

**Indian Institute of Technology  
Kanpur**

**NP-TEL  
National Programme  
On  
Technology Enhanced Learning**

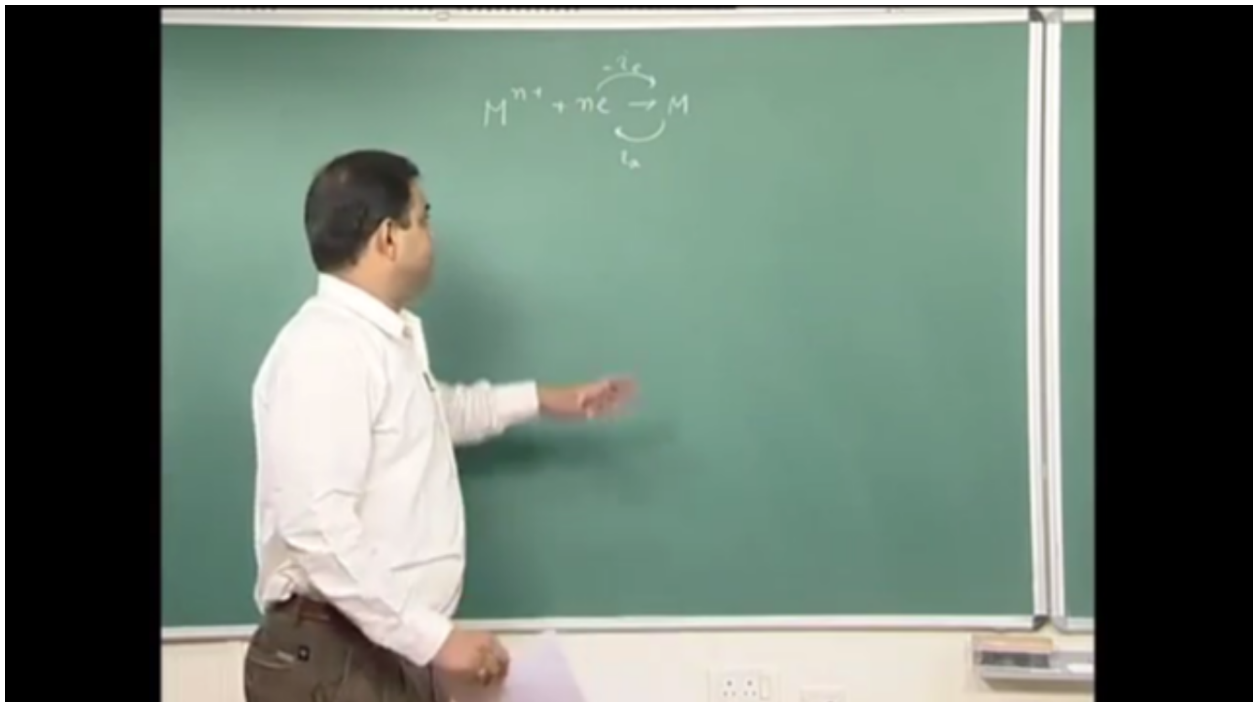
**Course Title  
Environmental Degradation of Materials**

**Module 01 Lecture 13  
Broad Subject: Activation polarization, Concentration polarization**

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Dept. of Materials Science & Engineering**

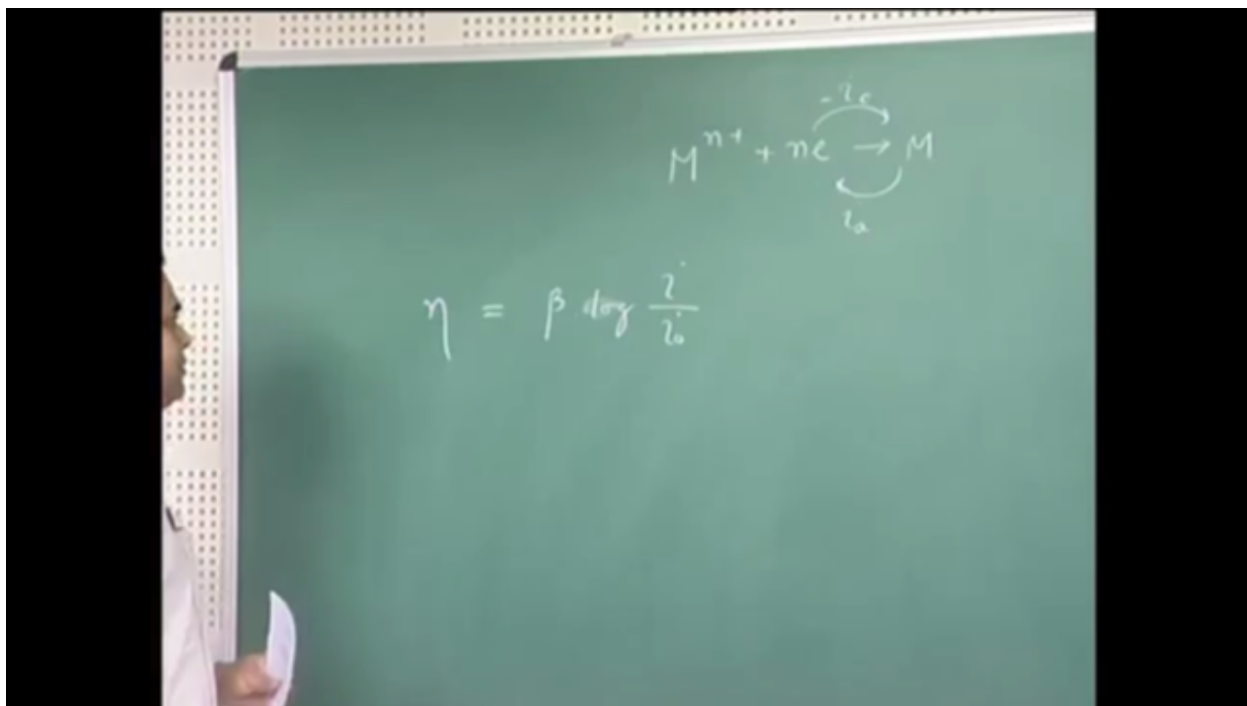
So we have found out an expression for overvoltage when you have a preferential charge transfer. For example, if charge transfer is taking the equilibrium reaction towards the more and more ion formation reaction, then it would be  $i_a$ , for example, if this is my reaction, and this reaction is preferentially happening, so that time I will consider  $i_c$  and if this reaction is preferentially happening, I will consider this as  $i_a$ .

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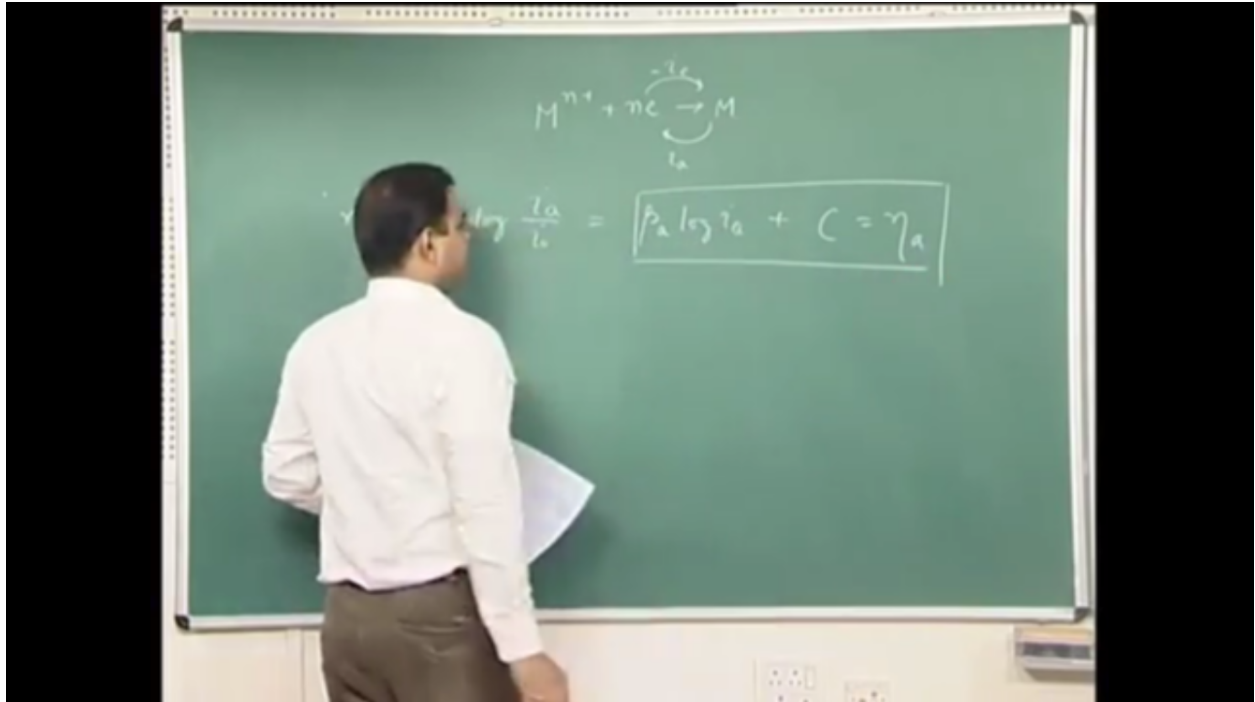
Now that time we see that we have a preferential if this side is going, the backward reaction is happening, so preferential ion formation is taking place. So, preferentially, you are taking out electron from metal atom. Now that time we have found out expression for overvoltage because when you have non-equilibrium for the formation of metal ion or formation of metal, that time we can find out what is overvoltage or the quantity -- we can quantify the polarization.

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We have found out the expression which is -- this is my -- this is my general expression where I initially started with the total polarization and then finally, if it is anodic side, then we have put it  $i_a$  and this is -- this is  $\eta_a$  and this is  $\beta_a$ , which is the Tafel slope and then we can also get it in the form of  $\beta_a \log i_a$  plus some constant.

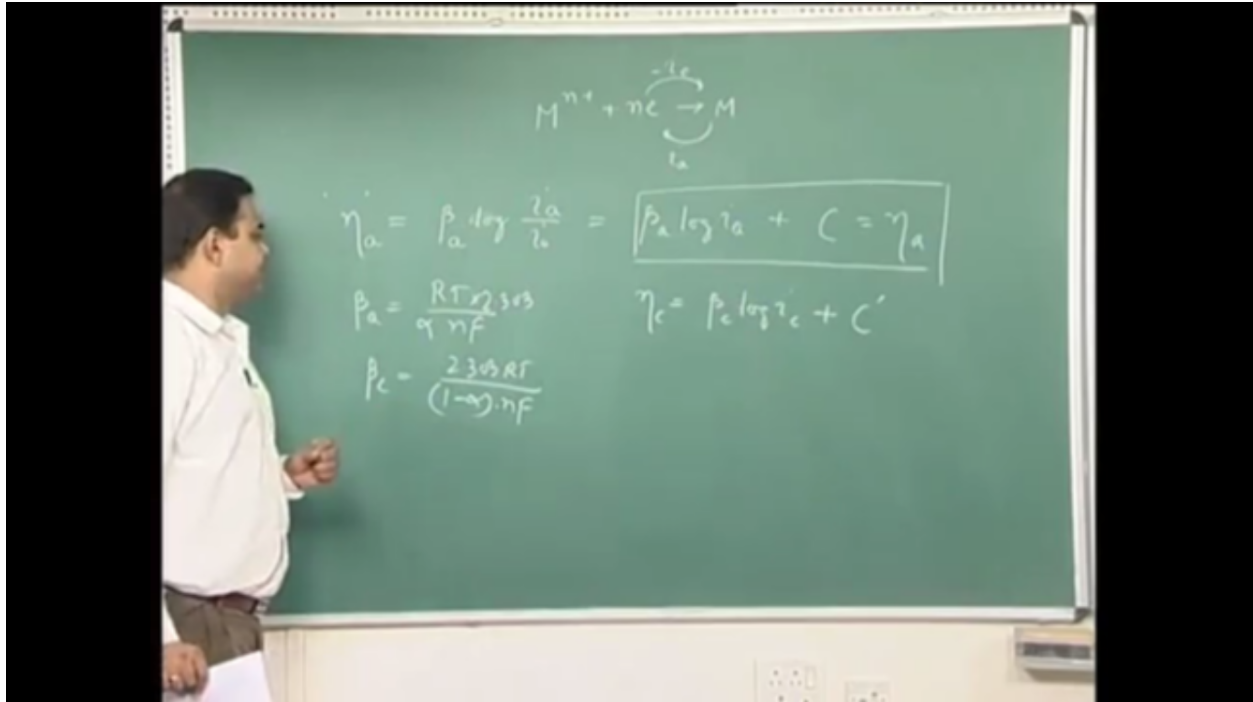
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So this is my Tafel equation. This is my Tafel equation.

Similarly, I could find out what is the Tafel equation for cathodic reaction. So that case  $\eta_c$  would be  $\beta_c$ , which is the Tafel slope cathodic process  $\log i_c$  plus  $C$  dash which is also a constant and now in this case  $\beta_c$  is  $RT/\alpha nF$  into 2.303 we have seen that and  $\beta_c$  is basically  $2.303RT/(1-\alpha)nF$  and where alpha is a symmetry factor and generally, we take it as 0.5.

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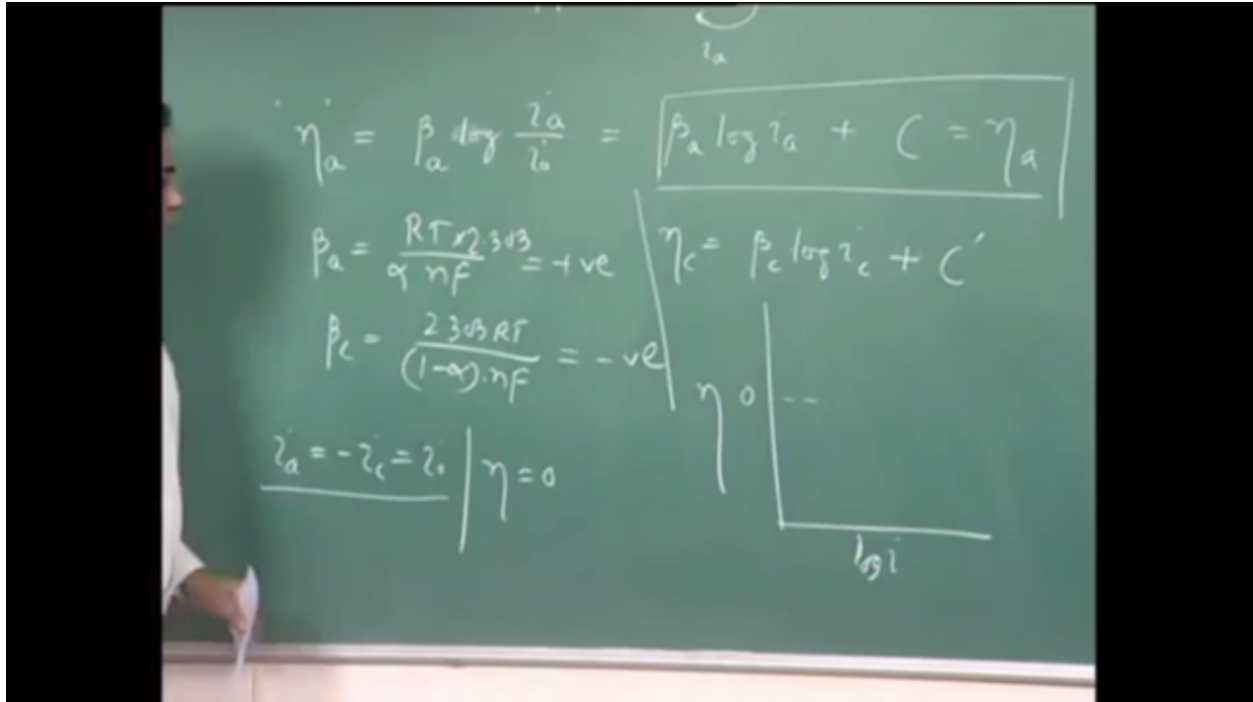


So the distribution of energy states or energy level of the ionic species as well as the atomic species will vary as per this alpha, and this alpha if it is 0.5 that there would be equal distribution or equal change in the anodic side as well as cathodic side, and we consider this to be a negative value just to have a sense that cathodic polarization is going towards the negative side that means potential drops from the equilibrium potential and this is considered to be positive. Anodic polarization means the increase in potential from the equilibrium value.

Now we have also seen that if you would like to see what is my overvoltage as a function of log  $i$ , as a function of log  $I$ , now when the overvoltage is zero that time I know if the overvoltage is zero, that time  $i_a$  equal to minus  $i_c$  equal to  $i_0$ .



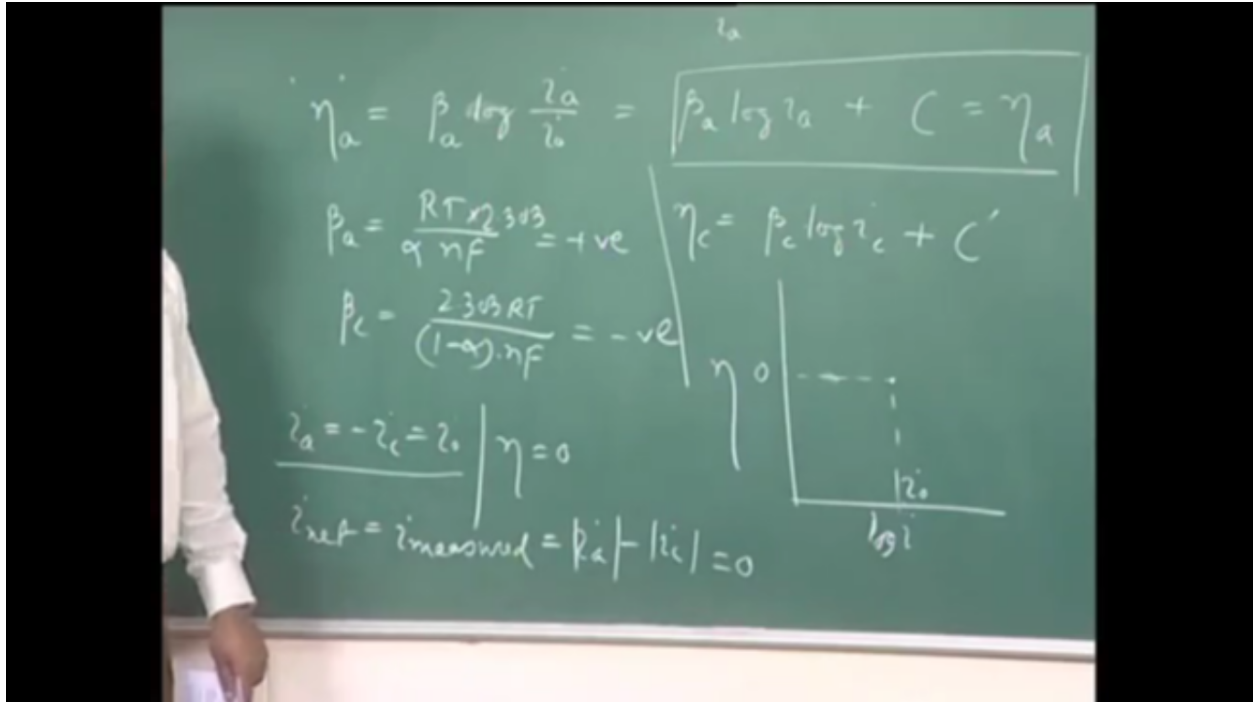
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So when  $i$ , this condition is satisfied or equal to zero, that time we know that there would be no net current flow in the system because I know what is my net current flow, I know that  $i_{net}$  or the measured current what you are seeing in the circuit that would be  $I_{measured}$  would be equal to  $I_a - I_c$ . I am taking mod just to indicate the value.

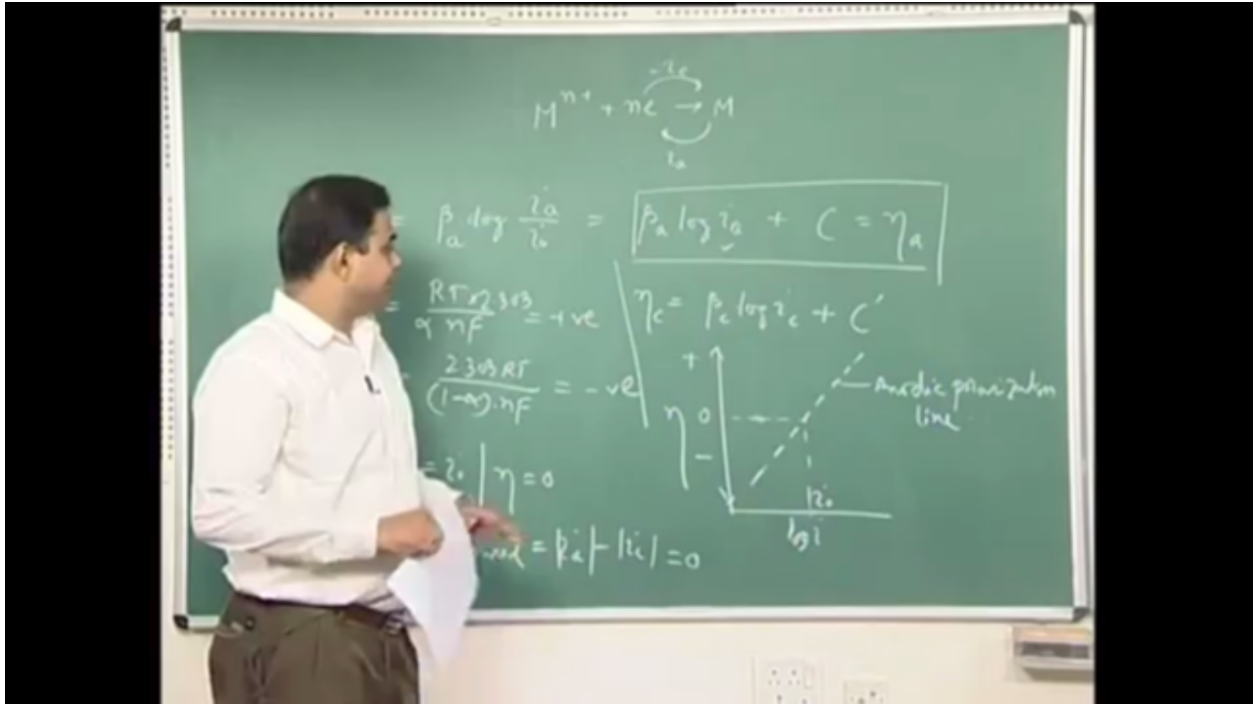
Now if you see that  $I_c$  is more, this would be along the direction of  $I_c$  and if  $i_a$  is more, then  $i_a$  is more than  $I_c$ , then this direction, the measured current direction would be along the  $i_a$ . So that case this would be zero. So I won't have any net current in the system.

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So I have this point. Let us say this is my point which is corresponding to some  $i$ , that  $i$  would be  $i_0$  and now if we would like to see the cathodic polarization or anodic polarization, I need to find out what would be my  $i_a$  and what would be my  $i_c$ . Let's say I know what is my  $i_a$  with the progress of polarization along the -- along the positive side. This is positive. This is negative side. So that will be governed by this equation. So this is my -- this is my anodic polarization line.

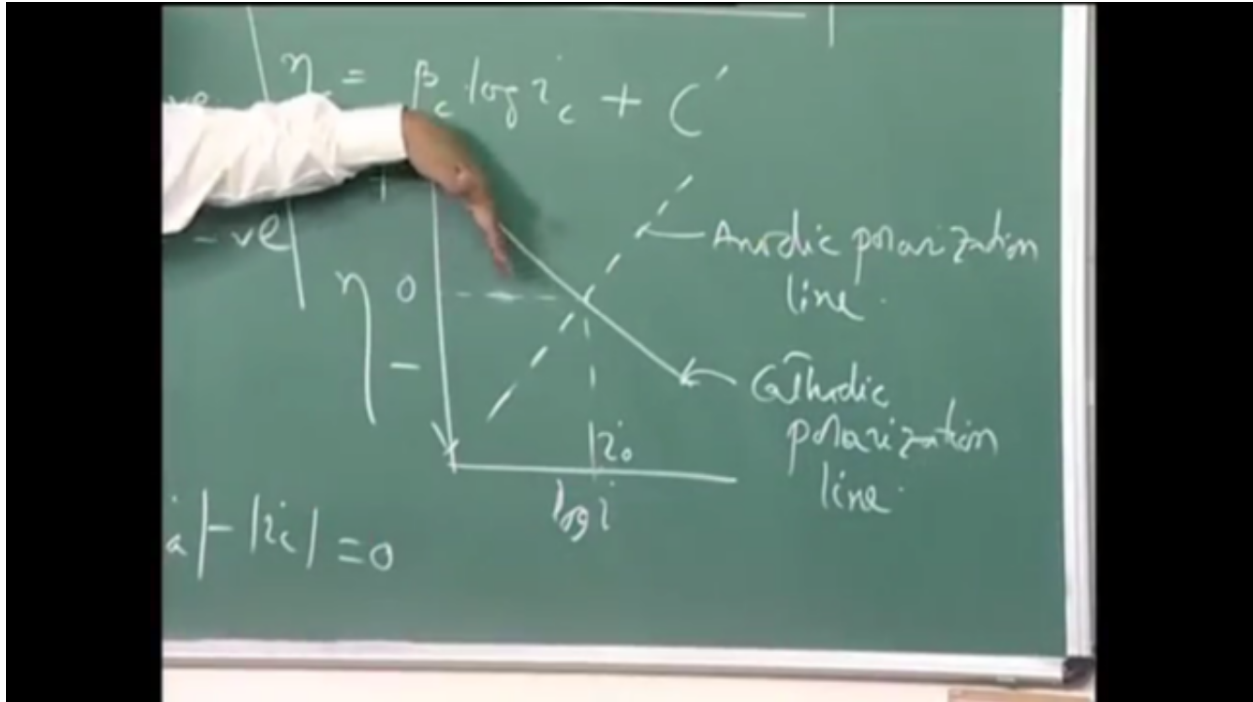
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Since this is plotting with respect to put in polarization as a function of  $\log i$ .

Now, similarly, I can also find out what would be my cathodic polarization if I know  $i_c$ . Okay. Accordingly, I will also find out  $i_c$ . This is my cathodic polarization line.

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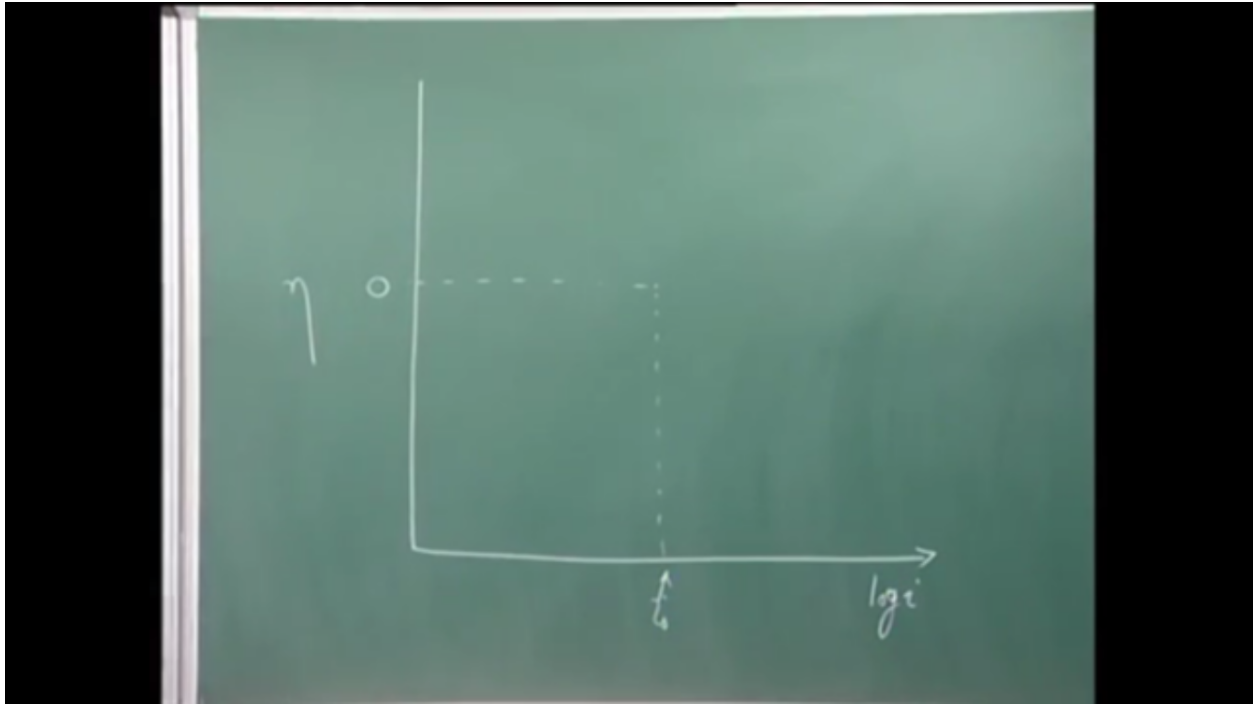
So now I have the both the lines and here you see has a negative slope that means because we have already considered that the slope for this cathodic polarization is negative and that is  $\beta_c$  and in this case it would be  $\beta_a$ , which is positive.

Now the point is initially, we have considered that initial when we have started with total polarization  $\beta \log i$  by  $i_0$ . Now out of that total polarization, alpha fraction would be anodic polarization and 1 minus alpha fraction would be cathodic polarization.

Now here we have shifted it from  $\eta$  to  $\eta_a$  and  $\eta_c$ . Now we have to see whether this change from this is going to have any difference or not. If we see that there is no difference, then we can easily put that. If we see that there is difference, then we should not convert this directly from this. We have to have some logic that why we are writing  $\eta_a$  and  $\eta_c$  from the total polarization.

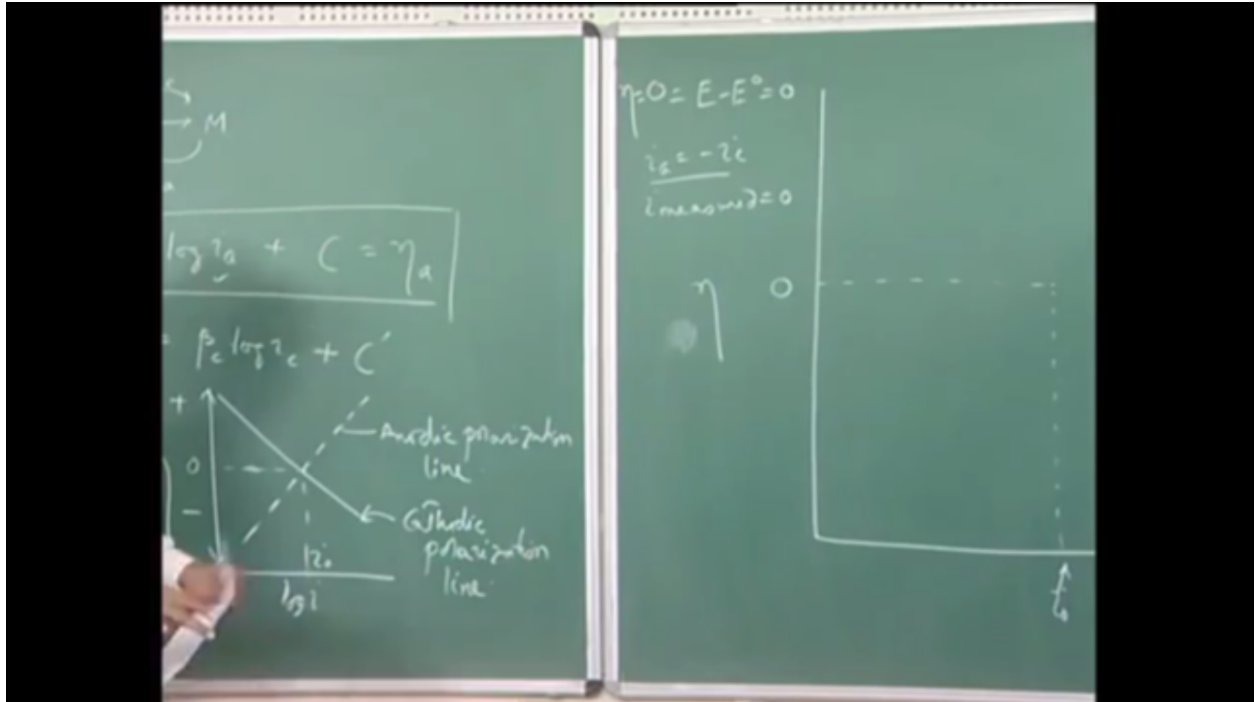
Now let us have a bigger graph. This is my  $\log$ ,  $\log i$ . This is my polarization. Now condition one, we have already seen, this is my condition one, where overvoltage is zero. Overvoltage zero means polarization is zero, and polarization zero means  $i_a$  equal to  $i_c$  equal to  $i_0$ . So I can pinpoint that point. Let me see that this point is this. So, correspondingly, I have this value. This is  $i_0$ . Corresponding value would be  $i_0$  and corresponding polarization would be zero.

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Now as zero means this means zero polarization means  $\eta$  equal to zero means  $E - E^0$ . In this case, let's say if we consider that the equilibrium potential is reversible, non-corroding potential or the standard reduction potential, that time it is basically zero. So we don't have any current flow because  $i_a$  equal to minus  $i_c$ , so  $i_{\text{measured}}$  is basically zero.

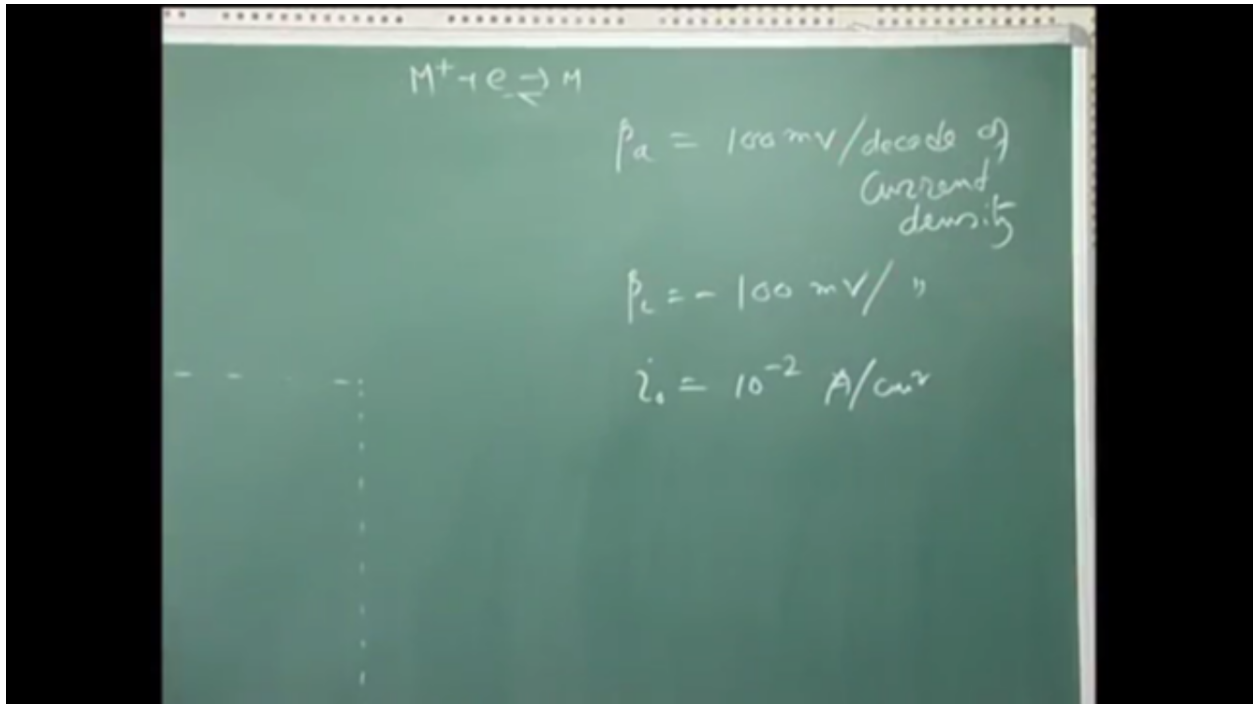
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Now let's say, let me take some reasonable value. Let's say  $\beta_a$ , let me take it as 100 millivolt per decade of current density. Since I have  $\log i$  on the x-axis, so millivolt, and  $\beta_c$  is equal to minus 100 millivolt per decade of current density.

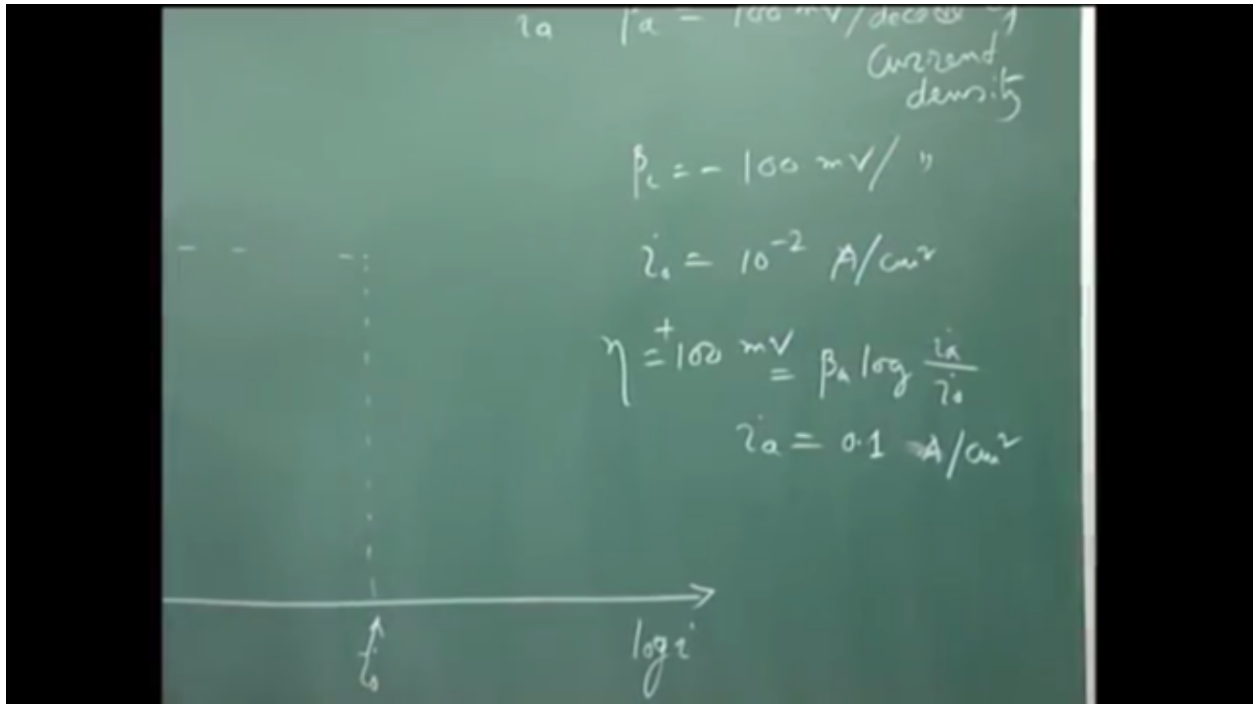
Now let me consider for a particular reaction that case in case of mono  $M^+$  plus  $e$ , for this reaction, let me consider  $i_0$  is  $10^{-2}$  ampere per centimeter square.

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Now in this case, if I take the potential to the positive side, that means I increase the anodic current, so this is my anodic current  $i_a$ . This is my  $i_c$ . So I increase my anodic current. So if I increase my anodic current, let's say at some position, I have the overvoltage to be 100 millivolt, plus 100 millivolt. So if it is plus 100 millivolt, let me find out what would be the amount of  $i_a$ . So this would be equal to  $\beta_a \log i_a$  by  $i_0$ . So from this, I would see that  $i_a$  is coming out to be 0.1, 0.1 milli -- ampere per centimeter square.

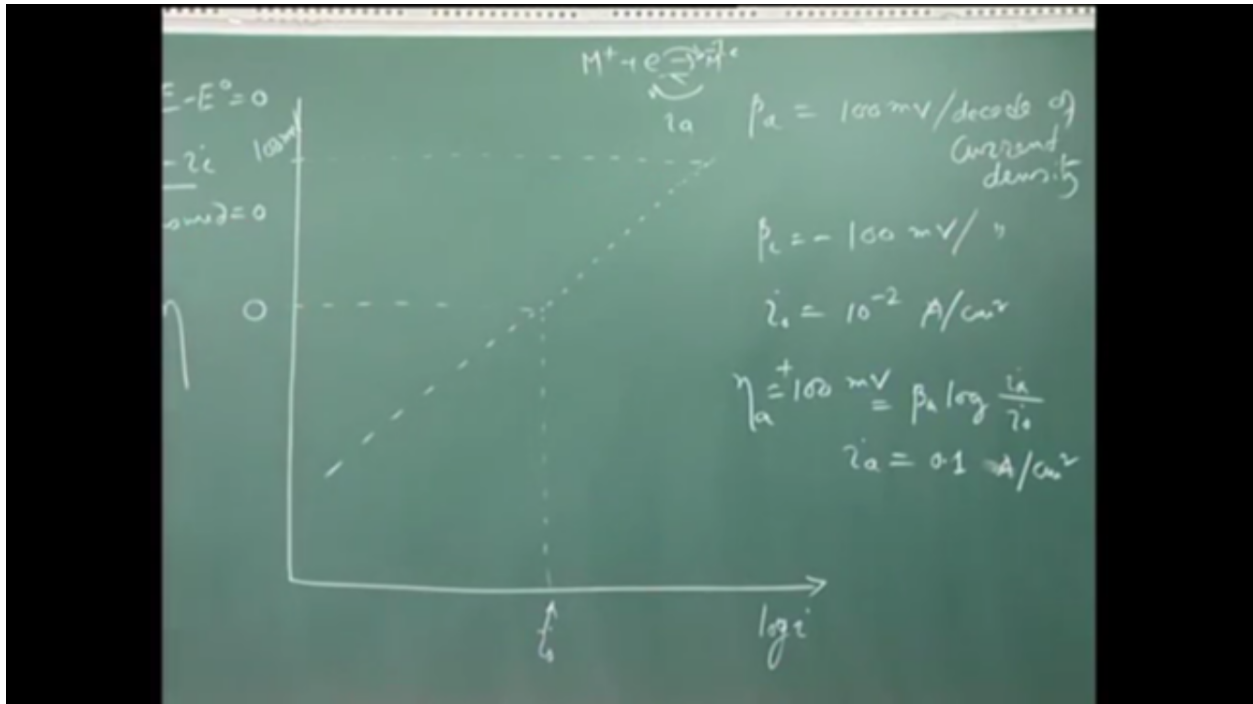
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Similarly, since I know that I have already gone to a positive side, which is 100 millivolt, let us say this is my 100 millivolt. This is my 100 millivolt. So I know that I have already reached there. So I can calculate what is my anodic polarization. Fine. So I can find out where is my point, this point, let's say this is my point. This is my point. So like that I can also find out what would be my cathodic current because say then I can draw this cathodic -- anodic polarization line. This equation, it will be governed by this equation. So I can have a line for anodic polarization.

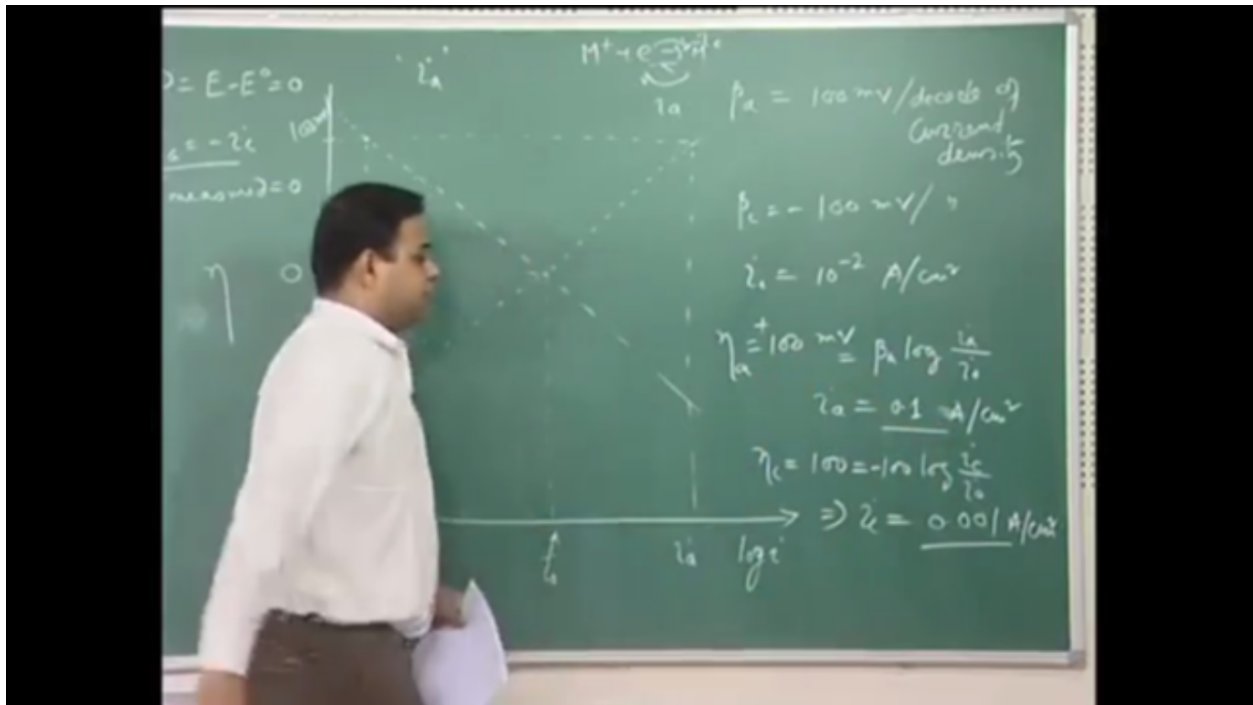


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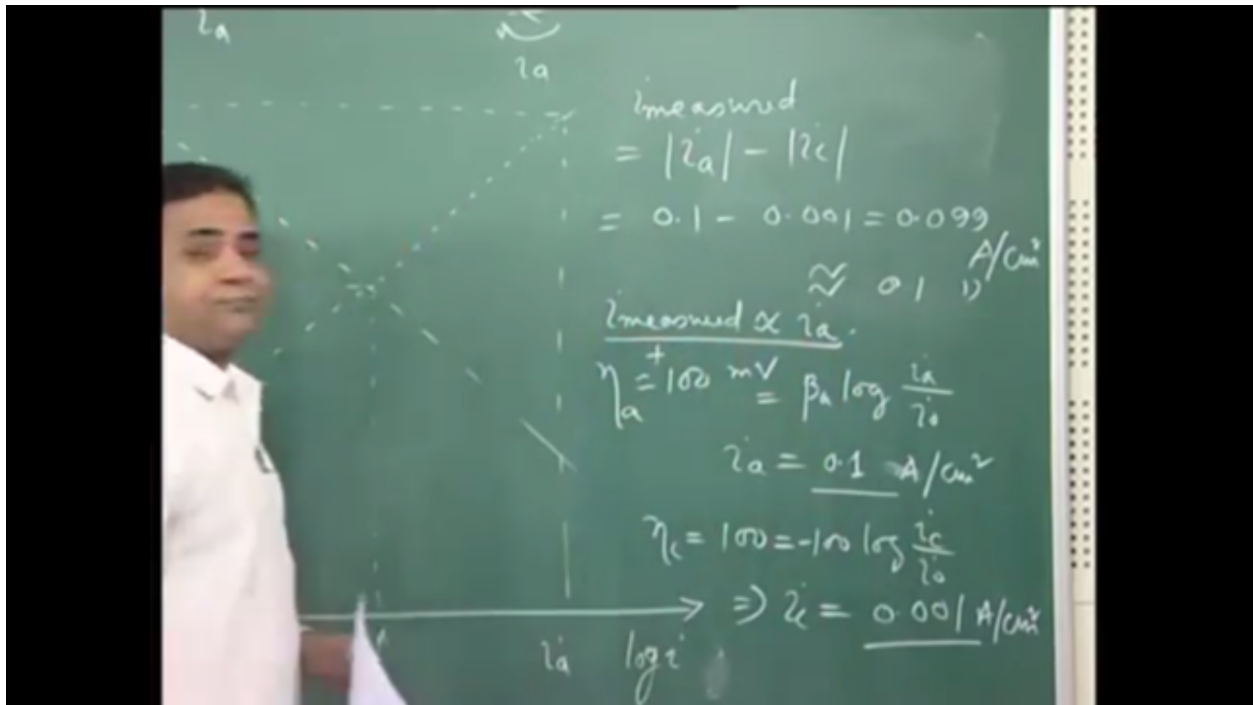
Now, similarly, when I see that  $i_a$  has increased compared to  $i_c$  that doesn't mean that a reverse reaction is not happening. Reverse reaction is also happening, but at a much slower rate. So  $i_c$ , so  $i_a$ , if I know  $i_a$ , similarly, I can also find out what is  $i_c$  because similarly, I can have an imaginary line for cathodic polarization. So my cathodic polarization line cutting the 100 millivolt at this point, so I also can be -- this is my  $i_a$  and then this should be my  $i_c$ . So I can also find out  $i_c$ . Just I would put in this equation, this equation, I will put 100 millivolt, which is plus, and I know what is  $\beta_c$ .  $\beta_c$  is minus and accordingly, I can find out  $i_c$ . So the  $i_c$  you will see that so I can put  $\eta_c$  equal to 100 since I know what is my over voltage, so would be equal to 100 millivolt equal to minus 100 millivolt per decade of current density because I have to put  $\beta_c$ ,  $\beta_c$  is negative, so minus log of  $i_c$  by  $i_0$ , and from that I can find out  $i_c$  is coming out to be 0.001 ampere per centimeter square.

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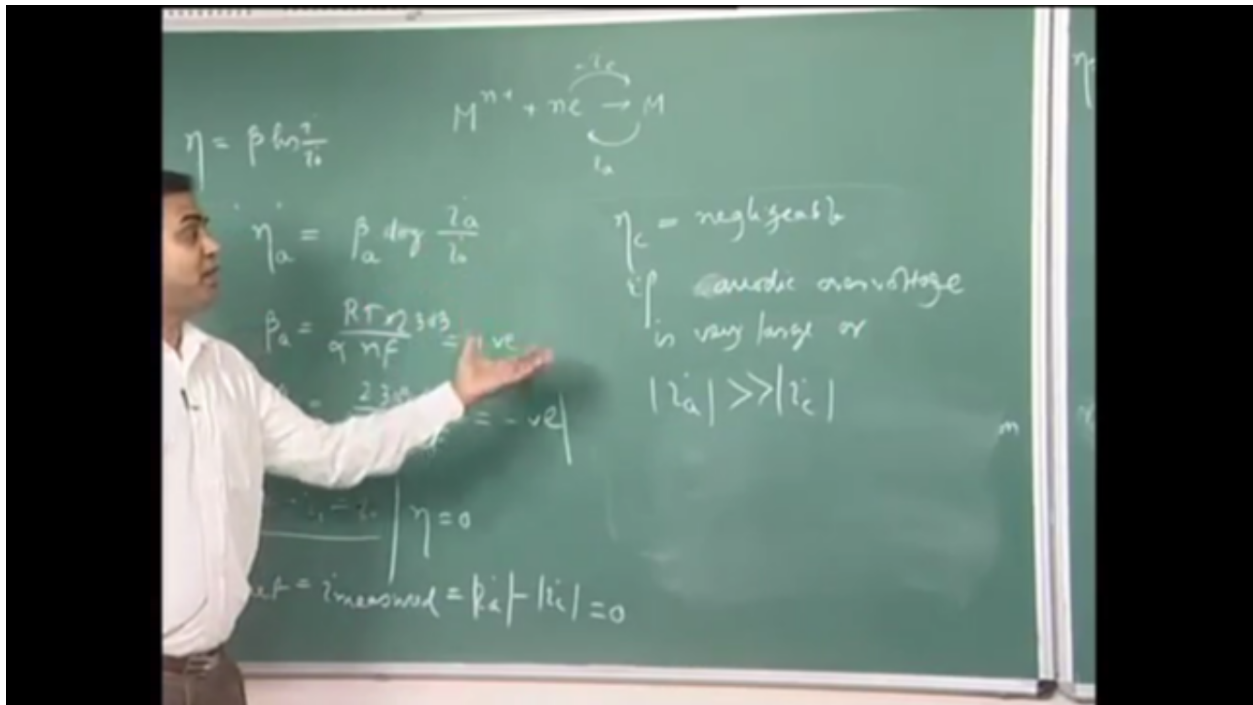
Now if you compare these two current, this is one current, this is another current, so current densities, rather not -- not comparison of current, rather current density, the current density if you see the anodic process is very, very large and if current density for the anodic process is very, very large that means that the cathodic process is very, very slow, and now if I would like to find out what would be my measured current, measured current would be then  $i_{\text{measured}}$ . So I know these two values. So  $i_{\text{measured}}$  would be equal to  $i_a$  minus  $i_c$ , so it would be equal to 0.1 minus 0.001. Now this is equal to 0.099 ampere per centimeter square is almost equal to 0.1.

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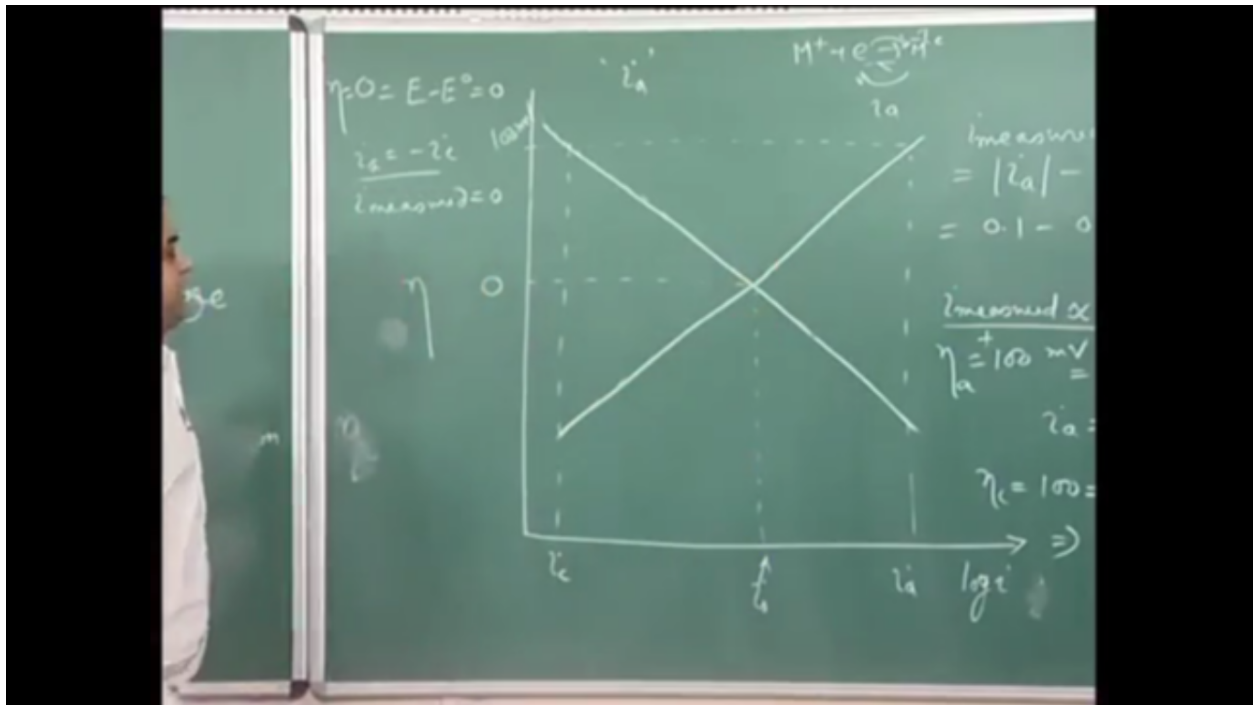


Now you see that  $i_{\text{measured}}$  equal to  $i_a$ . So a very important conclusion we have reached,  $i_{\text{measured}}$  equal to  $i_a$  if the overvoltage is very large at that case or on other side if the current density for the anodic process is very large compared to the current density for cathodic process. So that means if the polarization effect due to cathodic current when we have reached to a very, very high positive potential with respect to the equilibrium potential is going to be negligible. So  $\eta_c$ , so let me write it on this side,  $\eta_c$  would be negligible, negligible if overvoltage anodic voltage is very large or  $i_a \gg i_c$ .

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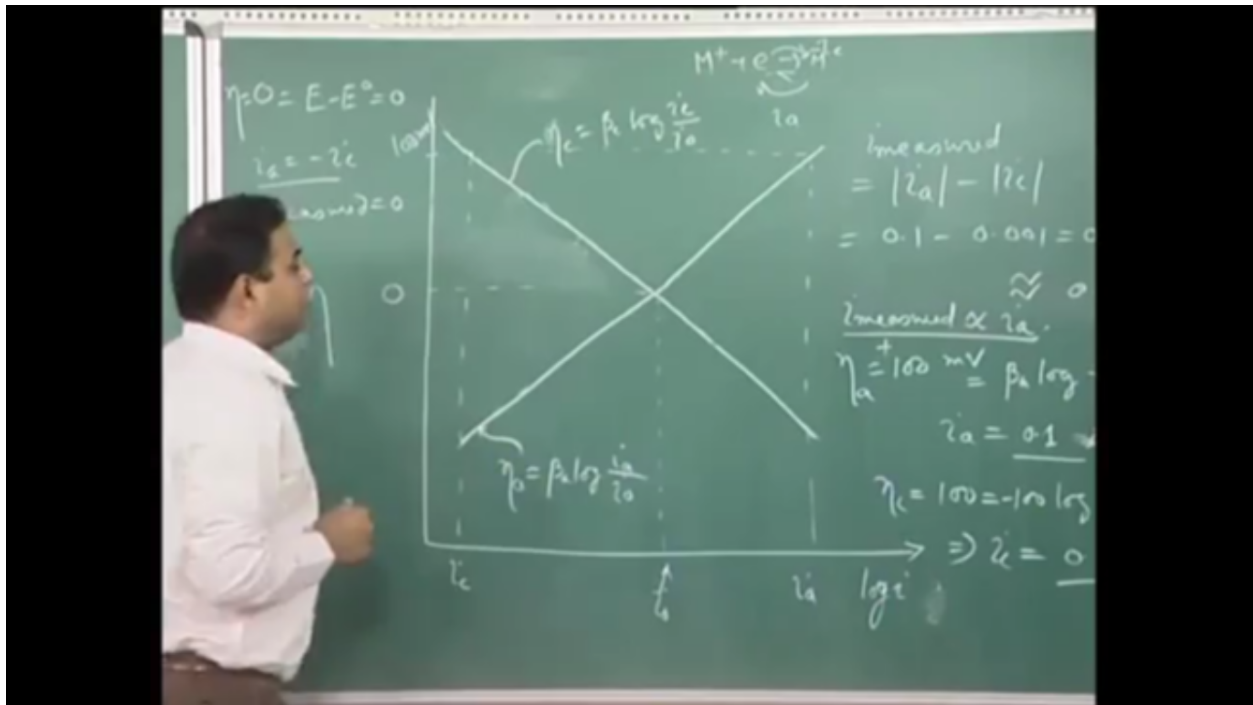


So that means the total polarization is going to be the effect of only the anodic current. So that's why from this we can easily write this. Since the total polarization is only the effect of this, in other way around, if you see this, if we consider what would be the effect of the cathodic current on the polarization since cathodic current always would lead to cathodic polarization or the potential should drop towards the negative value, here you see it is going to the positive side. Again, from the sign convention, it does not lead to any -- does not satisfy my polarization effect. So that means I can easily write this because of this. So now from this I can easily write this for cathodic polarization. I can write for cathodic polarization -- anodic polarization. I can also write for cathodic polarization. I can also this slash means you just replace a with c in case of cathodic polarization.



So now coming back to this curve, so now I can pinpoint what are the -- what is my cathodic polarization line, what is my anodic polarization line? So this is my cathodic polarization line. This is my anodic polarization line. So I can write those equation. This is my  $\eta_a$  equal to  $\beta_a \log i_a$  by  $i_0$  and this is equal to  $\eta_c$  equal to  $\beta_c \log i_c$  by  $i_0$ . Fine, no problem, but the point is I cannot measure  $i_a$  or  $i_c$  individually. Rather I always measure what is my measured current from the circuit. So I need to see what is my measured current. Now from this you can be easily understand, you can easily understand that  $i_{\text{measured}}$  equal to  $i_a$  at a very, very high over potential.

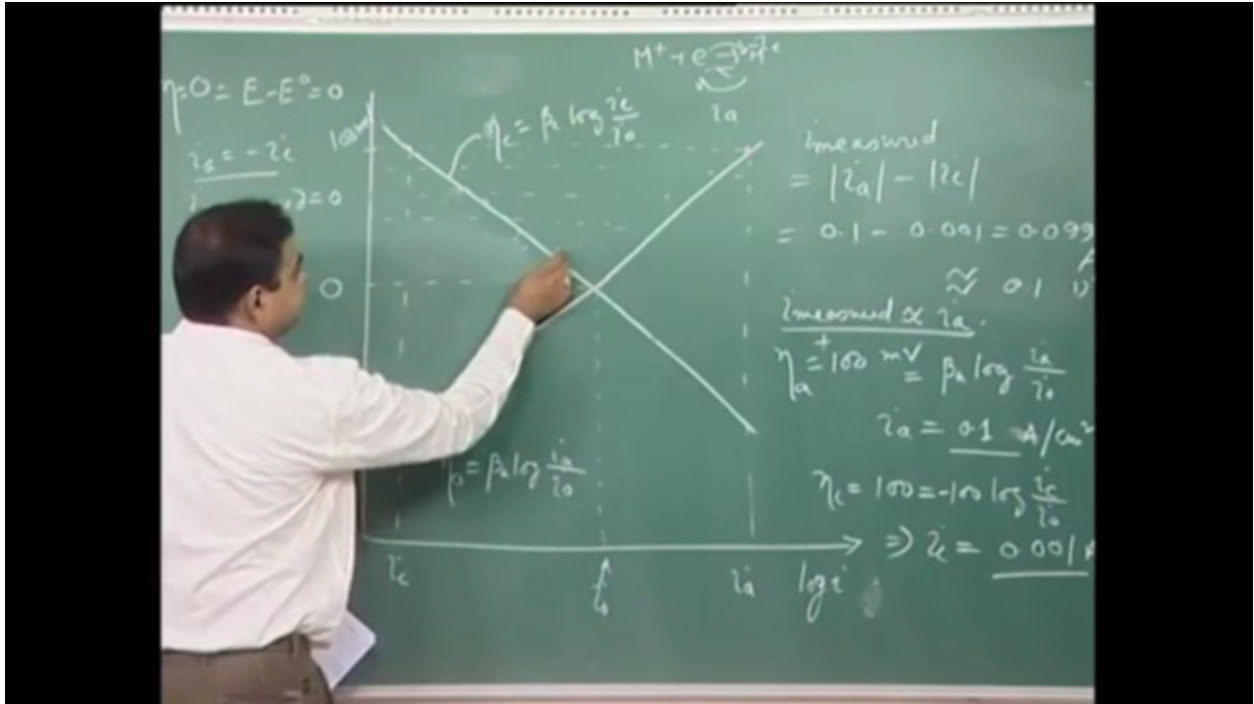
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Now let us say at this, now when the over potential is 100 millivolt, that time I see that  $i_{\text{measured}}$  equal to  $i_a$ . So what would be my corresponding point there? My corresponding point would be close to this, close to this. Similarly, I drop down to little more lower overvoltage. I will see this my  $i_{\text{measured}}$  point would shift to this. It would be very, very close to  $i_a$ . Similarly, if I drop down further, I will see that my current value is coming out to be this. This is my  $i_{\text{measured}}$ . I am just plotting  $i_{\text{measured}}$ . Gradually, I can see that  $i_{\text{measured}}$  will come here.

Now as I come close to this, so I will see that  $i_{\text{measured}}$  would have the effect of  $i_c$  also. At a very, very high positive over potential,  $i_{\text{measured}}$  would be equal to  $i_a$  as you go down because as you go down that means if you have a lower and lower anodic overvoltage or anodic polarization, you see that  $i_c$  effect is coming because that time  $i_{\text{measured}}$  cannot be equal to  $i_a$ . Rather  $i_{\text{measured}}$  would be equal to  $i_a$  minus  $i_c$ . So this point will shift.

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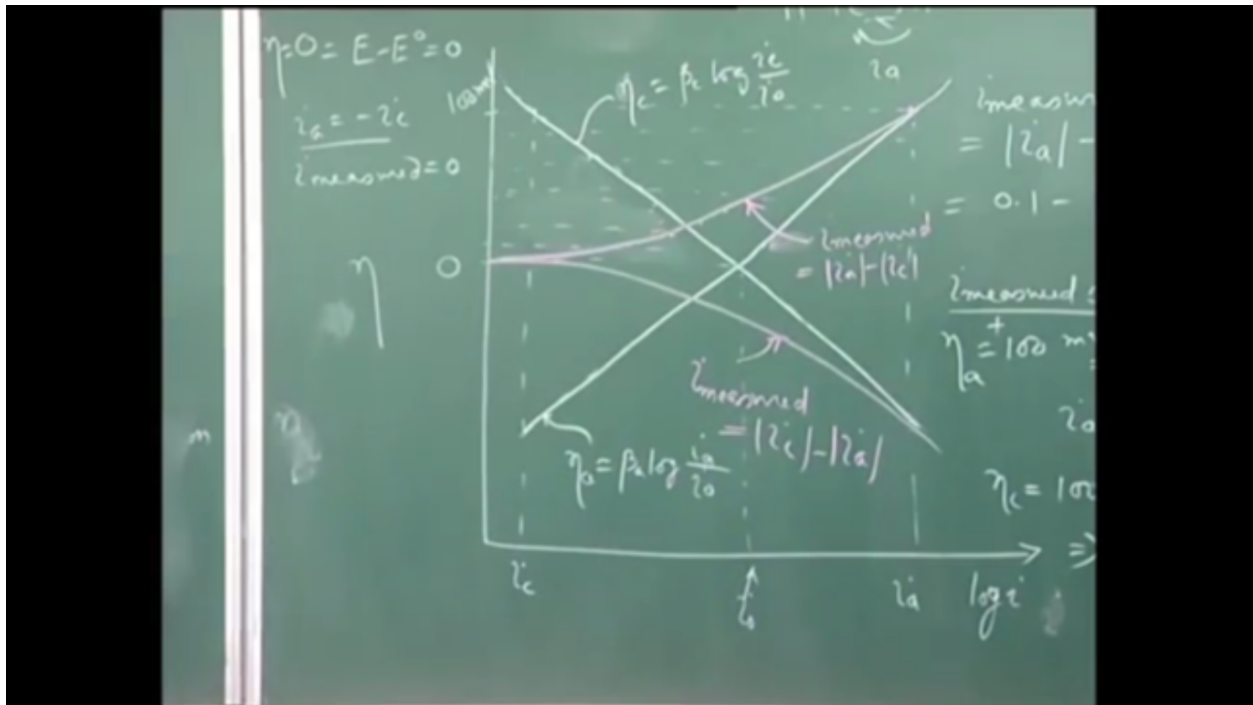


Fine. So now I can -- I can -- I can connect this all those locus, all those points. So now I can -- let me connect all those points. I have connected all those points at different overvoltage value. So at different overpotential values, I have just found out what is my  $i_{\text{measured}}$ , and this is the plot of my  $i_{\text{measured}}$  and  $i_{\text{measured}}$  actually we measure from the external from the circuit. We don't measure  $i_a$  or  $i_c$  separately.

Similarly, the other side also we can have similar plot. So this is my  $i_{\text{measured}}$  is nothing but  $i_c$  minus  $i_a$ , and this side is  $i_{\text{measured}}$  equal to  $i_a$  minus  $i_c$ . Sorry, this line. This line.

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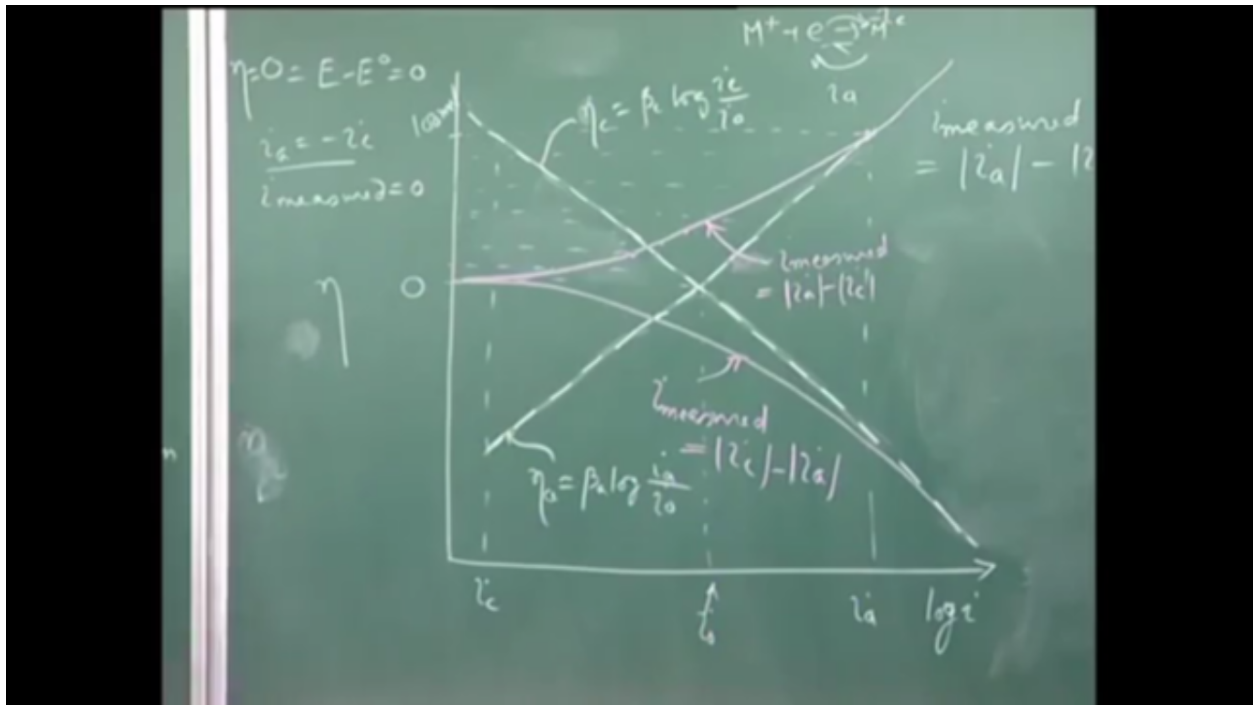
So now what curve we will see where, what experiment data we will see, when we do polarization, that means we forcefully take the potential towards the positive side or the negative side. That we can easily do by supplying positive current or negative current into the -- into this so that time I can have a cathodic current and we can forcefully take out electrons from metal. We can have anodic current. So that time I will have a plot like this, and from this it is very clear what is my  $i_0$ ,  $i_0$  and the important issue is -- important issue is you see at a very, very high overvoltage, this experimental line is merging with the straight line part because at a very, very high overvoltage line, over potential line, experimental line is basically the -- this line is experimental bio data, and this is my actual anodic -- cathodic current, and this is my anodic current and corresponding overvoltage.

So if you would like to find out what is my  $i_0$  for this reaction, I will have this curve, and we have to find out what is my straight line region, and the straight line really a region from the linear region I will draw a tangent, and also from the linear region I will draw straight line and I would like to see where it cuts along 0 overvoltage. That is my point for  $i_0$  for the particular equilibrium reaction or reversible reaction. So this is my experimental part.

So let me find out, let me put the experimental line as a solid line and other line as dotted line which are not experimentally found out. So my dotted line would be -- this is not my experimental plot. This is inherent in the system. This is inherent in the system. So I have gotten a polarization curve.

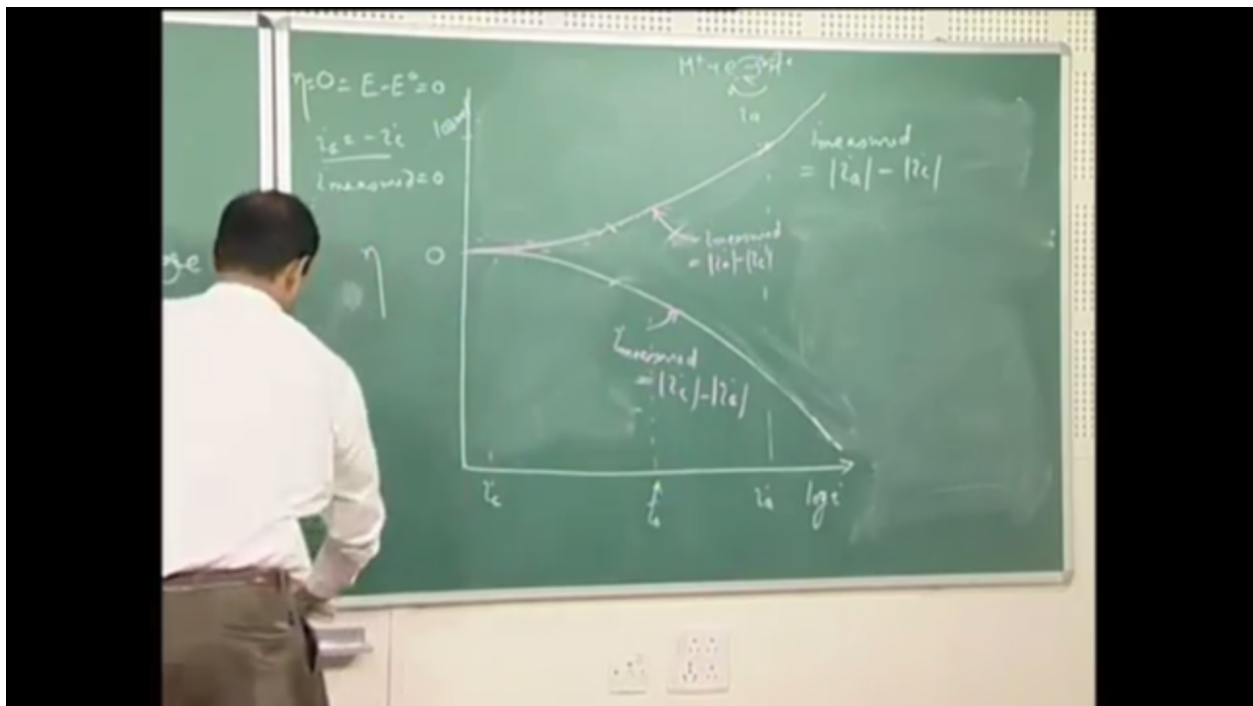
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So let me remove all the dotted lines and then I will only see the polarization curve.

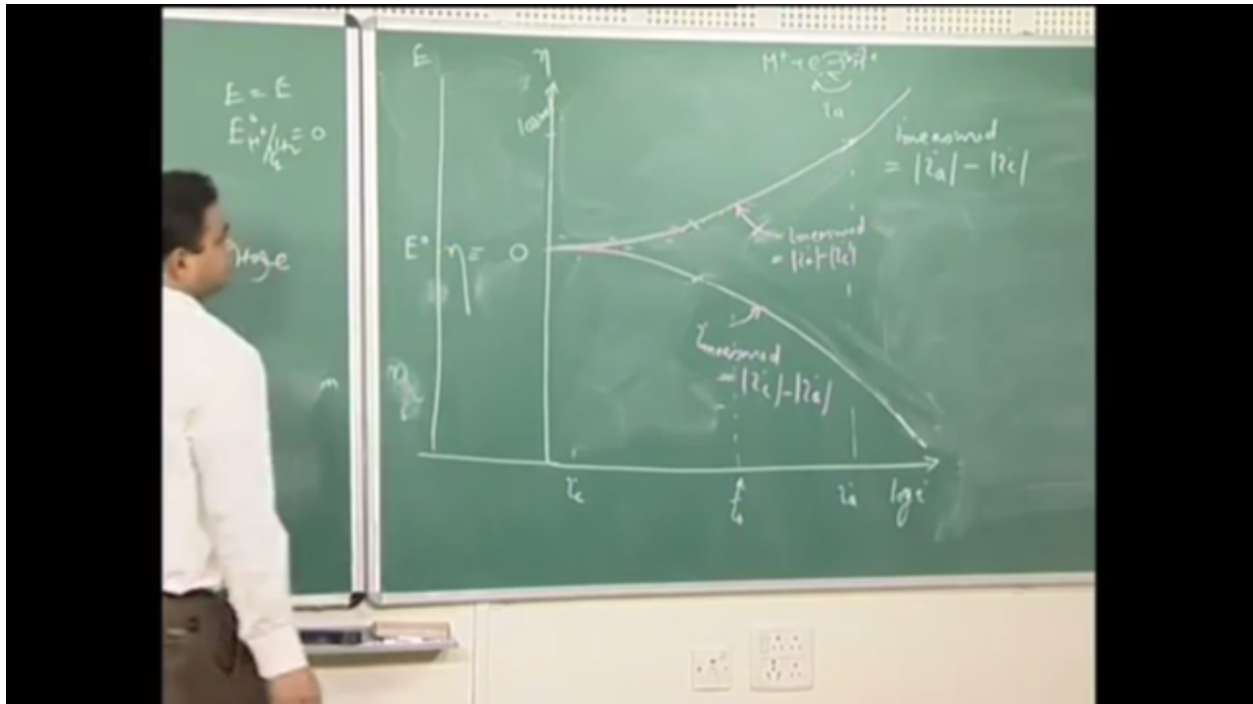
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This is my polarization plot and that plot you actually see experimentally. So I can find out what is my polarization curve that means overvoltage versus  $\log i$ . Now we can also convert into absolute potential. What we have to do? Add positive voltage. This is corresponding to  $E_0$ . Zero

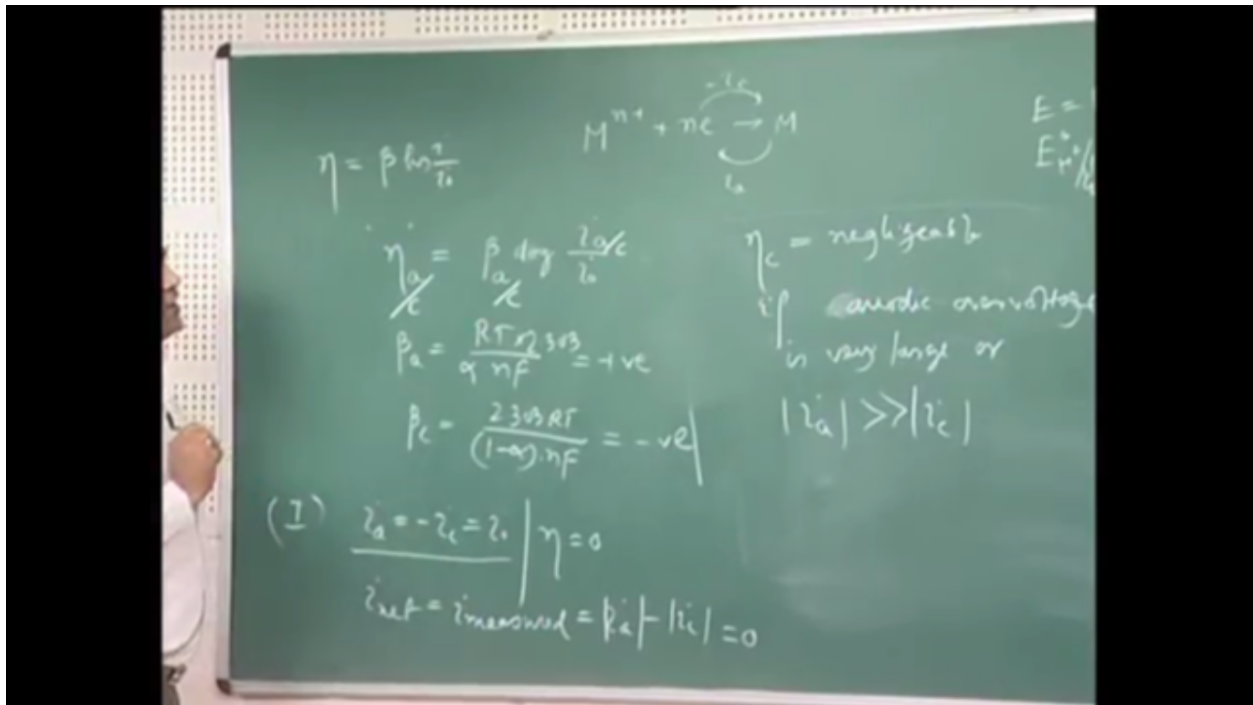
corresponds to  $E_0$  when we convert it into absolute potential. This is my overvoltage data. Let me see another axis where I would like to see what is my absolute potential? Let's say you have measured the potential with respect to standard hydrogen electrode potential, so that case  $E$  is basically nothing but  $E$  because standard hydrogen electrode potential is equal to zero. So this corresponds to  $E_0$ .

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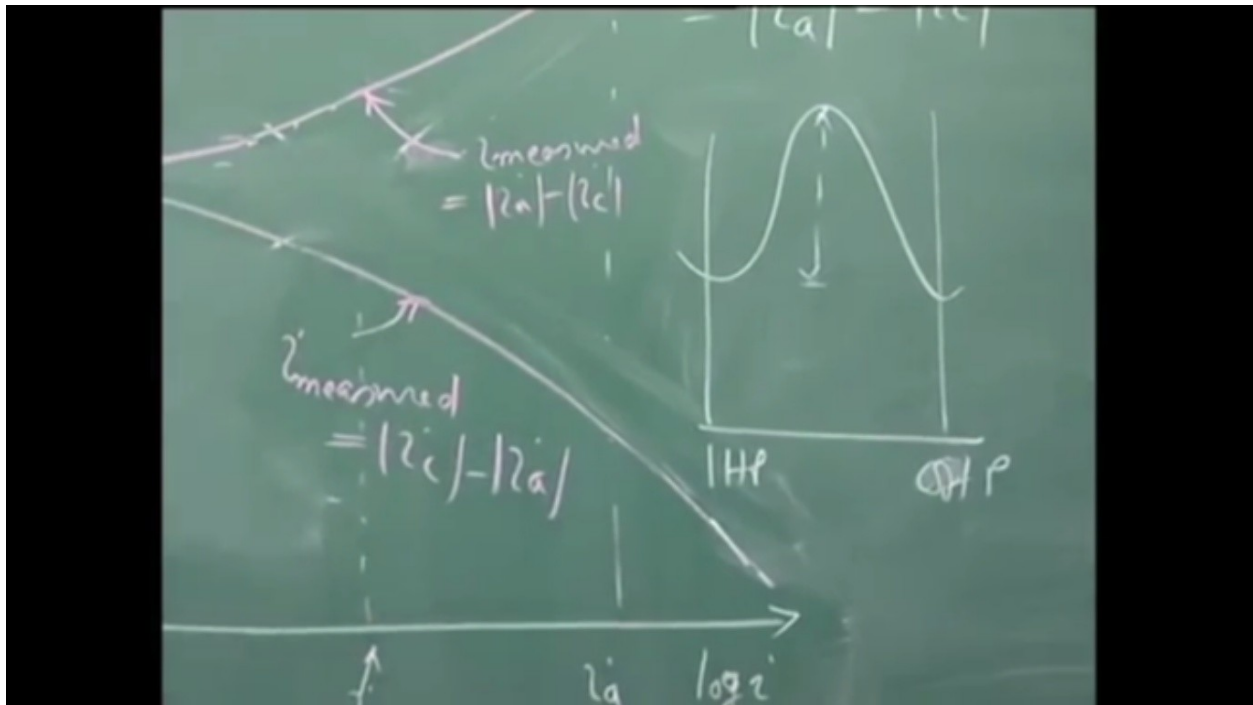
Now as you go up, this would be  $E$  positive compared to this definitely, and this would be  $E$  negative.  $E$  negative is  $E$  minus  $E_0$  along from zero point or  $E_0$  point would be negative, and if you compare what is my  $E^+$ , this is  $E^-$ ,  $E^+$  means this is minus  $E^0$  equal to positive value. So this is my  $i$  in the potential axis and actually, when you compare, when you see the actual measurement that time polarization by experiment you will see the potential but just current density. You can also convert into overpotential compared to the standard electrode what you have used in your particular experiment.

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Now we have seen that this is my overvoltage. Now if you see what is the origin, origin is basically nothing but the thermally activated process. So now we have seen that if this is my IHP, inner Helmholtz plane, and this is my OHP, outer Helmholtz plane, I have seen that how the my reaction barrier or the activation barrier is changing and accordingly, we have found out this expression.

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But the point is if you see this that means if this process is nothing but the activated, thermally activated jump of those species which are the part of this reaction over an energy barrier or activation barrier and that is guided by -- that is also an exponential function that means this is a sort of activation control, activation control. So that means we have to have, for example, if you would like to see what is my cathodic overvoltage or what is my anodic overvoltage, that time I will just see what is the energy barrier that is that the ionic species is facing in case of cathodic polarization or what is the activation barrier the atom is facing to go into ionic species during anodic overvoltage or anodic polarization. So it is an activation control, and this is the slowest step in the process, in the overall process.

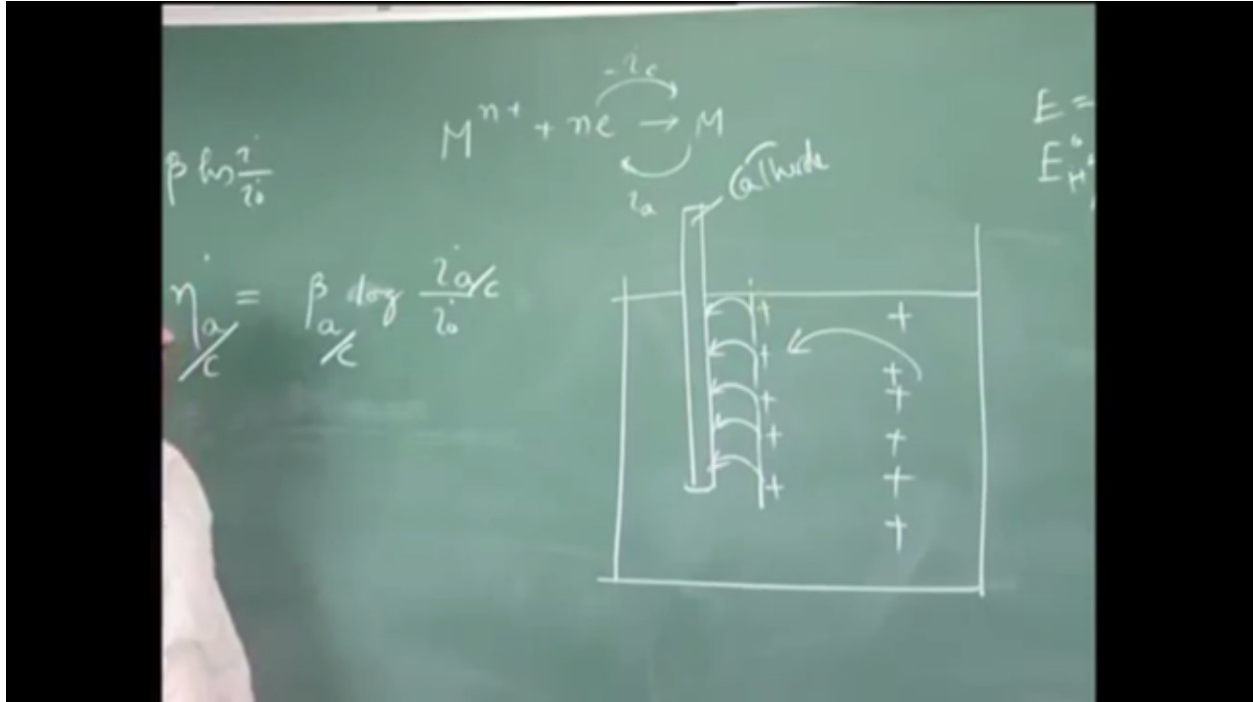
Now we have to understand why we are saying that this is a slowest step? Slowest step because let's say if you consider the cathodic overvoltage that means you actually having all the positive charge, and they are going and depositing on this IHP. Now let's say the rate at which this cathodic or the positive charges are getting deposited on the IHP or the inner Helmholtz plane, that rate exceeds the rate at which the further supply of the further the positive charges are being supplied from the bulk solution. Let me -- let us understand this more carefully.

This is my bulk solution. Let me just say this is my bulk. Let's say this is my cathode. This is my cathode. Now you have inner, outer Helmholtz plane. This is my outer Helmholtz plane. Schematic, I am just drawing a schematic. Now these positive charges are getting deposited.

Now in order to maintain this positive charge, the depleted positive charge, so once one set of a positive charges are getting deposited on this cathode surface in order to maintain the positive

charge ions, the number of positive charge ions on this surface, you have to have a diffusion of positive charges from the bulk of the solution.

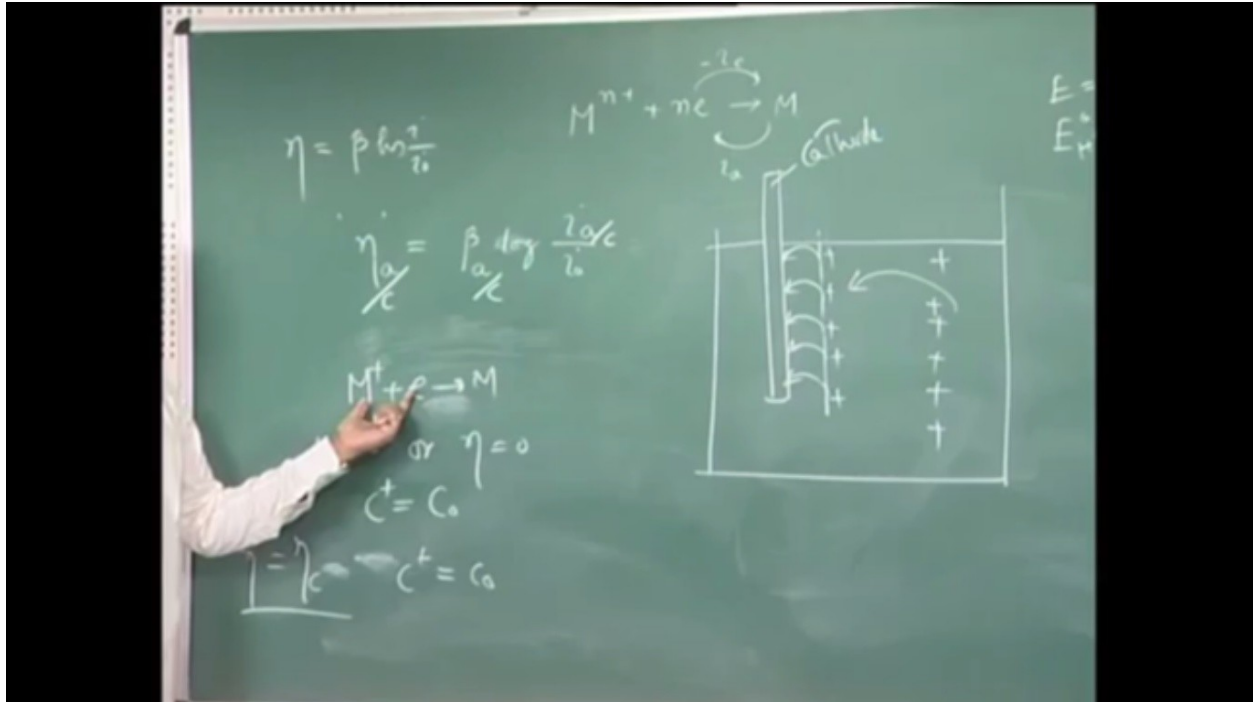
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So now, for example, during the start of the process, let's say this is my reaction. This is at equilibrium. At equilibrium means the rate at which metal ion is forming and the rate at which metal ion is getting deposited, both are equal. Now suddenly, you see that you have some external stimulant or current or you are supplying extra electron to this system. So you have forward reaction preferentially happening, so you are getting depletion of metal ion. So if  $t$  equal to zero and polarization is zero, so concentration of positive charge, let's say concentration of positive charge something around  $C_0$  at this surface.

Now when this equal to some let us say some value, let us say something around some value, let's say this  $\eta_c$  is my over voltage,  $\eta_c$  is my over voltage, that case if I see that  $C^+$  equal to  $C_0$  again, that means the rate at which metal ion is coming from bulk to this, that rate is more than the rate at which metal ion is getting deposited.

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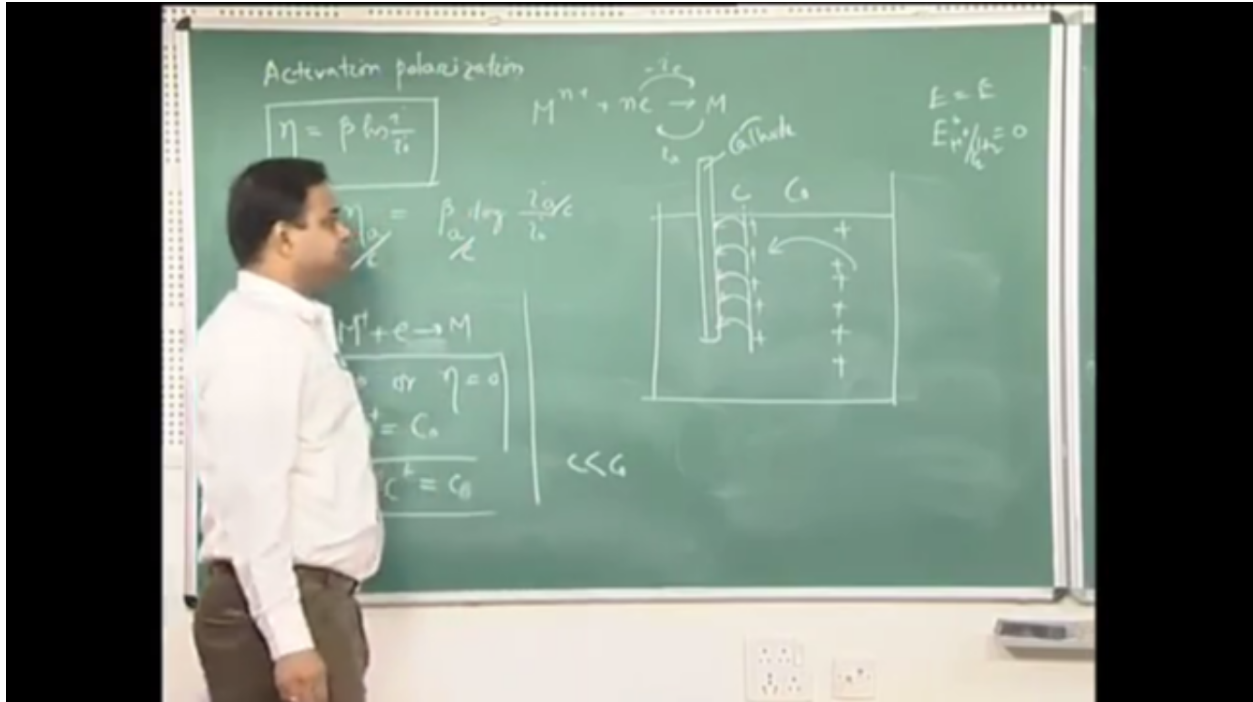
So I see that this process is slower than this process, the diffusion process. So that case my rate controlling step would be the rate at which the metal ion is galloping this activation barrier. So this is activation control.

Now there could be another situation. So, sorry, before that, since this is activation control, we call it as, this, we call it as activated -- activation polarization.

Now the point is same situation at time  $t$  this is happening. This is at time  $t$  equal to zero. Now the point is if you see that if the overvoltage is  $\eta_c$  and that time  $C^+$  plus at this surface is not  $C_0$ , rather it's  $C$  and  $C$  is less than  $C_0$ . So I know that initially, the overall potential -- overall charge concentration is  $C_0$  because that time  $t$  equal to zero and overvoltage is zero. So  $C_0$  throughout the solution we have  $C_0$  concentration of metal ion, but once we have started our polarization, at some polarization value, I see that  $C^+$  concentration at this surface goes to  $C$ .



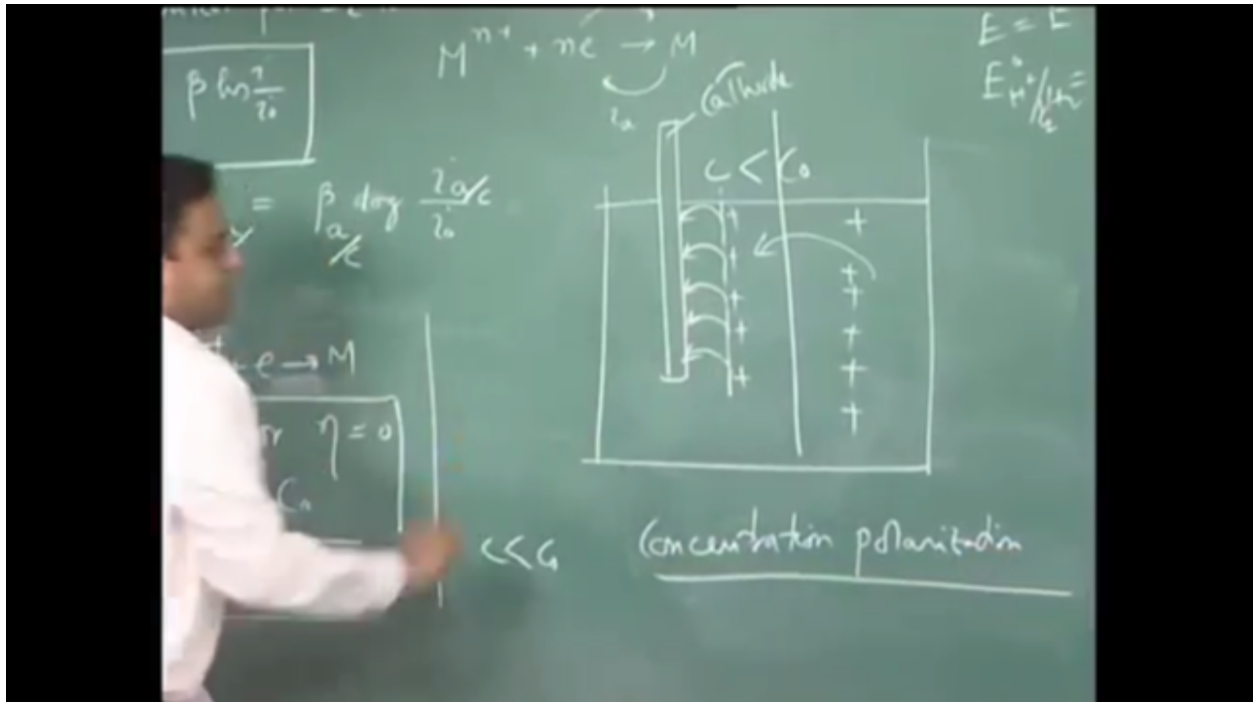
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So if this surface concentration is  $C$ , what does it mean? That means that the rate at which the metal charge is depleting or the depositing is higher than the rate at which this metal ion is coming and diffusing from the bulk to this substrate -- to this surface. So bulk concentration is still maintaining  $C_0$ , but that interface we have the concentration  $C$  and this is less than  $C_0$ .

So what is the slowest step here? The slowest step here is basically the diffusion of charge, positive charge from the bulk to this interface rather than the rate at which this activation jump is happening. So the activation polarization is the activation jump is faster rate is happening at a much faster rate than the diffusion, so I should have something which this polarization has some part which is guided by the diffusion. So this polarization which is happening because of this diffusion, which is the slowest step here in this case, that time it would be called as concentration polarization.

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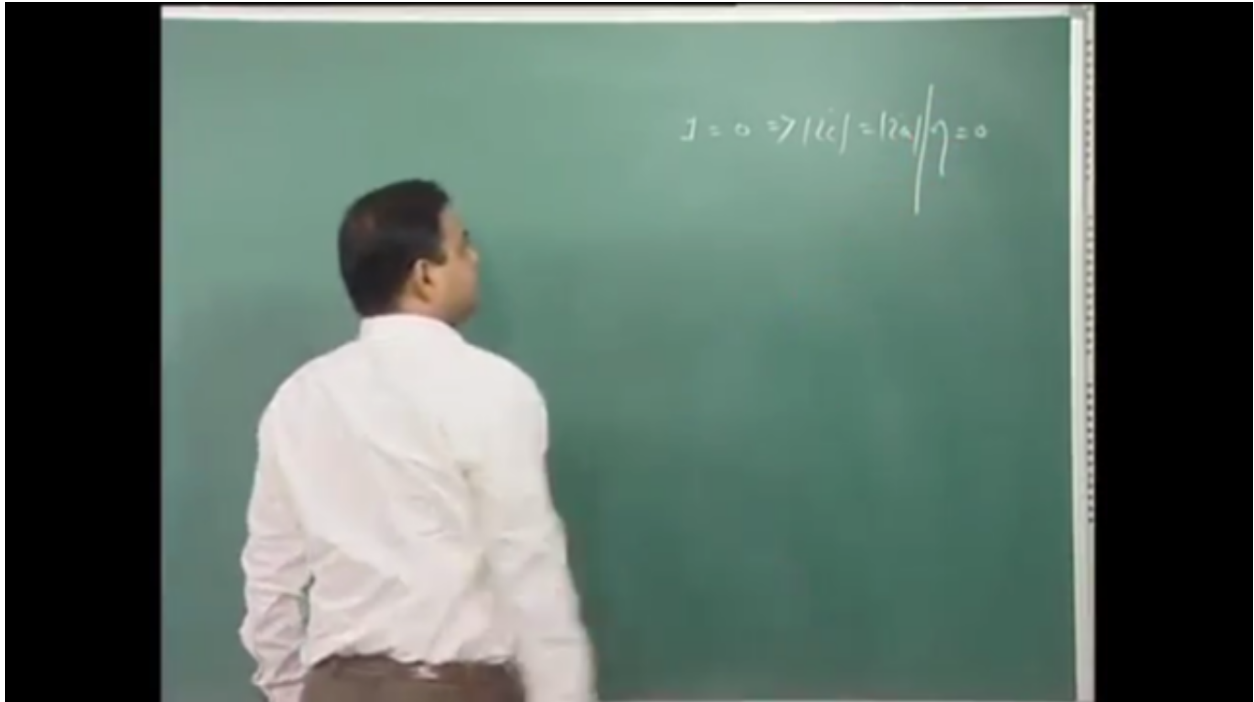


Concentration polarization. Why? Because you see that after some time because of this polarization, I see that there is a depletion of metal -- metal charge concentration, so  $C$  is less than  $C_0$  and  $C_0$  is still the bulk concentration, which is equal to the initial concentration that means in the start during the -- at -- just at the start of polarization, so I see a depletion of metal ion concentration at the interface. So the rate at which diffusion is happening is slower than the rate at which metal activation jump, ion activation jump is happening from this surface to this surface. So my activation, the -- the controlling step would be diffusion and the polarization because of this diffusion is called concentration polarization and that is happening because of difference in concentration at these two sections.

So you see this polarization which is happening because of concentration difference rather than the charge, actual charge transfer reaction, actual activation jump of this ionic charges from this surface to the surface. Now if you blow it up there, you will see what are the things that is happening. Let's say this is my metal surface and these are very closely spaced, so I can merge these two. So what would be the concentration when  $i = 0$ ? If  $i = 0$  that means the  $i_{\text{measured}}$  is zero. So this means  $i_c$  equal to  $i_a$ . Now that case what is my polarization? Zero.



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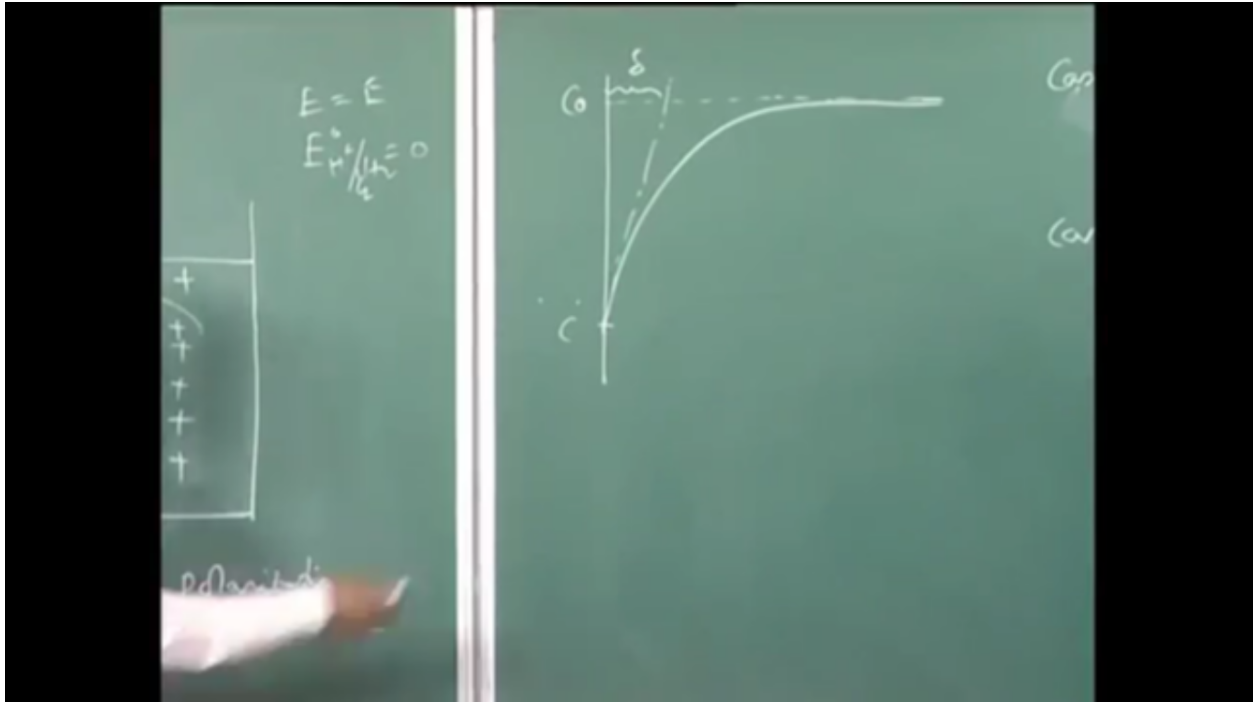


This is my polarization. What would be my concentration at this surface, concentration of metal ion? That is my  $C_0$ . Concentration is  $C_0$  zero when  $i = 0$  or overvoltage is zero. Now during the course of polarization, I see that the collision of metal ion just at the vicinity of cathodic surface is going to decrease because the charge transfer rate from the bulk solution is the slowest step. So the rate at which the metal ion is depositing there that is exceeding the rate at which metal ion is supplied from the bulk solution, so I have a depletion of metal charge at this surface of the metal surface, cathodic surface.

So this is my concentration when  $i = 0$  this is when this is my condition or condition case one. Case one. Now my concentration will change to  $C$  naught  $C$ , that means after some time when we have gotten some finite polarization. So case two is I have gotten  $\eta = \eta_c$  or the overvoltage due to cathodic -- due to cathodic -- due to the metal deposition reaction. So I have dropped this concentration, metal -- ionic species concentration has dropped to this.

Now at some larger distance from this metal surface, what would be my concentration? Concentration would still remain this, but you will see and this is a diffusion process. I can have a boundary layer. So I will see the distribution of metal charge concentration would follow like this. So that means at a wider distance or the bulk of the solution would still have concentration  $C_0$ , but at the metal surface, my concentration of the metal ionic species would drop to  $C$  and this is my boundary layer  $\Delta$ . This is by boundary layer thickness.

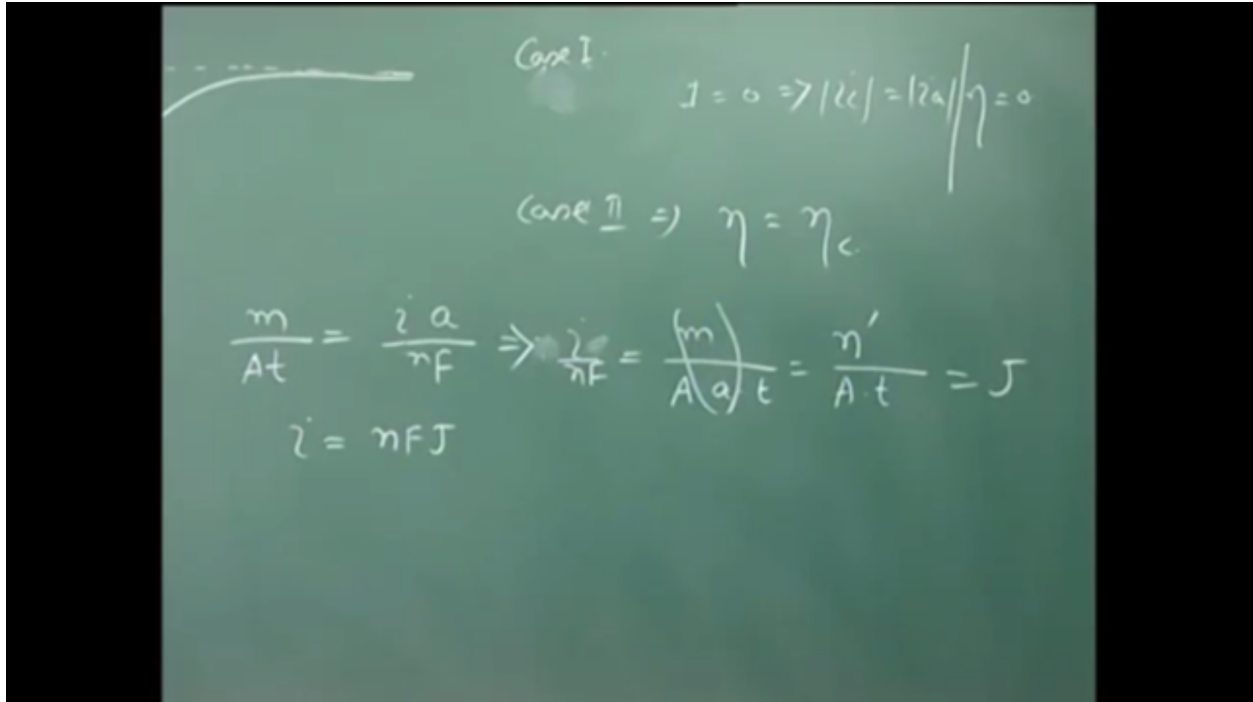
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So this is my boundary layer thickness, which is basically a tangent from this point on this line, on this curved line.

Now let me find out what would be the flux of metal charge that is existing there. So I know this equation  $m = i A t$  equal to  $i A t$  by  $n F$  where  $i$  is the current density,  $a$  is the atomic weight,  $m$  is the mass that is traveling through a section, cross-section,  $A$  is the area and  $t$  is the time. Now from this I can find out that what is my  $i$ ,  $i = m / (n F A t)$ , I can see that  $m$  by -- from this I can find out  $m$  by  $A$  into small  $a$  into  $t$ . And what is this? This is nothing but number of moles by area into  $t$ . So this is  $n$  dash is nothing but the number of mole, total mass that is transferring from one section to another divided by the atomic weight of that metal is giving rise to the number of moles, and you see the number of -- number of moles per unit area per unit time is nothing but the flux. So this is  $J$ . So I can find out what is my  $i$ ,  $n F J$ .

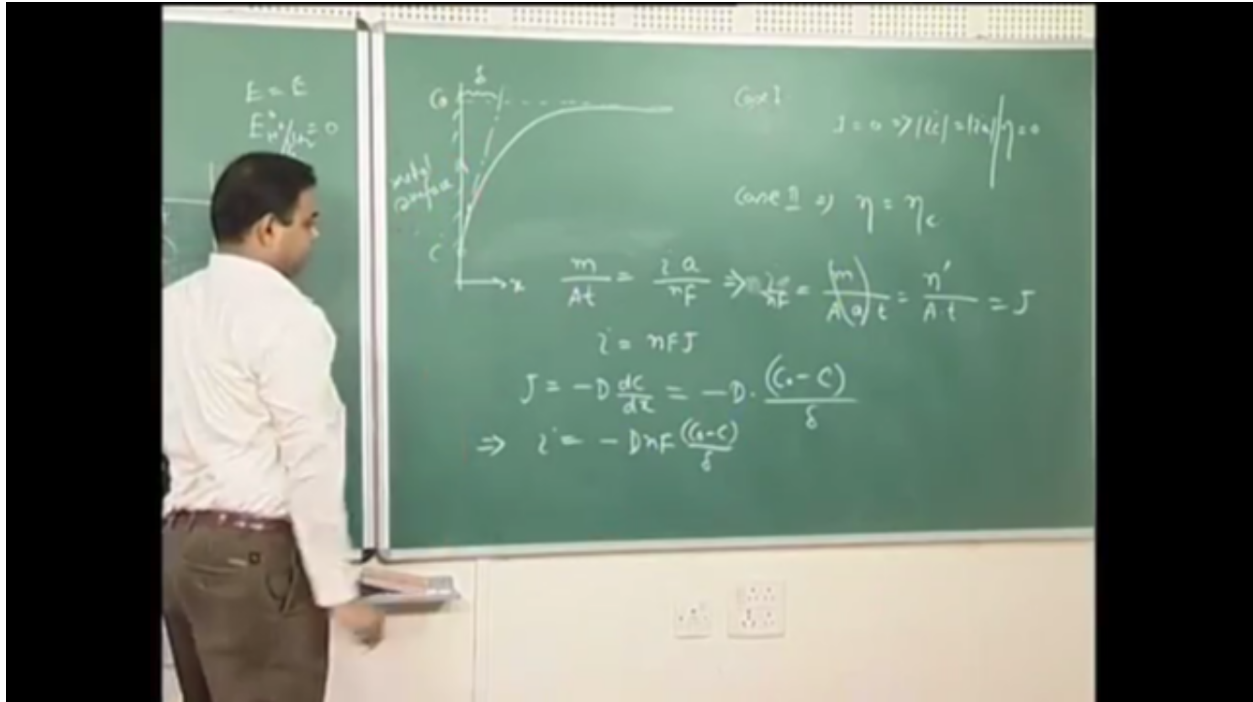
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Now if we consider that is the Fick's 1st law, then  $J$  is nothing but minus  $D \frac{dc}{dx}$  of  $C$ . This  $c$  is basically the concentration and  $x$  is the distance. So this is my  $x$ -axis and this is my concentration and the concentration is changing. This is my  $x$ -axis, and this is my concentration axis, and concentration is changing according to this and this is my metal surface.

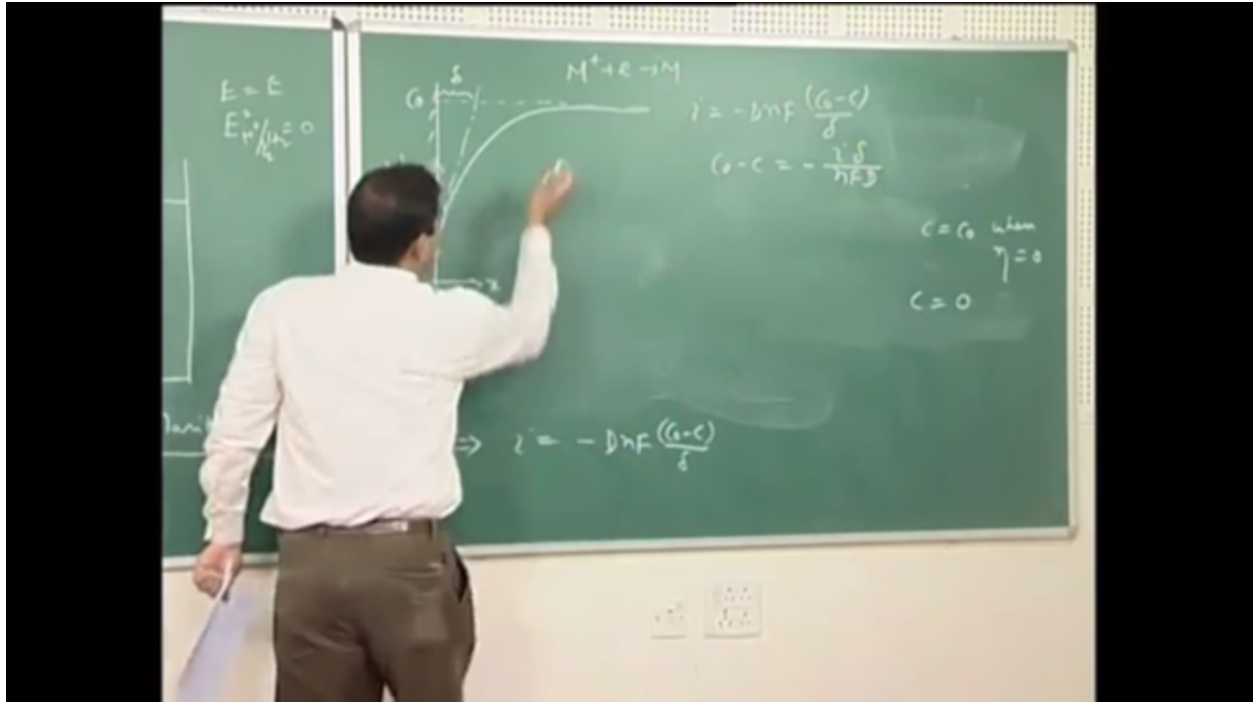
So now if we consider that the concentration is varying linearly, so I can see that what is my concentration difference? Concentration difference is nothing but  $D(C_0 - C)$  by  $\delta$  where  $D$  is the diffusivity of the metallic ionic species in the solution,  $C$  is the concentration when there is no current flow  $C$  is the concentration of the ionic species at this surface when there is finite polarization because of current flow. So from that I can write  $i$  equal to minus  $DnF(C_0 - C)/\delta$  and this is my boundary layer thickness.

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Now so I know  $i$  -- let me -- so  $i$  equal to  $-DnF(C_0 - C)/\delta$ . Now when -- so  $C_0$  minus  $C$  I can find out,  $i\delta$  by  $nFD$  with a minus sign and this minus indicates that the concentration is changing from higher to lower concentration. Now we have two equation -- two situations.  $C$  equal to  $C_0$  when this is 0, overvoltage is zero or there is no current flow. Similarly,  $C$  would be zero if we see that whatever charge that is coming from the bulk to this surface is converting, is basically going to deposit on this surface by charge transfer, by this -- by this equation.

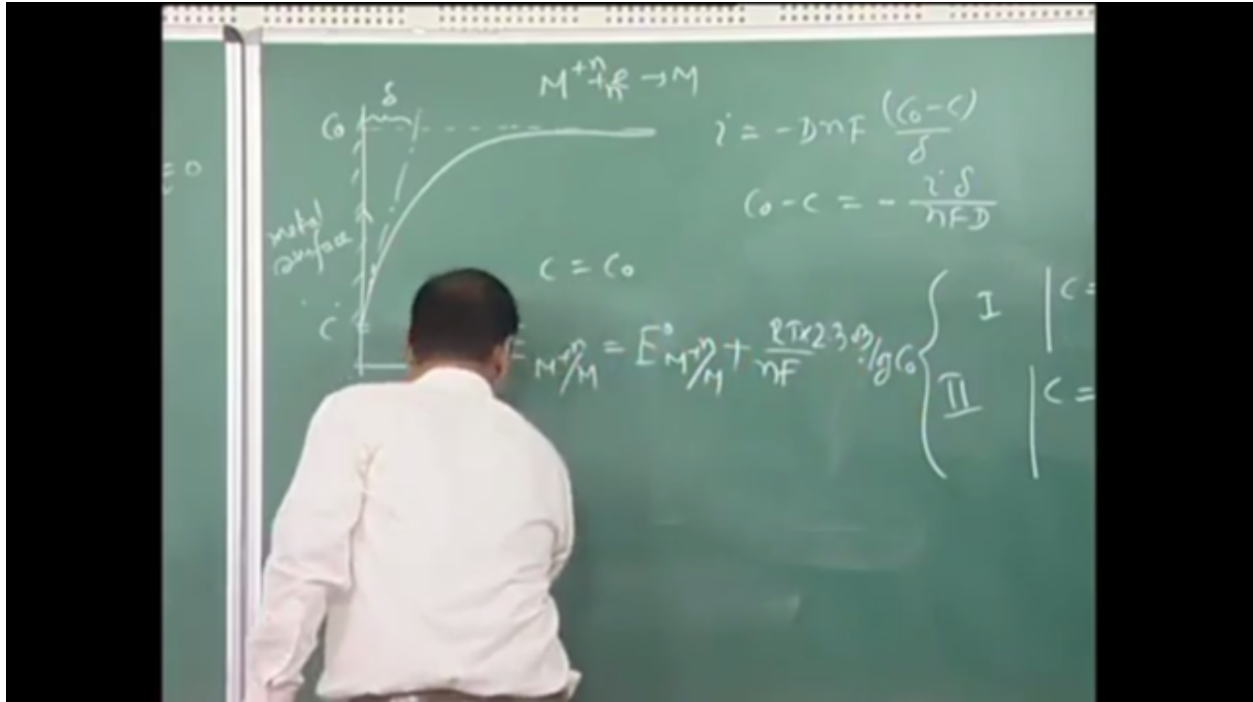
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So whatever metal ion is coming from bulk to this interface, those charges will immediately convert to metal atom because of deposition reaction. So what would be my concentration here? That time  $C$  would be zero and this is  $i$  would be zero in this case, case one. Case two,  $C$  would be zero when  $i$  would be  $i_{\max}$ . What does it mean? Current density is very, very large and the current density you have to find out. As I add some current density, we will see that whatever charge is coming, that will have this reaction and that will deposit. So the concentration at the interface will drop to zero, so that time I can find out what would be my  $i$ . This  $i$  would be the maximum because in this case,  $C$  is going to be zero. So I can have from these two condition, I can have some sort of potential conversion. How would I do that?

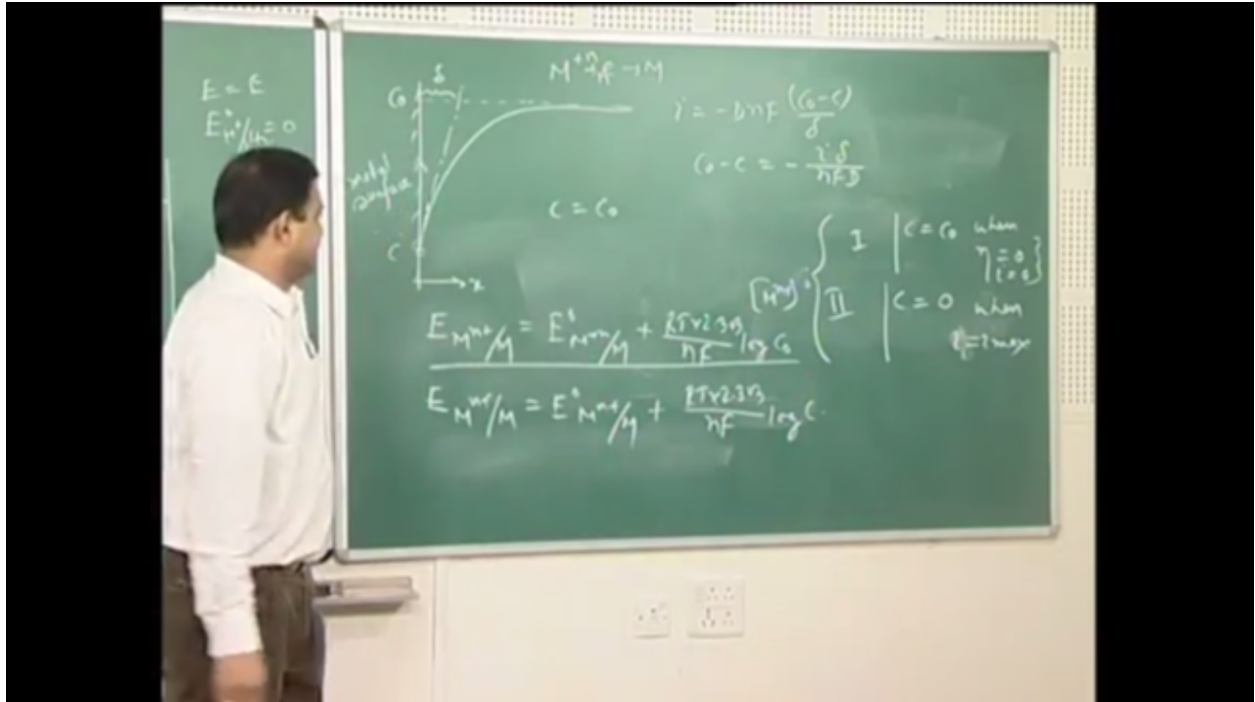
Now when  $C$  equal to  $C_0$ , I can find out what would be my potential  $M^+/M$  equal to  $E_{M^+/M}^0$ . I will just put Nernst equation  $RT$  by  $F$ . Now if we consider this is  $n$ , this is  $n$ , so this is  $n$ , this is  $n$  because if we consider  $n$  number of electrons are associated with this deposition reaction, so that case it would be  $nF$  into log of -- into  $2.303$  log of  $C_0$ .

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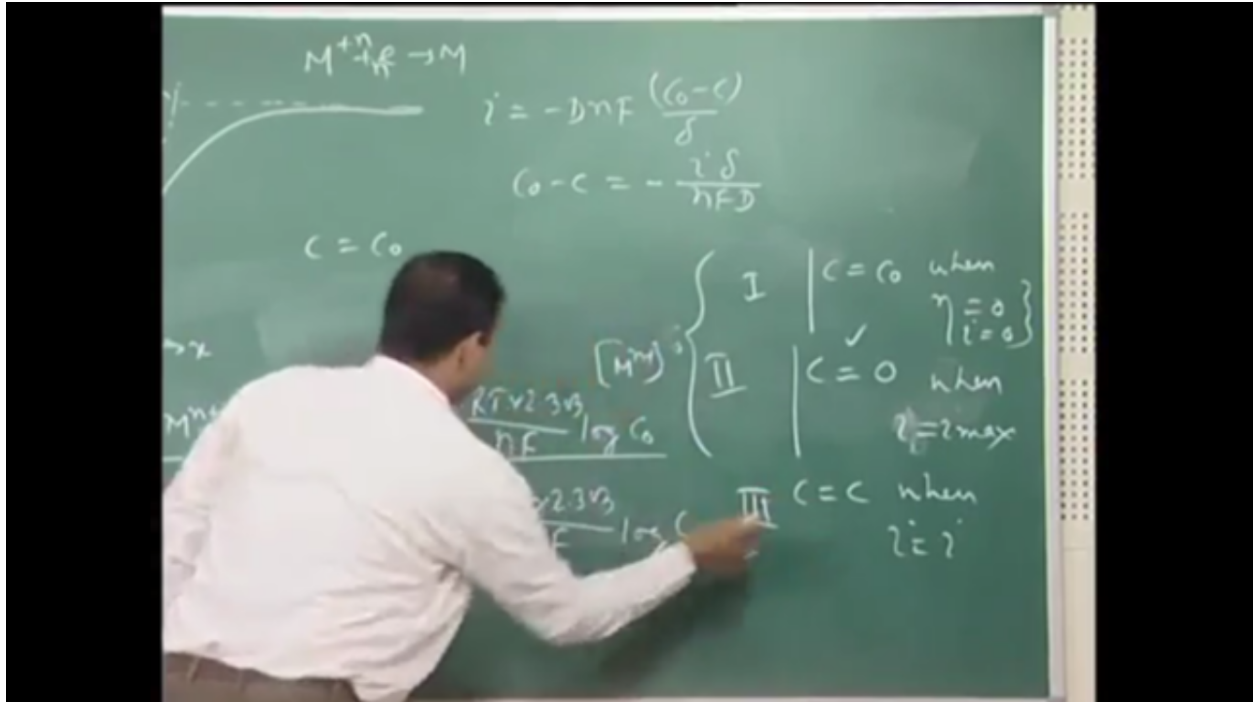
Let me write to little left.  $C_0$  means concentration of metal ion. So I -- I can write Nernst equation according to this formula, and I can put this concentration  $m^{n+}$  as  $C_0$  when  $i$  equal to zero, that time the concentration at the interface also would be  $C_0$ . Now if I find out what would be my potential if my concentration changes from  $C_0$  to  $C$ ? So  $n M^{n+}/M$  would be equal to  $E_0 M^{n+}/M$  plus  $RT$  into  $2.303 nF \log C$ .

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So this is case one. This is case two. That means case one means when  $I = 0$  at this interface, my concentration would be  $C_0$  and when  $i$  has some high value or  $i_{\max}$  that time  $C$  would be let's say some value in case of this would be  $C$  equal to zero or I can put  $C$  equal to  $C_0$  when  $i$  equal to  $I$ , some value.

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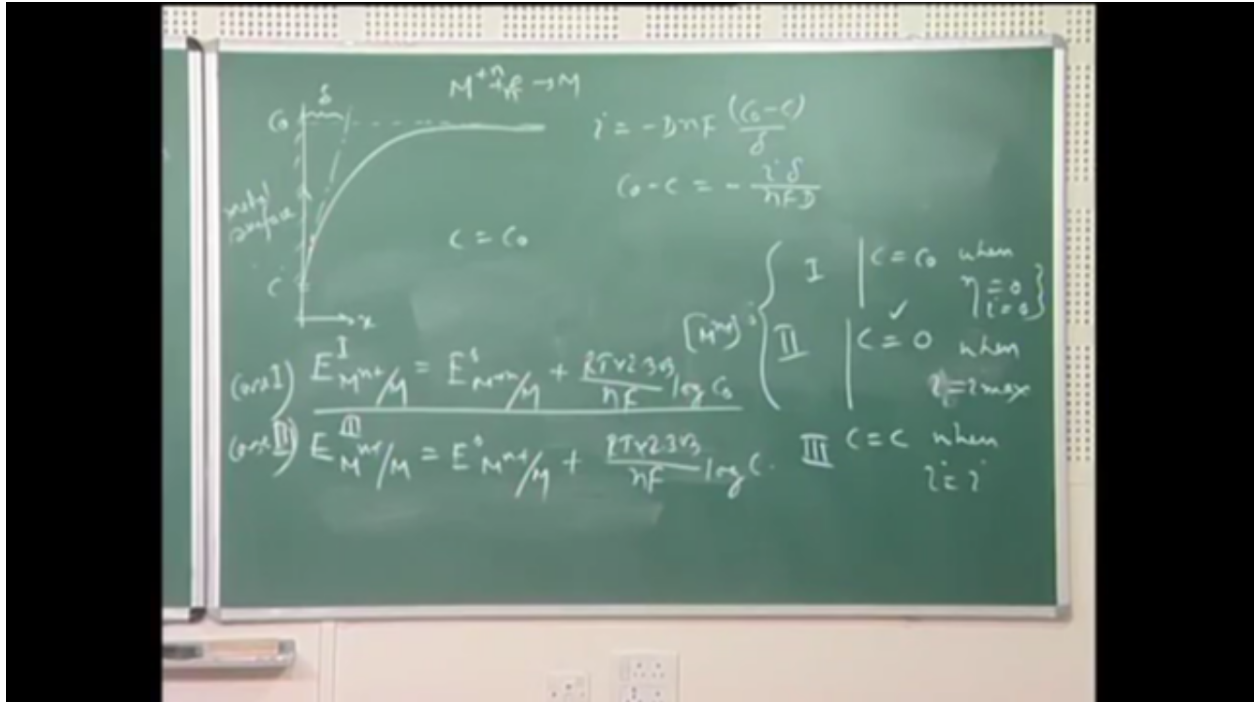


So this case, let me consider this is third case. So third case, let me put this is a third case. That case my -- I can find out what would be my potential because of this concentration  $C$  and when the current is  $i$ . From this two equation, I can see that this is 1, this is 3 corresponding to third condition. So I can see that  $E_{M^{n+}/M}$  condition one would be greater than  $E_{M^{n+}/M}$  condition third since  $C_0$  greater than  $C$ . So what would be my polarization? Because of concentration difference, polarization would be I can put concentration conc because that time polarization would be  $E$  final minus  $E$  initial.  $E$  final is this one,  $E_{M^{n+}/M}$  third,  $E_{M^{n+}/M}$  first.

This is my polarization, and you see we have considered metal ion this reaction. So it is basically nothing but the cathodic polarization. Okay. Here also this is cathodic polarization because we see that potential is decreasing since this one is greater than this, and this is happening because of the concentration difference, not because of the metal charge activation jump of the ionic species over the activation barrier from OHP to IHP.

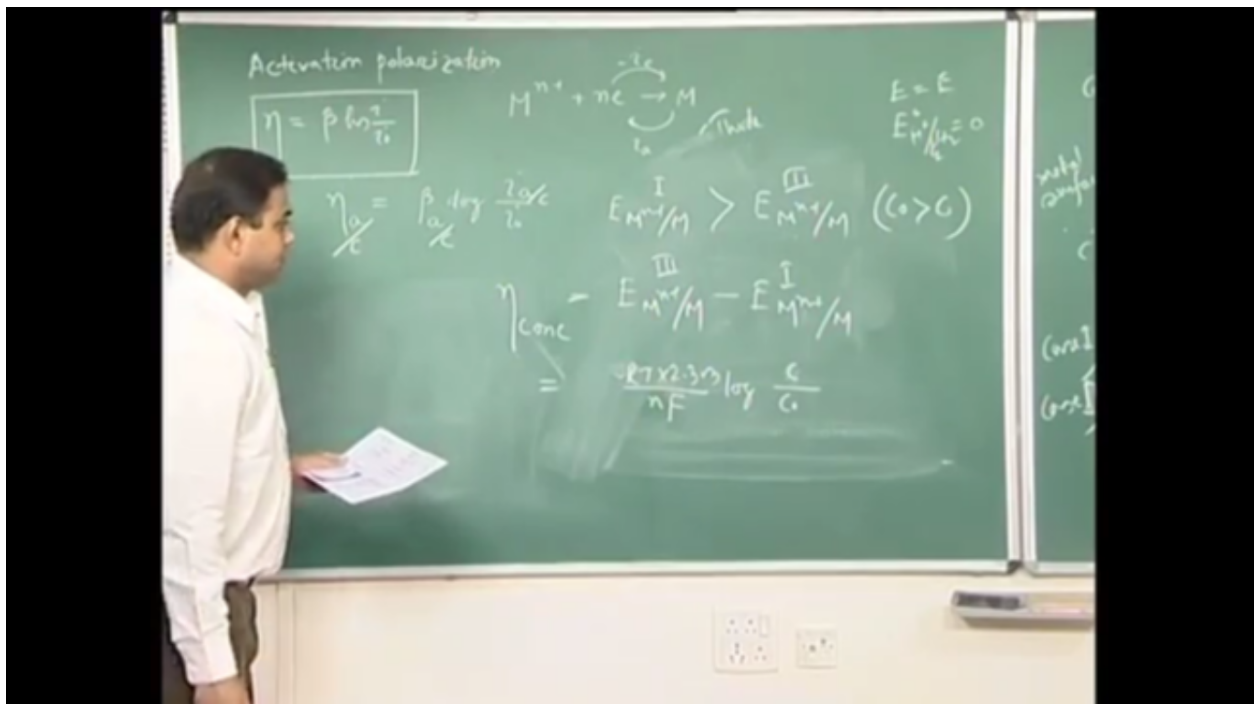


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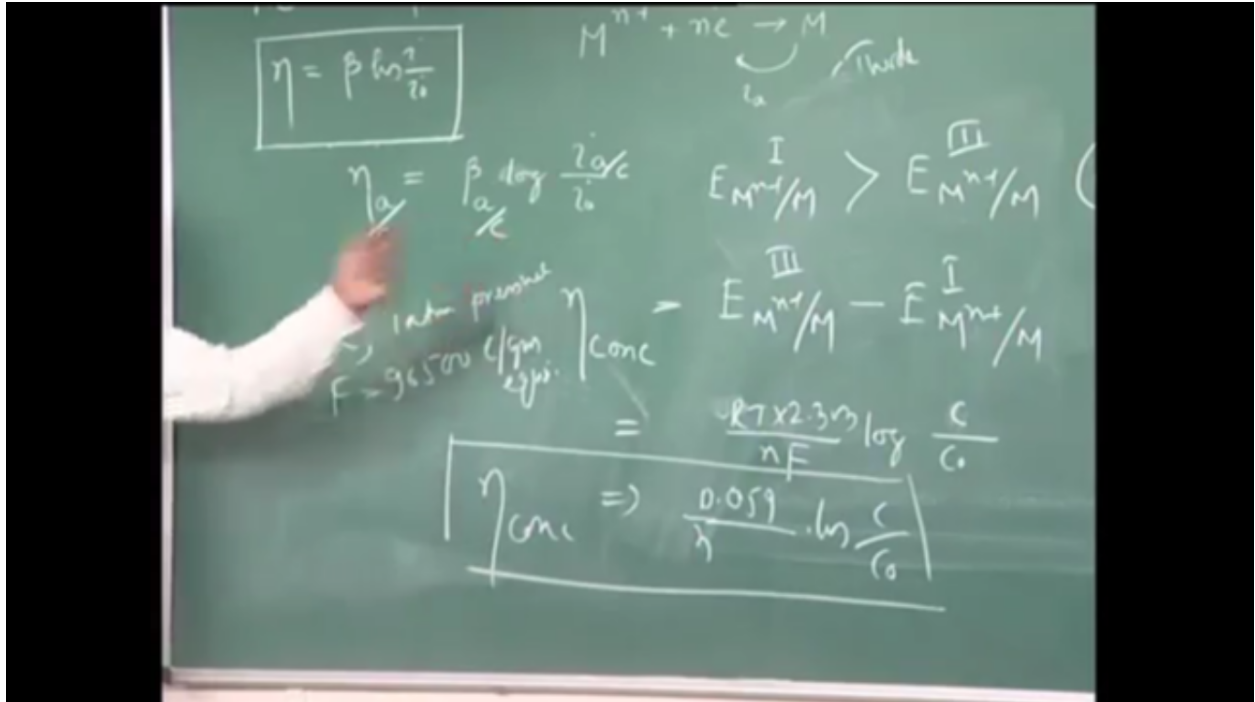
Now from this we can write this should be equal to these two will get cancelled because these are the standard reduction potential for  $M^{n+}$  to  $M$ . These two will get cancelled. So, finally, I would get zero point -- I will get  $RT$  into  $2.303$  by  $nF$  log of -- log of  $C$  by  $C_0$ .

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Now if you put -- if it is happening at 25 degree Celsius, 1 atmosphere pressure, and F equal to 96500 Coulomb per gram equivalent -- gram equivalent, then this value would be 1 by n 0.059. You just put all those values. R is 8.314 into log of C by C<sub>0</sub>. So I have gotten one important correlation with the overvoltage that is because of concentration difference I will get this.

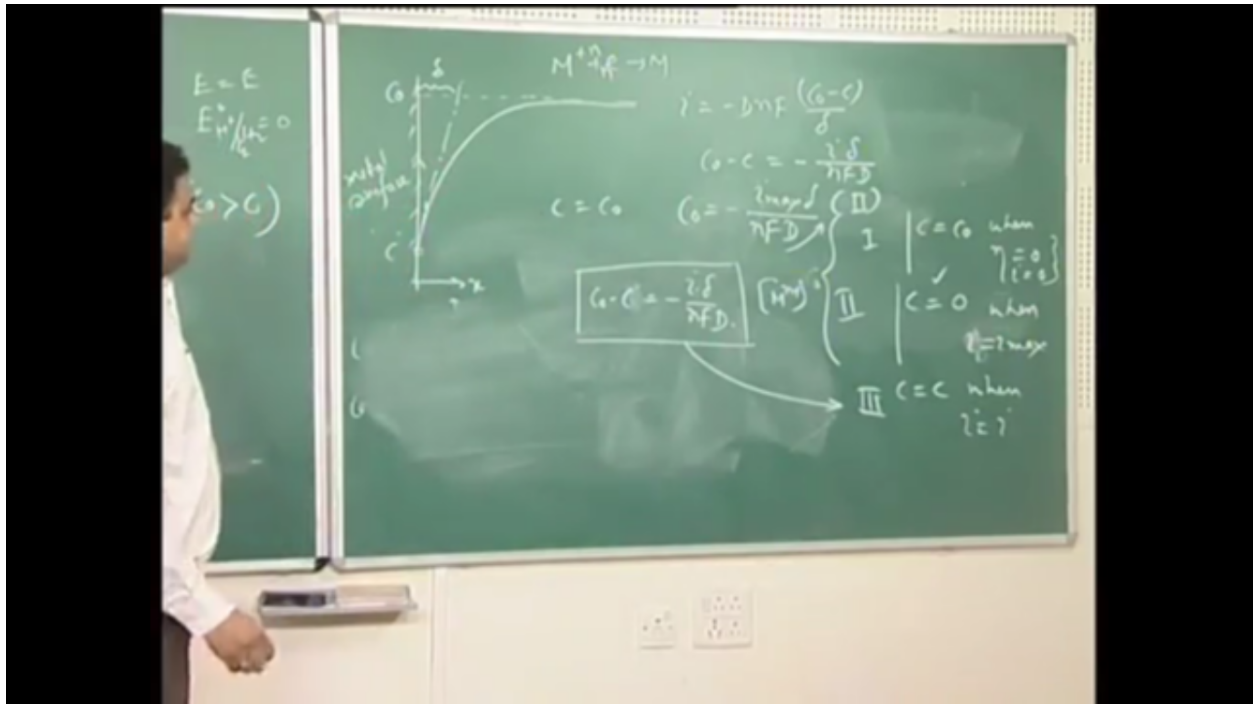
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Now -- now instead of C, I can -- I can write the concentration in the form of this. Okay. So if C equal to 0, that time, in this case, if C equal to 0, that time i is basically i<sub>max</sub>. So C<sub>0</sub> would be equal to minus i<sub>max</sub>δ/nFD, condition third, condition second. This is related to condition second.

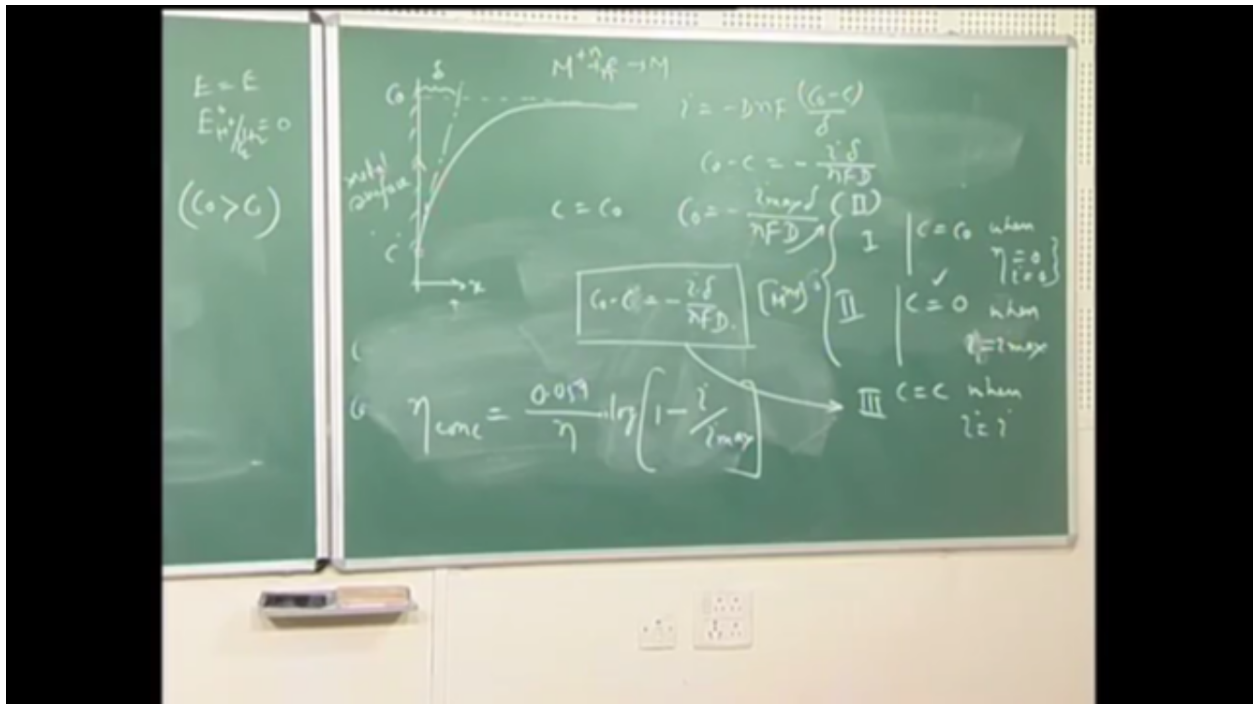
Similarly, I can write what is C. C would be equal to minus iδ/nFD. Sorry. C<sub>0</sub> minus C equal to this is condition this.

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So I can replace this  $i$  and  $i_0$ . So let me replace  $i$  and  $i_0$ , equal to  $0.059/n \log$  of -- you just replace this, you will get  $1$  minus ( $i$  by  $i_{max}$ ).

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So this is a very, very crucial expression and this expression tells you what would be my polarization because of concentration difference. So this is nothing but the concentration overvoltage. Thank you.

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