

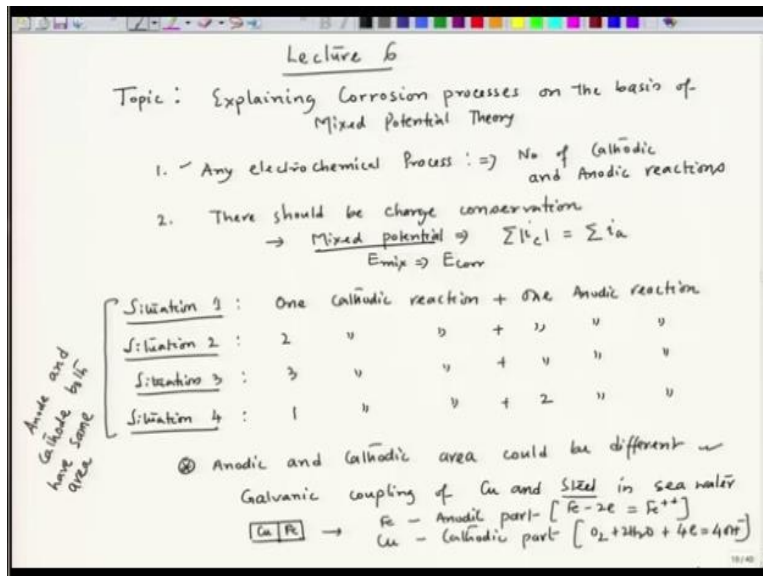
Corrosion -Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology - Kanpur

Lecture - 6

Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Introduction

Hello, everyone let's start lecture 6.

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And the topic since we have already covered little bit of background on the basis of which mixed potential theory has evolved. So, now we will gradually move into a discussing corrosion event on the basis of mixed potential theory. So, the topic could be explaining corrosion processes, I would say on the basis of mixed potential theory. So, when we talk about mixed potential theory we said that it is based on 2 hypotheses one is any electrochemical process can be divided by into a number of simple cathodic or anodic processes.

So that consist of number of cathodic and anodic reaction and there could be situation that one particular reaction, 1 particular electrochemical process let's say zinc dissolution in acid. It can have a situation like there could be 1 cathodic reaction, 1 anodic reaction, there could be situation like multiple numbers of cathodic reaction and 1 single anodic process, cathodic reactions and 1 single anodic process.

So, we will see those situations one by one and then the second part is there should be charge balance, charge, I would say charge conservation. And it also leads to of mixed potential which is lying in between the equilibrium potentials of those cathodic as well as anodic reactions. And at that potential we have a situation which is called $i_c = i_a$ and this summation sign means that it considers all the cathodic reactions the current density corresponding to that and i_a corresponds to the all the anodic processes anodic reactions.

So, this this is the mixed potential which we call it E_{mix} and later will see that this is nothing but $E_{corrosion}$. So, on this 2 hypotheses this mixed potential theory is built on and while we will understand while we discuss this we will see that we need to understand we need to make use of our understanding of polarization. And we have already seen these 2 polarizations one is concentration, one is on concentration polarization another one is activation polarization.

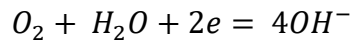
Initially we will see processes based on activation polarization and we will also consider some processes, corrosion processes where concentration polarization is used to understand that particular process. Now as we see that the first hypothesis there could be number of situations. Situation 1, let's say situation 1 there could be 1 cathodic + 1 anodic then situation 2, 2 cathodic + 1 anodic reaction, situation 3 there could be 3 cathodic reaction + 1 anodic reaction, this is one set.

So, that means we can have multiple cathodic and 1 unique anodic reaction, there could be situation like 4 where we can have 1 cathodic + 2 anodic reactions. Fine. So, this is another situation. Now while we consider these 4 situations we are going to assume that anode and cathode both have same area. But when we can have one more situation where anodic and cathodic area could be different that means this is 1 unique situation.

And what do we mean by anodic and cathodic area the area over which cathodic reactions are taking place and the area over which anodic reactions are taking place. So, this situation can arise and this example to this particular phenomena particular instance is also available. For example, if we consider galvanic coupling of let's say consider we consider galvanic coupling of copper and steel in and this steel means plane carbon steel in sea water.

Now if you go back and look at some of the lectures in corrosion 1 you will see that when cathodic let's say this is copper and this is steel, steel I consider to be Fe. So, if they are having similar area then the corrosion of anodic component which is nothing but the iron, iron is the anodic part and copper is cathodic part that time of course the anodic part would corrode and cathodic part would get protected because the cathodic reaction.

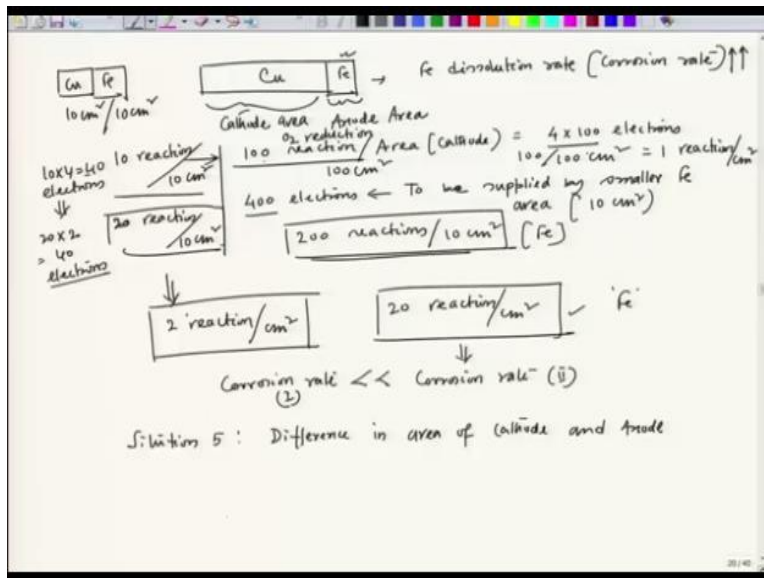
And in this case the cathodic reaction is



This is the cathodic reaction that happens on that copper surface, galvanic series if you see in the sea water is situating on top of iron that what copper would act as cathode. And the current will flow from copper to iron in the conductor but if we consider electrolyte then current will flow from iron to copper in the electrolyte and the anodic part anodic reaction would be this will be the anodic reaction.

So, if they have similar area the anode would corrode but the corrosion rate would be not that significant.

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But if we situation where copper area is large and iron area is small that time we come across a serious corrosion of iron, this part would corrode at a very very fast rate. So, in this case iron dissolution rate, so we call it corrosion rate would it would increase seriously. The reason is since

we have a very large cathode area, this is the cathode area and this is the small part is anode area very large number of cathodic reaction would happen on copper surface.

And in order to supply electrons for those cathodic reactions, so this cathodic reaction in order to supply those 4 electron per oxygen molecule reduction, iron has to dissolve. Now if there are 100 reactions over the area of A cathode area, so this 100 reaction needs 4 into 100 electrons and this of course cathodic reactions, oxygen reduction in neutral solutions. So, these many electrons need to be supplied by the smaller anodic area.

So, this 400 electron to be supplied by smaller iron area, so that means had it been equal area, so the 100 reactions is happening over area of let's say 10 centimeter square on the copper surface. The same 100 reactions are taking place 100 not 100, so it will be 200 because for the iron oxidation we need 2 electron to be taken out. So, that means 200 reaction need to take place on the 10 centimeter square iron surface.

But in this case if this is 100 centimeter square and this is 10 centimeter square, so then if I consider 2 electrons which are taken out from iron. Then 200 reactions per 10 centimeter square need to take place on iron surface and here it is 100 reactions per 100 centimeter square. So, we could see that in the beginning we had 100 reaction per let's say 10 centimeter square. Sorry.

So, if we consider equivalent reaction over this 10 centimeter square of the cathodic area, so the equivalent area would amount would be 10. So, that means here it is coming 1 reaction per centimeter square, so it would lead to 10 reactions part. So, now if I consider in the beginning let's say equal area, so this is copper, this is iron and 10 centimeter square for copper and 10 centimeter square for iron.

Then the number of reaction on copper would be 10 divided by 10 centimeter, so 10 reactions per 10 centimeter square area. And similarly for iron it will be 20 reactions per 10 centimeter square areas because when it is 10 reactions per centimeter square, so that means we need 10 into 4 electrons. So, which will be given by 20 reactions into 2 equal to 40, so this becomes 40, this

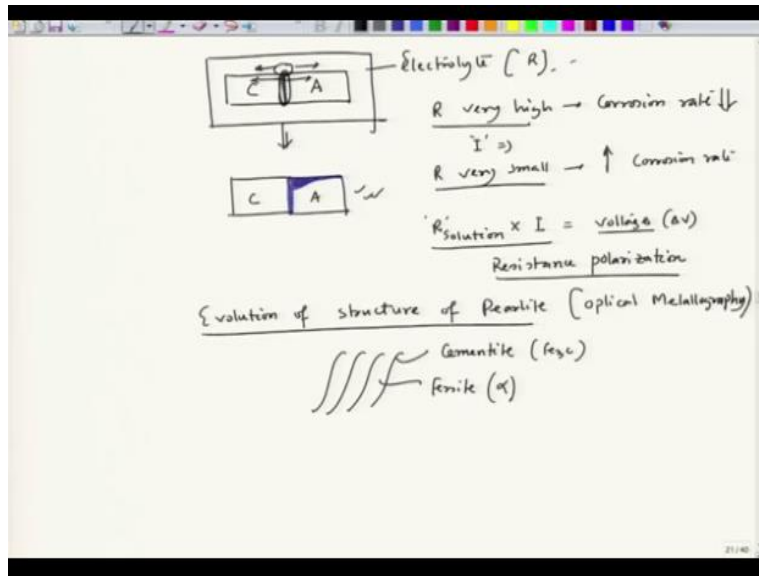
becomes 40. So, the 40 electrons from iron surface because iron we are taking out 2 electrons, so that means here 20 reactions per 10 centimeter square.

Now when the area of the copper surface has increased 10 times which is 100 centimeter square, now we are having 100 reactions because those reaction is statistically distributed. So, now, so this 400, so that means 100 reactions means we need to take 400 electrons. And this 400 electrons to be supplied by the smaller iron area which is 10 centimeter square, so that means 200 reactions by 10 centimeter square.

So, we could see the this amount and this amount if we compare, so that means here we have 2 reactions per centimeter square and here it is 20 reactions per centimeter square. So, that means for iron if we compare in those 2 situations this case we have larger electrons, larger number of electrons or greater number of electrons need to be taken out. So, the corrosion rate in this case okay in this case is much greater than corrosion rate, this is let's say case 1, this is case 2, case 2 the corrosion rate is much higher.

So, this is the situation we have understood before, now this particular phenomena, this particular observation we can also explain. Let's say this is situation, so here up to situation 4 we consider, so this situation 5 difference in area. We can understand this particular situation with the help of mixed potential theory okay, so this is another situation. Now while discussing this particular area factor, now though we say that the corrosion of the anodic portion when areas of cathode and anodes are similar is not that significant but there is a little insight to it.

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because when we consider let's say we consider equal area, so this is cathode, this is anode. C means cathode A means anode. Now if you have an electrolyte around that this is here we have electrolyte that time electrolyte would have some finite resistance this is R resistance. So, whenever we have a resistance in a path the current also faces obstacles this resistance actually obstacles to the current flow.

So, when you have obstacles then of course the current flow will be hindered and we will not have the degree of dissolution of the anodic portion had there been no resistance. So, in 1 case let's say resistance is very high, so that case corrosion rate would be very low because the current is having a resistance to flow. Now if R is very small, so then of course reverse will happen the corrosion rate will go up.

The classic example is let's say if we try to see the corrosion of any metal in a very pure water deionized water that case we all is come across the very low corrosion rate as compare to the situation when that water is contaminated with lot of ions. Because those ions allow that resistance to drop the solution resistance to drop and that allows the easy current flow on the corrosion rate goes up.

Now when we consider this situation this is the galvanic contact now as we go away from this even if the electrolyte have got a low resistance because of that contamination or presence of ions.

Now if we go away from this region as we are going away from this region the resistance increases. So, that means the corrosion effect due to the galvanic coupling will be felt more near this junction point.

Because near that junction point resistance offered by the electrolyte would be less as compare to the resistance offered by the electrolyte if we go away from that contact portion. So, that means if we have a situation like this then I would have a typical corrosion process, let's say this is anodic this is cathodic that case the corrosion process the typical corrosion process would be this portion this near to this junction the corrosion here would be more and the corrosion pattern would look like this.

So, this is the corrosion pattern, fine this blue shaded region is the corrosion pattern and the cathode of course it is being protected because all the cathodic reactions are taking place on that surface. So, the corrosion is always more near the junction of galvanic coupling this is due to the resistance affect or the electrolyte resistance affect, just to intimate here that because of the resistance and if I multiply R .

So, this is resistance solution resistance and if I multiply the current I will get voltage. So, this is also a drop we consider in that circuit, so this is called resistance polarization. Because of the resistance of the electrolyte I will have this voltage ΔV and these ΔV will take the equilibrium potential to some other potential okay, so that is resistance polarization will talk more on this resistance polarization later on.

But right now we assume that the resistance offered by the electrolyte is insignificant. So, this particular situation can be there could be there is a classical example of this situation in physical metallurgy. The evolution of structure of pearlite. So this particular and of course optical metallography. So, when we will do optical metallography we will have a typical micro structural pattern.

So, it is a lamellar micro structure where these black regions are cementite and these white regions are ferrite which is nothing but α and this is Fe_3C . Now why do we get a typical appearance

that the cementite becomes black and the ferrite becomes bright that can be explain on the basis of this particular phenomenon there we will take this explanation to our next lecture, thank you.