Electrochemical Impedance Spectroscopy
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Lecture - 19
Maxwell, Voigt, Ladder Circuits, Choice of Initial Values Illustrated

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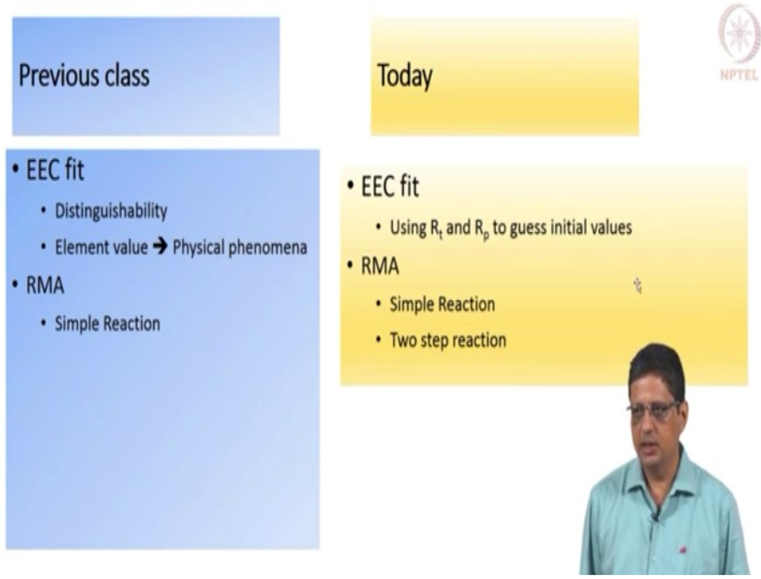

What we saw yesterday was few examples in EEC fit, what are the difficulties on my phase and the difficulties in interpreting the data or interpreting the value of the elements, when it is negative how do we interpret it when we have an inductance or capacitance, how do we interpret it? I want to (give) you one or two examples on EEC fit. ~~So~~ Yesterday we saw that the definition of R_t, charge transfer resistance and polarization resistance. The definitions are different. At infinite frequency, the impedance given by the reaction is called charge transfer resistance. At zero frequency, it is (called as) polarization resistance. I want to show an example on how to use that information for making good initial guesses in the EEC. We saw this example.

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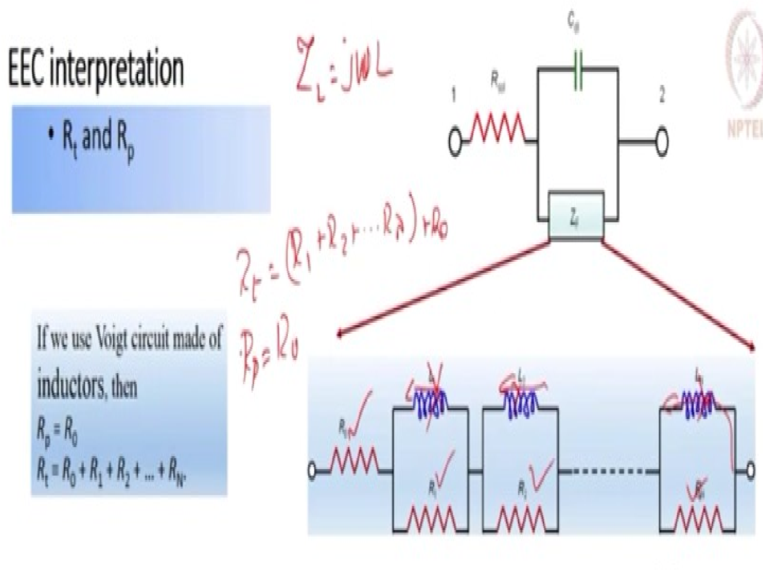

If I take a Voigt circuit and use that to model the Faradaic impedance. So I am not using the Voigt circuit to model the entire impedance. I have solution resistance here, I have solution resistance as R_{sol}. C_{dl} is the capacitor, Z_l is the Faradaic impedance, which I am writing as R_0 + R_1C_1 =+ R_2C_2 and so on. If I do this, can I tell what the Faradaic impedance is going to be when frequency is very high. When frequency is very high, capacitor will act as a short circuit.

That means R_0 is going to be charge transfer resistance. When frequency is zero, capacitance is basically open, it is cut off, that means R_0+R_1+R_2 and so on R_n. So sum of all the R_0 to R_n here, R_0 being still part of the Faradaic impedance, that is going to be polarization resistance. Only R_0 is going to be charge transfer resistance. Normally, I will not need many. I will probably use one or two or depending on the number of features I have there.

But in general, if you have a Voigt circuit based on capacitor, and use that to model the Faradaic impedance, you have a relationship between them. Instead of capacitor, I can use an inductor. Inductor based circuit here, if I say frequency is infinity, the impedance of an inductor is going to be $j\omega L$. So when omega tends to infinity, Z_L tends to infinity. When omega tends to zero, Z_L tends to zero.

That means when we go to very high frequency, charge transfer resistance is going to be R_0. This is broken + R_1 + R_2+ ...+ Rn, so because at high frequency, this is an open circuit. At zero limit, nothing is going to going through this. It is going to short circuit through this, and through this, and through this. It is going to see only the first resistances present there, which means if I use a Voigt circuit based on inductor, I know the relationship is here.

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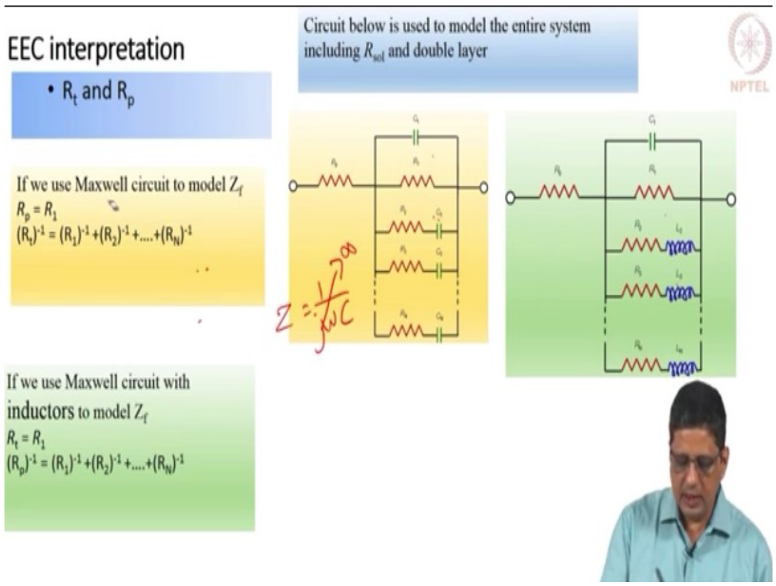

Now if I use a Maxwell circuit, Maxwell circuit here means this, so I still have R_{sol}. C_1 here is double layer capacitance. So it starts at R1, R_2C_2, R_3C_3 and so on, one resistance and then pairs of resistance and capacitance arranged in this fashion. So the circuit below is used to model the entire system, including the solution resistance and double layer. In this case, if I give zero frequency, this capacitor becomes open circuit.

So zero frequency, all the current has to go through this only, so polarization resistance is R_1. If I use infinite frequency, capacitance basically offers zero impedance, in which case, this becomes short circuited, this becomes short circuited and we have set of resistances in parallel, to represent the Faradaic impedance, which means at infinite frequency, I can write $1/R_t$ is $1/R_1 + 1/R_2 + \ldots + R_n$. Normally, I will not again need 10 elements, 15 elements for this. I do not think, we will have impedance with so many features in common cases, but one or two or three cases, you can have R_1, R_2. R_1 will anyway be there, but R_2 and R_3 and so on, you can use this. We have a relationship. I will show you an example to illustrate how you can use this information. Instead of Maxwell with capacitor, if I have Maxwell with inductor, at zero frequency, this is going to be short circuited.

So zero frequency means R_p at the limit of zero frequency, I can say $(R_p)^{-1}$ inverse is going to be $(R_1)^{-1} + (R_2)^{-1}$ and so on. At infinite frequency, the inductance will not allow any current to go through, therefore this becomes charge transfer resistance. So the expression for charge transfer resistance in the Maxwell circuit with inductor, if I am able to fit the data to this circuit, I can right away tell charge transfer resistance is R_1. If I fit it to this circuit, I can right away say, polarization resistance is R_1. Now I have not mentioned anything about their capacitance being positive or negative. The impedance of a capacitor is $1/j\omega C$. When ω tends to zero, regardless of the value of C, whether it is positive 10 mF or -10 mF, this will go to infinity. So I can use positive value or negative value it does not matter, this relationship is still valid.

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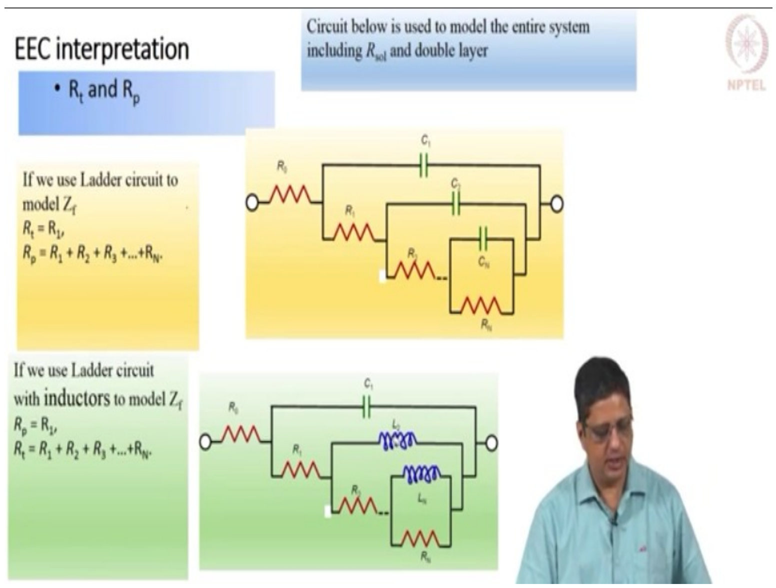

And the next possible is *ladder circuit*. Ladder and Voigt will look similar, except that here starting with R_1 onwards, we are taking this as a Faradaic impedance. This is solution resistance, this is double layer capacitance or you know in fact, if you want you can call this as R_{sol}, C_0, and then write this as R_0, C_1, R_1, etc., it does not matter. We are going to anyway put numerical values here. Now if I say this is the Faradaic impedance, if I give infinite frequency, this is the short circuit current that comes from here will just go through this, it will ignore everything here, because it is short circuited. So at infinite frequency, R_1 is going to be equal to charge transfer resistance. If I give zero frequency, it is broken here, it is broken here, so it has to come here, pass through this, any other resistance, so I am going to get $R_1 + R_2 + R_3$ and so on to be polarization resistance.

So when you come up with a circuit and fit this, you should first think what would happen, if I go to infinite frequency for the Faradaic part, what would happen if I go to the 0 frequency? That helps us get good estimate for sum of the resistance values there and if I use of course with inductance, you can arrive at similar conclusions here and say at zero frequency, one of it is going to be short circuited. Here at zero frequency, this is short circuited.

At infinite frequency, this is going to be open. So if it short circuited, all currents will go through this. If it is open no current will go through this, and you can come to conclusions on relationship between these.

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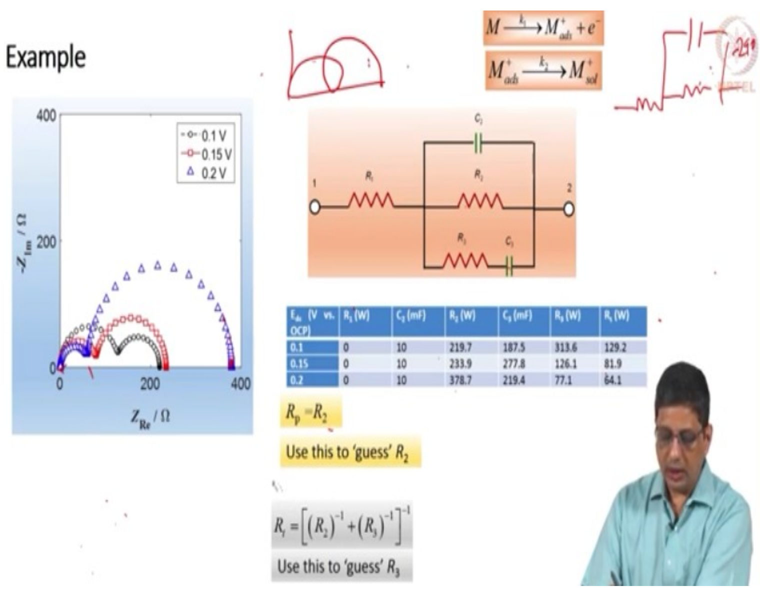

Now, later we will see that if you have a reaction like this, it is possible to get impedance spectrum like this. At different DC voltages, we will get three different spectra here. Now I want to fit it to the circuit. I have two capacitance loops; I am going to use one Maxwell circuit like this. Solution resistance is more or less zero. This is artificial data of course, so I made it as 0. (We should get the double layer capacitance, and all other resistances).

Now I can use the knowledge that this represents the Faradaic process. At infinite frequency, this first loop where it hits, that is more or less where the charge transfer resistance is. The second loop hits the real axis here, that is where the polarization resistance is, because solution resistance is zero. Otherwise I need to take the distance here and say that distance when expressed as Ω or Ωcm^2, will tell me the charge transfer resistance.

Starting from this point to this point is the polarization resistance. ~~If~~ Instead of this, it is shifted like this, I cannot call this as polarization resistance. This is $R_p + R_{sol}$. This is R solution. Resistance or impedance between these two points tells the polarization resistance. Now here because this point is 0, I can simplify it and say this is R_p. Now in the circuit, what is R_p? When I give zero frequency, current will not pass through this. Current will pass only through this, therefore if I am taking this data, I am going to estimate it and say, I will start with an initial value of 400 or something close to this. Where does it hit here? The values can be 200 here, this may be 100, this may be 80, of course, if you have access to the data, you can go in a little more detail, zoom in and then check. I will say this is roughly 80. Now what is R_t from the circuit. If I give infinite frequency, this is going to be short circuited.
That means it is R_2 in parallel with R_3, and $1/R_t$ is going to be $1/R_2 + 1/R_3$. Now I have an estimate for R_2. I have an estimate for R_3 also now. We can give this as initial guess and ask the program to optimize. Instead of giving the circuit and say optimize and give me, if I lucky to give you the values~~;~~. If not, you should not say this circuit is not a suitable circuit. You should look at the values, give appropriate initial values to the best extent possible, and then ask it to fit.

In fact, you can fix the value of R_p, if the data has come all the way here. If the data has stopped here, because beyond this, it will say it is noisy. You can still estimate where it is stop and give a value like this. Let us say, you have an impedance data, which has third loop. Then I have to use one more R_4, C_4. I still use R_p from this, no problem. R_t, if I want to use, I have to write $1/R_t=1/R_2+1/R_3+1/R_4$. Now I cannot guess two values from this. But still I can say, choose 1 value, the other value has to be such that there is some here is still valid. So although I cannot choose R_3 and R_4 very correctly, initial values I choose R_3 some value 100 ohm, 10 ohm, any value. R_4 I can choose is such that the first charge transfer resistance will still meet and then, from there I should start optimizing.

If I take this, this is representing the Faradaic process, means reaction. This is solution resistance and this is C_{dl}, double layer capacitance. Now at infinite frequency, we know the process will have only simple resistive behaviour, it need not be R_2. It is not R_2 here. It is sum of all these things at infinite frequency. Z_F at infinite frequency should come out as a resistor. When it comes out as a resistor, this is where it is going to (settl)e. Then when you go to lower frequencies, other capacitor or inductor or whatever that element is present that will also show up, and it will have loops like this. There the first high frequency loop hits the real axis, or tends to hit the real axis, is your estimate of R_t based on the data.

Now all these simplifications, I can use when that Voigt elements or the Maxwell elements are made up of capacitors only or inductors only. If you use a circuit with mixes up inductor and capacitor, you cannot get this simplification.

These are few other examples. In all these cases, we assume the points, frequency points settle at the location where I am just marking. This is solution resistance. This point is R_t+R_{sol} and if this is 0, we will just call it as R_t. This is R_p+R_{sol}. This is R_t, assuming solution resistance is 0. I am going to skip that phase now. I will assume solution resistance is zero and I will say this is R_p. This is R_t. It starts here, comes like this and then forms a loop. It can form a loop like this. It can form a loop here. It does not matter where is it going to hit the real axis, if only a resistance is there and it is projected out there and this is R_p, this is R_t. This is R_p. We have data like this. This point is going to be R_t. We have data like this, and we can simulate it, meaning we can show reaction, which can give you a spectrum like this. This is R_t, this meaning where it hits here. I am not very sure whether it hits right here or right here. That is okay. I do not remember it well. But maybe I will draw it a little better. I will project it here and call this as R_t, wherever that settles, that is R_p, provided solution resistance is zero. Otherwise you just have to add the solution resistance all these and that is what you would do. Now R_t you can get it from impedance spectroscopy. R_p you can get it from impedance as well as other techniques. Now I also want to show you that instead of using a Maxwell circuit with capacitor, only R resistor only, I am going to draw this. In one of the earlier classes, we have looked at a spectrum, which looks like this and then I showed you if I take a circuit like this, it does not seem to fit well. Zsimpwin says it is not able to fit it. Well, it does not say that, it fits it, but we are not happy with the fit. Whereas, instead of this, if I use, negative values for these to model this inductive loop, then I am able to fit it very well and then we used the equivalent circuits say these two circuits are equivalent, meaning capacitor in resistor series in parallel with the resistance can be modeled by a resistor, inductor and a resistor and then we found that this resistance has to be negative, - 200 Ω or -290 Ω or some such number. Whereas if you look at the data, it never goes to negative in the real axis. So when you mix up and get an inductor and capacitor in a circuit to represent Faradaic impedance, you cannot get a simple expression for polarization resistance or charge transfer resistance.

Previous cases, where we looked at the examples, one of them will be simple equation, that is R_0 is R_t. I use a slightly different representation R_0 is R_p. Other one is sum of this or inverse of this resistance is going to be sum of inverse of all these things, etc. I use Maxwell circuit with capacitor, 1 resistance can be identified quickly. With inductor, another resistance can be identified quickly. This is R_t can be identified, previously R_p can be identified.

Ladder, again, I can identify R_p or R_t quickly. If I have a mixed circuit, when I give zero frequency, this is broken, this is short circuited. So I have two resistances in parallel, at the minimum, I may have more elements. If I do infinite frequency, this is short circuited, but this is broken. So, you should not mix inductor and capacitor when you are modeling Faradaic impedance part. If you have film on the surface and you are modeling the film + reaction, then you may get inductor.

And you may not have a choice, that is different. When you assume, there is only simple meaning, a reaction without any further film formation and so on, then this part which represents Faradaic impedance, it is better to keep it as set of inductor or set of capacitor. Usually we keep it as set of capacitors, you should not mix up. So if I use this and say this set of three spectra I can model using the circuit, I can guess the value of R_2. I can guess the value of R_t. Not guess the value of R_t, yeah I can guess the value of R_t from that I can guess the value of R_3, and then optimize it, I can get the circuit fit. Not just that.

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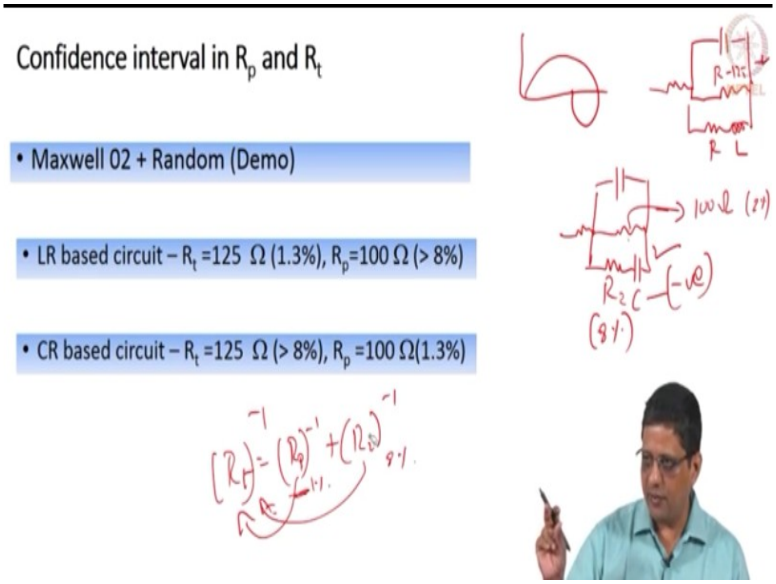

I want to show you another example.

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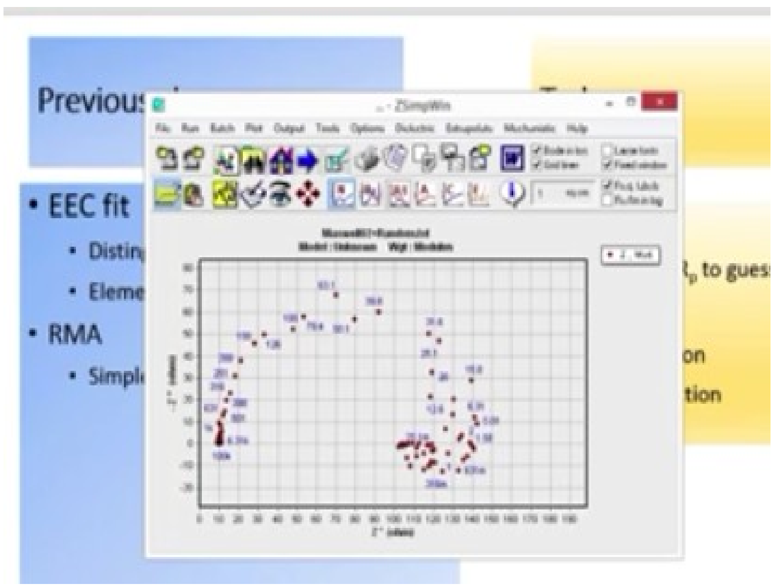

This is a data that I have generated, this is something we have seen before. It actually comes from a data which looks like this, which you can model using solution resistance, double layer capacitance, and either I can use, resistors and inductor. I can model this or I can do something similar for the first component and I will say (for the) resistor and capacitor, allow negative values. Either case, I can model it. What I have done now is to add some noise to that artificially and then what happens, when we fit it. This is the original data, which looks like this, suppose to come nicely and sit here, but if it comes very nicely and sits there, because I have given artificial data, then confidence interval in all parameters will tell, I have 100% confidence or it is 0%

standard deviation. But I want to show you what happens when you have a real data. This is of course not real data, but noisy data.

In the Zsimpwin, I can use this circuit to model. Any other software you can use it is okay. You will get pretty much the same result. It fits it and then says, it is noisy. The data is noisy, fit is okay and this has come from artificial data. It does fit well, I created random noise and added over this, so it is going to be, on the average it is going to be still following the original value with slight deviation.

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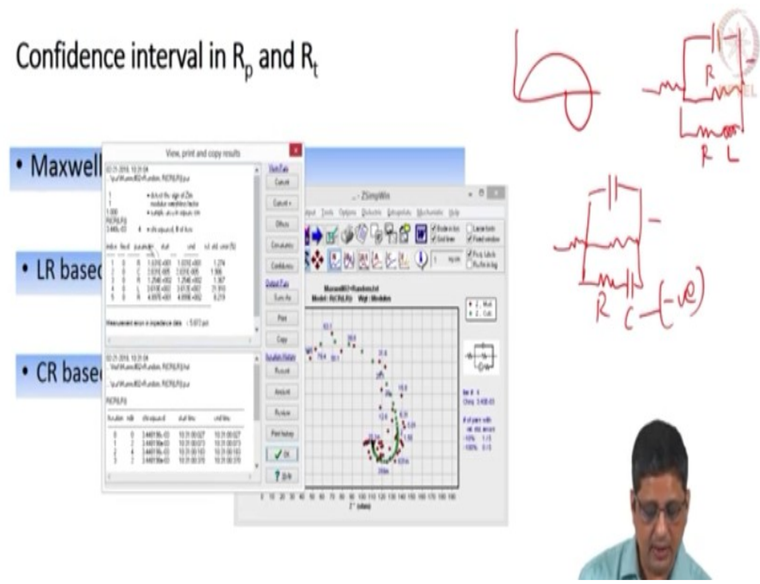

I want you to look at the values of the elements. The resistance, the first resistance here is 10 Ω , it is 1.03×10^1, relative standard error is 1.3%. Capacitor is 20 μF that is also coming correctly 2%. 125 Ω, is the resistance here. So this resistor is 125 Ω. Standard deviation is 1.4%. That means in this representation, I know at infinite frequency, current will not go through this, so charge transfer resistance here is 125 Ω.

Look at the confidence or the percentage relative standard error in L. It is about 22%, low frequency data has lot of noise, therefore it is not very sure that this is the correct value. It has come up with the value of 361 H. Resistance is about 489-490 Ω, so it has got a value for this resistance here in the inductor, it is 361 H. Resistance is about 490 Ω. We are not very confident. It is okay, 8%, 9%, 20% in that range, we have the relative standard error.

So I am confident about R_t. I am not confident about R_p, because from this, if I have 1% error in R_t and 8% error in the next element, I have to take them in parallel to estimate R_p. I will get poor estimate or I will have less confidence in that, because one of the element has low confidence and the final value also will have low confidence. Actually, it depends on how much weightage each element contributes to the final value.

But unless you do the calculation very carefully, you will say I can estimate R_t well, I have some problem in estimating the R_2 or whatever the second R representation is. I do not have that much confidence in the L. I do not have that much confidence in the R. Therefore, I may not be able to tell you R_p very well. Data also looks noisy in that region. Now instead of this, I can use C, except that I have to say that this has to be negative only then, I can model. So I have given it negative and ask it to model. It will fit equally well. Because those circuits are actually equivalent.

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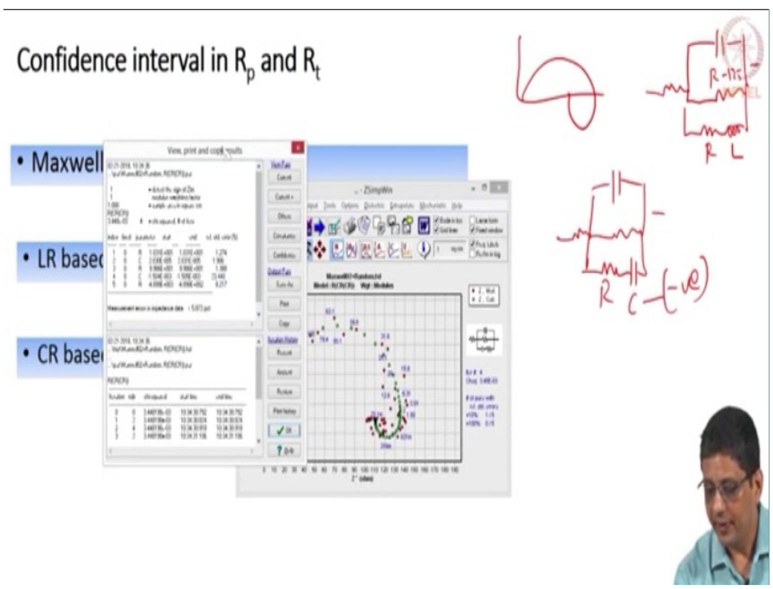

The percentage standard deviation, relative standard deviation is different now. Because of the way that each element is related to the impedance. So you have 23-24% relative standard error for the capacitance. We have 8% standard error in the resistor, which is associated with the capacitor. This value the one associated with R_p, we have confidence now. So now we have good confidence in the value of R_p, R_p is close to 100 Ω.

R_t was close to 124 Ω. It starts at 10 Ω, it hits close to 135 here, that means 125 Ω is the R_t. It hits close to 110 Ω here, that means 100 Ω is the R_p, but it is not apparent that you have reasonably good confidence in R_t and R_p, but you will have to use different circuits to get that quickly. If I want to estimate R_t from this, effectively at infinite frequency, this is going to be a resistor in parallel with another resistor.

So it is $(R_t)^{-1} = (R_p)^{-1} + (R_2)^{-1}$. If I am confident about this value, it is within 1%, this is 8%, I have to do it correctly. I can say this contributes mostly to this, this contributes less to this, but when you do it in one form, one form meaning capacitor based, you have to do the weighted averaging, and say even though this element has a lot of error for a total calculation, it does not contribute much. Therefore, I am still confident. What that means is, when you look at real data and analyse, you have to look at the confidence interval for the parameter values to know whether your circuit is good, whether you have to do one more element, you have to do it with care.