# Corrosion Part - II
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## Lecture - 20
## Concentration Polarization and Activation polarization: Numerical Analysis

Hello welcome to lecture 20.

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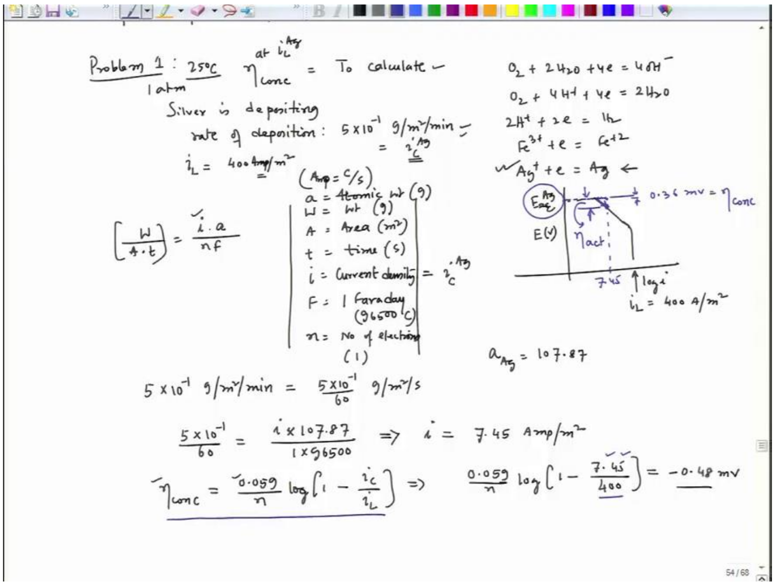

Problem 1: $25^\circ C$, 1 atm $\eta_{conc}$ at $i_L^{Ag}$ = To calculate

Silver is depositing

rate of deposition: $5 \times 10^{-1}$ g/m²/min $= i_c^{Ag}$

$i_L = 400$ Amp/m²

(Amp = C/s)

$$\left[\frac{W}{A \cdot t}\right] = \frac{i \cdot a}{nF}$$

a = Atomic wt (g)
W = wt (g)
A = Area (m²)
t = time (s)
i = Current density $= i_c^{Ag}$
F = 1 Faraday (96500 C)
n = No of electrons (1)

$O_2 + 2H_2O + 4e = 4OH^-$
$O_2 + 4H^+ + 4e = 2H_2O$
$2H^+ + 2e = H_2$
$Fe^{3+} + e = Fe^{+2}$
$Ag^+ + e = Ag \leftarrow$

$a_{Ag} = 107.87$

$$5 \times 10^{-1}\ g/m^2/min = \frac{5 \times 10^{-1}}{60}\ g/m^2/s$$

$$\frac{5 \times 10^{-1}}{60} = \frac{i \times 107.87}{1 \times 96500} \Rightarrow i = 7.45\ Amp/m^2$$

$$\eta_{conc} = \frac{0.059}{n} \log\left[1 - \frac{i_c}{i_L}\right] \Rightarrow \frac{0.059}{n} \log\left[1 - \frac{7.45}{400}\right] = -0.48\ mV$$

So the topic of course it the broad topic is explanation of corrosion event on the basis of mixed potential theory and on lecture 18 and 19. We have talked about the effect of concentration polarization as well as activation polarization on the corrosion of an active metal. And we have taken the instance where active metal the polarization is controlled by activation mode.

Whereas the cathodic reaction can have either activation control mode or concentration control mode. And at the same time we could also see how the experimental plot looks like in case of a situation where the corrosion is activation control that means both activation polarization lines are cutting across and in another case where the concentration controlled a situation.

Where or at a concentration polarization control corrosion event where the activation control part of that dissolving metal is cutting across the concentration polarization segment of the polarization plot of the cathodic reaction. Now we will do little bit of numerical problem solving and we will start with one problem on concentration polarization effect and then we will also start looking at another aspect that in practical situations.

We seldom use hydrogen electrode rather standard hydrogen electrode is seldom reused. So we generally use a much better stable reference electrode while we do experiment in the lab. We either use Ag/AgCl electrode which are actually and this is one reference electrode. Then we can use standard calomel electrode or copper copper-sulphate electrode. We use copper copper-sulphate electrode is more preferred in the industrial application point of view.

For example, when we see the cathodic protection in order to see the polarization effect of the electrodes means either anode or cathode when those cathodic couples are placed inside soil or seawater that time we do see time to time the polarization potential of those electrodes that time we mostly copper copper-sulphate electrodes are used.

So because those electrodes are much stable electrodes that means every time it will give the same reference potential but in case of hydrogen electrode maintenance of the stable electrode potential is be tricky. And that is what the potential many a times we measure with reference to those standard hydrogen electrode standard electrodes which are not standard hydrogen electrode so the potential part will be little different.

Till now whatever calculations we have done we have done on the basis of standard hydrogen electrode. Now we will do see or the effect of calomel electrode will take calomel electrode this time and see how to calculate the polarization how to solve a problem when something is corroding and there also will make use of mix potential theory. So the first problem let’s take up the problem 1.

And the statement is like this we have to calculate concentration polarization we have to calculate to calculate and the situation where silver is depositing. See the cathodic reactions and in this case we are considering cathodic polarization. Cathodic polarization for the understanding of concentration polarization part. So now cathodic polarization cathodic reactions could be several data types.

For example, one type could be oxygen reduction which is

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

There could be reaction like

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

So these are 2 cathodic reactions. There could be reactions like this. There could be reaction like + 2 this is also reduction reaction or cathodic reactions. There could be reduction like Ag+ + e = Ag. So the Ag since Ag is very strong Ag + is a very strong oxidizer.

So that means it has always a tendency to get reduced so this reduction reaction can happen. Now here Ag is dip silver is depositing that means we are considering this reaction. Now depositing at a rate of if I try to find out the rate so the rate of deposition it is 5 into $10^{-1}$ gram per meter square per minute.

So this is the deposition rate and in that situation iL = 400 ampere per meter square. So that means this is the maximum deposition when this reaction if I try to see its polarization effect so let's say this is my E equilibrium Ag at the concentration what we have in that particular Ag solution. So it will have its plot like this so this is the plot we are getting so this is log i this is E voltage and here we are considering standard hydrogen electrode reference electrode.

So this particular indication is iL which is nothing but 400 ampere per meter square. Now we have to find out the concentration polarization. So this value at the rate of deposition which is corresponding to some current ic at ic Ag. So because this deposition rate can be taken in the form of cathodic current density. So in order to attack that we have to find out this value.

So how to find out that value so we can find this value as we know this equation nF this equation you know and what are those values this W = weight in gram, A area in meter square in this particular instance, t I can take it as time. Let's take it as second because we will come to see the why we are taking second because we have to convert this particular thing into in the form of ampere.

And one ampere is nothing but Coulomb per second. so that is what we are this is this a and this a these are similar so let me put it as amp. So i is current density, F 1 Faraday 96500 Coulomb, n is number of electrons. In case of Ag this value is 1 because we are considering this reaction. So if we see this particular quantity it is basically 5 into $10^{-1}$ gram per meter square per minute.

So, I have to convert in this particular thing into gram per meter square per second so 5 into $10^{-1}$ divided by 60 it becomes gram per meter square per second. So I can find out this ic corresponding to ic Ag because this is nothing but ic Ag which is cathodic current density corresponding to the deposition rate of silver. So 5 into $10^{-1}$ by 60 = i.

And now a here we missed one point, a is nothing but atomic weight of silver. This is also in gram and a of Ag = 107.87. So into 107.87 divided by 1 into 96500. So I would get i to be 7.45 ampere per meter square. Now once we get this then I can find out

$$\eta_c = \frac{0.059}{n} log\left(1 - \frac{i_c}{i_L}\right)$$

Now remember that calculation what here we are doing every all the calculation we will be doing at 25 degree Celsius as well as one atmosphere pressure, fine.

So this is the condition so that condition only this value will become 0.059. So I can calculate this value like this

$$\eta_c = \frac{0.059}{n} log\left(1 - \frac{7.45}{400}\right)$$

So this becomes - 0.48 millivolt. So we could see that the potential drop sorry here we have to put a - sign this becomes +. But actually since we are considering concentration polarization so this will be going downwards.

So other way around I can still I can remove this part just to take that - sign so here I can put a -, Fine. Because it is concentration polarization for the cathodic reaction will always go downwards because we are considering cathodic polarization. Now this is the value you are getting. Now if I try to let's say this that means we have a very, so if we try to see the current value.

So if the current this is the current value we are considering 7.45 ampere per meter square. So at this condition, the polarization and this is the equilibrium silver potential equilibrium potential so the drop would be from this E equilibrium Ag very miniscule which is 0.36 millivolt. Now if we just for sake of taking an example that what will be the effect of the current on the polarization concentration polarization.

Of course there if we try to find out the activation polarization I could see the activation polarization this is = neeta concentration. But activation polarization is substantial okay.

Because here it is going along this line but concentration polarization effect would be very miniscule because of this very equation this very equation we have to see okay.

So this is one sort of problem but you just try to put this current value different value and keep going towards close to this iL which is 400 ampere per meter square. You will see that the influence of that increase in current here until unless it reaches close to that 400 meter ampere per meter square it will be very small change. Because of this again I am telling this because of this very equation.

Now this is one problem on this cathodic polarization part. Now in the next lecture onwards will be start will be taking up passivation and then mixed potential theory will consider for explaining corrosion rate of passive metals. Before we get to that let's as we have mentioned in the beginning of this lecture that we have to consider influence of a measurement by different other reference electrodes so let's solve some problems.

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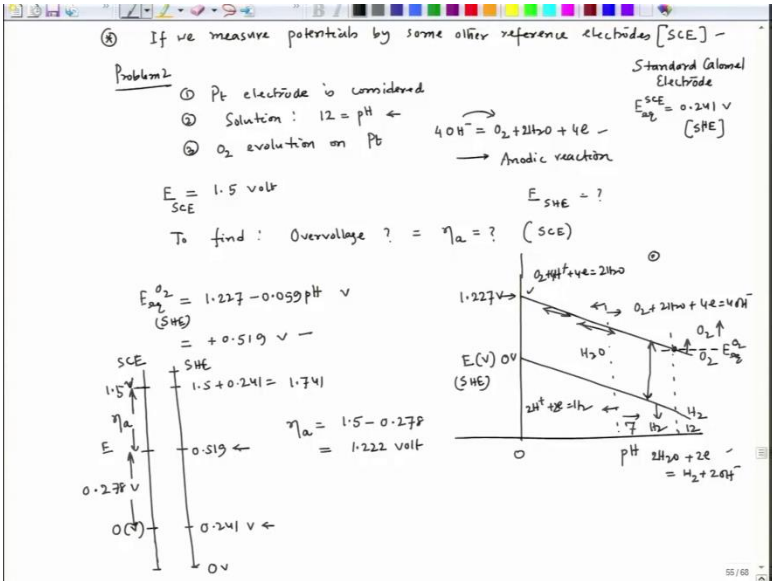

(*) If we measure potentials by some other reference electrodes [SCE] –

Standard Calomel Electrode

$E_{aq}^{SCE} = 0.241$ V [SHE]

Problem2

① Pt electrode is considered

② Solution : 12 = pH ←

③ $O_2$ evolution on Pt

$4OH^- = O_2 + 2H_2O + 4e$ –

⟶ Anodic reaction

$E_{SCE} = 1.5$ volt

$E_{SHE} = ?$

To find : Overvoltage ? = $\eta_a = ?$ (SCE)

$E_{aq}^{O_2}$ (SHE) $= 1.227 - 0.059\,pH$ V

$= +0.519$ V –

$\eta_a = 1.5 - 0.278$

$= 1.222$ volt

One problem this is let's say problem two, problem 2. So that situation what we are considering if we measure potential by some other reference electrodes other than of course standard hydrogen electrode and here we are considering standard calomel electrode this SCE means Standard Calomel Electrode and the potential, the equilibrium potential for SCE we take up 0.241volt and this is measured with reference to standard hydrogen electrode okay.

So if we measure any potential with reference to this electrode so what will be the situation so one problem could be considered like this. Let's say a platinum electrode is considered. So if we take a platinum electrode and if we consider that platinum electrode is in a solution and this is in a solution or the electrolyte is having pH of 12 so this is the pH solution pH is 12 and this is and in that situation we are seeing oxygen evolution on platinum electrode.

So these are the three statements. Now since it is pH 12 and since it is oxygen evolution immediately we could make out that the reaction what we have to consider is

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

So these are the reaction we should consider. Now we could see that oxygen evolution can take place if the reaction is anodic. That means the reaction is moving this way so that means anodic reaction we are considering.

And if the potential let's say we are using the standard calomel electrode that time the potential over platinum is measured to be 1.5 volt. So this is the voltage what we have measured with reference to standard calomel electrode so this is the way it is expressed if you are measuring potential with reference to hydrogen electrode. It is always better to mention SHE volt.

And in case of standard calomel electrode so we are writing SCE. Now if we see this that means this is the volt what we are measured on platinum so you remember here platinum is not dissolving. The Platinum is acting as an electrode on top of which oxygen evolution is taking place. So we are taking the reaction this reaction and here since it is anodic reactions we are considering anodic polarization.

Now if we take anodic polarization and if the potential is this now our problem with the part what is to be determined is we have to find out to find over voltage is how much is the over voltage. So over voltage since it is an anodic of course we have to find out neeta a and this is to be found out with reference to Standard Calomel Electrode. So this how to solve this? So let's plot this in order to solve this.

We have to see what could be the correlation of this polarization with reference to Pourbaix diagram. See if we see the Pourbaix diagram for water. So this is E voltage and that is always plotted with reference to Standard Hydrogen Electrode and this is pH so we could see that hydrogen lines are 2 parallel lines this water lines are 2 parallel lines.

Where H2O is stable between these two lines and this is the line which is hydrogen line this is oxygen line. And if we see the pH 7 below pH 7 the reaction which is governing is 4 + 4e = 2 H2O. And then on the right side it is

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

and this side is

$$2H^+ + 2e = H_2$$

and in this side the reaction that happens is water reduction H2 + 2 OH -. So this is the reaction that happens.

When the pH is more than seven or = seven this reaction takes place and now in this zone we have stable water and this particular potential is 1.227 volt. When pH = 0 and this voltage is 0 volt when pH = 0. Now since we have taken pH to be 12 so this is 12 pH now when you are taking 12 pH and we are considering oxygen evolution that means of course we are looking at this particular line.

And since it is oxygen evolution is taking place beyond this line oxygen evolves and below this line hydrogen evolves. So the beyond this oxygen is evolving. So we have to first consider the equilibrium potential at that pH so this is going to be my E equilibrium O2 reaction. So E equilibrium O2 would be we have we know the equation governing this particular line which is nothing but 1.227 - 0.059 pH.

So this is the equation that will tell me the point here so this is volt and remember this is with reference to standard hydrogen electrode. And now once we determine that so this becomes - zero point sorry + 0.19 volt. So we know what is the equilibrium. Now we let’s draw E versus log i plot. So since we have a considered Standard Calomel Electrode these put in first let’s draw those potential axes.

Now, Standard Calomel Electrode has got a potential this becomes + 0.241 volt this is with reference to hydrogen electrode and then hydrogen electrode has got a potential let’s say this side is hydrogen this is Standard Calomel Electrode and this is hydrogen electrode. So this potential is 0 volt so with reference to standard hydrogen electrode so this is 0 volt and here this is 0.241 volt.

So, now we are seeing this with reference to Standard Hydrogen Electrode this potential is 0.519. With reference to Standard Calomel Electrode this value becomes because when standard calomel electrode we are using this is my reference potential so that becomes 0. So 0.519 - 0.241 = 0.278 volt and we have gone up to 1.1 volt. So we Standard Calomel Electrode this is 1.5 volt okay.

So, now if this is 1.5 volt and now this value have we have considered this is the potential what we have considered with reference to a standard hydrogen electrode. So this potential would become 1.5 + 0.241 = 1.741. So that means this potential is way beyond this Potential. So of course oxygen evolution would take place. So now we have to find out the polarization with reference to Standard Calomel Electrode.

So, the standard calomel electrode the over voltage would be this would be the measurement of standard this over voltage so this n a becomes, neeta a becomes 1.5 - 0.278 = 1.222 volt. So this is going to be the over voltage what I would experience. So this become because why because this point corresponding to Standard Calomel Electrode, I will see the voltage to be 78 volt. So this becomes my neeta a and this is the value what we are going to see. So let’s stop here we will continue our discussion and try to see some other problems in our next lecture, thanks a lot.