Electrochemical Impedance Spectroscopy
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Lecture – 37
Porous Electrodes

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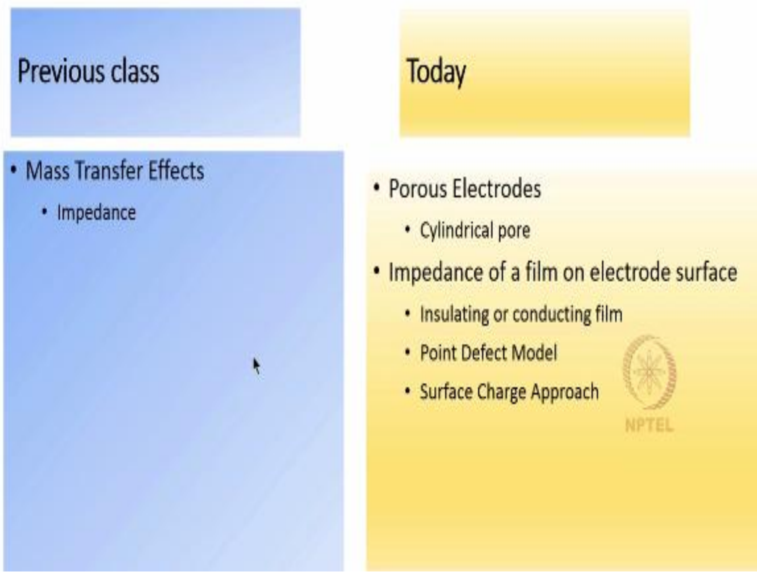

So next what I want to show you, when you have porous electrode, how does the impedance vary. Within the domain of porous electrode there are lot of possibilities, what we are going to see is basically only one example and after that if time permits we will go on to look at what happens when you have a film present on the surface. There are different models for it, there are simplified models, which say the film is either insulating or conducting.

And they can also assume that the film is dense or it is porous. The first case, which is given as porous electrodes, the first case what we are going to see is a conducting metal, but that is porous. If the conducting metal is just a solid metal we know how to handle them, if it is a very thin film, so we have one metal on top of which you have another thin metal film, nonporous proper film, on top of which we have the solution, we can model that.

If you have a film that is porous, we are going to see what it is. If we say the film is insulator, we can model that, that we will see little later and then if the film is insulator but it is porous, we can model that also. For a film which is clean insulator, it is pretty straight forward. For a film that is normally present in metals in solution usually the film is not a clean dense film, it has defects and fill many times continues to form and dissolve. That model is little more complex, so there are models for that, description of those models we will see at the end of that.

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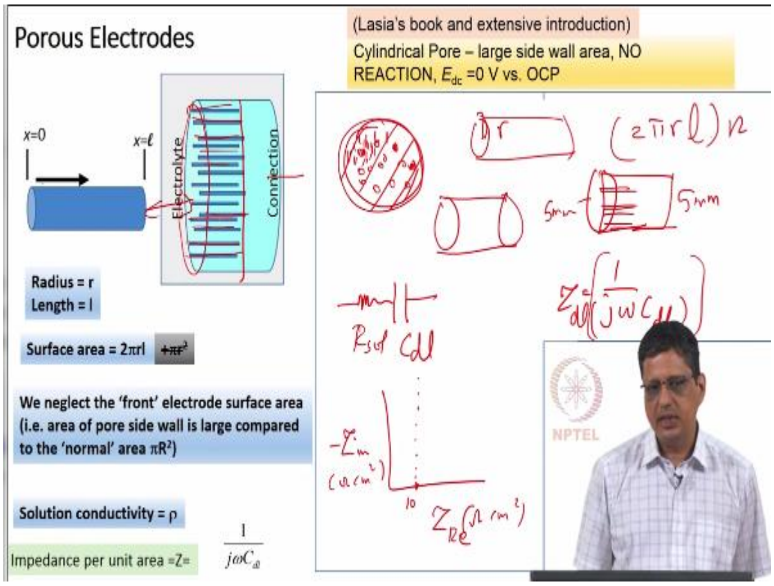

First what you want to see is case where you have an electrode. [Please refer to video 2.10] So I tried to draw this here. You see the dark blue lines here; they represent cylindrical pores. This is the front surface of the electrode that is exposed to the solution, and this is of course connected. These pores extend into the electrode and the electrode is the conducting material, typically a metal. This front surface has an area, so if I draw this here I see lot of pores here, right. At the bottom of this, you will have an area, surface area for this. At the top when there is no pore, those areas will also give rise to a particular area. The total area of the bottom of the pore, and the nonporous area is going to be equal to the geometric area of this if you assume there is no pore. So that is one area, look at this pore, we are going to say it goes from x = 0 to x = L and this has a radius of small r and the side wall area is 2πrl and if there are n number of pores the side wall area is n2π rl. So we are going to start with the assumption that the side wall area is very large compared to the geometric area of this solid electrode, that means we are neglecting the bottom area of the pore, we are neglecting the front area of the electrode where pores are not present.

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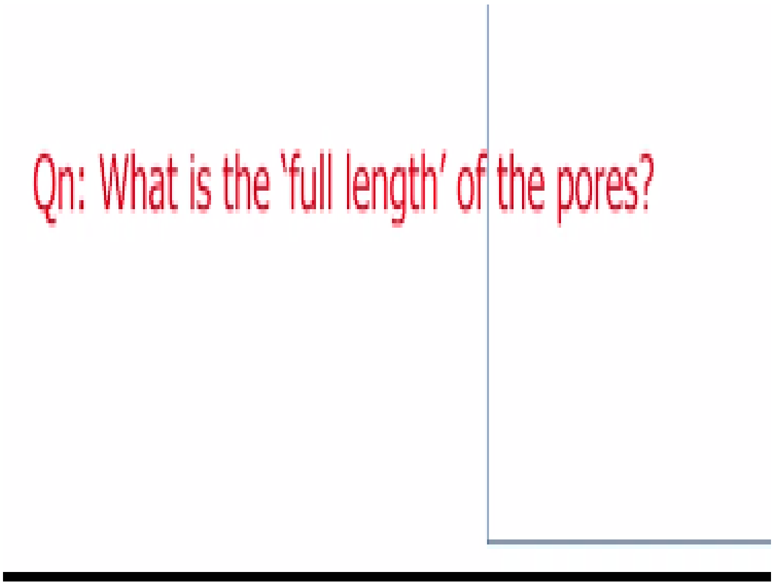

Full length meaning?

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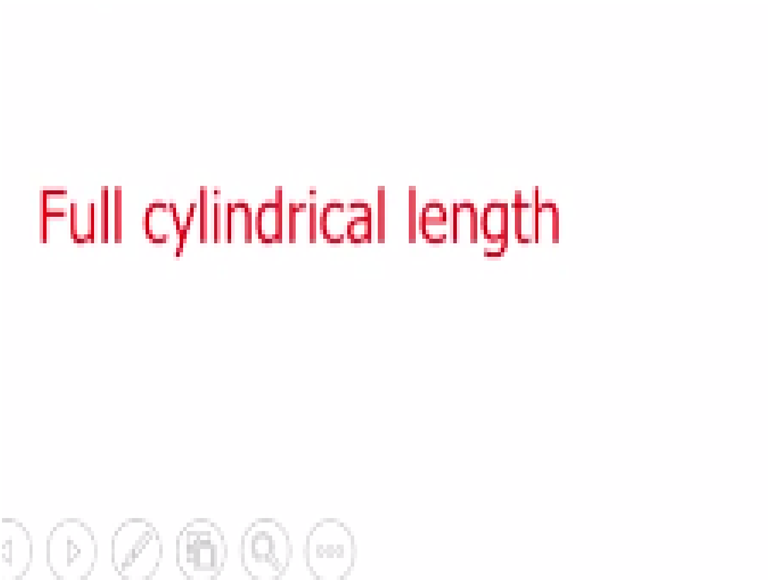

Full cylindrical length. They travel up to a length l, we are making some simplification right. In porous electrode, you are not going to have necessarily cylindrical pores, you are not going to have all of them with same radius, and we are not going to have all of them placed evenly positioned evenly. We are not going to have all of them with the same length, but we are making the assumption that they are identical pores.

But other than that, they travel up to some distance and beyond that it is solid electrode. So if we have an electrode which is 5 mm diameter, 5 mm length, it is a small electrode. We assume the pores are very small in terms of the radius and relative to the length of this it is still small, maybe it is 0.5 mm in length. Maybe it is 1 micron in the pore diameter or pore radius.

So it is going to be many pores, very small pores compared to the diameter of the electrode the pore diameter is nothing. Compared to the length of the electrode the pore length is nothing, very small~~, nothing means~~. So we are going to say the surface area of a single pore is $2\pi rl$ and if you take this as a pore we are going to, we should say $2\pi r l + \pi r^2$because the bottom area also is part of the pore but we are neglecting that, that is why I have crossed it out.

So what we want to do is find the impedance of a single pore and then we can calculate the impedance of n number of pores and find the impedance of the electrode. We are going to make certain assumptions. There is no reaction here, there is only capacitance, double layer capacitance associated with the solid-liquid interface. We are not applying any dc bias, even if you apply dc bias there is no dc current.

If I take the electrode, if I take the pore, it has a double layer which can be represented by a capacitor. [Please refer to video 6.15] Now this is the wall that is present, if there is no ac potential, you apply only dc potential, all that will happen is the double layer will get charged to some level because of the dc potential and that is all. There will be a transient current for charging the double layer, but after that you will not have any dc current.

Only when you apply an ac the double layer will get charged and discharged, so you will see and ac current and since there is no species here which can react they are not going to have ferro-ferri solution. So if you apply dc nothing will happen as long as I stay within the electrolyte breaking potential, as long as I stay within the water, if it is water based solution I should not go to a potential where water can split.

Now if you apply ac potential some current will pass here, there is a solution resistance. Solution resistance is not negligible; we are going to say it is significant because of that the potential here is going to be less. So some potential comes, some of it is taken out here, it is going to be less potential. Some of it is taken out less potential, some of it is taken out it is going to be less potential.

So potential will decrease with respective distance and we will find a way to account for that. In case this is a solid electrode, it is not porous. If I apply in ac, I will get the ac current, which can be modelled using a solution resistance outside the electrode from the reference electrode to this porous electrode is one solution resistance plus a simple double layer capacitor, that is all we need to describe the situation. If I plot this in a complex plain plot, high frequency it will be close to the solution resistance, just make up a number and say 10 Ωcm^2. Capacitance will offer almost zero resistance, because the capacitance is going to be giving as an impedance like this and when ω tends to large value or infinity you are going to say that is going to give a zero, this is going to be R_{sol}. And when we reduce the frequency we are going to get an impedance from this, it is going to contribute only to the imaginary part and then we are going to add the R_{sol}, so it is going to be vertical line, starting at R_{sol} and then it is going vertically up for various frequencies you are going to get various points. You can visualise this part and correspondingly bode plot you can plot it and see.

When you have pores here and solution is present inside the pore, and it is going to cause a decrease in the potential as we go inside. This will have an effect on the absorbed current here. So this is just to reiterate that we neglect the front electrode surface area and actually the bottom of the pore also and the solution conductivity we are going to denote that by ρ.

If you take unit surface area, then the impedance corresponding to the double layer is given by $1/j\omega C_{dl}$.

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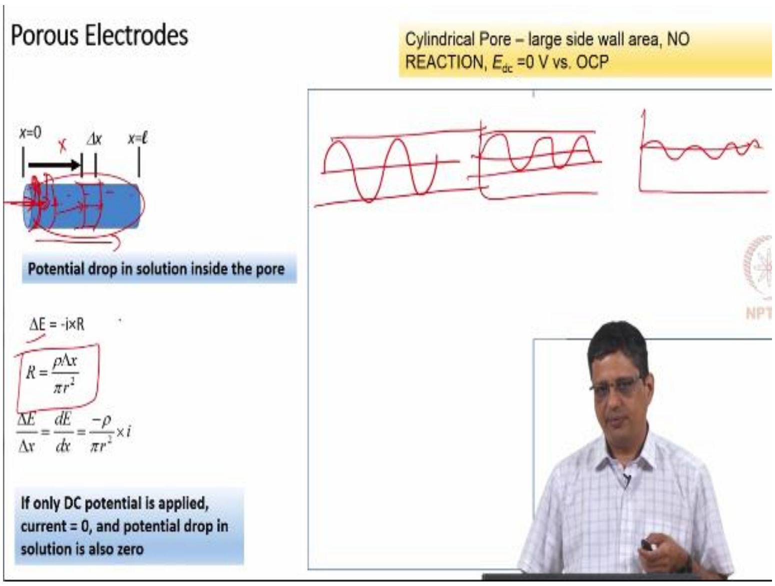

[Please refer to video 10.00] So what we want to do is take a small section here, potential will get it will decrease here when we move from location x to $x+\Delta x$. You take any small section here we are looking at a cylindrical surface and that is going to be i x R, because when we go here potential is decreasing, we are going to write it as i x R with a negative sign. R is given by connectivity multiplied by the length divided by the area.

The relationship between conductivity and the resistance is how long is it. If it is longer you are going to have more resistance. If the area is more you are going to have less resistance. So that is given by area here is for the cylinders. The block, cylinder block which is containing the liquid. So solution resistance causes a drop in potential and that solution resistance for this small section cylinder is given by $\rho\Delta x/ \pi r^2$.

Now if I want to find as I go in the length what is the potential drop, dE/dx, it is going to be given by $\rho/ \pi r^2 i$. So I write here as $\rho \Delta x/ \pi$ r square. So I rearrange it and say $\Delta E/\Delta x$ at the limit of Δx going to 0, it is going to be written as dE/dx and the remaining terms are $\rho/ \pi r^2 x i$. We do not know what the i is yet.

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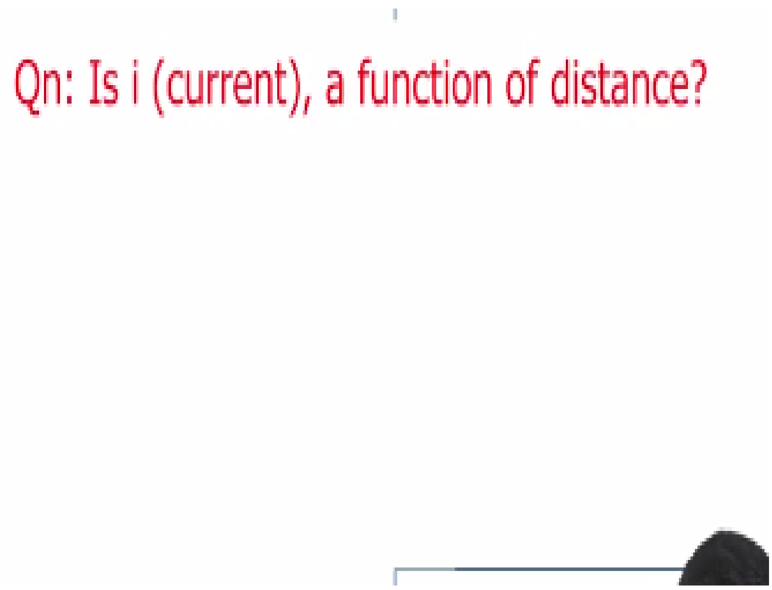

so i is the function with distance. Yes, i is the function of distance.

So if you visualize this. You apply an ac potential, so it is going to go with an amplitude. At the wall, current that is coming in, this potential is going to be large potential or whatever we are giving that is the maximum potential. It is going to oscillate like this at whatever frequency you are giving in.

[Please refer to video 12.25] Little later, what happens is some of the current is taken here and the potential is decreasing here, because it offers a resistance. This small section offers a resistance. Remaining current, it is going to see a relatively smaller compared to this, this is going to be little smaller, smaller amplitude and that will take up some current here. Then that means the potential oscillation here is going to have an even smaller amplitude and that will take up little current. So what happens is, the current that is taken up is going to be higher here and it is going to be lower as you go along. Sum of all these currents has to come from here. Now if you want an analogy think that you have a pipe and the pipe has pores. If you send in liquid with the particular pressure of course there dc is possible, equivalent of dc is possible, send in with pressure, some will go here. Some fluid will leak out of this, pressure will decrease here, because of it some more fluid will go out but it will not go out at the same rate as in the beginning. Some more fluid will go and likewise it will keep going, pressure will keep decreasing along this, the total fluid flow rate here under steady state condition should be equal to the integral or some of the fluid flow rate at all these sections.

This assumes the points or the holes are of similar size. I will not get even flow out of this when I go along this line. I will get higher flow rate and lower flow rate. Higher flow rate in the beginning and lower flow rate at the outlet, but the net flow rate here is going to be enough to tell what is the total flow rate here. So this is at any location, this i is equivalent to flow rate at any location. Of course it is going to depend on x. Now as we mentioned before if you apply only dc potential current will be zero. If current is zero, there is no pressure drop here or there is no potential drop here, that equivalent is not there in the flow in a pipe line. So if we have cancelled the flow in the pipe line that will be equal to having a redox reaction with present here. We are not considering this, we are saying there is no reaction.

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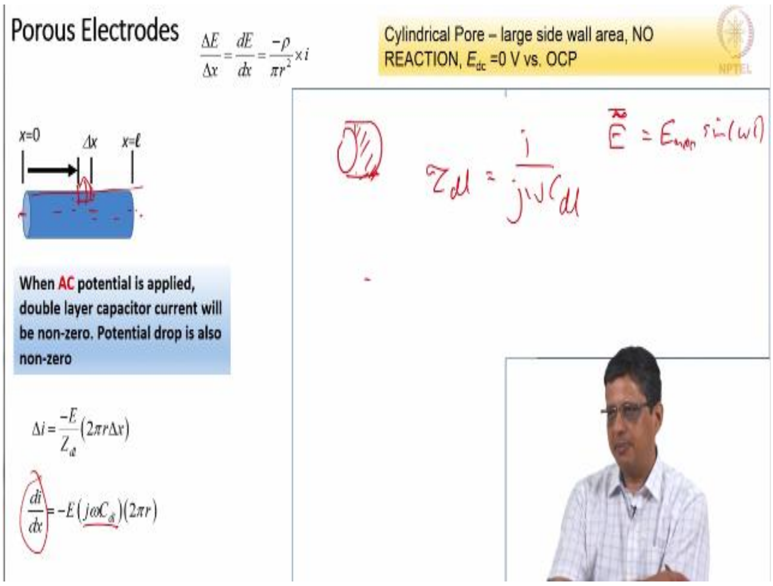

But when you apply ac, you will have an ac current here. So double layer capacitance will give you a current and that is not zero, potential drop is also not zero. Now, if I take a small section and look at the cylindrical surface area, so surface area here is the sidewall area. Impedance is going to be ΔE/Δi. Impedance per unit area is given by this. If I want to look at the current, not current density what I have to do is find this value, ΔE/Δ i.

Here it is E here is not the dc potential, it is actually E here is E_{ac} which is E_{ac0}, sin ω t except this E_{ac0} is the function of location. In the beginning what we specify is $E_{ac\ 0}$, as you go along the amplitude keeps decreasing, so this phasor is what we mean by E here, that means it is an ac with a particular frequency, but with varying magnitude, the magnitude vary as the function of location.

This ΔE, this ΔE if it is a dc it will tell E_2-E_1 if I say this is location 2, and this is location 1. Here what it means is if I draw, this is how the sinusoidal potential will go. As I go in the amplitude will keep decreasing. Here this is, E_{ac0} at location 2 – E_{ac0} at location 1, that is the Δi here. This is not E_{ac}, earlier we would have taken ΔE is E_{ac} and that is = E_{ac0} sin ωt.

That is not the ΔE that is used here, the notation is different, it has to be interpreted little differently here. So this ΔE is the dependence of the amplitude with respect to the location x. So the current that is going here is related to the potential, current density. So here Δi means the amount of current that goes in a small section here. So if I integrate all the Δi, I will get the total i, it is like the quantity of liquid that is flowing out of the porous pipe.

So in a small section, small section here means through the surface area of $2\pi r\Delta x$ how much current is going, that is going to be given by potential by impedance. Now if I shrink the Δx to 0 at that limit I can write it as di/dx, E is kept as E, remembering it is an ac potential, Z double layer or ZC_{dl} is going to be $1/j\omega C_{dl}$. So all that we see is the capacitance current here.

Except the AC potential's amplitude keeps decreasing, therefore the current through the sidewall for given sidewall area will keep decreasing as we go along. So that is what is given here, di/dx as we go along it is going to be decreasing therefore it is negative, how much is the current that depends on how much is the potential, how much is the frequency, diameter of this or radius of this pore, double layer capacitance.

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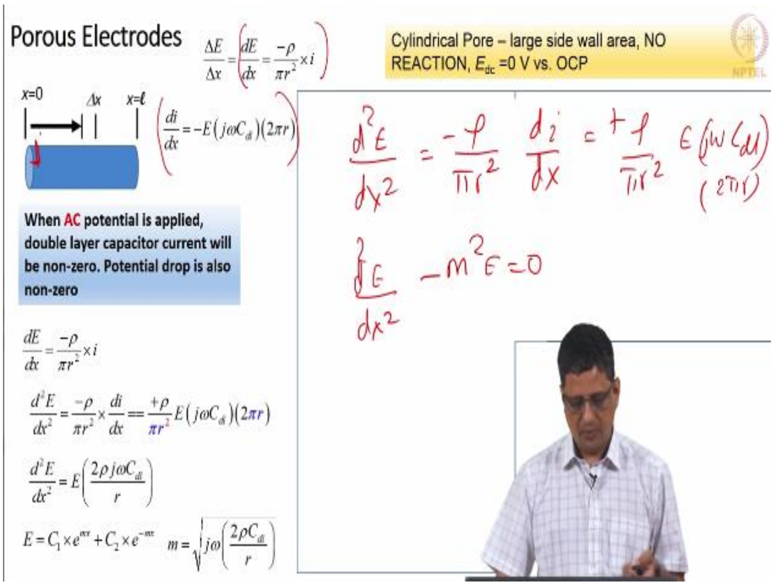

So I have 2 equations one is dE/dx relating to the current, another is di/dx relating to the potential. So we take the dE/dx and take a derivative with respect to x. [Please refer to video 19.20] You are going to get, see what we want to do is find the current, find the impedance for this one pore. We want to find E/i, E here is the E_{ac} and correspondingly i, in order to find E/i, we need to find E as it goes along the pore it is changing. We know the e at the entrance, we know the pore diameter, we know the pore length, we know the conductivity, we know the double layer capacitance of the sidewall per unit area, from this we want to get an expression for the total current that is going in as a function of potential. So we want to write E/i remembering that E and i are vectors. So we want to solve for E, in terms, that is one you can solve for i, we will solve for E here.

This you can rearrange and solve, correct, ρ is a constant, r is the constant, C_{dl} is a constant, ω for a given frequency it is fixed number anyway it is not dependent on x. So you have a question which goes like $d^2E/dx^2 - m^2E = 0$, where m square is a constant.

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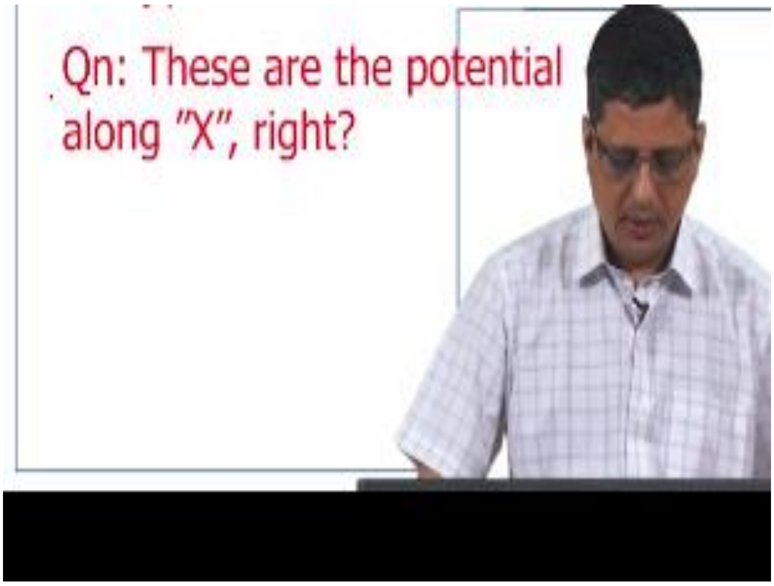

Sir, these are the potential along X right. Yes. So we are looking at it like this like, not along the length? No we are looking at along the length.

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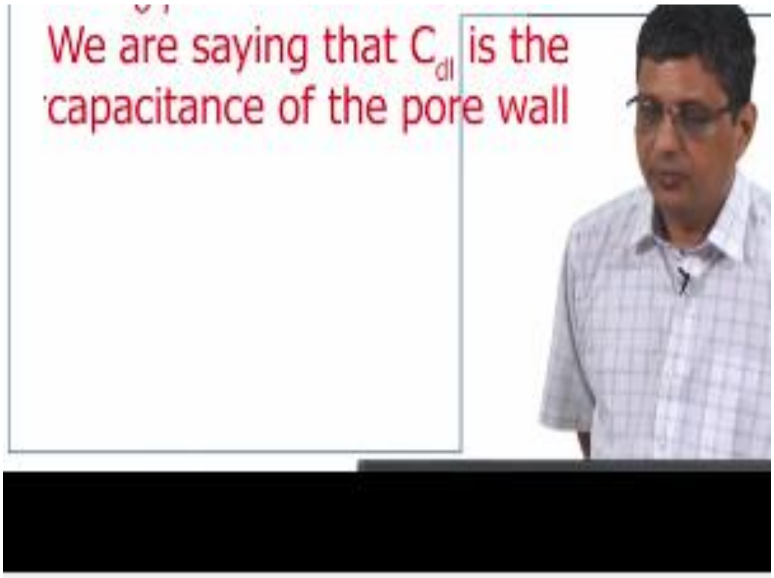

I think we are saying C_{dl} is the capacitance of the pore wall. Yes.

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And we are saying the current that goes though will be same. one assumption we make is potential at the center and potential along the radius, they are all the same. Potential decreases as you go along the length of the pore. It does not decrease as you go from the centre to the edge of the pore, that is another way of saying the length is lot longer compared to the diameter of the pore.

So we will see numbers little later, to indicate what is meant by lot longer? When we neglect the front area and the back of the pore area and then say this pore sidewall area is much more significant than this, what numbers would give us this? You can do this yourself and see, but we will show examples. So you are okay with this? We get solution in terms of exponential functions with m given by j ω 2 $\rho C_{dl}/r$.

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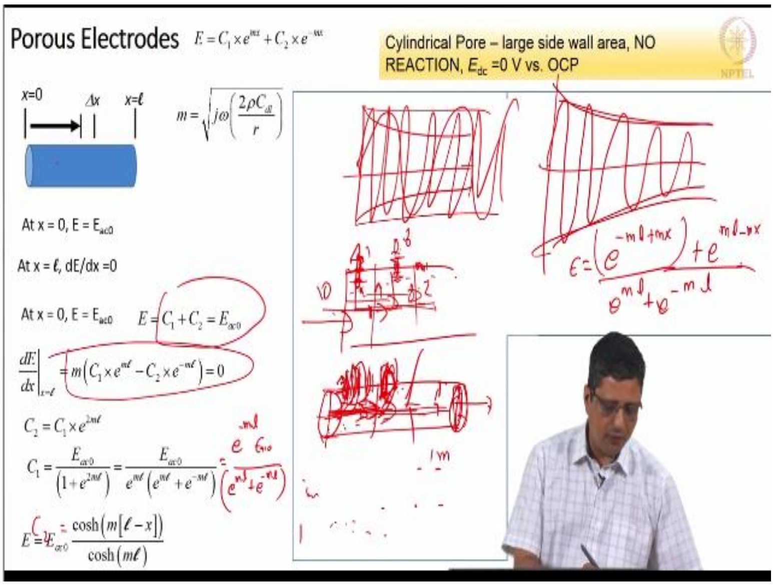

We need boundary conditions right, one at x = 0, E is actually E_{ac0} sinωt, but I just want to find the maximum of the sin that means I want to find how the envelope of this sinusoidal current will go as I go along, that means if I do not have any resistance here, it is just going to be a sinusoidal wave throughout this, whether it is high frequency, low frequency it does not matter, this is going to be the envelope.

Because the solution has resistance and it is going to be sinusoidal wave bounded by an envelope which is decreasing with respect to distance, so here I am going to just say E = E_{ac0}, remembering it is part of AC wave.

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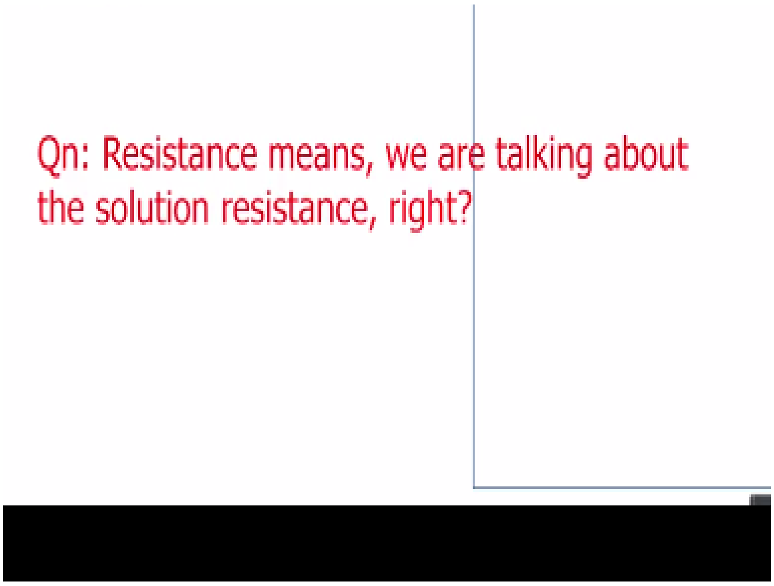

So resistance means we are talking about? Solution resistance.

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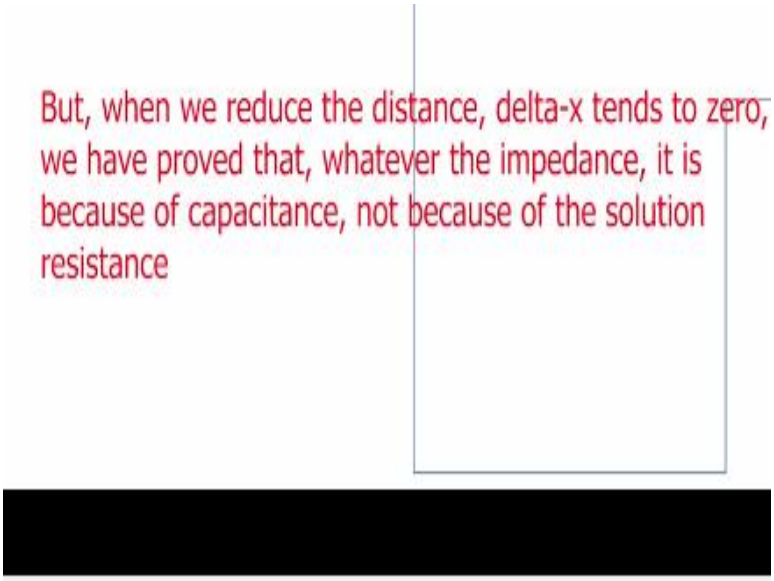

But when we reduce the distance, Δx tends to 0, we have proved that, whatever the impedance, it is because of the capacitance, not because of the solution. See the impedance at the side wall, is because of the capacitance, total impedance, it is going to be because of the resistance plus the sidewall capacitance. Whatever current that is going through the resistor has to go through the capacitor. So it is like saying the flow rate here, if I take a pipe, flow rate here, some of it is going to go here, some of it is going to go in the next section, some of it is going to go to the next section, but whatever comes hear that has to be split into all this, and if I take a small section here and there is a pressure drop even from centre to edge for example, that flow rate is going to be equal to the flow rate through the pore.

So whatever current is going through, there is a potential drop, but current that is going through, right, because of the potential drop current will be less and less because potential will be less and less as it goes along, but the current that is going through this resistance is going to be equal to the current that is going out, meaning if you take this current that is going through this has to be equal to current that goes out plus current that comes here.

This current, this may be some unit, write 10 units, out of which 1 unit go here, 9 units come here. This may be 0.8 goes here, 8.2 comes here. So I am just taking into multiple discrete sections. So solution resistance will play a role, but if I want to know the current here, all that I need to know is the potential here, it is like saying I need to know the pressure here and the pressure here and the resistance offered by this hole. Outside pressure is uniform, inside pressure will keep decreasing. The resistance offered by this will be the same. If the pressure drop is less as you go along the flow rate will become less, but we cannot say this does not offer any resistance. If you want, we can also consider the case where there is a pressure drop here along with the pressure drop here. The net pressure drop across this is enough to tell us and the resistance there is enough to tell us how much fluid will flow.

Finally, the i that is coming here has to go out of all these. Now I will give you, maybe a slightly better analogy. You have a pipe which is porous,. [Please refer to video 26.10] Now if there is no pore there, I will give a pressure, pressure will be uniform everywhere and then stop, it is going to be static. If there are pores here, the pores will offer a resistance but flow will happen. In addition, I can also say, this pipe does offer a resistance.

It is not that it does not offer any resistance, that means if I open this and have many pore here I will have a pressure drop here, significant pressure drop. Now, imagine this situation some flow rate occurs here because there is a pressure drop here, it offers lot of resistance, but not infinite resistance, that is why flow is occurring, but some pressure drop will also occur here, right?

Accounting for that pressure drop is occurring across this, pressure drop is occurring across this, if I want to look at the fluid flow here, I have to say whatever has gone out the pressure drop because of this distance there is a pressure drop. The total pressure drop here will tell how much is pressure here and we can calculate this is going to be the flow rate because of this.

Whatever fluid that is coming here still has to go out through this only and when I want to calculate the flow rate here, I need to know the local pressure and the local pressure, that is all I need to know and the resistance. Whether the pressure here is low because lot of fluid has flown or whether it is the case where there is no porosity here, but there is a pressure drop, after this there is porosity.

This also will give you a flow here correct, but this case will be different from a case where you have porosity from that beginning it. So I can look at this section, this maybe 1 meter, this may be 1 meter, I can say I will take this section and just cut this and put it here 1 metre here. This flow rate will be different compared in this flow rate. Does it make sense? Same pressure in, this will offer a pressure drop.

As long as there is a flow there is going to be a pressure drop. This will cause a less flow rate compared to the same P in with no initial section. Now I can have a combined one where from the beginning itself there is pore, this will offer pressure drop, it will offer some flow here, it will offer pressure drop here. This pressure drop will keep varying because there is flow on the site.

If you look at a straight pipe, same diameter, $\Delta p/\Delta x$ when I have opening only here, $\Delta p/\Delta x$ will be a constant for Newtonian fluid. When we have flow around this $\Delta p/\Delta x$ will a constant, that is effectively what we are accounting here. I do not know whether it answered your question, but at $x = 0$ the amplitude is maximum , at $x = l$ it is blocked therefore de/dx is going to be 0. Potential is not going to vary with distance.

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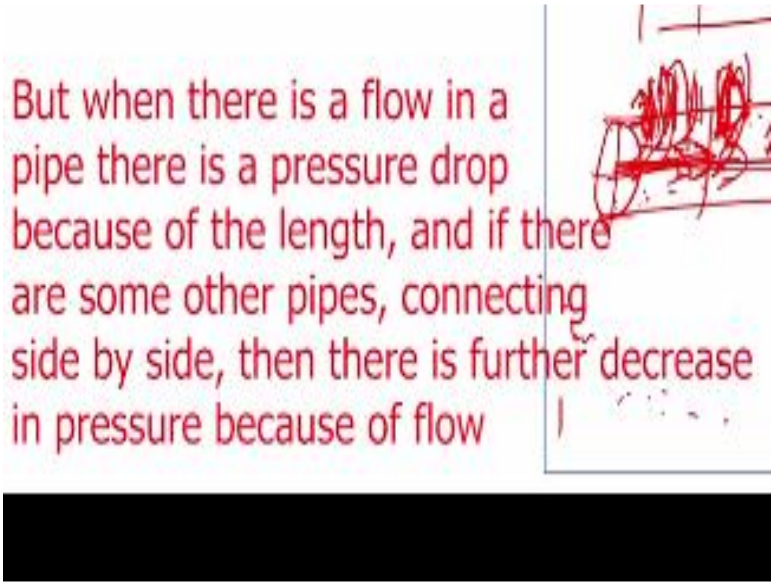

Sir, but when there is a flow in a pipe, there is a pressure drop because of the length and if there are some other pipes connecting side by side then there is a further decrease in the pressure drop because of flow.

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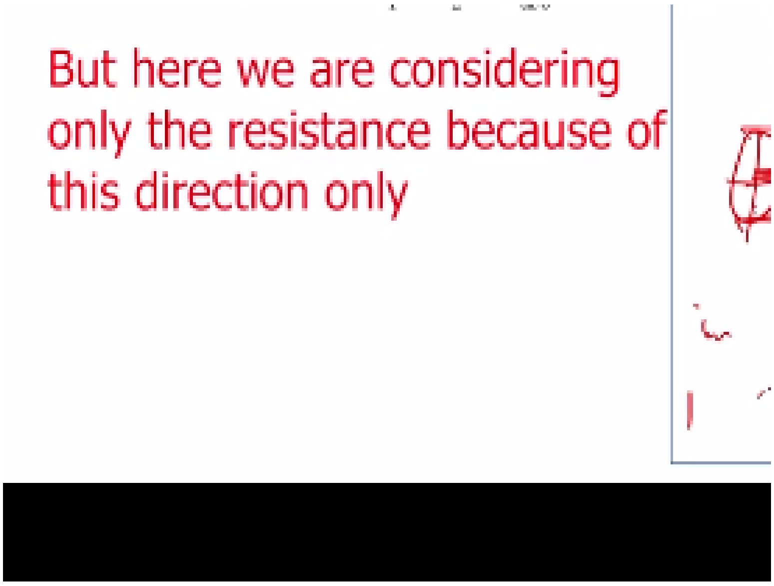

But here we are considering only the resistance because of this direction only. We also considering double layer capacitance.

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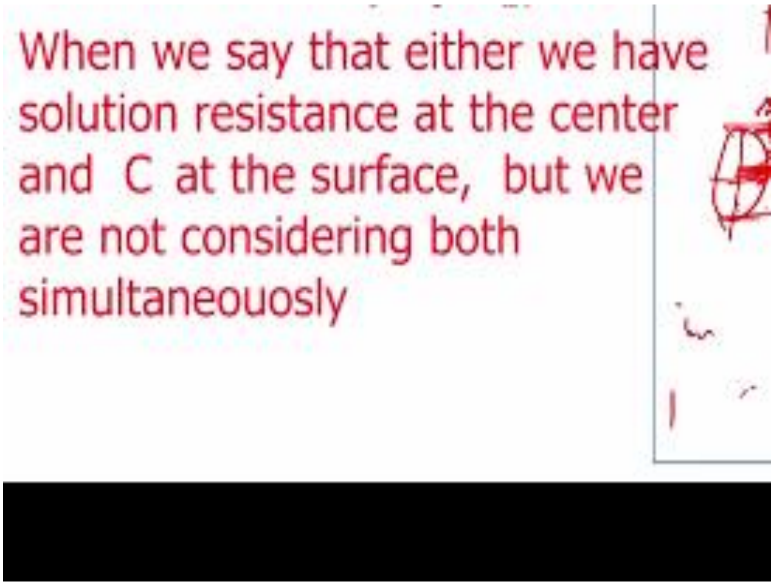

No, when we say that either we have solution resistance at the center and we have a C_{dl} resistance at the surface of the. Yes. But we are not considering both the things as simultaneously.

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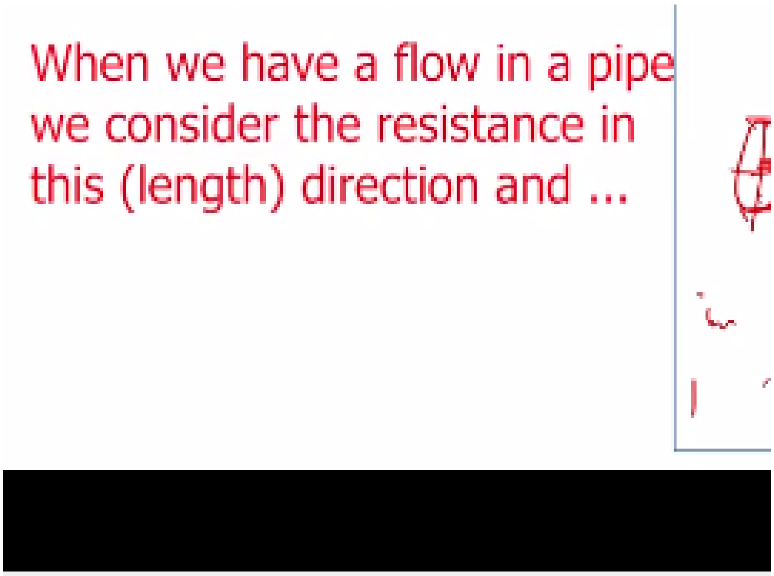

When we have a flow in a pipe we consider the resistance in this direction if there are some other points. We are considering them simultaneously. See one of them, this tells, the first equation here tells as you go along how it varies with length. The solution resistance comes into play, we are denoting i but we are recognising that i is a variable.

And that i takes into account, the double layer capacitance. So double layer capacitance and solution resistance are taken together, that is why we get an equation which has both ρ and

C_{dl} together and in fact when we finally come to the expression we will see the ratio of these 2 impedances will also be a dimensionless factor, that comes into play.

So the impedance or admittance because of the double layer capacitance and the impedance offered by a solution filled in a cylinder of particular radius and particular length you can calculate the impedance. The ratio of these two is giving you a dimensionless factor that will tell how the impedance of the entire pore structure will vary. So this much we are okay. We have two boundary conditions.

[Please refer to video 32.00] First boundary condition you can put x = 0, it will become C_1 + C_2 and that is = E_{ac0}. Second boundary condition you take the derivative and then substitute x = l, so you were going to get mC_1exp(ml) then –m C_2 exp(–ml). So we have two equations and two unknown C_1 and C_2. So the second equation tells us the relationship between C_2 and C_1, substitute it into the first equation you can write C_1 as exp(–ml)E_{ac0} and C_2 is going to be exp(+ml) E_{ac0} correct.

[Please refer to video 32.50] So you can get E as the function of x, that is going to look E as a function of x because E is going to be exp(–ml + mx), substituting for C_1 and C_2 you can write it as hyperbolic cos(ml – mx) divided by hyperbolic cos(ml). At x =0 it is going to be 1, where the factor is going to be 1. Of course you are multiplying that by E_{ac0}. As you go along this is going to decrease. At x = l, it is going to be, it is not going to be 0, because it is going to decrease by a factor of cos (h ml) that is all.

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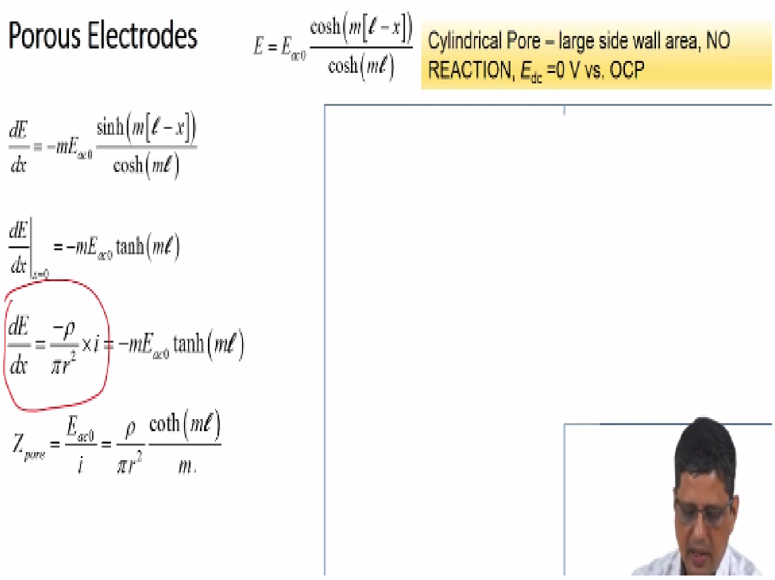

Now we want to find the current at x = 0 because that current is going to be distributed inside, right. So in order to find the current we take the derivative with respect to x and use the relationship that dE/dx is going to be –ρ π r square i, dE/dx at x = 0, so if you take the derivative you are going to get m outside and then cos h is going to give you –sin h, x =0 you are going to get tan (hml) and therefore you can relate the current and potential.

We want to find the value of E_{ac0} by i, i here is the current not the current density that means z pore is the impedance, written in Ωs. I am sorry, i at the entrance is going to be distributed throughout this right. So what we do is this, when we apply E_{ac} potential we measure the current. We measure the magnitude and phase of the current and we take the ratio and say this is the impedance of the system.

So what is going to be the current at the entrance, that is all we are going to measure. That current gets distributed unevenly inside, that is, but what are we going to measure. What can we measure if we have an electrode of this pore structure? This is the current that we are going to measure, and this is the impedance we are going to see from the instrument. So we want to predict that. We assume we know the impedance inside the pore, that is how we are getting the total impedance out of this. The impedance inside the pore is given by this resistance plus that capacitance except that this resistance and capacitance are all differential quantities and we are integrating them. How much is the potential drop that depends on what is the conductivity, what is the radius and what is the length of this, not the full length, but whatever length we are going up to.

At that level what is the impedance that is what we have, what is the impedance, or what is the potential there, we are calculating and that is how we have come to this. we assume that we know the double layer capacitance on this pore wall. We assume of course that we know the radius, length and the conductivity. If you rearrange and get E/i here I gave as E_{ac0}/i, but essentially it is E/i. I would get a factor like this and I can rewrite it with capital λ.

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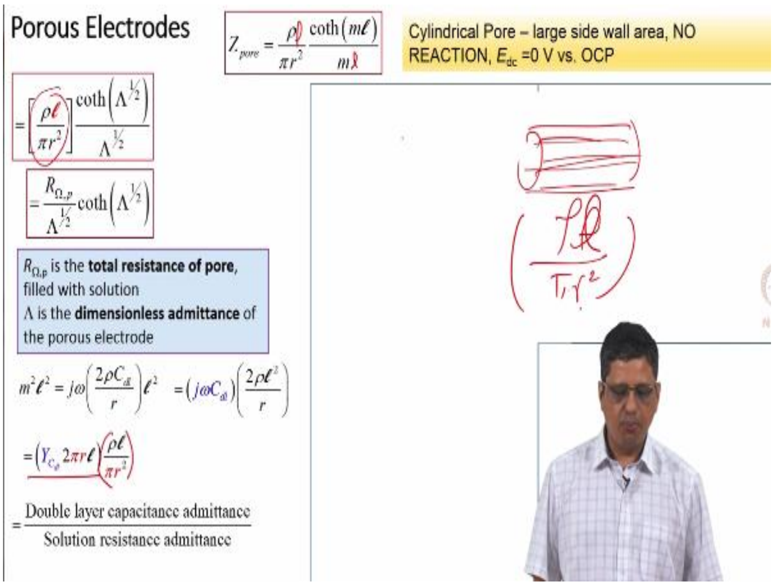

I am going to write capital λ = m^2l square. I can write this as capital λ as ml but there is real reason why you want to do this because it gives you a dimensionless number. So multiply and divide this by l, I will get $\rho l/\pi r^2$, and this is going to give me tan h is going to give me cot h here because I take the inverse and basically the derivation here whatever I am showing you is from the book by Lasia.

It is also available in the web not the entire book but the significant part of that, that has extensive introduction to as. Now this first part is denoted as capital $R_{\Omega, p}$ to say, this is the resistance of the solution inside the pore. Look at this, you have a pore, consider this as a cylindrical block filled with a liquid of conductivity ρ, length l, πr^2.

So this is the pure resistance offered by this pore, that is all without worrying about the sidewall double layer capacitance. What about the ml or what about that capital λ, instead of ml if you take m^2, l^2 , m^2, l^2 we can write it, m we know it is square root (j ω 2 ρ C_{dl}/r), right, so $m^2$is going to be just the same factor without square root, l square we keep it as it is.

I am going to rewrite that a little, I am going to keep jω C_{dl} on one side, 2 ρ l^2/r on the other side, I am just rearranging it and the blue coloured factors I am going to call them as admittance of the double layer capacitance, multiply by 2 πrl or multiplied by π r, divide by π r and bring the 2 to that side. This will tell you, this admittance for this area of 2 π r l.

The ρ l/ π r^2 is the resistance or impedance, so if this is the admittance I can write this as ratio of admittances or ratio of impedances, double layer capacitance based admittance divide by solution resistance based admittance. This is the impedance so I can say inverse of this is the admittance and I can bring it to the denominator. So the factor m^2, l^2 is basically dimensionless admittance.

Capacitance based admittance versus just the pure solution resistance, that based admittance and this is for 1 pore.

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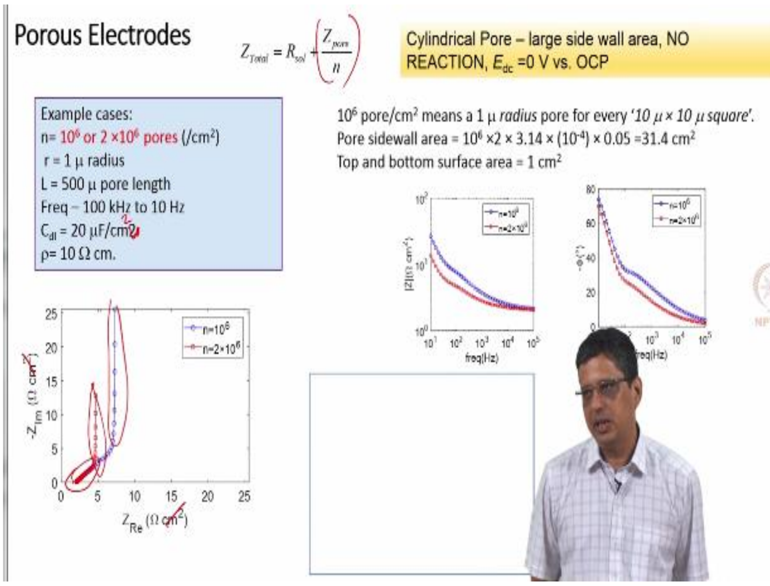

If I take n pores in parallel that net resistance is going to be given by Z pore/n, I have to add the admittances, to get the net admittance and then invert it to get the net impedance and then there is a solution resistance here that is the R solution from the reference electrode to this porous electrode there is some solution resistance, that is what I give by R solution there. We have accounted for the solution resistance inside this porous electrode in our expression for Z pore.

So I want to give you couple of examples, so I want to say there is 1 million pore or 2 million pore per square cm. Each pore is of 1 micron radius, it is pretty small and 500 micron pore length. So compared to the radius or diameter the length is pretty larger, it is 250 times diameter. Frequency I am going from 100 kilo Hz to 10 Hz, we can go lower, but the scales become such that you cannot see some of the patterns in this complex plain plot.

So I have not gone below 10 Hz, but it is easy to use the formula and plot it for you know any range. Double layer capacitance we take it as 20 microfarad per cm^2 which is a typical value.

Solution resistance here, the conductivity, we take it as 10 ohm cm. So these are number made up which are sort of realistic numbers. Now what is 10 power 0 pore per cm^2.

One centimetre length is going to be 10 power 4 micron, 10 power 3 micron is mm, 10 power 4 micron is cm, 10 power 8 micron square is going to be 1 cm^2. So if we take 10 micron by 10 micron area that will contain a pore of 1 micron radius, 2 micron diameter. So divide this into 10 sections, divide this into 10 sections, take radius of one section here, this how it is going to look like.

So roughly if I take this I can take it as a square for just an approximate number. So I get 2 by 2 out of 100. So 96% is still covered by solid electrode only 4% or little < 4% is corresponding to the opening of the pore, that is what I would get if I take 1 micron radius and 10^6. If you say 2 * 10 power 6, 2 million it is going to have 2 such. So it is going to cover 8% or 7% of the surface area.

So it still has lot of area left on the surface. The sidewall area corresponding to that if I have million pore, it is going to be 31 cm^2. The area of the top and bottom surfaces of course 1 cm^2 that is how we have taken this. So compared to 31 we are neglecting one means we are leaving around 3%. So you should have some feel for the numbers. You cannot just put 1000 number of pores 1 micron radius and assume that the side wall area there.

Because 1000 is the large number, you cannot neglect the side wall area in that case, I mean you cannot neglect the front and back area in that case. This case you are justified to say I will lose 3% of area, I am okay with that. If you plot the impedance in the complex plane plot using this expression you can calculate and then plot it in fact this is not correct, it should be written as ohm, but that is alright.

Or because I see here what it means is we are taking the geometric area of this electrode, it is 1 cm^2 area therefore we are writing it as so many Ω cm^2. Normally when you take a porous electrode, all that you know is it is porous. If you get a pattern like this in a solution without any reaction you would say this comes from a porous electrode, let me see if I can recalculate the diameter and length.

Or if I have some way of estimating the diameter using SEM on that you would not get uniform diameter anyway right, so you will measure these pore diameter and then take an average and say this can be representative diameter, or representative radius. See if you can estimate the length. Length is again going to vary depending on where you cut it. Even if you put in SEM it is going to vary.

So you can say can I model this using this particular description then you take an average length, you take the average radius and then see if it can model this. When you plot it initially you will not know all these things right. So you will just plot it based on the geometric surface area. Now if you look here note this complex plane plot looks like this that up to some level they are overlapping and maybe at the low frequency there is a difference that is what it looks like.

Put it in the bode plot you will see even at mid frequency there is a difference. Just because on the same path the points have moved. It is like saying I have one simple resistor, one simple reaction, solution resistance reaction, double layer capacitance changes in two cases in the complex plane plot all the points will just keep moving there, you may not see the difference.

Bode plot you will see the difference likewise in this case it is better to display that in bode plot and show that when you have twice the number of pores magnitude decreases, phase follows similar trend, but they are not identical. Couple of more minutes I will leave you. If I take smaller radius, same number of pores, smaller radius, you expect naturally it will offer more impedance, it does offer more impedance. Pattern looks like going up but look at this phase, it goes up, comes down and goes up.

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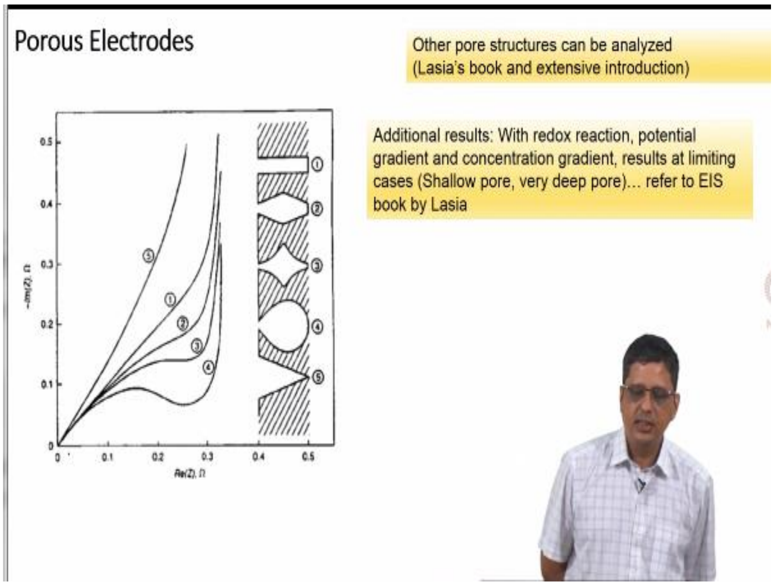

All that we have done is for a cylindrical pore, right? You can have pores of different geometries. So there are equations, cylindrical pore gives like this, different geometries, different groves will give you different shapes here. You can also have a distribution of cylindrical pores of different diameter, different radii, you can derive for those. You can have variety of cases with reaction, with diffusion inside.

When you have reaction species will A and B will react and depending on which way the reaction is happening you can have increase in concentration of A decrease in concentration of B or vice versa. Diffusion of that can become rate limiting, it becomes lot more complex many cases you have to make approximations, but it is possible to see how that will happen. Here all that we see is a introduction to porous electrodes. So you get an idea that it is going to be quite different from what you would see for a solid electrode.

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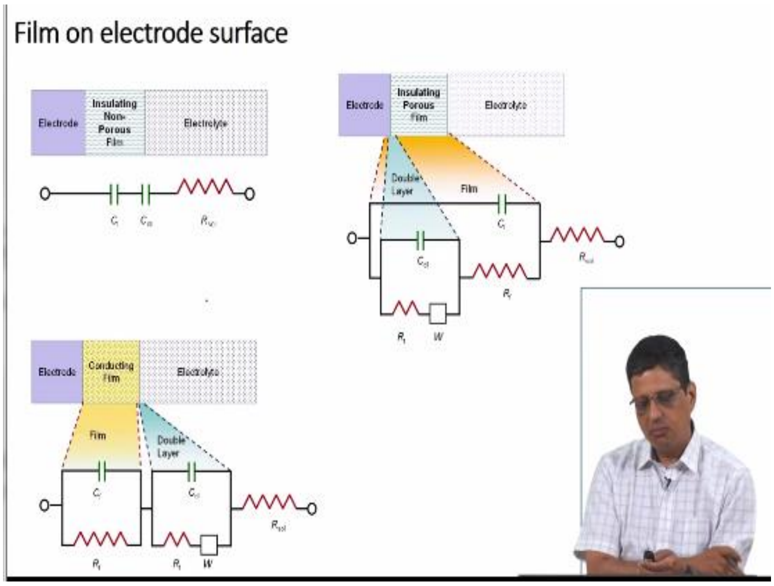

We will continue with this other part tomorrow. We will stop here today.