, let’s stop here. We will continue our discussion on the Active Passive metal. And we will take two more instances one is the influence of alloying on the attainment of passivity in some critical metal like titanium. And the second part is, we have to also talk about anodic protection of metal.

Where in the anodic side if you polarize, we do get a lower corrosion rate and protect the structure. So, let’s stop here. We will continue our discussion in the next lecture. Thank you.