Corrosion - Part II
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Lecture - 4
Activation and Concentration Polarization: Mixed Potential Theory

Hello everyone, let’s start lecture 4.

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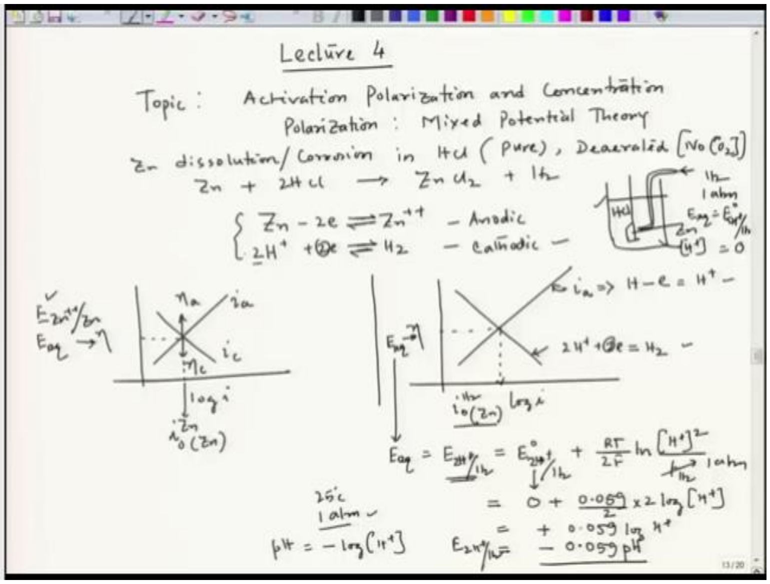

Lecture 4

Topic : Activation Polarization and Concentration Polarization : Mixed Potential Theory

Zn dissolution/ Corrosion in HCl (Pure) , Deaerated [No (O_2)]

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

$\begin{cases} Zn - 2e \rightleftharpoons Zn^{++} & - \text{Anodic} \\ 2H^+ + 2e \rightleftharpoons H_2 & - \text{Cathodic} \end{cases}$

$E_{eq} = E^{\circ}_{2H^+/H_2}$, $[H^+] = 0$

$E_{eq} = E_{2H^+/H_2} = E^{\circ}_{2H^+/H_2} + \frac{RT}{2F} \ln \frac{[H^+]^2}{P_{H_2}}$ 1 atm

$= 0 + \frac{0.059}{2} \times 2 \log [H^+]$

$= + 0.059 \log H^+$

$E_{2H^+/H_2} = - 0.059 pH$

25°C
1 atm

$pH = - \log [H^+]$

And the topic it is continuation of what we have been discussing for the last 3 lectures. So, it is activation polarization and concentration polarization and now we will try to get into mixed potential theory we have already talked little bit at the end of lecture 3 mixed potential theory. So, we saw we wanted to explain dissolution of zinc in acid medium which is HCl at some pH and you could see that the overall reaction would be

$$Zn + 2HCl = ZnCl_2 + H_2$$

So, this is the overall reaction and we are trying to explain zinc dissolution or corrosion in HCl which is pure and deaerated means no dissolve oxygen. Now you could also see that the anodic process is and cathodic process is, so this anodic, this is cathodic. Hence these are electrochemical reactions and we could also see the separately if we consider a zinc plate dipped in zinc containing solution we will have a situation like this situation will get.

This is ia, this is ic and in this way neeta a and this direction neeta c and this point corresponds to i zero of zinc or I can just go down little bit which is i zero zinc on zinc surface and this corresponds to E equilibrium or E zinc++ zinc. Now this value would depend on what is the concentration of zinc ion in that electrolyte. Similarly, for this reaction we can also have similar type of polarization where this is log i and if I see the 2 segments.

This segment corresponds to ia which corresponds to this reaction which is nothing but H - e = H^+ and this part is nothing but H2. So, this is anodic process, this is cathodic process because both these processes I can have anodic as well as cathodic. So, I can here also I will have E equilibrium and now here E equilibrium which is nothing but E H+ H2 E zero H+ H2 this is we are considering reduction potential + RT 2F because here we are considering 2 electrons, this is 2 electrons.

So, now ln activity of H+ because there are 2 H+ ion and partial pressure of hydrogen sorry this there should be nothing like this. And if I take 25 degree Celsius temperature 1 atmosphere pressure, so then this value is zero and this becomes 0.059/2 * 2log H+. Because if it is 1 atmosphere, this is one atmosphere then this becomes - 0.059 log H+ and it can be written as pH. Since we know

$$pH = -log\ [H^+]$$

So, now these value will be decided by the pH of that HCl medium. So this is equilibrium value and this point is nothing but i zero of hydrogen on zinc surface. Because this particular electrode will be constituted like this you have HCl medium and you have a zinc plate. So, this is zinc now you have hydrogen gas which is flowing in and this is at 1 atmosphere pressure this is HCl. So, and we are maintaining H+ ion concentration if it is 1 then the pH will be zero.

And that time E zero would be E equilibrium would be E zero H2 which is nothing but zero. But if this H+ ion concentration has got some other value other than 1 then it can have equilibrium potential value related to this equation which is E 2H+ H2. Fine. And since it is happening on the zinc surface we are taking a zinc electrode, so then that hydrogen evolution exchange current density we have to write in the with respect electrode that is what this subscript we are taking zinc in the bracket it form zinc.

Now these 2 situation can have if we have a separate process like zinc dipped in zinc containing solution and if I consider a hydrogen electrode like this.

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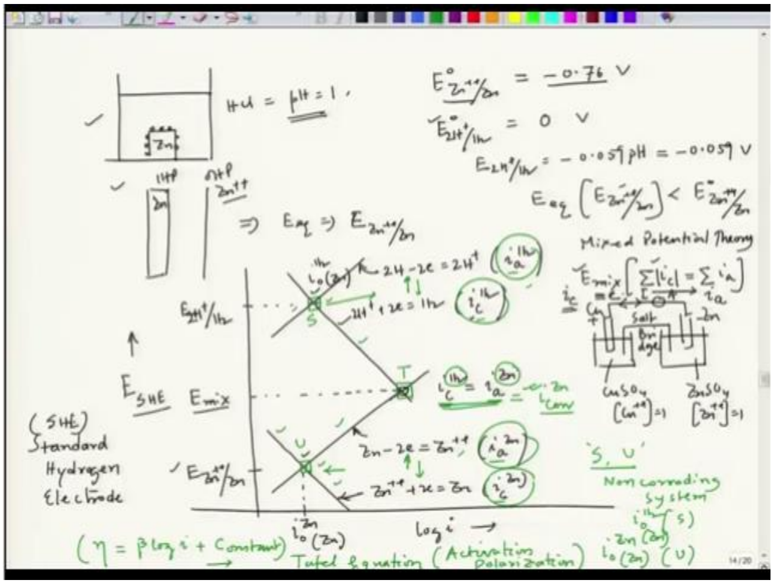

But once we combine them. Okay. So once we have a situation like in an HCl solution with a pH let's say 1 there if I put zinc pure zinc then we will have this reaction this 2 reaction will start happening. Depending on the concentration of zinc in the when the double layer forms on the zinc surface that means on the zinc surface we will have a double layer which is here it will have zinc ion and this is zinc.

So, we will have a double layer and that double layer formation we will have IHP, OHP and then it can also have E equilibrium which is nothing but E zinc++ zinc depending on the concentration of zinc++ ion in the vicinity of that zinc plate. Similarly, the hydrogen will start bubbling on this particular surface it will also form double layer and then that will also decide it's equilibrium potential depending on the pH value.

See if we combine in a plot these 2 plots we are now combining assuming that the zinc ion concentration we are taking whatever zinc ion concentration will experience here. So, that time here we will have E zinc++ zinc and here we will have E hydrogen H2. These 2 levels will have. Since we already know that

$$E^{o}_{Zn^{++}/Zn} = -0.76$$

or I can write volt and

$$E^{o}_{H^{+}/H_2} = 0$$

So, that means in the potential access with reference to the hydrogen standard hydrogen electrode this SHE is nothing but standard electrode SHE. Fine. So, with reference to that these value will be on top of this value, if we consider in the standard state of that 2 partial or the half cell but since it is not a standard condition we have some pH 1. So, in this case the potential will not be same as this or potential would be - 0.059 PH is nothing but 0.059 volt.

And in this case we are not maintaining zinc ion concentration to be 1 rather it is much lower than that. So, these potential value will further go down in this case, so E equilibrium which is nothing but E zinc++ zinc would be less than E zero zinc++ zinc. Because zinc ion concentration in the actual system is lower than the unit activity or unit concentration. Now that case of course that level would be like this but of course here the value would be decided by what is the concentration that zinc metal is facing in front of it.

Now it will have its own polarization individually we will have polarization like this, this value is i zero zinc on zinc surface and similarly I can have i zero hydrogen on zinc surface. So, this line is nothing but

$$2H^{+} + 2e = H_2$$
$$H_2 - 2e = 2H^{+}$$
$$Zn - 2e = Zn^{2+}$$
$$Zn^{2+} + 2e = Zn$$

So, this is corresponding to ic of zinc correspondence to ia of zinc, this is corresponding to ic of hydrogen, this is corresponding to ia of hydrogen, fine.

So, these are the current densities we could see, now whenever we have a system, 2 system working in tandem particular system like this we have to make use of mixed potential theory. We have already explained mixed potential theory at the end of third lecture saying that there could be number of cathodic and anodic reactions and at the same time the system will try to find the mixed potential where the net current density corresponding to cathodic current.

And the net current density corresponding to anodic current these 2 will be similar. So, we will find E mix where I will have summation of ic = summation of ia and of course I am taking mod. Since we have considered ic to be the negative current it is the direction not the value magnitude wise it is height is having a finite magnitude but the direction is opposite to the current ia and remember this ia is nothing but the current in the outer circuit and the ic is the current corresponding to electron flow.

Now let us just analyze this for example if we have a cell like this, this is let us say copper sulphate solution this is zinc sulphate solution. And let us say concentration of copper ion is equal to 1 and here zinc ion concentration equal to1 and then if we have as copper rod and if we have zinc rod in those solution. If we allow them to stabilize we will develop some potential here, we will develop some potential here.

Now if we connect with salt bridge this is salt bridge and now if we connect them with conductor we will see if we put an ammeter here will see that the current is flowing this way. This is the system current and the electron flows this way, so now the electron flow corresponds to ic and the current flow corresponds to ia. So, now we could see that the current in the external circuit or the conductor it flows from positive terminal to the negative terminal.

And in the solution it is basically from negative to positive terminal but the system current is opposite to the electron flow and the electron flow direction nothing but the ic that is the concept. Now we have to find out here we could see that there are 2 reactions 1 cathodic and 1 anodic now it has to reach a situation a potential which will be between these 2 potential and at that potential we could see that the net current density for the cathodic process.

And the net current density for the anodic process will be similar and I could see that situation is arriving when they are approaching and intersecting at this point. And here I could see that these ic, ic hydrogen = ia zinc and this potential corresponds to E mix and that is the whole concept of mixed potential theory. Fine. So, this is the potential the system will achieve. Now coming to some salient features in this diagram.

So, this is of course log i scale because these 2 plots are done on thus basis of log i. So, this is also log i, log i cell this is potential axis, now if we consider this point, this point and this point, 3 points they are having some unique features. If I consider let us say I am giving some name let us say S, T, U. now if I go to if I talk about S and U there the potential which is nothing but the non-corroding system or non-corroding situation.

And I achieve i zero in case of S it is nothing but hydrogen on zinc surface and in case of U it is i zero zinc on zinc surface this is U. And interestingly at this 2 points I could achieve steady state and forward and backward reactions are equally the rate of forward and backward reaction at this 2 points are same. And in this case is basically this 2 reactions and in this case this 2 reaction they are happening at the similar rate.

Now coming back to this point this is an interesting point, this point you see that the ic and ia both are same. Here also you see ic and ia are same here also ic and ia are same this point these 2 values are same here also these 2 values are same at this point. But they are corresponding to the same species zinc, zinc++ and here it is H+ H2. Now but in this case though it is ia = ic but they are of different species. In 1 case it is zinc and here it is hydrogen.

So, though here you somebody can say that these are 2 rates are similar because i is nothing but the rate of the process that means rate of the cathodic reaction is similar to the rate of anodic process. Here also the rate of cathodic reaction and rate of anodic reaction both are same but in this case there are different species then that means we cannot say that this point is an equilibrium position.

But we can say that the rate at which zinc dissolution is taking place is steady, that means it is happening at the same potential all throughout of course it is a open system that means hydrogen is continuously going out and that is what the reaction is continuously taking place at that particular rate. So, this condition it is though we can say that the rate is fixed but it is not equilibrium but here the rate is fixed but it is equilibrium.

Now coming to further just to add it to this particular thing, so here I can say this is nothing but i corr of zinc. Why? This is ia, is nothing but the dissolution of zinc in the form of zinc ion, so that is what it becomes the corrosion current density of zinc in HCl of pH 1. So, this is the connection between activation polarization and mixed potential theory because both the cases we are actually expressing all the lines this line, this line, this line all 4 lines we are expressing with a general expression beta log of i+ some constant C.

So, this is nothing but tafel equation and the tafel equation is valid in the case of activation polarization. Fine. So, this is the connection between activation polarization and mixed potential theory for a simple system. Now there will be one more important aspect of polarization which is called concentration polarization. Fine.

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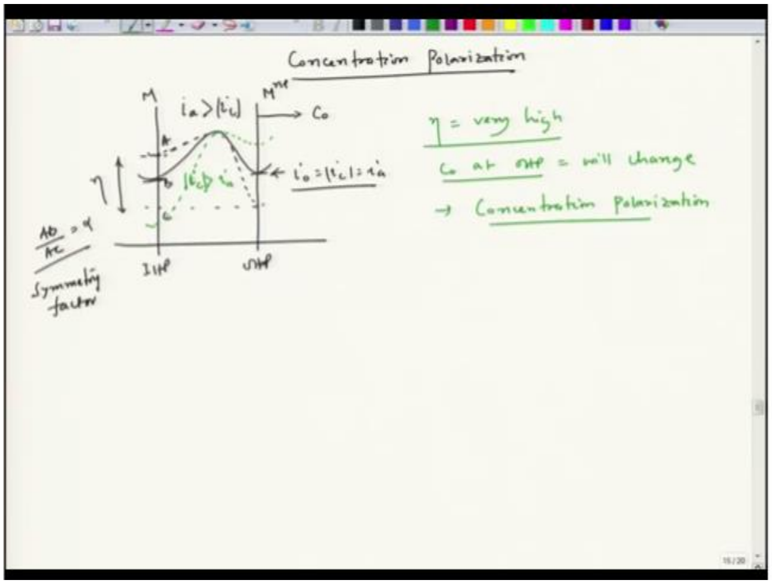

Concentration Polarization

η = very high

C_o at OHP = will change

→ Concentration Polarization

So, let us look into this part, now when we consider activation polarization. We have considered this is IHP, OHP. We have considered atomic jump from one into another this is M n+ M and if ia is more than that. So, this will be the distribution of energy free energies, so this becomes my over voltage and if it is A, B, C so (AB/AC) =α which is symmetry factor. So, that means this particular case and in this case ia greater than ic for the dotted case.

And this is the corresponding situation for i zero = ic = ia. Now in this case if I look at it is basically the thermal activator jump process and it happens at a smaller current density level. And the basic assumption is when these happens the concentration at this particular end does not change. So, if the concentration here is C zero in the beginning, so the C zero concentration remains there, okay, with the polarization.

But if we go to higher and higher current density that means if we switch to higher and higher level of polarization then I would have a different situation. Okay. So, now even if it is for ia and ic for if I do it for ic greater than ia, so that case the plot will be like this. Fine. This is the green colour for situation ic greater than ia, okay. So, if we go to a higher polarization, so that is over voltage becomes very high though situations C zero at OHP will change.

And that lead to another kind of polarization we call it concentration polarization. Fine. So, let us stop here we will continue our discussion on concentration polarization and it is relation it is interaction with the mixed potential theory. Thank you.