Corrosion - Part I
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Lecture – 38
Mixed potential theory–II

So, in the last lecture we just started discussing on Mixed potential theory. And this lecture is lecture number 38.

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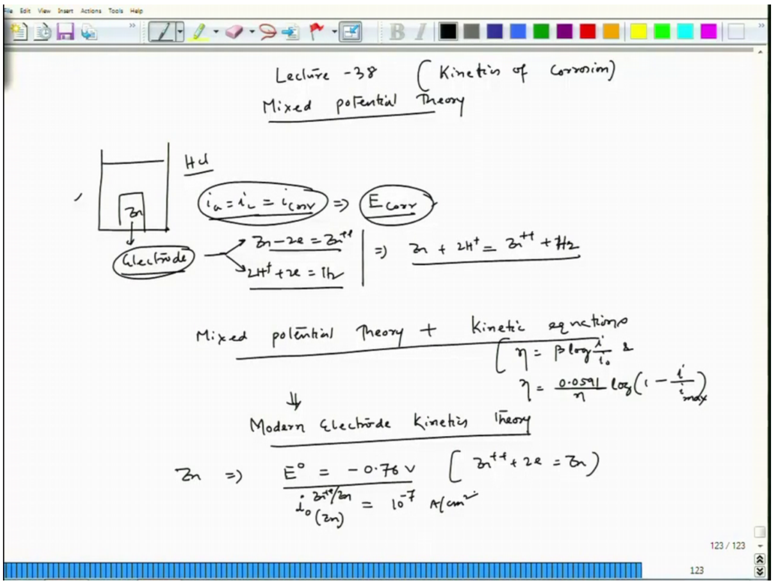

Lecture -38 (Kinetics of Corrosion)

Mixed potential Theory

$i_a = i_c = i_{corr} \Rightarrow E_{corr}$

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

$2H^+ + 2e = H_2$

$\Rightarrow Zn + 2H^+ = Zn^{++} + H_2$

Mixed potential Theory + Kinetic equations $\left[\eta = \beta \log\frac{i}{i_0}\right.$ &

$\eta = \frac{0.0591}{n} \log\left(1 - \frac{i}{i_{max}}\right)$

$\Downarrow$

Modern Electrode Kinetics Theory

$Zn \Rightarrow E^\circ = -0.76\,V \quad [Zn^{++} + 2e = Zn)$

$i_{0\,(Zn)}^{Zn^{++}/Zn} = 10^{-7}\ A/cm^2$

And here we will continue kinetics of Corrosion. And now we are our discussion mode would be mixed potential theory.

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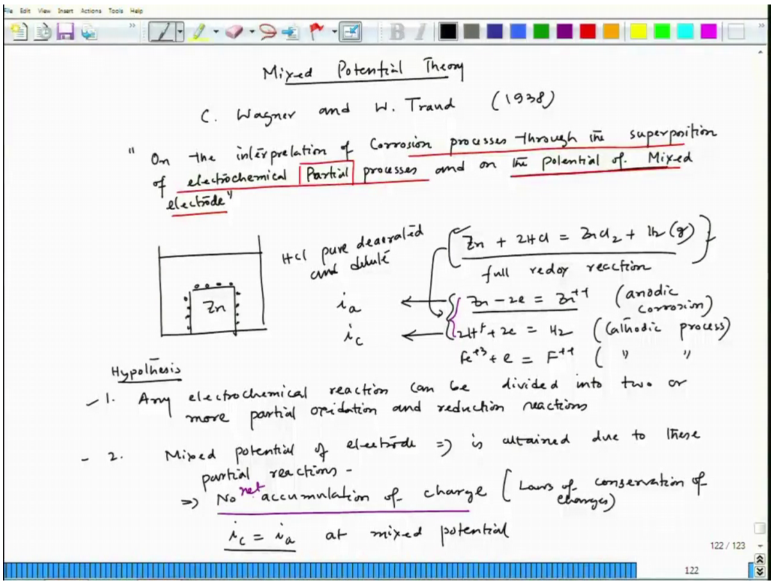

Mixed Potential Theory

C. Wagner and W. Traud (1938)

" On the interpretation of Corrosion processes through the superposition of electrochemical Partial processes and on the potential of Mixed electrode"

HCl pure deaerated and dilute

$Zn + 2HCl = ZnCl_2 + H_2 (g)$

full redox reaction

i_a ← $Zn - 2e = Zn^{++}$ (anodic corrosion)

i_c ← $2H^+ + 2e = H_2$ (cathodic process)

$Fe^{+3} + e = F^{++}$ (" ")

Hypothesis

- 1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions
- 2. Mixed potential of electrode => is attained due to these partial reactions -

=> No net accumulation of charge (Laws of conservation of charges)

$i_c = i_a$ at mixed potential

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In fact, in the last lecture if we see that we have put forward 2 hypothesis and those two hypotheses are basically any electrochemical reactions this is first hypothesis can be divided into 2 or more partial oxidation or reduction reactions.

And the second hypothesis says that because of this process, that means more partial oxidation and 1 or 2 or more partial oxidation and reduction reactions, the electrode will achieve a mixed potential which is attain due to this partial reactions definitely and there should be no net accumulation of charges. And this no net accumulation of charge would basically indicate the laws of conservation of charge and that time i a should be equal to i c. And that i a equal to i c means, there is for example a metal, when it is electrically isolated and then there should be no current flow. In fact, if I try to look at this particular example where, zinc is immersed in Hcl.

So, actually there is no net current flow in the zinc rather, when this mix potential is achieved i a equal to i c. And that also indicates i corrosion because, at this rate the corrosion will take place. And that also corresponds to a mixed potential which is also called Ecorr. Since zinc is acting as that electrode. And on top, you have cathodic as well as anodic reaction, zinc minus 2e equal to zinc plus plus and H plus plus 2 e equal to H 2.

So, this leads to 1 redox reaction which is zinc plus 2 H plus zinc equal to zinc plus plus plus H 2. So, and these electrode would achieve, unique mixed potential which is not same as the potential for zinc zinc plus plus, that is single redox reaction this half cell reaction they would also have their reversible potential to begin with. And this potential is not the same as that particular begin with the potential where from it has began to shift from that potential to this Ecorr due to this combined reactions.

So, now we see that the concept of i corr and Ecorr. Now let us try to understand this mixed potential theory and kinetic reaction, kinetic equations rather in the form of and i max these two equations. If we combine them we would see that it leads to modern electrode kinetics theory kinetics effects rather, electrode kinetics theory or effect.

So, it would lead to modern electrode kinetics theory, so this combination of these 2. Now to begin with when we have this situation let us say that for zinc, it would have a potential E 0, which is minus 0.76 volt and in that time I have zinc plus plus plus 2e equal to zinc for this reduction reaction is actually happening in the standard state. Let us assume that in the beginning it has zinc ions and then we have this potential to achieve which is the equilibrium potential.

So, at that potential I have i 0, which is exchange current density of course, it is on zinc surface zinc plus plus zinc has got some value it is let us say, it is values around 10 to the power minus 7 ampere per centimeter square to begin with.

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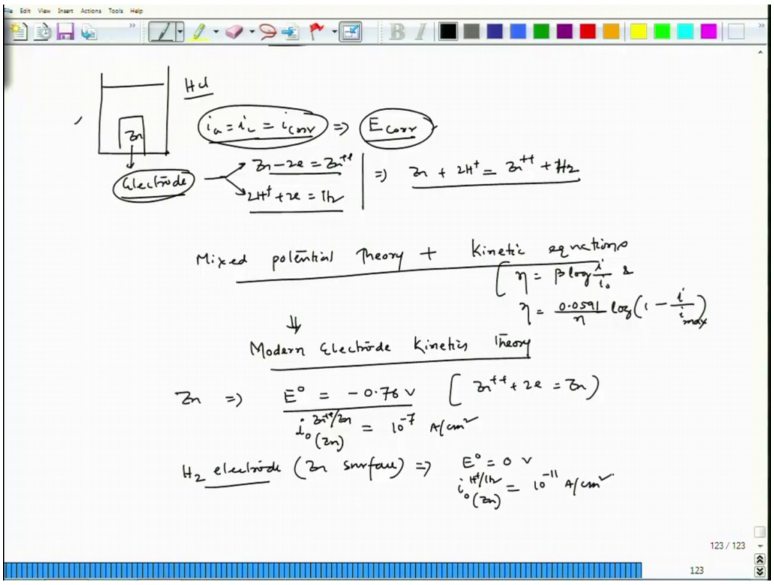

$\boxed{i_a = i_c = i_{corr}} \Rightarrow \boxed{E_{corr}}$

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

$2H^+ + 2e = H_2$

$\Rightarrow \underline{Zn + 2H^+ = Zn^{++} + H_2}$

Mixed potential Theory + Kinetic equations

$\left[\eta = \beta \log \frac{i}{i_0} \right.$ &

$\eta = \frac{0.0591}{n} \log\left(1 - \frac{i}{i_{max}}\right)$

$\Downarrow$

Modern Electrode Kinetics Theory

$Zn \Rightarrow \underline{E^\circ = -0.76\,V}$ $\left[Zn^{++} + 2e = Zn \right)$

$i_{0\,(Zn)}^{Zn^{++}/Zn} = 10^{-7}\ A/cm^2$

H_2 electrode (Zn surface) $\Rightarrow$ $E^\circ = 0\ V$

$i_{0\,(Zn)}^{H^+/H_2} = 10^{-11}\ A/cm^2$

Now, similarly if I consider hydrogen electrode, which is forming on zinc surface, so hydrogen electrode the standard hydrogen electrode what we have seen before it isbasically platinum electrode or platonized platina electrode is used. But on zinc surface, we can also constitute an hydrogen electrode and that time I have E0 to be 0 volt and I 0 of hydrogen exchange current density which is actually on the zinc surface would be let us say some value around 10 to the power minus 11 ampere per centimeter square.

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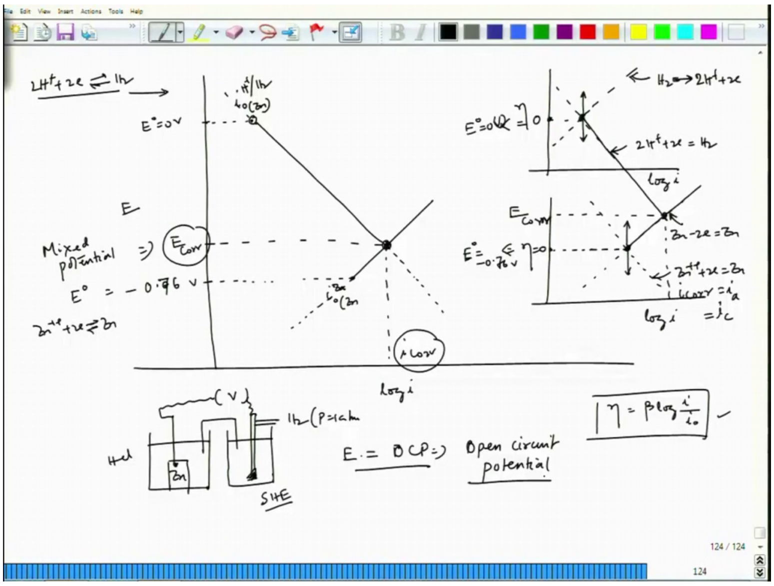

If I try to plot them on Log i versus potential axis let us say this is my zinc potential which is 0.76 minus volt which is equivalent to E0. And this is my E0 for volt for hydrogen. Now exchange current density of hydrogen on zinc surface i 0 zinc, H 2 and exchange current density on zinc surface for zinc reaction so this is I 0 zinc, I simply put zinc without putting that zinc plus plus plus zinc because, it is taking little bit of space.

This is the situation in the beginning to begin with. So, here it indicates H 2. This is non corroding reversible situation at this point. Here also this is zinc plus plus plus 2 e equal to zinc. This is non corroding and reversible condition and this was the potential in the beginning for both these half cell reactions because we have to consider these two half cell reactions. This is oxidation and this is reduction these are basically two half cell reactions and to begin with we have assumed that they are starting from the standard potential.

Now, for both the cases for hydrogen and zinc let us say you let us draw that, this is for hydrogen this is for zinc; if I try to see over voltage as a function of log i, this is let us say 0 over voltage is equal to 0, which is actually indicating e 0 to be 0 volt and here eta equal to 0, this is indicating 0, which is actually indicating e 0 for e 0 equal to minus 0.76 volt for zinc. They would have their own cathodic and anodic polarization plot. And let us say that we are in the activation polarization region, that means, in the low current region because, concentration polarization starts at a very high current density.

So, if I consider the activation polarization for hydrogen reactions, it has also has its own cathodic and anodic reactions. So, this is cathodic part, anodic part for hydrogen. So, this is 2 hydrogen equal to 2 H plus plus 2 e and this is cathodic part H 2 and in case of zinc, this is anodic part which is zinc minus 2 equal to zinc and this is cathodic part zinc plus plus plus 2 equal to zinc.

So, they have their own cathodic as well as anodic tafel plots. I would say that this equation eta equal to beta log i by i 0. According to this equations they have their own plots. But since they are potential as far off are far off, 1 is at 0 and another 1 is 0. minus 0.76. As per this mixed potential theory, if I look at that mixed potential theory it says that the mixed potential of electrode will be achieved due to partial reactions.

Now, there are 2 different potentials, so they must achieve some potential which is in between these two potential and that is unique for this particular situation. How can they achieve? That can only be achieved for example, if it goes anodic side and if it goes cathodic side, they cannot achieve a single unique potential because, their potentials are basically moving away from each other. So, the only way they can achieve a mixed potential by moving this one on the anodic side and this one on the cathodic.

Then only they can reach unique potential. And when they would like to do that so; that means, they would follow their own anodic polarization plot and cathodic polarization plot as per these equations. So, in this case, in case of zinc case this polarization would follow according to this line and here the polarization of hydrogen reaction would follow this line. So, now, they will meet somewhere here.

Once they meet somewhere here, you see that the potential is Ecorr which is in between this and this. And for that you could see that polarization for zinc is on the positive side and the polarization for hydrogen is on the negative side. So, hydrogen is cathodically polarized and zinc is anodically polarized, in order to achieve this mixed potential.

Now, interesting thing the second postulate or the second hypothesis is also met here. If you see this it says that, when it reaches that mixed potential there is no net accumulation of charges. So, that means the current density for cathodic reaction which actually accepts electron and then current density for anodic reaction which actually leaves electron, these two equation these two rates are same. So, that means, the rate at which electrons are consumed due to cathodic reaction which is hydrogen evolution reaction is same as the rate at which electrons are generated by this zinc dissolution which is anodic or corrosion reaction and they are meeting at this Ecorr point.

And corresponding current density should be icorr which is nothing, but i a equal to i c. And whenever we have this situation there is whatever electrons are generated are basically consumed. So, there is no net accumulation of charges for this electrically isolated zinc piece in Hcl medium. So, if I try to plot here. So, it would be, so this is Ecorr and this is icorr, this is the crux of mixed potential theory.

So, this potential is called mixed potential. And the system would like to stay here and the corrosion of zinc would take place as per the rate decided by this icorr. Now how do I get this icorr and Ecorr experimentally? Now whenever this zinc plate is zinc block is put up put immersed in Hcl medium after some time it will try to achieve this because, this rates are going at a different this icorr and this i a as well as i c, they are actually taking time because finally, it has to reach to this constant rate and then there will be no net current flow in the system.

So, the system this zinc would remain at this potential. So, if I try to measure this potential of zinc without sending any current through that particular zinc plate by a standard hydrogen electrode. So; that means, if we have this zinc Hcl medium and then I connect it to hydrogen standard hydrogen electrode and I connect a wire with this zinc and then if I try to measure the potential, it gives me potential, after achieving this potential these potential we call it without sending current remember without sending current we are not connecting that circuit. So, that time we see that the potential is termed as OCP Open Circuit Potential.

Remember once we try to measure this same potential with a standard hydrogen electrode then initially that potential is actually switching from one potential to another until unless it reaches to this potential. So, once we allow little bit of time we see that the potential is actually potential has achieved this particular Ecorr or OCP and it is maintaining at that potential with time.

So, this open circuit potential is the new point from where we have to consider the polarization during experimentation. And that is what in the lab we do polarization experiment and that time we give we try to achieve this open circuit potential which is rather stable open circuit potential and then that one would be considered as a 0 over voltage, the new 0 over voltage and then we try to go positive or negative side and then try to see that what is my what is my net current flow or i applied. In case of single electrode system, we see we have seen that the actually in case of single electrode system, what we have done?

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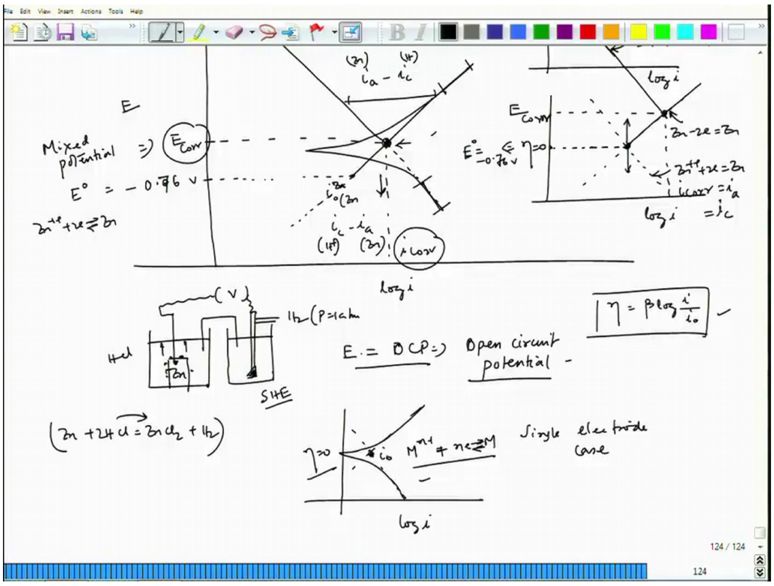

So, this is eta equal to 0, this is i 0, these are the 2 sides and then we saw that if I send applied current; that means, when the rate of cathodic anodic reactions are different then the plot would look like this So, this is my i 0 and when i 0 is achieved there is no net current flow in the.

Similar way here it is M N plus equal plus ne equal to M as well as this forward as well as backward reactions; this is a non corroding situation or single electrode case. But, here we have 2 different reactions, it is not single electrode reaction, one reaction is zinc dissolution, another one is hydrogen evolution. And this point would be the new set point the way we have considered eta equal to 0 for single electrode case.

Or then if I try to do the same experiment, we will get a curve like this. And then the linear portion we have to consider, this linear portion and the linear portion we have a extend and then finally, we will achieve to this point. And this linear portion is achieved the way we have done for this case, it is the same way in this case we have to consider i c minus i a and this is for hydrogen and this is for zinc. And in this case also we have to consider the difference between i a minus i c and this is for zinc and this is for hydrogen.

So, that is what we get this Tafel plots and accordingly we can extend this linear portion and these 2 linear portion backward and we can achieve this particular point and that is basically nothing, but icorr and Ecorr. This is one important information what we achieve what we what we get by doing Tafel experimentation. So, these particular part will come in the corrosion part 2, but still when we have considered this we are just explaining little bit.

So, if I try to look at the mixed potential theory in nutshell we could see that the new potential is achieved and that new potential is when it is achieved due to the polarization of those partial reactions; one definitely would be cathodic, another one is definitely anodic polarization in this simple situation where this entire reaction is divided into two parts. One is one single cathodic reaction, another one is one single anodic reaction.

Then once we reach to that mixed potential that mixed potential at that mix potential, I could see that if it is isolated metal block in that particular solution there is no net current flow and that can achieve if I could see that i a equal to i c at this point. That is what we have understood in the in these particular diagrams. In addition to this remember this is an open system. If it is an open system, so since this is open system the hydrogen bubbles are forming and they are actually going out.

Now, if we have it is habit in a closed system, definitely this reaction would arrive at equilibrium. This reaction will arrive at equilibrium. That time also it will be Ecorr and i 0, which is equal i naught i 0 is basically icorr the same point will be achieved. But if it is an open system, if we do not change the temperature, then hydrogen will keep on going out and then this reaction will go forward. So, the zinc will keep on corroding.

So, that time it will not be equilibrium situation, it will be non equilibrium spontaneous situation; since hydrogen is going out. So, now, let us consider some of those effects of mixed potential theory; some of those consideration of kinetic factors.

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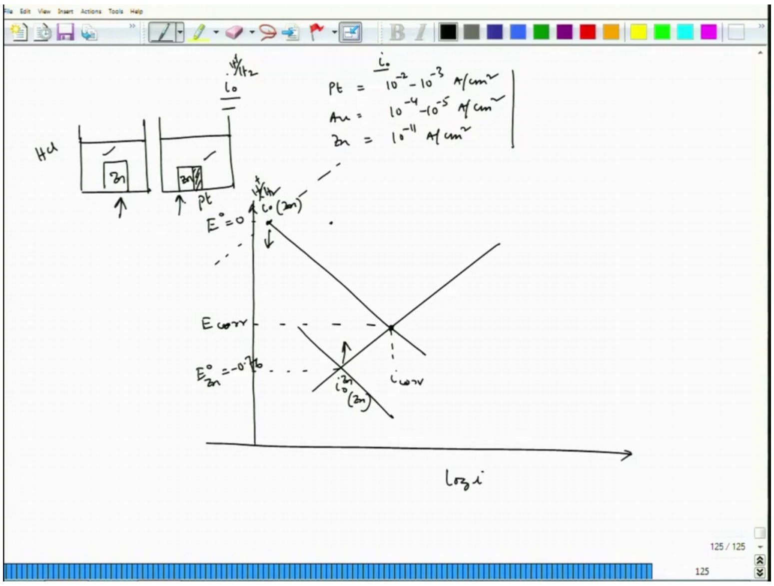

So, one such kinetic factors is definitely i 0. Now i 0 for let us say hydrogen evolution reaction on different metal surface surfaces are different. For example on platinum surface as we have seen its value is around 10 to the power minus 2 to 10 to the power minus 3 ampere per centimeter square. For gold it is around 10 to the power minus 4 to 10 to power minus 5 ampere per centimeter square and for zinc for this hydrogen evolution reactions remember this i 0 value I am just putting this i 0 value it is around 10 to the minus 11 ampere per centimeter square.

All these values would have definite effect on the zinc corrosion rate. Now how we are considering? For example, if we have a particular beaker, let us say 2 beaker, 1 beaker we have a zinc plate, zinc block and the concentration of both the electrolytes that is acid medium Hcl is same and another case I have a zinc in connection with a platinum plate, this is let us say platinum plate and this is zinc.

Now, we would see that in this case we would have very very high rate of corrosion of zinc, why? This can be explained by using mixed potential theory. So, when we try to see these 2 situations, we have to first look at the diagram. Which the diagram, the diagram what we have shown here these diagrams are called Evans diagram. So, this Evans diagram are basically not considering the practical diagram which is i applied versus potential or potential versus i applied, this is basically potential versus log i as per this polarization or the Tafel equation. We will not consider there this what happens if we go on positive side or negative side and what would be the variation of i applied.

So, that case we have to again consider this for zinc this is E 0 zinc and this is i 0 zinc, on zinc surface and then we have E 0 for hydrogen which is 0, this is minus 0.76 volt and then we could see that this is my i 0 of hydrogen reaction on zinc surface. And accordingly we are achieving the mixed potential theory, as per the theory this is the potential what we would achieve, this is the mixed potential which is Ecorr and this is icorr, isn't it? So, that is what we have seen.

Of course, it will have its own anodic over voltage also, but since as per the discussion what we have seen that it will go to negative side and this will go to positive side, isn't it? Now if we have another reaction this in this case, this is the situation this diagram this Evan's diagram is indicating this situation. Now in this situation it will be little complicated and if I have understood this mixed potential theory it can be analyzed very easily, but we will take it up in our next lecture and let us stop here.

Thank you very much and wait for the next lecture where we will talk about this effect of increase in exchange current density for a particular cathodic reaction by changing the metal surface and then its effect on corrosion of metal. Let us stop it.

Thank you.