Corrosion – Part I
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Lecture - 30
Exchange Current Density and Standard Hydrogen Electrode

Let us start lecture 30.

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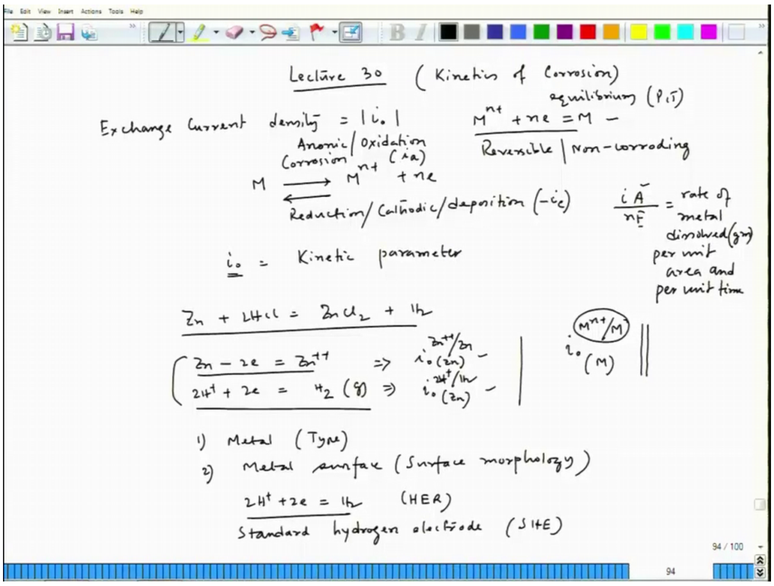

Lecture 30 (Kinetics of Corrosion)

Exchange Current density $= |i_0|$

equilibrium (P, T)

$M^{n+} + ne = M$ –

Reversible | Non-corroding

Anodic / Oxidation (i_a)
Corrosion

$M \rightarrow M^{n+} + ne$

Reduction / Cathodic / deposition ($-i_c$)

$\frac{i\bar{A}}{nF}$ = rate of metal dissolved (gm) per unit area and per unit time

i_0 = Kinetic parameter

$Zn + 2HCl = ZnCl_2 + H_2$

$Zn - 2e = Zn^{++} \Rightarrow i_0^{Zn^{++}/Zn}(Zn)$ –

$2H^+ + 2e = H_2\,(g) \Rightarrow i_0^{2H^+/H_2}(Zn)$ –

$i_0^{M^{n+}/M}(M)$

1) Metal (Type)

2) Metal surface (Surface morphology)

$2H^+ + 2e = H_2$ (HER)

Standard hydrogen electrode (SHE)

And will continue our discussion on kinetics of corrosion and we have been discussing on current density and we saw the concept of i 0 also which is called exchange current density, which appears when for a particular redox reaction. For this particular redox reaction when it reaches equilibrium.

So; that means, then this is a kind of situation which is reversible as well as this is non corroding. Why it is non corroding? Because, when a metal is dipped in an aqueous medium the metal ion comes out from the metal surface as well as the reverse reaction which is the metal ion gets reduced to metal.

These 2 processes happen at the same rate and that is the condition when we have the exchange current density, the metal ion formation which is M goes to M n plus plus n e this is corrosion or we can take it as anodic reaction or oxidation reaction. And then this backward reaction which is reduction or cathodic reaction or deposition reaction both this process happens happen at a very same rate and the rate is termed in terms of i which is the exchange current which is basically the current density.

Since, we have seen that i A divided by n F is nothing, but the rate of metal dissolved in ground per unit area and per unit time. Where A is nothing, but atomic weight of that particular metal, n is the number of electrons that participate for this reduction reaction or oxidation reaction F is 1 faraday.

So, this particular term we call it as i c and this one as i a; i a is nothing, but the corrosion current density. And in order to indicate the direction of flow of these 2 currents we have put a negative sign in front of i c, these negative sign does not indicate that the value of current is current density is negative. It indicates that it flows opposite to the anodic current or the corrosion current density.

Now, when they reach equilibrium we come across i 0 which is the exchange current density and that is basically the reversible condition and non corroding situation because, whatever metal ion forms that metal and goes and deposit on the metal surface.

Now, once we know this i 0 we need to look at little bit carefully on this i 0 because, this is i 0 is a very very strong and fundamental kinetic parameters. And this parameter would have a huge importance on the corrosion of a particular metal in a particular medium. And that will see little later when we start discussing on mix potential theory.

Now, if you see this i 0, this i 0 we have said that this is specific to a particular redox reaction. It is not for the complete cell reaction, this is for a half cell reaction I would say. For example, if we take this consideration like zinc plus HCL equal to zinc chloride plus H 2. For this reaction it can be broken into 2 half cells, one is zinc minus 2 e equal to zinc plus plus and 2 H plus plus 2 e equal to H 2 this is the gas that forms on the zinc surface.

So, it is experimentally we have seen that when zinc is dipped in HCL, let us say that HCL is pure HCL and it does not contain any oxygen so; that means, it is a deaerated solution that time we have these 2 half cell reactions. So, for each half cell reaction we will have corresponding i 0 and in this case how do I how do I denote this? It should be denoted like this. This is i 0, this is also i 0 for H plus H 2.

So, for the reduction, reaction we are considering this is the notation would use and now question is this i 0 indicate some equilibrium reaction of that particular metal ion disposition or dissolution or hydrogen ion formation or hydrogen gas formation.

Now, those reactions happen on a particular surface and in order to indicate that this is taking place on that on a particular surface we have to also indicate on which surface this is taking place. So, in the bracket we have to mention zinc because, on the zinc surface only that zinc dissolution takes place as well as hydrogen evolution also takes place on the zinc surface so, zinc.

So, now, exchange current density i 0 on a metal surface and then. So, this is the notation and now these particular redox reaction which is half cell reaction. So, for examples this is for a half cell so, this is for a half cell and they are combination they are may constituting one complete full cell reaction. Now, these particular reaction might change it could be metal dissolution or it could be any other cathodic or anodic reactions that are taking place on this metal surface.

For example, in this zinc case the zinc dissolution is taking place on zinc surface and that is what we are considering i 0 for zinc dissolution on zinc as well as hydrogen evolution is also taking on taking place on zinc surface, that is what we are considering hydrogen evolution exchange current density on zinc surface also.

Now, when we consider this another important aspect is since we are considering the material aspect. So, of course, this exchange current density would depend on materials. Similarly, it would also depend on the surface condition. So, these are 2 important issues we would like to consider. So, one is metal surface and of course, a kind of metal.

So, let us put it in 2 ways, one is metal, which is type depending on zinc platinum or palladium or gold this i 0 would change for a particular reaction. Second is metal surface so, the metal surface condition would also change the i 0 for a particular reaction. So, this is surface condition I would say, surface morphology morphology. So, let us look at this 2 situations, one case is metal surface depending on the type of metal. Let us say we consider this reaction, this hydrogen evolution reaction state, this we call it HER, Hydrogen Evolution Reaction.

Now, depending on this reaction we can constitute a cell which is called Standard Hydrogen Electrode, which we in short we call it as SHE. And when we talk about standard electrode, standard hydrogen electrode we need to also see the how it how what is the importance of the standard hydrogen electrode as well as it is constitution.

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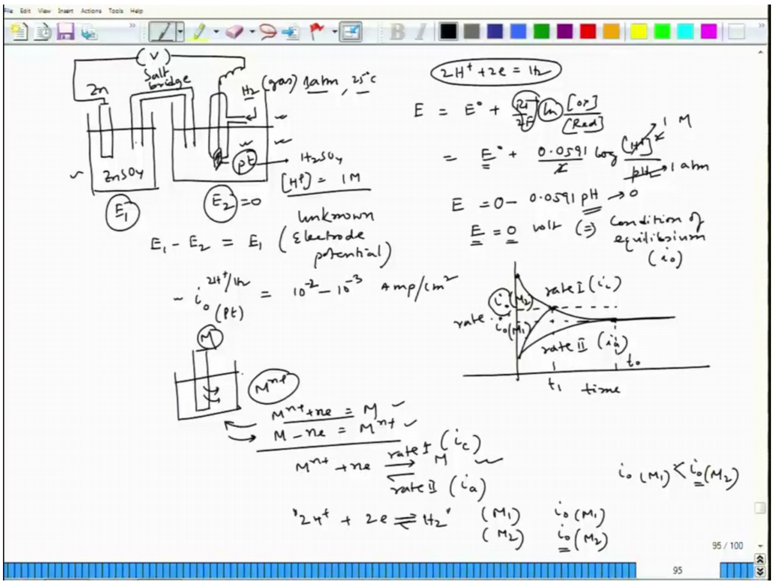

So, it looks like this, symmetrically you have acid solution where you can make it as H 2 SO 4 where H plus ion concentration is maintained at 1 molar 1 mole.

Now, this is the glass, simple a glass electrode where this is a metal wire which is connecting a platinum plate which is dipped in acid medium and through this route we send hydrogen gas and that pressure is maintained as 1 atmosphere.

And when you do that that time we get potential would be E 0 plus RT 2F ln OX red, which is E 0 and if we consider 25 degree Celsius and 1 atmosphere pressure. So, then this quantity would become 0.0591 divided by 2 and that time this quantity this is be in terms of log instead of log and then OX is nothing, but H plus ion concentration square and pH 2 the reaction is H 2.

Now, this is maintained at 1 atmosphere. So, it will become this is 0 minus 0.0591 pH. So, these 2 they will get canceled so, this is the equation. So, finally, we are getting E equal to minus like this. And I would like to put this 0 value.

Now, when this is maintained at 1 mole 1 molar solution so, then this goes to 0 so, E equal to 0 volt. So, now, once we maintain this E 0 so, if it is connected to let us say another cell with a salt bridge, this is the salt bridge. And if we have a zinc rod here, see if we connect like this is zinc sulfate we would see some voltage here and this voltage is the difference between the electrode voltage between this 1 and this 2.

So, here we have electrode voltage which is E 2 now if we maintain this situation 1 molar as well as 1 atmosphere hydrogen pressure, then E 2 would be always 0 and that is what the E 1 is nothing, but E 1 minus E 2 which is the difference between these 2 electrodes is equal to E 1. So, now, this becomes my unknown electrode potential isn't it? So, that is the use of the standard hydrogen electrode.

And why we are calling standard because, we are maintaining 1 atmosphere pressure and 25 degree Celsius and the activity or the concentration of hydrogen ion is also maintained at 1. So, now, in order to maintain so, we have to make sure that this particular cell stays at 0 volt all the time; that means that standard reduction potential for this reaction in this particular hydrogen electrode is to be maintained at 0 volt. In order to do that, we have to maintain those concentration as well as pressure.

Now, if it and this is taken as platinum now if we take some metal and why we take platinum? Because, the on platinum surface it is around 10 to the power minus 1 to 10 to the power rather 10 to the minus 2 to minus 3 ampere per centimeter square, which is considered to be very very high current density.

Now, what is why we should choose rather we should choose some particular metal where this hydrogen reduction exchange current density should be very very high. Now, what do you mean by very very high and what is the advantage of very very high value of i 0 for this particular hydrogen reduction reaction or hydrogen reaction which is the half cell reaction?

Now, when you have this, then if we see the rate part, let us say this is the time and this is the rate, once the metal is introduced in a solution. So, this metal ion would form or other way around if we have the solution maintained at with the metal ion concentration in maintain with some metal ion presence there. So, then there could be reduction reaction as well as oxidation reaction. So, reduction reaction is nothing, but M n plus

plus n e equal to M or oxidation reaction M minus n e equal to M n plus. So, these two reaction would happen.

Now, let us say initially the reduction reaction would be very high because we have already the presence of M n plus, depending on it is reduction potential M n plus would try to reduce and then form M. And as this reaction is starting this reaction would also start, but they will be sluggish in the beginning, but as the time passes on they will pick up the rate will pick up.

So, and the forward reaction which is this reaction the rate would reduce. So, M n plus plus n e M this rate initially would be very high because, already they are M n plus ion presence and then initially this particular reverse reaction which is M going to M n plus would be less because initially if I assume that the first the M n plus would ion would get reduced first and then metal would release electron and then form metal ion.

So, this is rate 1 and this is rate 2. So, rate 1 is nothing, but i a sorry i c because this is the cathodic reaction and rate 2 is i a in terms of current density if we like would like to express them. So, the i c, the first rate is this one and then second rate this is rate 2, this is rate 1. Now, at some time after some time they will reach equal and then they maintain if we do not disturb the equilibrium because they would reach equilibrium.

So, this is the condition which is basically the equilibrium rate and or i 0. This is i c, this is i a. And now interestingly you see this i 0 is arriving at this time, this is the time let us say t 0 and this of course, happens in a metal surface that is for same metal surface. So, this is for this particular redox reaction. So, similarly, if we can consider this hydrogen reaction here also this forward reaction and backward reaction they will reach equilibrium after some time on a particular metal surface let us say metal 1.

Now, this on metal 2, this is i 0 on metal 1, i 0 on metal 2 and when we talk and consider about i 0 metal 2. If i 0 metal 1 is less than i 0 metal 2, it means that equilibrium on metal 2 for this reduction reaction or that this particular half cell reaction would arrive at a much fast time. So, means it will arrive here so; that means, this is my mu i 0, you see the i 0 this is on metal 1, this is metal 2 so; that means, i 0 in case of metal 2 arrives at a much faster time this is let us say t 1.

Now, what it indicates? It indicates that that the equilibrium achieves or is arrived at much quickly in case of higher exchange current density.

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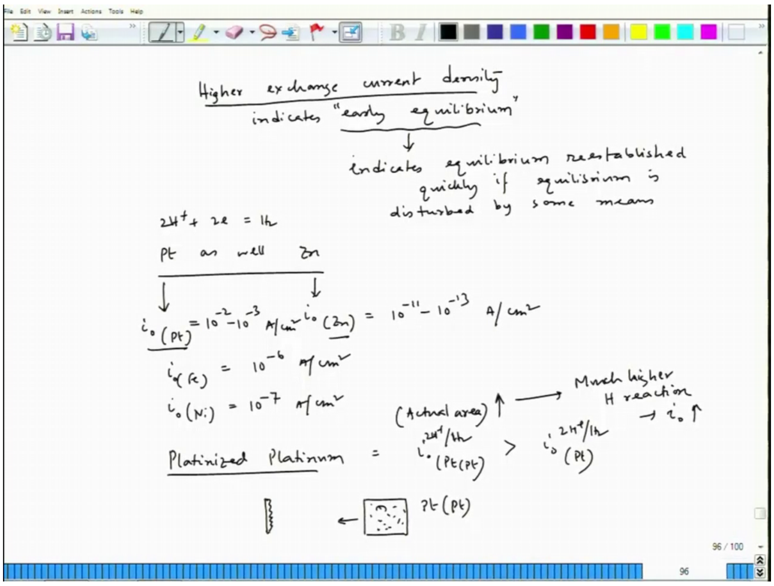

Higher exchange current density

indicates "early equilibrium"

↓

indicates equilibrium reestablished quickly if equilibrium is disturbed by some means

$2H^+ + 2e = H_2$

Pt as well Zn

$i_{0\,(Pt)} = 10^{-2} - 10^{-3}$ A/cm²

$i_0\,(Zn) = 10^{-11} - 10^{-13}$ A/cm²

$i_0\,(Fe) = 10^{-6}$ A/cm²

$i_0\,(Ni) = 10^{-7}$ A/cm²

(Actual area) ↑ → Much higher H reaction → $i_0 \uparrow$

Platinized Platinum = $i_{0\,(Pt(Pt))}^{2H^+/H_2} > i_{0\,(Pt)}^{2H^+/H_2}$

Pt (Pt)

So, higher exchange current density indicates early. Now, early equilibrium also indicates, this particular early equilibrium also indicates now let us say somehow on this metal 2 surface we disturb the equilibrium because of some situation. And since it has got a higher i 0 like the situation what we have seen higher i 0 so, the equilibrium will be reestablished much quickly. Now, interestingly when equilibrium reestablishes quickly it indicates if E is disturbed.

So, higher exchange current density it indicates early equilibrium and early equilibrium indicates that if the equilibrium is disturbed by some means it will reestablish quickly. What is the importance of that part? Now, this particular cell is basically a reference cell which is the hydrogen reduction, hydrogen standard hydrogen electrode.

And in case of standard hydrogen electrode we have to maintain this voltage which should be known beforehand, otherwise we cannot know the potential of the unknown electrode. So, in order to know that, in order to maintain this particular potential all the time similar potential and known potential we have to also see that potential is stable. And in order to make it stable, we have to also see that the equilibrium is reached quickly because, these potential is actually condition of indicating a condition of equilibrium.

This also indicates a condition of equilibrium. So, and; that means, indirectly it also indicates that it has to have a non corroding reversible condition and when it is a non corroding reversible condition; that means, it is also related to i 0. So, higher i 0 means, the condition equilibrium condition of equilibrium is established and if there is a disturbance then higher i 0 also indicates that condition of equilibrium will be reestablished quickly.

So, all the time we can maintain this standard reduction or standard potential or standard reduction potential to be at the known potential. So, it will help us in determining the reduction potential or the electrode potential of some unknown cell. And there could be possibilities that that equilibrium is disturbed some by some means, during the experimentation during measurement of this unknown electrode potential measurement.

And since platinum has got a very very high deduction exchange current density of hydrogen reaction, it will reestablish the equilibrium and so, we are we will be with this reference electrode.

Now, if I try to see platinum as well as zinc, now in that case on zinc for this particular reaction i 0 is of the order of 10 to the power minus 11 to 10 to the minus 13 ampere per centimeter square. And here it is as we have mentioned is equal to 10 to the power minus 2 to 10 to the power minus 3.

And also if I try to see other values of i 0 on top of let us say if iron it is of the order of 10 to the power minus 6 ampere per centimeter square i 0 of hydrogen reaction on nickel is of the order of 10 to the power minus 7 ampere per centimeter square.

So, these are the values; that means, on platinum surface hydrogen reaction would achieve equilibrium quickly compared to zinc surface it will take much longer time. And when it takes much longer time; that means, if we make some standard reduction, standard for cell with by using zinc it will not be a good practice. Because, it will take long time to reestablish to establish equilibrium and then if somehow equilibrium is disturbed it will also take long time to reestablish that equilibrium.

So, that is what the platinum is very much preferred electrode for hydrogen cell hydrogen standard electrode. Now, instead sometimes we use platinized platinum and in case of platinized platinum. So, i 0 for this hydrogen reaction is much higher than i 0 on platinum, see the when it is platinized on platinum platinum is plated. So, when platinum is plated it is actually forms a very rough surface and it means that if we have a particular area of platinum and if it is platinized platinum. So, then the actual area increases if we see this one from cross section so, it would be look like this. So, this is the cross section from the side if you look at.

So, actual area increases this so, here actual area increases which leads to much higher hydrogen reaction or i 0 increases. It suggests that if we use platonized platina in place of platinum, standard hydrogen electrode would be much better compared to if we use platinum. Because, in case of platinized is platina i 0 is higher so, the equilibrium would be much stable equilibrium or if we disturb this it will come back to the equilibrium quickly. So, that helps us to maintain this standard potential of that hydrogen electrode so that we can measure the another potential of an electrode with certainty or surety. So, this is about the effect of different electrodes, different metals as well as the surface conditions.

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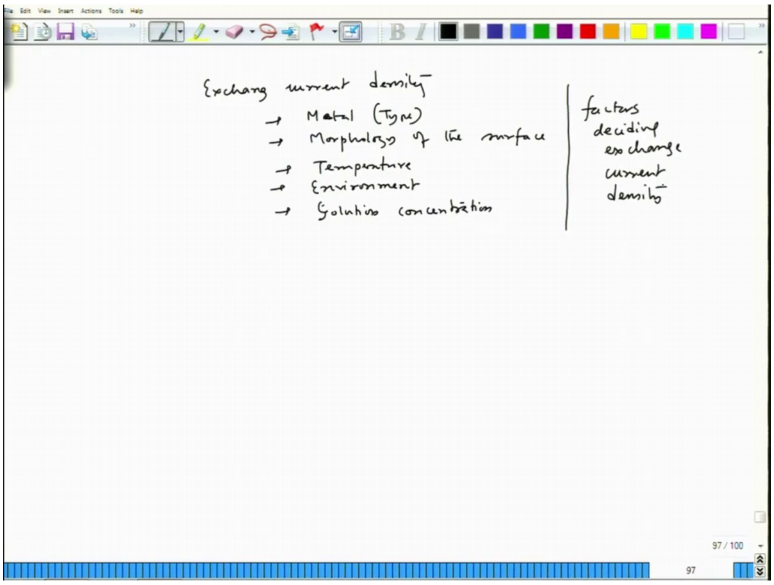

Exchang current density
→ Metal (Type)
→ Morphology of the surface
→ Temperature
→ Environment
→ Solution concentration

factors deciding exchange current density

So, now, there are other factors on which this exchange current density depends. It depends on as we have said metals type, morphology of the surface, then we have temperature environment. Why environment because sometimes we have a situation like in one place we have higher salt content or in other place we have less salt content. Then for example, in seashore area salt content is very high and if we go to Himalayan belt the salt content would definitely be less.

So, in those 2 cases even we use the same temperature and pressure and the same metal and solution we would have a difference exchange current density of a particular reaction. And then we have solution concentration, this would definitely change the exchange current density also. So, these are the some of the factors on which density. So, will talk about exchange current density more in our next lecture so, let us stop here.

Thank you.