Indian Institute of Technology Kanpur

Present

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Module Lecture 012

Broad Subject: Exchange current density, Polarization, Activation Polarization, Tafel Equation

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We have been discussing the number of – the transfer of charges from iron surface to the metal surface and transfer of metal atom from metal surface to iron surface in the solution and on that way we have seen that if these are the two surfaces and then this is metal surface and this is metal n+ and the reaction if you consider equilibrium n++ ne M for this equilibrium the ion is coming from this surface to this surface and metal atom is going from this surface to this surface and this transformation -- this transfer of species is not a very simple process. It doesn't go like this. It has to cross a barrier and that barrier is nothing but the activation barrier and we have already seen that if you draw G versus free energy versus a distance plot now here you have a well and now you have two this is my second position. Now if and this metal atom it will move across this barrier and metal charge will also move across this barrier to come to this side and we have seen that if this is my free energy barrier and we have started having some sort of equation with respect to the free energy barrier as a function of free energy barrier as a function of number of moles per unit area on this surface or on this surface and with a vibrational frequency of atom or charges and then we have also included a part which is a f, f is nothing but the small f is nothing but the fraction of atom let's say from here to there the atom is moving from atom from this surface to this surface and it's forming charge, the fraction of atom which is actually going and sitting there.

Now we have seen that if you consider the flux, now we have to see the flux of moles or the species transferring from this surface to this surface or this surface to this surface and this if we consider that is the forward reaction. Now if let's say this is my forward reaction and this is my backward reaction, then the forward reaction flux would be equal to we can consider r1 is nothing but or flux is nothing but the rate of transfer of species per unit area per unit time would be equal to n1 f1 n1 v1 exponential minus delG star by RT. Now similarly we can put this if you consider r1 this is r2. r1 this arrow means it's a forward direction, rate of flux and this is the backward direction rate of flux. Similar way r2 will be equal to n2 f2 n2 v2 exponential minus delG star by RT, and we have also seen that if these two rates are same we can equate this two equation we will get our important relation which is f1 n1 v1 equal to f2 n2 v2 and also will see that this if generally the value is roughly considered to be one, V is around 10 to the power 12 to 13 per second and n1 and n2 if let's say the charge the number of charge which is coming from this to this or metal atom going from metal atom to this these two are equal and if you consider unit area let's say one centimeter square area let's say this is one centimeter square area. This is one centimeter square area and also this is my one centimeter square area now I will also say that n1 and n2 they are not – they will not be if we assume that these two are same then this is basically all the time even if there is some sort of non-equilibrium or the rate of forward direction or rate of backward directions these two are different the only change would be here this term will remain constant or fixed.

Now if these are fixed now we know what is my rate equation as a function of current density. We know that the current density part if we remember the previous calculations we know that dn dash dt by 1/nF dq/dt since this is basically the charge transfer rate and this is the rate at which number of moles are transferring from metal surface to ion surface.

Now this we can write in the form of per unit area so I can divide unit with area term which is nothing but A. here also I have to divide it with area. Now this is nothing but the current so now this is n dash/Adt equal I, now this by this by this is becoming i small i by nF. Now this term is nothing but so this is this term is nothing but this because the unit of this is number of moles per unit area per unit time you see that this unit is also same, if n dash is the number of moles so this is nothing but r1 or r2 equivalent to r2 equal to i/nF.

Now this i if these two are equal here I have put equivalent means equivalence their units are same. Now if these two rates are different r1 and r2 are different so they will not be equal but if these two rates are equal then r1 equal to r2 I can write it then I know that when this has reached equilibrium and if the activity of this species is one unit activity if we maintain all those species then this is nothing but the non-corroding item and the potential develop will be standard reduction potential which is nothing but E0M+n/M and when we have already seen the concept of exchange current density that exchange current density it says that when the system is at equilibrium and non-corroding system or the reversible condition where you do not have a net formation of metal ion and net formation of metal ion is nothing but the corrosion so that since there is no net formation of metal ion whatever metal ion is forming that metal ion is getting deposited and there is an equilibrium so that non-equilibrium --- that non-corroding system reversible equilibrium condition I can think of exchange current density of this reaction on the surface of the metal and that surface is nothing but the same metal surface.

So this is here I can consider i0 I can write on metal surface and this is – so exchange current density for this reaction on metal surface M and this thing I can write I can have a correlation if we consider the reverse and forward direction reaction rate so r1 equal to r2 equal to i0/nF. So I can write i0/nF. Now if I put this i0/nF instead of r1 or r2 since these two are equal in the equilibrium so I can get i0 equal to nFn1v1f1 exponential minus delG star by RT, and if you see that this term is becoming on is basically fixed for this case because n, f both are constant for this particular reaction and we have already seen that this is equal to this and this value does not change much and we can assume that this is with the reasonable assumption we can have that is f1 n1 v1 are fixed value in this case.

So now we can say that i0 is nothing but A dash, we will consider it as a constant so, so this A dash this all the things are included in this A dash. So I can have a good relation for this exchange current density.

Now this relation will come into our – it will be will be an important issue when we consider polarization. Now I have included this word polarization. Now let me come to this term or it is a polarization. Let me talk about polarization now, and this polarization this equation would be an integrated part of the polarization equation. Now let us say I have this reaction. This is my equilibrium reaction for metal deposition as well as metal formation, metal ion formation. Now that case this is nothing but ic, this is nothing but ia. We have already come to this. This is the cathodic current density. This is anodic current density and there would be a negative sign here and if it is equilibrium so ic equal to ia equal to i0 which is exchange current density. Now what happens if there is a net metal ion formation? Now net metal ion formation it means that the equilibrium is disturbed, and if equilibrium is disturbed I can write it in the form so that means equilibrium is disturbed so I have preferentially this reaction. It does not mean that this – the backward reaction is stopped. Backward reaction is also happening. So if you consider this is to be r2 dash so backward reaction r1 this is basically in this case this is my r1 forward reaction and this is my backward reaction. Now in this case I know that equilibrium is disturbed and metal ion formation is preferred. So I am having preferentially metal ion formation but since that means that r2 is greater than r1 and that means the rate at which the metal ion is forming is exceeding the rate at which metal ion is getting deposited. So you have a net metal ion formation and in that case for the net metal ion formation you have to see that you have to take the current charge or the electron from the metal at a faster rate and for this if we know that this is the metal ion formation so corresponding current is nothing but ia and it means that ia should be greater than ic. I am taking the mod value because just to avoid the negative sign. If ia greater than ic then r2 would be greater than r1 and when it happens you will see that the potential is deviating from the equilibrium potential and the potential here also you will see that here you know this is E0 Mn+M this is E0 Mn+/M. So this potential which is existing here if you have preferentially this reaction then you will see that potential for this reaction is changing towards the positive side.

So you can also do the measurement of the potential for this if the deviation is taking place in the potential. So let us say after some time the potential become E for this you will see that E1 -- E dash minus E0 Mn+/M it is a positive quantity. It is a positive quantity that means because of this disturbance in equilibrium or because of the preferential formation on metal n+ ion you are deviating the potential from the equilibrium value to some positive value that is why this becomes positive and here we are considering only the reduction potential. So reduction potential goes from E nut which is equilibrium potential to a higher potential.

Similarly if you have deposition reaction at a faster rate that means r1 should be greater than r2, so ic should be greater than ia. So deposition rate is faster than the production rate of metal n+ and in this case this is case number one and in this case this is case two you will see that after some time if you measure the potential E double dashed and if you find out what would be the difference in potential from the equilibrium potential so this minus E0 Mn+/M would be negative. Negative value. Negative value. That means in this case if you have a deposition reaction or the reduction reaction at a faster rate compared to the production reaction or the metal ion formation reaction then potential goes towards the negative side from the equilibrium potential and who is the culprit for this transfer of equilibrium potential from positive to negative or negative to positive, for example here potential goes towards the positive side compared to equilibrium potential. In this case potential goes to the negative towards the negative side compared to the equilibrium potential. So who is the culprit? The culprit is preferential transfer of electron. In this case, case one the electron is taken away from the metal at a faster rate than the consumption and in this case where ic greater than ia or ic greater than ia the electron is getting consumed by metal ion at a faster rate compared to the electron generation. So and charge transfer is nothing but the current. So whenever you have a current flow then you will see that the potential shift and potential shift from the equilibrium value and this shift in potential is nothing but the polarization from the equilibrium value.

So how do you define polarization? How do you have a conceptual -- how do you have concept of polarization? Polarization implies deviation of potential from equilibrium potential because of current flow or charge flow, net charge flow I should mention net charge flow because when you have equilibrium then also charge flow is taking place but the rate at which charge is flowing for the forward reaction as well as backward reaction these are same and when you have polarization you have a net electron flow. In this case electron is basically you are taking away from the metal at a faster rate and in the cathodic case where ic is greater than ia we consume electron at a faster rate than the production of electron.

So this is my concept of polarization.

Now we see that in this case, case one I have a positive quantity. We call it as anodic polarization and in this case it is cathodic polarization. Now the point is how do we quantify polarization. The polarization is quantified in the form of overvoltage and it's given as this form eta. Now the overvoltage in this case the overvoltage is nothing but the difference between the final potential and equilibrium potential. So in this case this is the positive quantity. I can term it as anodic overvoltage, and in this case I can term it as cathodic overvoltage a subscript a means anodic, subscript c means cathodic. So here anodic polarization or anodic overvoltage and this is cathodic overvoltage and if you would like to see what would be the sign, so if this is na is positive so nc would be etac would be negative. So this is positive and this is negative. So this is concept of polarization and overvoltage. Now getting back to this picture we know that the metal ion surfaces forming metal is forming and this picture if you can see what is happening from the start of the reaction let us say you have dipped a metal in a solution where you have metal ion already existing or salt of metal is existing so you can have an equilibrium. Now when you have that let us say first thing is there would be formation of metal ion from metal and similarly metal ion would go into the metal. So there will be a sort of equilibrium or dynamic equilibrium that would be existing at constant pressure and temperature or the temperature or pressure in that condition there will be a equilibrium.

Now when you have that when you form metal ion it will always be solvated by water molecule because it is a positive charge so salvation will occur. So you have positive. Now you can have this water molecule will encompass the positive charge and because this is water molecule has a polarized effect so there will be dipoles and this dipoles the negative side will come close to this positive side so this is nothing but the solvation. So you have a solvation there. Now also you have left electron at this surface. So there would be so you have positive charges here, there would be negative charges here. So you see there would be a formation of capacitor. This is a negative side. This is the positive side of the capacitor, and also this surface is called as inner Helmholtz plane and this is called outer Helmholtz plane. and H here it is Helmholtz. So this side is inner Helmholtz plane. This is a plane and this is outer Helmholtz plane. Now we know that if this is at equilibrium so you have this sort of formation of reaction barrier or this is the activation energy and that time if you would like to see what is my relation between the rate flow or the flux from this to this surface and inner HP to outer HP so you can come across the concept of exchange current density.

Now when you have preferential metal ion formation or you are breaking this equilibrium and you are increasing ia compared to ic so ia greater than ic if you consider their value or other way around if you consider the reduction process that time ic would be greater than ia and in that case polarization will occur so what would be -- how can we measure ia and ic as a function of over potential?

Now that thing let us have a relation. From this we can have a relation from with respect to over potential and current. What is current? Current is the kinetic part and over potential is nothing but the difference in potential and potential is nothing but a thermodynamic quantity. So we have to relate over potential or the polarization with the current value. Now let us consider this plot again. Let me put it here. Let me remove this part. Let me draw it here. Now this is IHP and this is OHP. When this is at equilibrium that time I will have -- this is my let us say this is my free energy. This is distance. This is IHP. This is OHP, and now here what we have, we have metal atom in the elemental condition and that we are putting as zero. Zero means this nut value means it's in – we are considering the equilibrium concept. Now that case this level and this level both will be same because it is in equilibrium so the state here and the state here the free energy state and the free energy state both these cases would be same. So that's why they are at equal distance from the reference distance, from the reference plane, reference value.

Now this side I can put it as M0mn+, this 0 I am putting just to indicate equilibrium. Now when and this is ia and this is my ic with a negative sign just to indicate that the rate, forward rate is given as ia, backward rate is given as ic which is the cathodic process. Now you disturb this equilibrium. If you disturb this equilibrium you can see that this would be greater than this. That is what we have seen. If this is greater than this now we know this relation if you see this relation in this relation if this term increases this term would go down, and if this term decreases this term will go up.

Now since I know that ia is greater than ic which is the anodic process. This is ia is greater than ic. So I should see that the barrier, reaction barrier should decrease for the anodic process or the metal ion formation process. Then only this would be higher, this would be higher than this. So what would be the rate of backward reaction. Let me put it as backward reaction would be equal to same way I can do the whole treatment but since we know that this is considered as A dash I can put it as A dash. So I can put it as A dash exponential minus delG star by RT. Now here I should see that this is let me put it as a again here just to indicate that this is the anodic reaction rate. So this a or this I am correlating with this. Now in that case my distribution of the figure this figure would change. How would that change? So I should see that overall value of this should decrease. Similar way this would go down so overall value of this side this side would go -- would increase. So if I have a process like this let me put it a different color. So what would be my barrier? My barrier would be this much for the forward reaction, and similar way I should see that the barrier for the reverse reaction that means this one should topple this barrier and this barrier should increase. So my distribution of curve would be like this. So in that case my barrier for the reverse reaction or the ic would increase.

Now this may, let me put it as delGa and this let me put it as delGc. So instead of delG star I should put delGa. Just let me consider only the ia value with respect to anodic process. Now what would be the value of this and we know that this one is delG star. Now if any number of electrons are involved for this process and let us say I have a fraction f alpha which is the symmetry factor for this related to this diagram and if we consider that this is my total overvoltage and then this is alpha fraction of this total overvoltage is contributing towards the anodic polarization so then what would be my anodic polarization if this is my total and this is my alpha which is the fraction of the total polarization that is going -- that is coming as anodic polarization. So my anodic polarization value would be and here alpha is symmetry factor or it can be called as the extend of polarization of cathodic/ anodic process. So if alpha is the extent of polarization for the anodic process and this is my total polarization then what would be my anodic polarization value, alpha eta. And this polarization is happening because we have already disturbed this equilibrium. So no longer I am having this equilibrium and we are having this process where this rate is more than the reverse rate and when you have that this process that time I know that alpha is the extent of polarization. So my total anodic polarization would be alpha eta.

Now if this is my polarization which is basically nothing but volt what would be the energy associated with the or free energy associated with it? Now I know that the free energy is nothing but -nFE and what is the voltage here alpha eta. So I know that what would be my free energy change alpha eta.

So my free energy change would be this, and now let us see what whether the free energy change is positive or negative. Here I leave the potential of this mo to let me put it as ma which is in activated condition or anodic polarization condition so that case this is my level. So I have reduced the barrier. So that case I should decrease, I am decreasing basically the overall activation barrier is decreasing by the amount of this much. So the value of this would be this minus this so there will be a negative sign associated with it.

So we see that this is my nothing but Ga which is – sorry this is my free energy change for this anodic polarization and that should be this part and this is nothing but delG, delGa would change to delG star minus this, delG star minus alpha nF eta. So I know, I am now coming to the value of ra. There is a small mistake here. You see A dash is nothing this nF part is included in this in part so then you can term it as i0. So I can put it a different constant which only constitutes the A double prime is nothing but n1f1v1. So ra which is the anodic rate so that is nothing but A double prime exponential minus this.

So then what is my relation between ia and ra? ra which is nothing but moles, number of moles per unit area per time would be equal to ia/nF would be equal to A double dash which is nothing but n1f1v1 into exponential I can separate, rewrite these two things delG star by RT into exponential minus,minus so it will get canceled it will be become plus, alpha nF eta by RT.

Now I can write it so this would be equal to ia would be equal to nFA double prime exponential minus delG star by RT into exponential alpha nF eta by RT. So what is this? This is nothing but i0. So I can write ia equal to – I can write ia would be equal to i0 exponential alpha nF eta by RT. Now you see that the anodic current which is nothing but the rate of electron transfer from the metal or the rate at which the electron is taken away from metal to form metal ion formation, to form metal ion so that is my ia, that current value, current density for anodic process and that lead to polarization or the shifting of potential and here also we see that shifting of potential we have already seen the shifting of potential for the anodic polarization is positive and we see that the polarization value and this term is coming positive. So I can write would be equal to RT/ alpha nF ln [ia/i0]. So I can have the polarization or the amount of polarization or overvoltage for the anodic process from if I know the current density and the current density can be easily found out experimentally. So if this is my expression now since I include I have ia here which is anodic process I can easily term it as na which is nothing but the anodic polarization.

Now the confusion starts. Confusion is initially we started with total polarization, the eta is considered to be total polarization. Now I am considering as anodic polarization. You will see that whenever you have a high rate of forward this reaction or if you see that ia is very much greater than ic because of this ic the polarization or the cathodic polarization would be very much negligible compared to the anodic polarization. So if ia value is very large so n eta total eta a. You will see that later we will see that. I am straight away putting anodic polarization and this relation is the relation between the anodic current density or the rate at which anodic process is taking place that would be related to the overvoltage or the anodic polarization through this equation, and generally this symmetry factor is considered to be half. So symmetry factor is considered to be half. So 0.5, and we know R, we know T. if we know the T at the temperature where this process is taking place we know this nF are constant for this process so this term we put it in terms of beta. So that case I can write beta, I am putting a value because I am considering the anodic process ln ia by i0. So a small change I can write na equal to i0 I have to convert this ln part into log, so RT into 2.303 by alpha nF log of ia by i0. So this part we put it in the form of beta i0. So I can write it like this I eta a would be equal to beta a log of ia minus beta a log of i0. You see this beta a if you consider alpha to the symmetry factor if you know this process in F, both of those are constants R is also constant, universal gas universal, T is the temperature at which the process is taking place. So this beta is a constant. Again i0 for this process on that metal surface in the solution is also a constant. So this is a constant. Now if you would like to see this so this expression you can straight away write in this mode. I can put it as a constant C, because is a constant here. This equation is known as Tafel equation. This equation is known as Tafel equation where is the Tafel constant and this unit of this Tafel constant or the Tafel slope, this is the slope Tafel slope is volt per decade of current density. Why per decade of current density because I am considering log of ia. So this unit would be volt per decade of current density. This is Tafel slope. beta a is Tafel slope and this is a very very fundamental equation which relate overvoltage with current density.

Now similar way we can have a relation between ic and overvoltage, cathodic overvoltage. So that case we have to start --you have to see the reverse process and the reverse process what would be my cathodic polarization with respect to the total polarization eta so that case I should see that this value is to be added. This value is to be added because then you have to start from this and that time this I can write it as in a MCn+ C is nothing but I am putting it in the form of cathodic side. So this is cathodic side. This is anodic side. So that case my total free energy that is to be put in in this equation is nothing but delG star plus this and I am putting 1 minus F, 1 minus alpha that means that if alpha is the extent of anodic polarization and we know that anodic plus cathodic polarization is nothing but the eta so now the equation is this is total na plus nc so now if we – if this contribution is alpha so in this case it would be 1 minus alpha. So extent of 1 minus alpha plus alpha equal to 1. so this constant also, this is also right. So the na would be the overall with respect to overall of the total polarization would be 1 minus alpha nF eta. So that case I just replace delG star with delG star plus this and if I do the same process I will get a relation, C dash, that case Tafel slope anodic Tafel slope since I am putting a here so this beta c is basically nothing but cathodic and C dash is constant here and if you would like to see the value of beta c and beta a so let me put the value here, and here is it is fine.

So now we know this equation and this equation also relates a thermodynamics with the kinetics of corrosion process and what is the corrosion current here, corrosion current is nothing but the ia which is the formation of metal ion and the current associated with the current density which is associated the metal ion formation.

So now we know these two relations. Now if we would like to see the polarization effect let us say I am at this position where I know that this equilibrium is existing so that case what would be my let us say this is my log i what would be my current density, the rate of forward or backward process. That is nothing but i0. So let me see that I am here okay. Now what would be the potential here or the polar – let us say I am putting the overvoltage. What would be my net overvoltage? The net overvoltage would be zero because at this condition when it is at equilibrium I know that potential always will be standard reduction potential. So now if I would like to see that if ia is increased compared to the ic so it would go into the anodic polarization side that time I have to consider this equation. And now this is a straight line equation with a slope of beta a so I will see that the line is like this. That time this is C. Now let us say that time ia is greater than I ic and if I would like to see if potential goes to the negative side this is positive side. this is anodic polarization. So I can see that this is na I am writing positive. Now if I see that cathodic current density is more than the anodic current density so it should move towards the negative side compared to the standard reduction potential or the reversible potential. So again this will follow this equation that time I will see that this is my cathodic side negative, the equation would be C dash.

So I see that if I have preferential anodic process I will move towards this. If I have preferential cathodic process I will move towards this. Thank you.

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