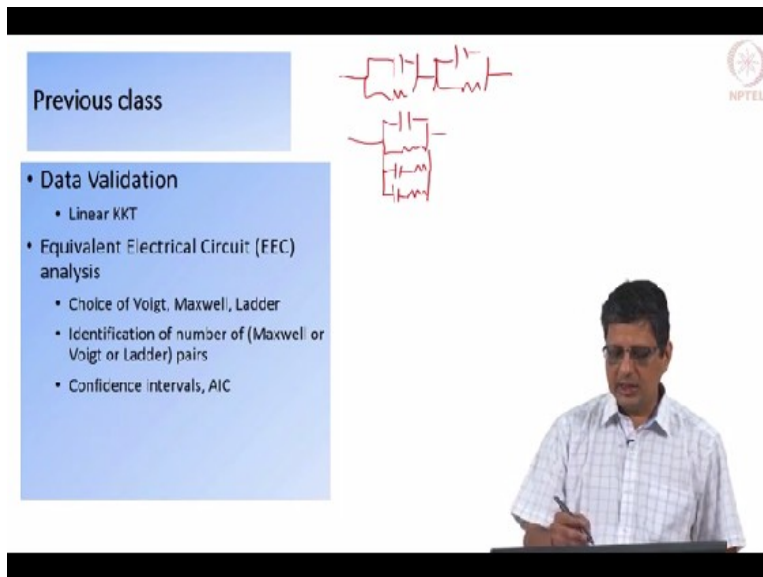


**Electrochemical Impedance Spectroscopy**  
**Prof. S. Ramanathan**  
**Department of Chemical Engineering**  
**Indian Institute of Technology - Madras**


**Lecture – 17**  
**EEC Fitting, Initial Values, Distinguishability**

**(Refer Slide Time: 00:13)**




In the last class, we saw example with Linear KKT. We also started using the electrical circuit to model the data. we said there are different types of circuits possible. You can use what is called Voigt circuit which goes like this (refer video, 0.:30). You can have Maxwell circuit in which case, the first capacitor used for modelling double layer and this resistor along with a set of resistor and capacitor pair. You can have 'n' number of this or you can have a Ladder circuit which is slightly different from these.

**(Refer Slide Time: 00:58)**



Previous class	Today
<ul style="list-style-type: none"><li>• Data Validation<ul style="list-style-type: none"><li>• Linear KKT</li></ul></li><li>• Equivalent Electrical Circuit (EEC) analysis<ul style="list-style-type: none"><li>• Choice of Voigt, Maxwell, Ladder</li><li>• Identification of number of (Maxwell or Voigt or Ladder) pairs</li><li>• Confidence intervals, AIC</li></ul></li></ul>	<ul style="list-style-type: none"><li>• EEC fit<ul style="list-style-type: none"><li>• Initial values</li><li>• Distinguishability</li><li>• Element value <math>\rightarrow</math> Physical phenomena</li></ul></li></ul>



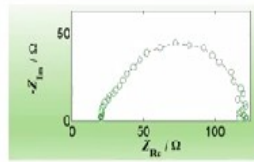
How do we select how many number of elements should be used? We saw an example before. I will also refresh your memory by showing that example again and then I want to show you using one particular software that we have. You can have access to other software and you can model this but the basic idea that you learn from here will be applicable whether you use this software or any other software.

How do you choose initial values? Normally, the software will give an automatic guess and will work. If it works fine, we are fine. If it does not work well, can we do something before we say we have to add one more pair of Voigt element or one more pair of Maxwell element. earlier I showed you an example how many elements should we use.

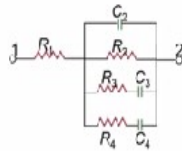
**(Refer Slide Time: 01:40)**

### Identify circuit

- How many elements should we use?
- Example: Synthetic data with 'noise'



• Confidence in the parameter values



Element	Till C2	Till C3	Till C4
$R_1 (\Omega)$	22.4 (< 3%)	19.9 (< 1%)	19.97 (< 1%)
$R_2 (\Omega)$	95.2 (< 3%)	100.6 (< 1%)	101 (< 4%)
$C_2 (\mu F)$	16.6 (< 5%)	10 (3%)	10 (< 3%)
$R_3 (\Omega)$	--	52.2 (< 6%)	52.1 (< 6%)
$C_3 (\mu F)$	--	9.8 (< 3%)	9.8 (< 3%)
$R_4 (\Omega)$	--	--	23370 (~ 767%)
$C_4 (\mu F)$	--	--	7.5 (~ 1704%)



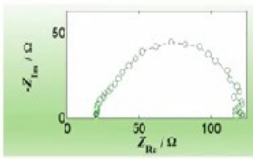
In this example, we have used a synthetic data with noise and we said we will use  $R_1 C_2 R_2$  in this example. Then we fitted to one more pair of Maxwell element. We look at 2 pairs of Maxwell elements. Confidence interval is poor in  $R_4 C_4$  case. We also did estimate of AIC and said, this circuit can be fitted well with  $C_2 R_2, R_3 C_3$  and we do not need  $R_4 C_4$ .

But here, we have assumed that when we fitted with this circuit with  $R_1 C_2 R_2$  or when we added one pair of elements, we did our best and these are the best-case values. It is possible that this example I showed here for example till  $C_3$ , I showed the value as 19.9, 100.6, 10  $\mu F$ , etc. This may not be the best case. In which case, I should not come to the conclusion that this is the good solution or this is the incorrect solution. I have to know, before I move from one column to the next column, I have to make sure that I have done the best in the first case. This example is straightforward. I will show you examples where it is not so straightforward.

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**Identify circuit**

- How many elements should we use?
- Example: Synthetic data with 'noise'

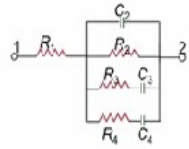


Residual sum square (RSS)  
Akaike Information Criterion  
Corrected AIC [AIC<sub>c</sub>]

$AIC = 2k + n \ln(RSS)$

'n' - number of observations  
'k' - number of parameters

$AIC_c = AIC + \frac{2k(k+1)}{n-k-1}$




Circuit	# of Residuals	AIC	AIC <sub>c</sub>
Till C2	3	1196	296.6
Till C3	5	76	187.3
Till C4	7	76	191.5

In this particular case, we have done the Akaike information criterion comparison where we add more parameters and corresponding to the parameters addition, you have penalty. And we showed that if you use more elements, beyond a limit, there is no significant benefit. And we should settle at some place here. But this involves the assumption that at each case, I got the minimal residual corresponding to that case.

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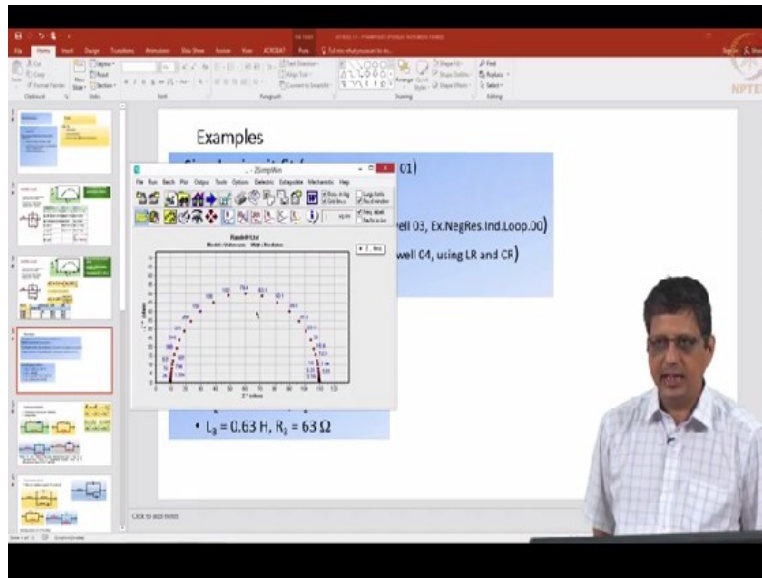
**Examples**

- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex.NegRes.Ind. Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)



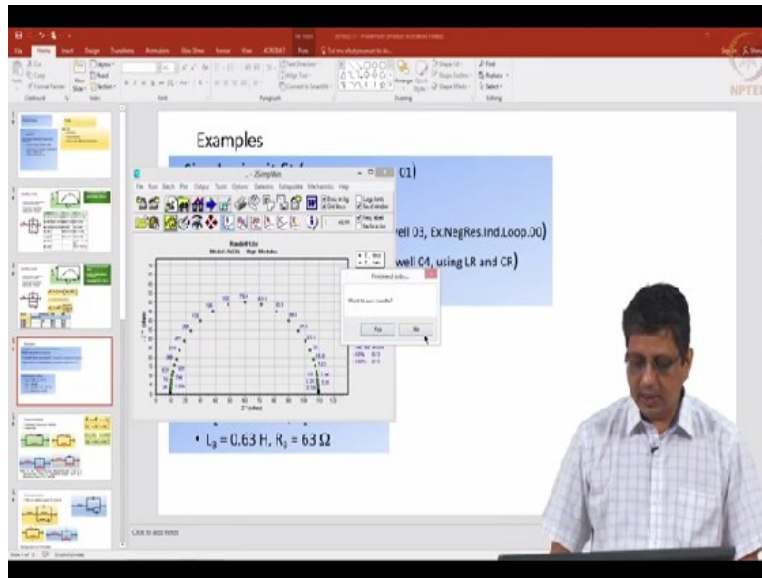
Now I want to show you how you can use the software to fit the data, fit the model to a particular set of data. starting with simple examples.

(Refer Slide Time: 03:32)



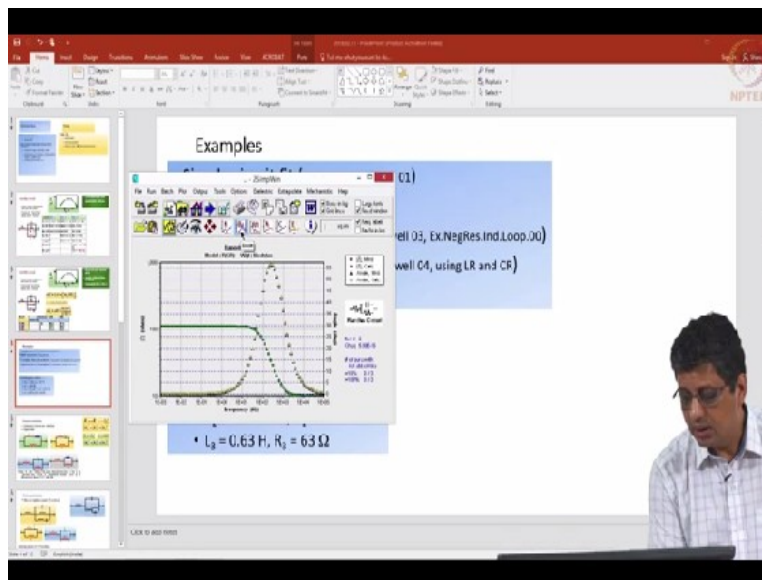
We will proceed to more difficult choices later. First I want to show you what is called Randle's circuit. Basically I have opened the software, opened the data. It is already in the correct format (refer video, 3:30). It has frequency, Z real, Z imaginary and it gives a semicircle. It is a synthetic data. And you can imagine that this can be fitted to a circuit with 1 resistor and a capacitor in parallel with the resistor. The capacitor parallel with the resistor will give you a semicircle and you add a resistor to shift that semicircle from origin to the right side. In the notation of this software, this is a model that you have to choose. Icon is to denote an electrical circuit and the way they denote this Randle circuit is CR tells the capacitance and resistors are in parallel. It is within the bracket and then you have R in front of this to say there is a resistor in front of it. This is a relatively straightforward model. Data is created from this.

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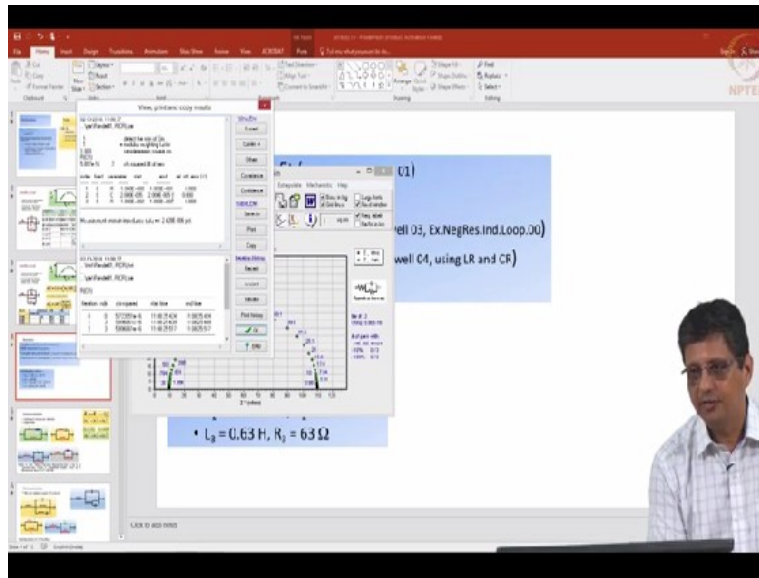
I will say I want to save the results. I want to save the parameters. It fits very well. You can look at it in the Bode format (refer video, 4:40).

**(Refer Slide Time: 04:50)**



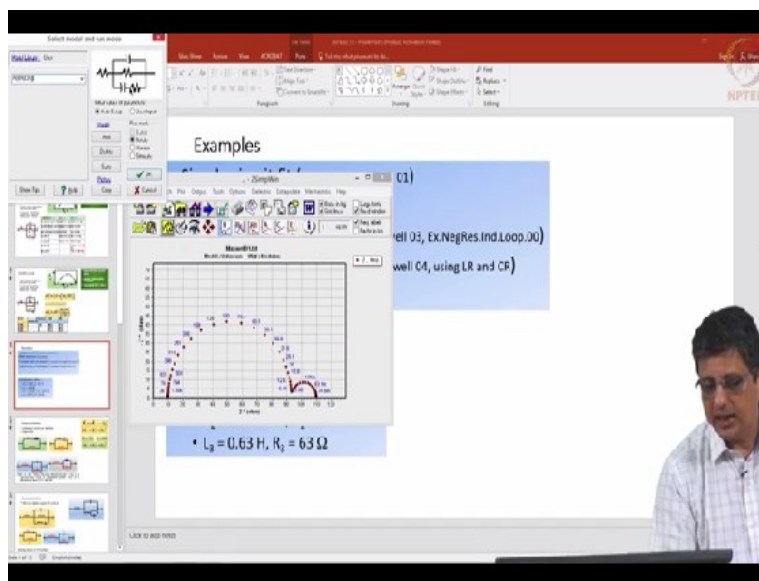
They overlap, so you cannot even see the 2 sets of data.

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The point to note is when we look at the parameters, it also gives me relative standard error. They are zero here. It is created from  $10 \Omega$ ,  $20 \mu\text{F}$ , that is  $2 \times 10^{-5} \text{ F}$ . And  $1 \times 10^2$ , that is  $100 \Omega$ . It is a resistor,  $10 \Omega$  resistor, it is in series with a capacitor and resistor. It is  $100 \Omega$  and this is a  $20 \mu\text{F}$ . It is a typical value for a standard system. The chi square value is only -16 of that order. That is basically a round off errors in this synthetic data. If this value is large, it means the deviations are high. That is one way of looking at it. This is 0% error, that obviously means it is fitting perfectly. I want to take another data. I will call it as Maxwell 1.

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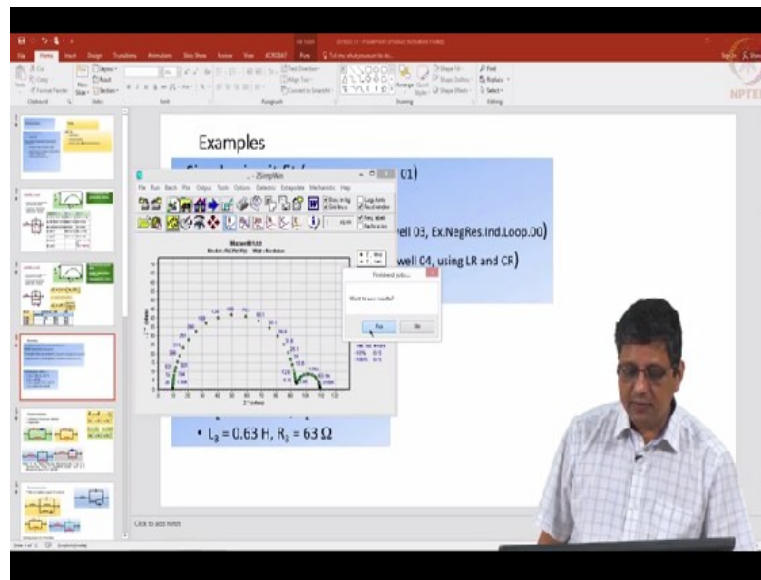


When you look at this, you can see there are 2 semicircles (refer video, 5:56). I can fit it with one more pair of capacitor and resistor. I can arrange it as a Voigt circuit, Ladder circuit, or



Maxwell. I am going to try this with one more CR and this shows up a Maxwell circuit here. In this particular software for many such combinations, you have example picture. So the picture here will change. But you can come up with your own circuit and they may or may not have a picture there. It does not matter. As long as the coding is correct, coding here means, R start with the bracket, CR start with another bracket, CR and end the bracket. It is going to give you Maxwell circuit. If I give a different circuit, as long as the coding is correct, it will try to fit it. The picture may not appear correctly. But here I am going to fit it with a Maxwell circuit.

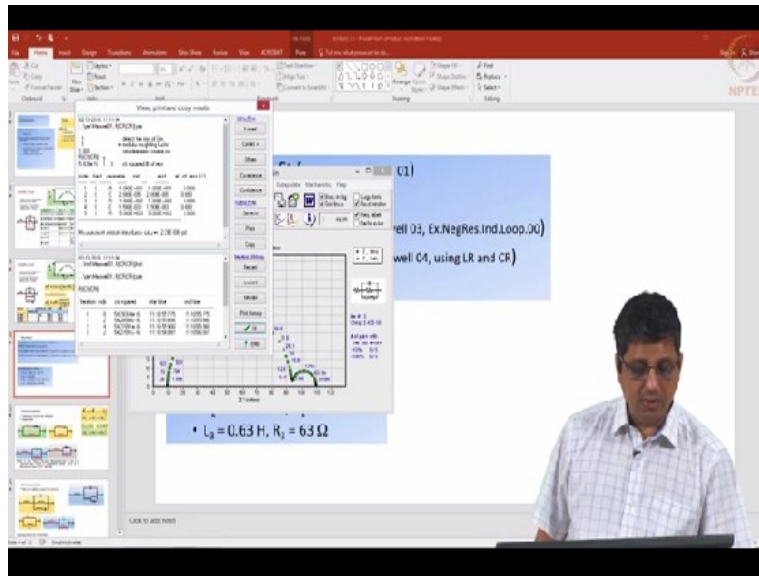
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And here also it fits very nicely (refer video, 7:03). I want to save the results because I want to look at the parameters.

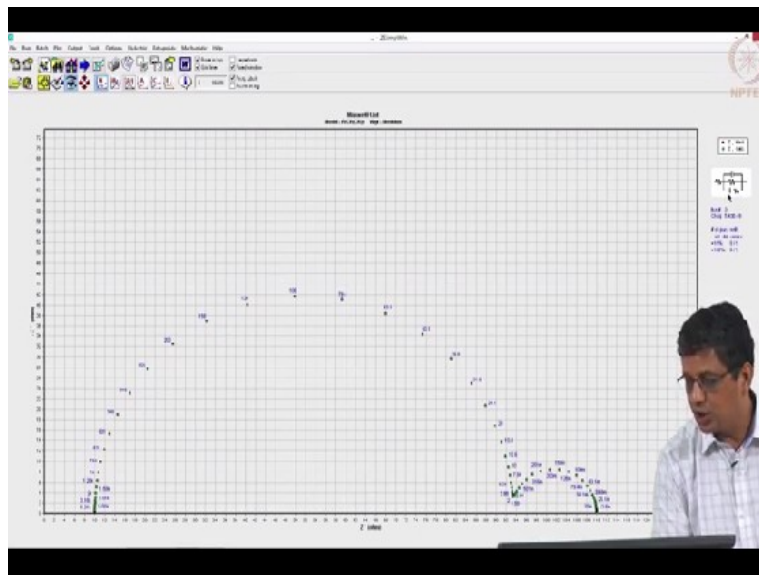
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The error is negligible and confidence interval is very tight that is a relative error is very low. And of course, it is again a synthesized data with  $10\ \Omega$ ,  $20\ \mu\text{F}$ ,  $100\ \Omega$ . This is  $1.5\ \text{mF}$  which fairly large capacitance and another  $R$  is  $500\ \Omega$ .

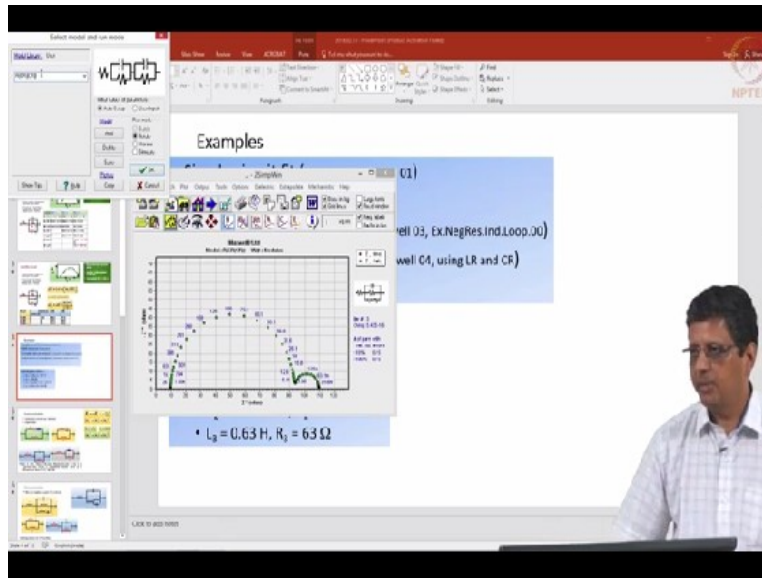
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This capacitor and resistor are large values ( $1.5\ \text{mF}$  and  $500\ \Omega$ ). Still I can tell that if I use this model, it fits well, no problem.

**“Professor - student conversation starts”** But if sir we change, as you go with the previous one when we have single semicircle and we do it in the series of. . what you want to do is to fit it to a circuit like this (refer video, 7:57).

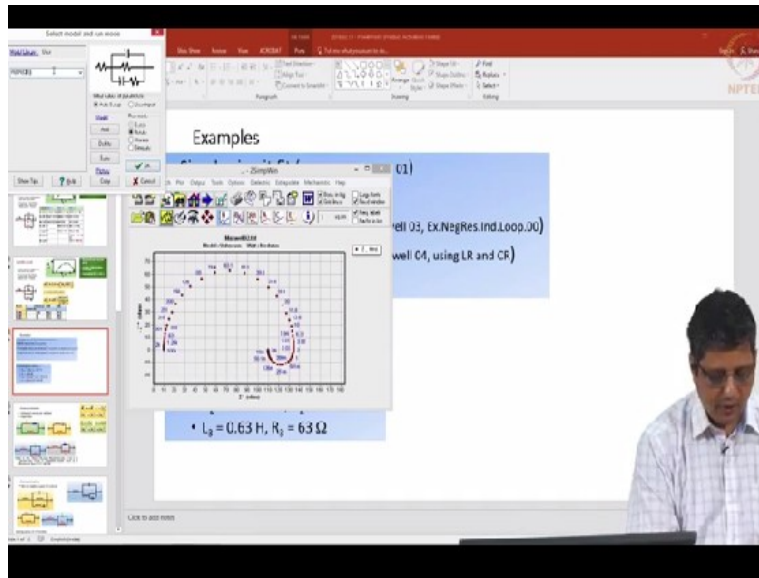
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If we had one more resistance also because the center resistance will have to shift the circle towards. No, we already have a resistor in the front. This will fit equally well. **“Professor - student conversation ends.”**

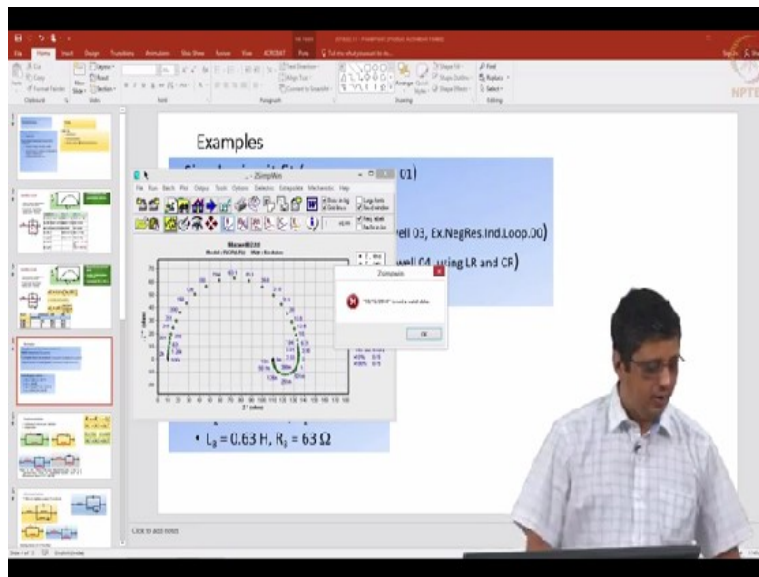
I want to save the results and this again gives me negligible error, 0% relative standard error, 10  $\Omega$  to 20  $\mu\text{F}$ . Now look at this, the value of resistance and capacitance will change. But this circuit and that circuit are equivalent (refer video, 8:42). That means, if you can fit it with that Maxwell circuit, you can fit it with this circuit with exactly same error. Those 2 are equivalent meaning if you tell me that it fits well with this circuit, these are the Maxwell elements. I will give you another circuit which is the Voigt circuit. In this example, Voigt circuit is this. Without fitting the data from the Maxwell element values, I can show you that this is how you can calculate. They are equivalent meaning if one model fits, an equivalent model will fit equally well. No better, no worse. And not just that. I can also fit it to a Ladder circuit. You can see the fit is good. You can see chi square value is same. Numbers will change. Obviously, the resistance and capacitance will be different but all these 3 circuits are equivalent.

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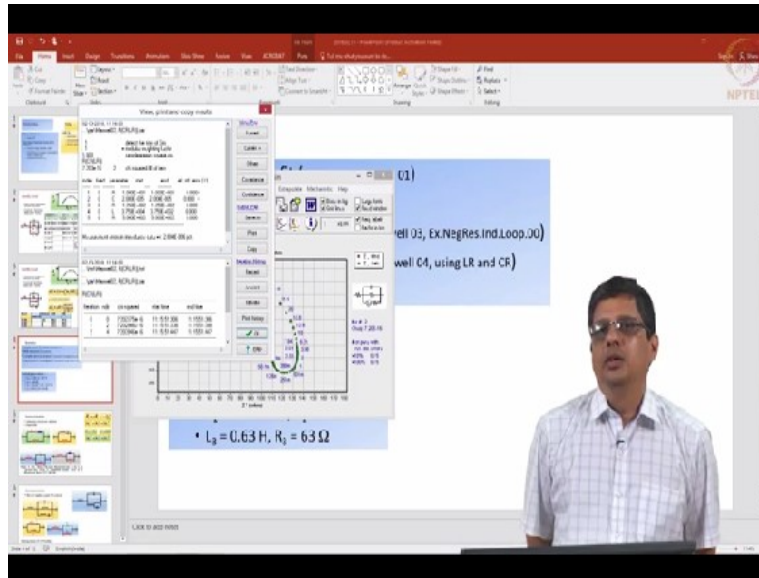
Now I want to fit it to a data which shows what is called inductive loop (refer video, 9:55). if you look here,  $-Z$  imaginary is zero here, goes up and comes down, this is the capacitance. If it comes below that axis, we will call that as inductive loop. It need not even come below this. If it goes like this here, it is still an inductive loop. So instead of fitting it to RCRCR, we can use the following circuit where you have L here. And similarly, you can use a Voigt circuit with LR. You can use the Ladder circuit with LR.

**(Refer Slide Time: 10:57)**



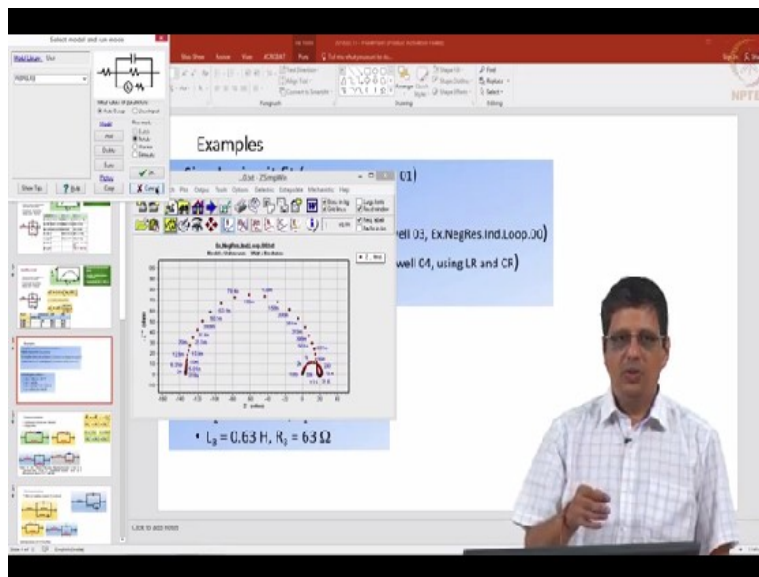
This example it fits well again.

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Values are good. You have 0% relative error. In some cases, you cannot fit it. You have to go to the next level of complexity. But before we go there, we had to be sure that we had done our best here.

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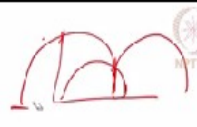



I want to show data which looks like this (refer video, 11:30). That means in the complex plane, it has an inductive loop and a capacitive loop that goes to the negative side. It has 1 capacitive loop at the high frequency. It has 1 inductive loop in the mid frequency. And 1 more capacitive loop except that it is going back.

(Refer Slide Time: 12:16)

Examples

- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex NegRes.Ind.Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)

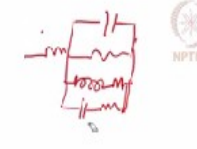




If I have to draw, this 1 capacitive loop, 1 inductive loop. If it goes to this side, I will say capacitive loop. If it goes here also, it is a capacitive loop except that it ends up in the negative value.

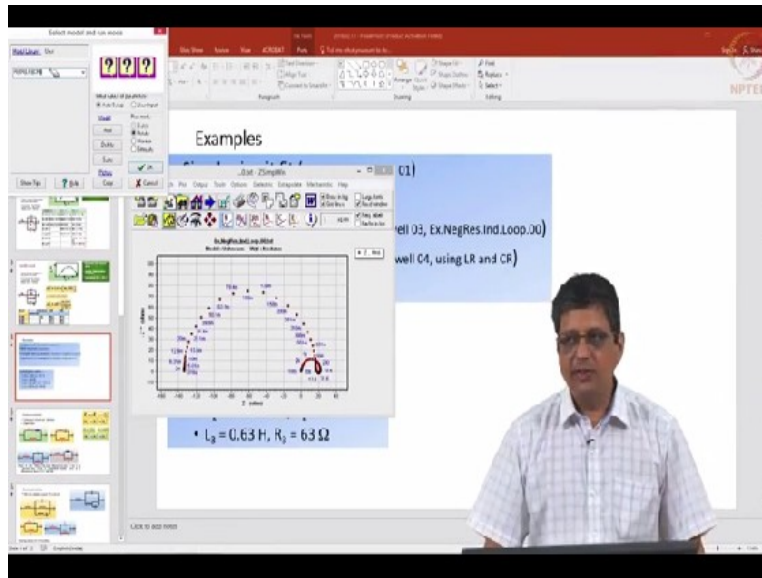
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Examples

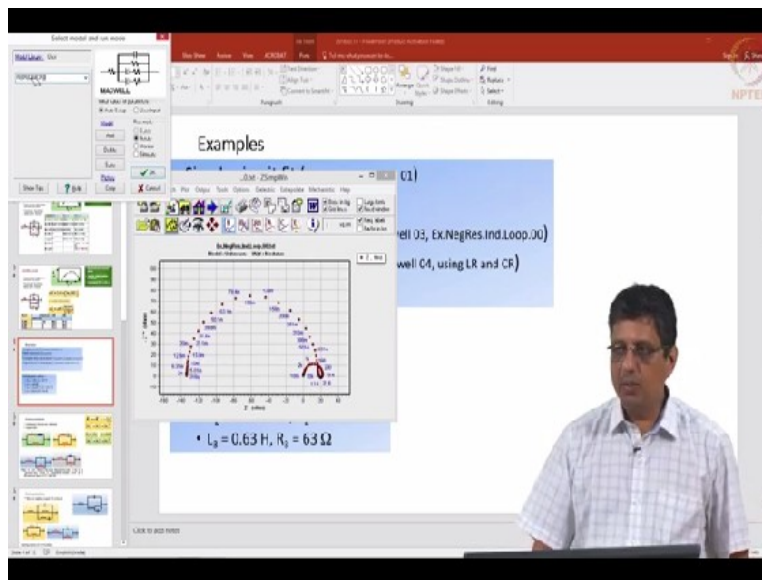
- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex NegRes.Ind.Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)

For this, I will use the following circuit (refer video, 12:37). This circuit will give me 1 capacitive loop. This is offset, this is capacitive loop. This element here is an inductor. And this is a resistor. I will use a capacitive loop here. But I also need to know that it will end up in a negative resistance. At the low frequency, it has to end in a negative resistance. **(Refer Slide Time: 13:20)**



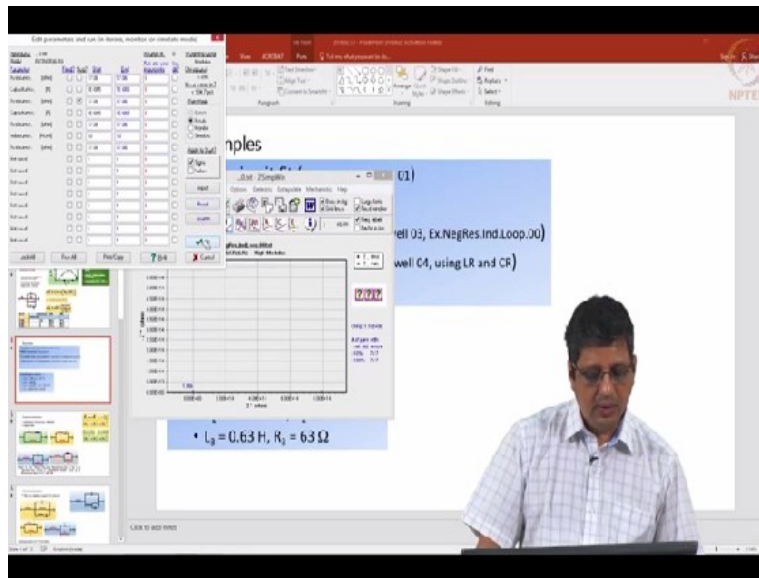
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If I give CR, I will get a picture here. Because of few systems, the library has the icons. Other system, it will still fit correctly except that it may not have an icon. we want to replace one of them with LR. In addition, I do not want it to be under auto mode. I have to go to user input here.

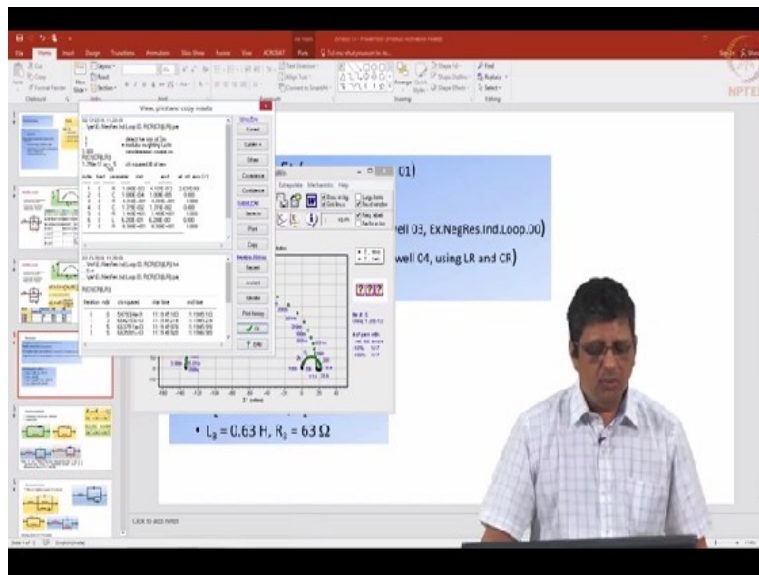
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And I want to tell the first resistance, capacitance, next resistance can be negative and in the beginning itself, it is going to give a negative value here in the guess value. Let us see how it works. Seems to work well (refer video, 14:05).

**(Refer Slide Time: 14:16)**



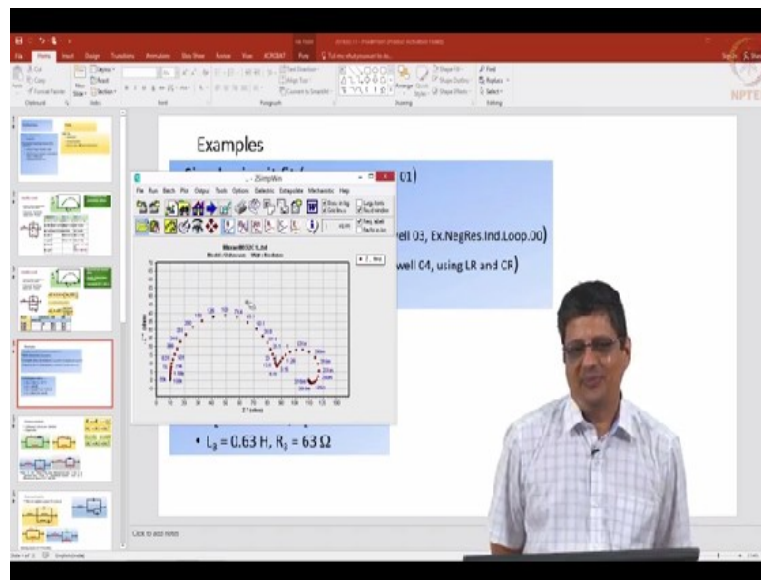
Now  $\chi^2$  is low and the first value, resistance is actually 40e-12 and it has very high standard error. This means I had created the data with zero solution resistance. And the software cannot have a zero value, therefore it gives very low value. You can ignore it and make it as zero for your model. You have to intelligently use the numbers. We cannot just say if it is 2% error, we are happy. If it is 100% error, we are unhappy. If it is 100% error, we are unhappy but in this particular case, we do not need to worry. We can use a model without the initial resistor or you



can still use the same thing and say I will make it zero and it will fit even better. The rest of them are fine. Notice this value (refer video, 15:20). The values are  $0\ \Omega$ ,  $-42.8\ \Omega$ ,  $1\ \mu\text{F}$ ,  $13\ \text{mF}$ , and  $14.69\ \Omega$ , inductor is  $0.62\ \text{H}$ , and  $63\ \Omega$ . The inductor is large inductance. See  $100\ \Omega$ ,  $10\ \Omega$ ,  $1000\ \Omega$ , resistors are easy to imagine. Milli Farad capacitance is not that easy to get if you really get a physical capacitor. It is a large capacitor. Also, large inductance is not easy to achieve.

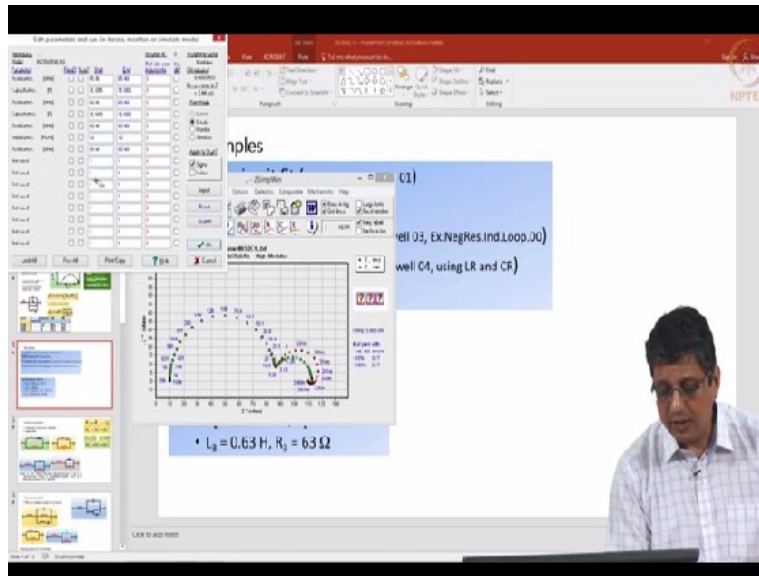
It means this comes from an electrochemical system. This circuit with this inductance and capacitance can give similar data. It does not mean that the actual system has some inductor or has any magnetic field. It does not necessarily mean it stores lot of energy like a capacitor. It just means this is an analogy. This physical system can be represented by a set of elements like capacitor and resistor arranged in this way. And negative resistance is always a headache to explain in the framework of this simple circuits.

**(Refer Slide Time: 16:38)**



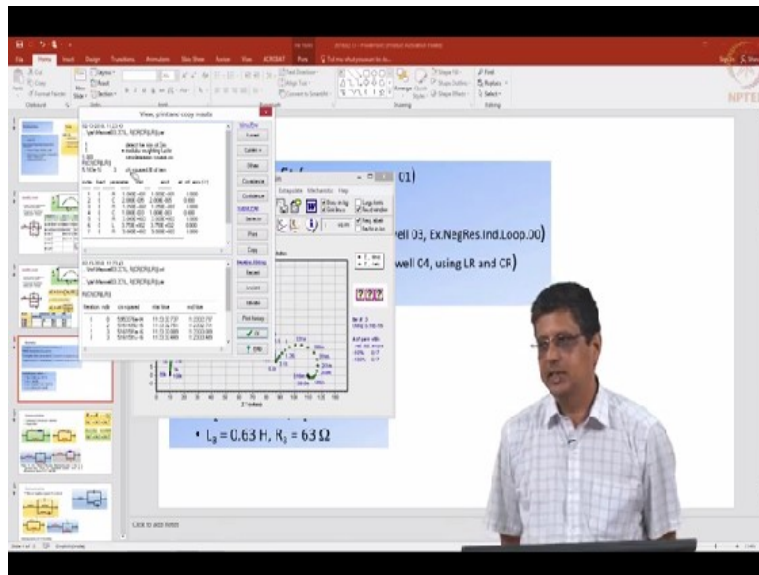
Here, we have another complex plane plot (refer video, 16:39). First high frequency loop which is starting from these  $10\ \Omega$ . It needs 1 resistor and capacitor. You can start with the Randle circuit. Then you have 1 more capacitive loop. You need to add 1 Maxwell with capacitor. You have one inductor at the end. You need 1 LR at the end.

**(Refer Slide Time: 17:04)**



And here also, I am going to use the circuit RCR. RCR for the first loop. Second loop is another CR. Third loop is LR. Except that I do not need negative values anywhere. I can go with the auto setup or I can give initial values. capacitive loop, another capacitive loop, inductive loop, it fits well.

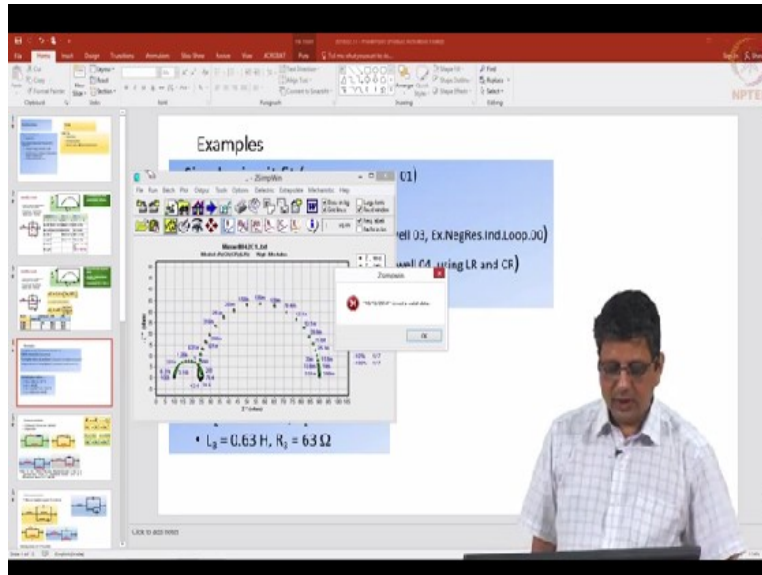
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And we can confirm by looking at the parameters. They have 0% standard error, relative standard error.  $\chi^2$  is  $10e-16$ . This is good. All these cases, we do not have any doubt. It fits well. We are fine. We have to choose carefully in the beginning whether the circuit needs a negative resistor. Now how do I know that that particular resistance has to be negative? Why not use another?

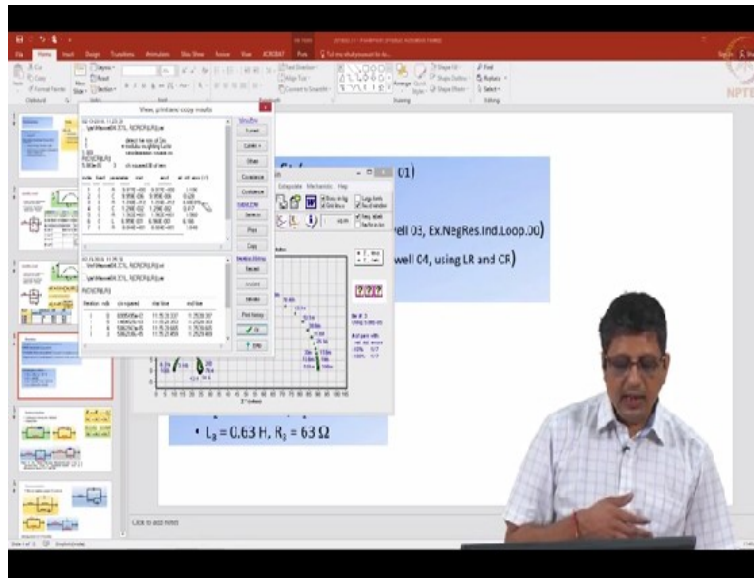
Previously I have tried these examples. I know this works, that is why I have given it to you or shown here. When you get a new set of data, if it works like this, you are happy. Does not work like this, what do we do?

**(Refer Slide Time: 18:23)**



This is another example where first you see a capacitive loop is there (refer video, 18:20). It is a small loop. Next you see an inductive loop is there. Next you see a large capacitive loop is there. I can use the same circuit that I used before. I need one R CR for the first capacitive loop, LR for the second, CR for the third. Now if I have LR here and CR here in parallel, it does not matter whether it is CR and LR. Similarly, if you have 2 elements in series, it does not matter whether you put it this way or that way as long as nothing else is connecting. It seems to fit. It is not fitting very well here. High frequency index is fine. Mid frequency fit is not that great.

**(Refer Slide Time: 19:31)**



And when I look at  $\chi^2$ , it is  $5e-5$ . Normally it is still a good data if it is experimental data. But this is synthetic data, I would expect  $\chi^2$  something in the range of  $1e-10$ ,  $1e-12$ ,  $1e-16$ . Moreover, the relative errors are not that good. I am not happy considering this is synthetic data. Previously, when the relative error was high for the solution resistance, I had a justification in saying it is fine. Solution resistance is zero. The software does not allow that element values to go to zero. Therefore, it is giving like this. I could have modelled it without the trailing resistor and it would have fitted perfectly. I did not show you but you can try it. You will see it is working fine. Here I am not very happy. Does it mean I should add 1 more CR or LR or any other element? Now I am going to claim that this is not fitting well because we are not doing our best.

(Refer Slide Time: 20:30)

### Examples

- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex NegRes Ind Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)

**“Professor - student conversation starts”** (refer video 20:35) This shows that we have 2 capacitance and 1 inductor here. Yes. And previous example also we had capacitance. Yes. What is the difference? Answer: It depends on the element values. Inductive loop need not come at the end or at the middle. It depends on the values of these elements. All that you can say is if it contains 1 capacitive loop, 1 inductive loop and another capacitive loop, you will need minimum these many pairs of Maxwell elements to model this. But the capacitive loop came in the end here and in the previous case, it came in the middle, it means the element values were different.

Student: nothing about order?

Professor: No. Nothing about order. Meaning if you change the values here, it can change from this to this. I do not need to change the circuit. The same circuit with different values for these elements will give me different patterns. **“Professor - student conversation ends.”**

**(Refer Slide Time: 21:40)**

Examples

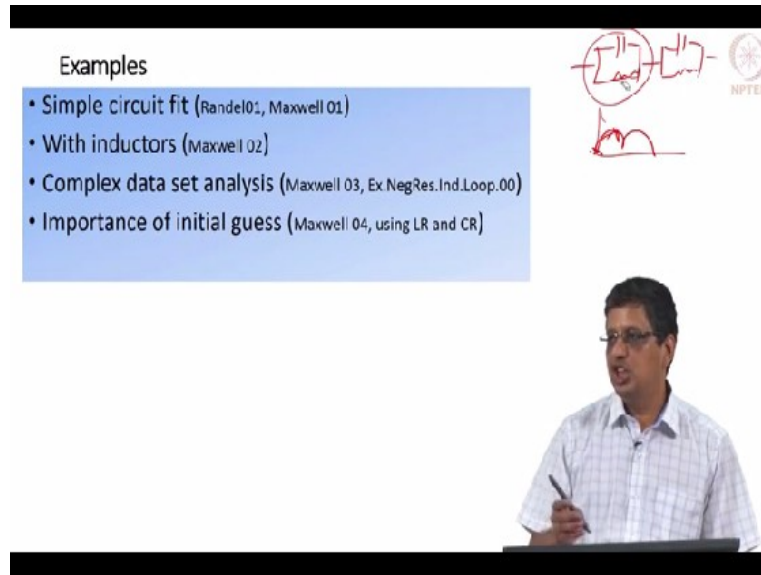
- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex NegRes.Ind.Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)

The slide also features two hand-drawn circuit diagrams in red ink. The top diagram shows a series combination of a capacitor, an inductor, and another capacitor, with labels  $10\mu F$ ,  $100\Omega$ , and  $10\mu F$ . The bottom diagram shows a similar series combination with a different arrangement of elements.

Let me show you another example (refer video, 21:42). I will make up these numbers. This in general can give me a capacitive loop, two loops like this starting at the origin because I have removed the initial resistor. Now imagine this is  $10\mu F$ . This is  $100\Omega$ . This is  $10\mu F$  and this is  $100\Omega$ . They are identical in terms. So, all that I need to do is calculate this, call it as  $Z1$ , multiply by 2, I will get the effective circuit. I can model this with only one, that means it will become a semicircle. If you just give me that data from, synthesized from  $10\mu F$ ,  $100\Omega$ ,  $10\mu F$ ,  $100\Omega$  here, if I look at the data without knowing where it came from, I will say one pair of elements is sufficient to model this. Because that is all that is needed. If they are identical, two semicircles

will become one semicircle. we can distinguish between them only if the elemental values are quite different. And we take data in the correct measurement range.

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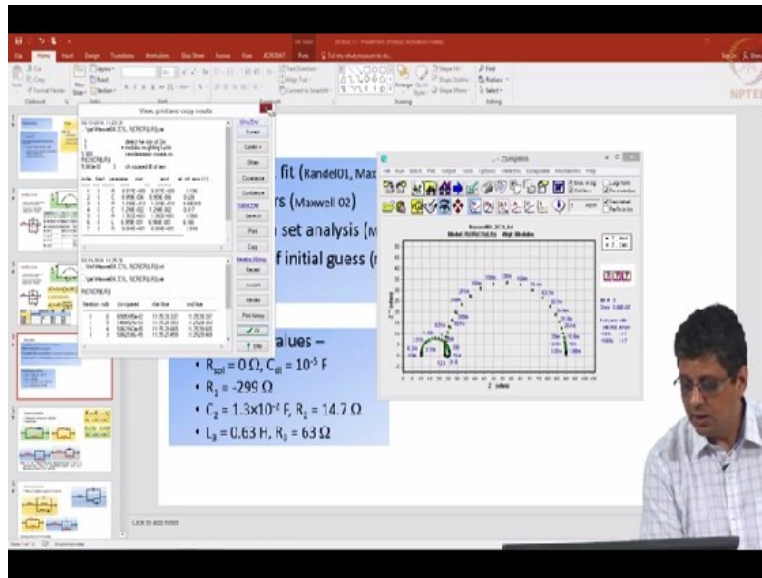


The video frame shows a presentation slide titled "Examples" with a blue background. The slide lists four bullet points: "Simple circuit fit (Randel01, Maxwell 01)", "With inductors (Maxwell 02)", "Complex data set analysis (Maxwell 03, Ex.Neg.Res.Ind.Loop.00)", and "Importance of initial guess (Maxwell 04, using LR and CR)". To the right of the text is a hand-drawn circuit diagram in red ink, showing a series combination of a resistor, an inductor, and a capacitor. Below the diagram is a red signature. In the bottom right corner of the slide is the NPTEL logo. A man in a light blue checkered shirt is visible in the bottom right corner of the video frame, holding a pen.

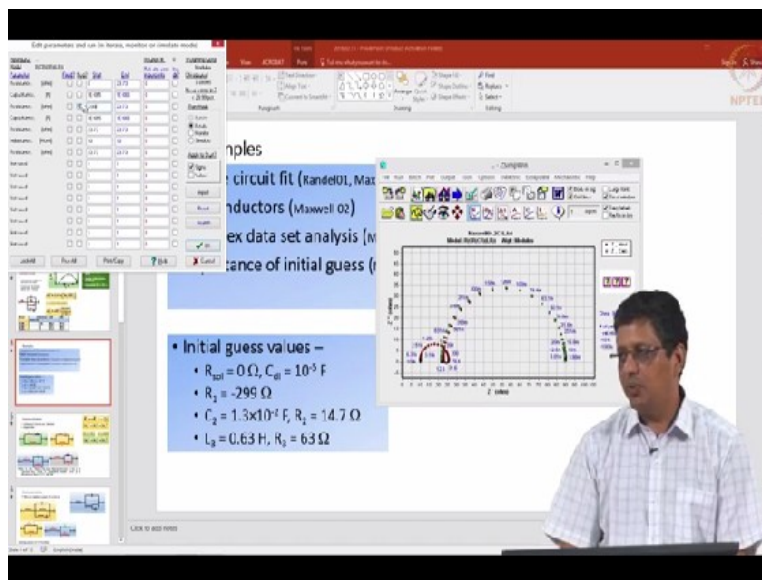
What do you mean by that? Again the same circuit (refer video, 23:08). Let us say they have very different values here. If I go to Voigt frequency range, I will get this data. If I take data in only one small frequency range, I will get data here which will be mostly arising from one of this and I may not need two pairs of this to model this. Data acquisition must be in a Voigt frequency range. Anything that has a time constant falling beyond this frequency range, it may not show signature here. But you cannot tell it occurs before it occurs later; therefore, I needed different circuit. I need different values for the elements, that is true. But I do not need a different circuit.

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Now I am going to claim that the same circuit if I give different initial value, it will work well. You can see if it does not model well,  $\chi^2$  is  $5e-5$ .  
(Refer Slide Time: 24:00)

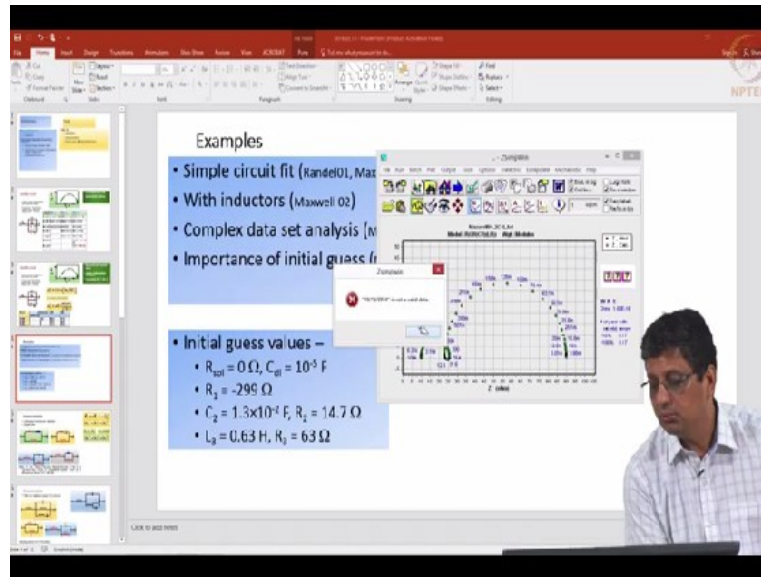


Now I do not want to change the circuit but I do want to give initial values myself instead of letting that guess it. Solution resistance, I will give it zero. That is not a big problem. This is  $1e-5$ . This resistor, I am going to give negative value. Now looking at the data, you cannot guess that you need to give negative value. It did not end up in the other side. How I came to know that this is the value that will work. Right now, let us try this value. And the capacitor is  $1.3e-2$ , that is actually 13 mF, pretty high capacitance. This I am going to give 14.7. H, I am going to give 0.63. I will say use these starting values for optimization. In this particular software, this is the



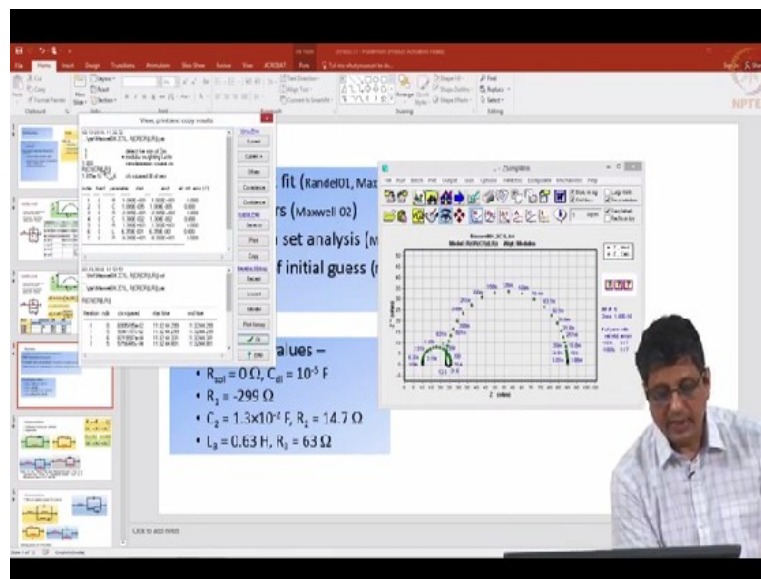
interface and this is how we have to feed. Another software, you will have a different way of feeding it but by and large I think any good software will give you the ability to either auto guess or take your inputs.

(Refer Slide Time: 24:30)



First thing to note is it looks very good. Save the results.

(Refer Slide Time: 25:40)



$\chi^2$  is  $1e-16$ , this is good. The results have 0% relative standard error.

**“Professor - student conversation starts”** Sir, negative resistance means, you have mentioned that, you had given the value negative to the resistance. What does it mean? normally the value of this either a resistance or is no resistance. Negative resistance means?

Answer: Negative resistance basically means here if you put a negative value, it shows up. **“Professor - student conversation ends.”** Physically, you do not get a negative resistance, correct. If I give positive terminal here and a negative terminal here, maybe a resistance, it may be capacitance, inductor. It may be something else. Electron will flow from negative to positive and by convention we take current to go from positive to negative. Negative resistance here if you just take it blindly, it means if you give high potential, positive potential here and negative here, current will flow from this direction but that is not what it means here. We model it negative resistance here. But it is actually called negative differential resistance. This circuit predicts the behaviour when we apply AC, because impedance is obtained using AC. This circuit if you just take it in isolation, you can tell I will give DC. And it will tell the negative resistance means I give high positive potential here. Current is going to go in this direction. But that is not correct. What it means is this. I have positive potential here, I got negative potential here. Current is still flowing in this direction. I will increase the potential here, current will decrease. Instead of having more current going, I will have less current going. And when I decrease the potential here, more current will flow. Physically, I will explain that. When you go to electrode surface and how it behaves, I will explain to you. here negative differential resistance means it is a differential resistance. It is not resistance. Earlier we saw  $E/i$  is the impedance, but what we measure is differential impedance which is  $dE/di$ . when I apply sinusoidal, now imagine this is the potential, this is the time axis. Apply sinusoidal means it is going to go like this, right. When I increase the potential, current decreases. But I am not starting at zero. I am starting with an offset. potential is not starting at zero, it is starting at, let us say, 200 mV. From here, I go to 205, come to 200, 195, come to 200. 5 mV amplitude. Then current decreases, comes to the same value, goes up, comes to the same value. Current is still flowing in the same direction. But it has a  $180^\circ$  phase offset. Therefore, it appears as a negative resistance here. It does not mean at the DC limit, current will go in the opposite direction. And when you are at zero voltage, you will not see this behaviour. At 0 voltage if I increase the potential, current may flow to a lesser extent or to a more extent but it will not flow in the opposite direction.

I need to have an offset, either in the positive or negative direction. And then you can look at this and say this has a negative differential resistance but that is usually silent. We do not write every

time we are differential impedance, we just say we measure EIS and this is the result. But it is always understood that you are measuring differential resistance.

**“Professor - student conversation starts”** Sir, what is the meaning of differential resistance in this.

Answer: Differential resistance means when I change the potential, what is the change in current.  $dE/di$ , differential impedance.  $Z$  here is  $dE/di$ . It is not  $E/i$ . These two can be very different.

**“Professor - student conversation ends.”** Early in the class, may be few classes earlier, 3 or 4 classes earlier, I showed you a graph which goes like this (refer video, 29:45). This is  $y$  versus  $x$ , goes like this. At this location, slope is going to be negative. But  $E/i$  still positive. what we measure is actually a negative value here because it is  $dE/di$ . And when I try to fit a circuit to this, I will end up with the circuit with negative resistance and the circuit if I take it in isolation to DC, it will tell this is the value. But the circuit analogy is not appropriate under all conditions. That is appropriate under the assumption that you are applying sinusoidal potential, you are looking at the current.

you cannot take that analogy and tell I can predict the value of the current at that potential. You can predict the value of  $di$  at the  $dE$  when you are at that potential. That means I am finding  $dy/dx$  at this  $x$ . I am not finding  $y$  at this  $x$ . the spectrum is  $dy/dx$  at a particular  $x$  for various frequencies. If I move fast, what is the response? If I move slowly, what is the response? That is what given in the spectrum.

We do not get the value of current at that potential by looking at the spectrum. And the circuit is fitted to the spectrum. So we should not estimate the current value from the circuit at the DC. You can say omega tending to zero, that is still means you are slowly changing the potential and watching the current change. We are not fixing the potential and watching the current and getting  $E/I$  and comparing with this.

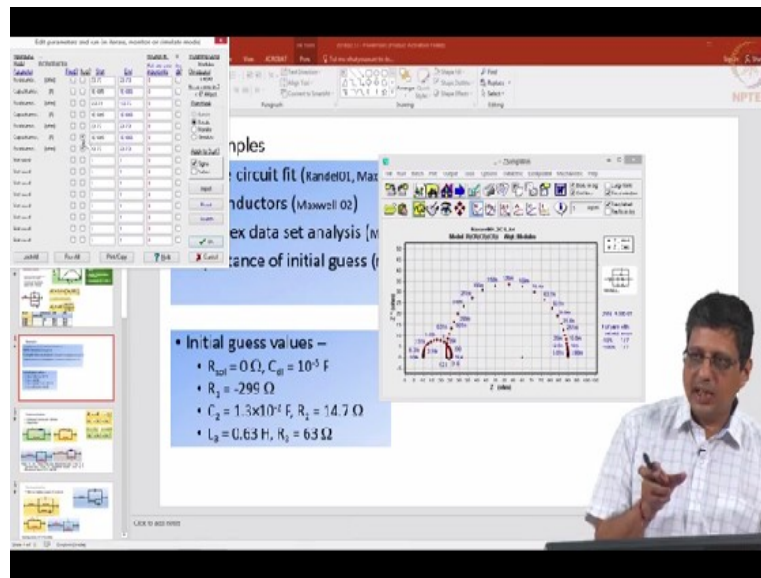
**“Professor - student conversation starts”** DC means infinite frequency or zero frequency?

Answer: DC means 0 frequency, not changing, right. **“Professor - student conversation ends.”** Changing slowly is low frequency. if I have a sinusoidal wave, 1 Hz, 1 second it goes like this. 10 Hz, it goes fast. if I say 0.1 Hz, it takes 10 seconds to complete a loop. DC means it is zero,

as it tends towards that, you can still use the circuit. Exactly at zero, you cannot use this circuit to predict the current value. You can still predict the slope from the circuit.

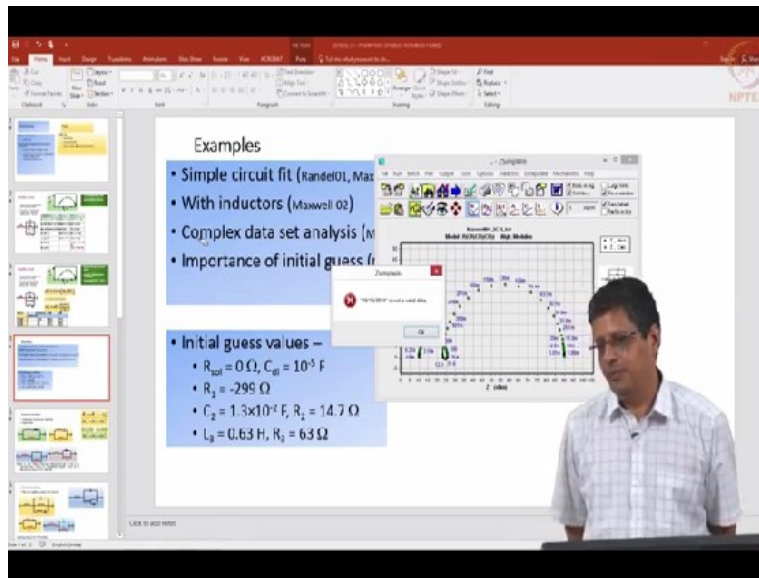
Now I did not know the value is going to be 299, 0.63, etc, etc. by looking at it directly. What I did was the following.

**(Refer Slide Time: 32:16)**



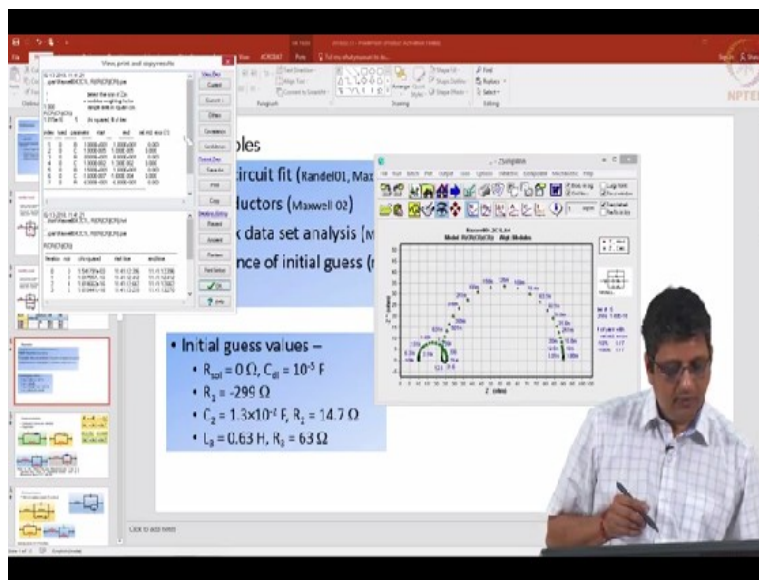
Instead of fitting to the circuit, I used the CRCR. We know that we have 1 inductive loop. We cannot model everything with capacitance. However, a Maxwell pair with negative RC can model an equivalent with positive LR. That is something that you will learn. I leave the original resistance, double layer capacitance, 1 more resistor, then parallel CR as positive, 1 more parallel CR, I keep it as negative.

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It models very well. Which means this particular model R CR CR CR CR arranged in the proper way is able to model this well.

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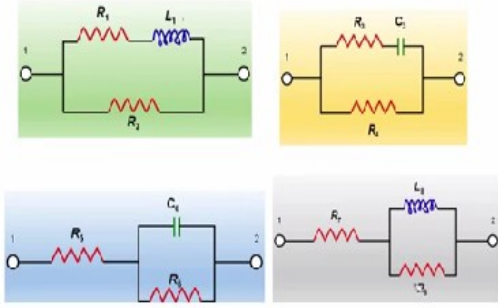


And I get very low  $\chi^2$  value (refer video, 33:22). Now I want you to translate this CR into LR. I know the values here, right. I know the values. These values are -1.6e-4 for the capacitor. -63 for the resistor. We still do not worry about what does it mean; we will say this can model it well. But I am not interested in modelling it with CR. I want to model it with LR. If I can model with this, I can model with the other one and you can translate from one to another.

(Refer Slide Time: 34:00)

**Distinguishability**

- Following 4 circuits are identical
- Degenerate



$$R_3 = -R_1 \quad C_3 = -\frac{L_1}{R_1^2}$$

$$(R_4)^{-1} = (R_1)^{-1} + (R_2)^{-1}$$

$$R_1 = -R_3 \quad L_1 = -C_3 R_3^2$$

$$(R_2)^{-1} = (R_3)^{-1} + (R_4)^{-1}$$

Fletcher, S. (1994). Tables of Degenerate Electrical Networks for Use in the Equivalent-Circuit Analysis of Electrochemical Systems. *Journal of the Electrochemical Society* 141(7), 1823-1826.

And I want to show you an example. There are 4 circuits here (refer video, 34:00). These can generate identical spectrum, not approximately equal, roughly equal. These are called degenerator. That is another way of saying that these are equal. And there are many more such combinations available. For 3 elements, these 4 circuits are sufficient for us to work with. You can have 6 set of even more complex systems. I had given  $R_1 L_1 R_2 R_7 L_8 R_8$  and capacitor and so on. Previously we have seen some examples where we model this with Voigt element, Maxwell element, Ladder circuit, and we showed that, you can model with all of these, it will work well.

if you give values saying 100  $\Omega$ , 20 H, 20 H, 200  $\Omega$ , you can translate and get the equal values in this. Only thing is when you go from inductor to inductor, if these are all positive, this will be positive. When you go from inductor to capacitor or capacitor-based circuit, inductor-based circuit, you will get negative values. What it did was to use this set. If you go in to go from top left to the top right, you can calculate the value of  $R_3$ ,  $C_3$  and  $R_4$  using this formula (refer video, 35:22). You give any omega and you predict the impedance, calculate the impedance on the top left, I can give you the value of  $R_3$ ,  $C_3$  and  $R_4$ . For any omega, it will give you the same impedance and you do not need to tell me the omega upfront. You just need to tell me  $R_1$ ,  $L_1$  and  $R_2$ , I will give you  $R_3$ ,  $C_3$ ,  $R_4$  or  $R_5$ ,  $C_6$ ,  $R_6$ ,  $R_7$ ,  $L_8$ ,  $R_8$ . Then you can decide which omega I want. Basically, if I write the equation in omega, they will be identical.

I can do the reverse also. If I know  $R_3$ ,  $C_3$  and  $R_4$ , I can get the value of  $R_1$ ,  $L_1$  and  $R_2$ . Likewise,



equivalent formulas are available for all the circuits.

(Refer Slide Time: 36:11)

The screenshot shows a software window titled 'EquivalentCircuitUtility'. It displays four different circuit topologies for conversion. Below the circuits, a blue box lists the following parameters:

- $R_1 = -295 \Omega$
- $C_2 = 1.3 \times 10^{-4} F, R_2 = 14.7 \Omega$
- $L_3 = 0.63 H, R_3 = 63 \Omega$

To the right, a 'Calculate' window shows a table of results for the 'EquivalentCircuitUtility'.

I have written a small utility (refer video, 36:10). This says, I want to convert the CR to LR but I cannot convert the CR to LR. I have  $C_3R_3$ . But what I can do is to convert a part of the circuit. I cannot convert  $C_3R_3$  to  $L_1R_1$ . I can convert  $C_3R_3$  in parallel with  $R_4$  to  $L_1R_1$  in parallel with  $R_2$ .

(Refer Slide Time: 36:39)

The slide is titled 'Distinguishability' and lists two points: 'Following 4 circuits are identical' and 'Degenerate'. It shows two circuit diagrams. The top diagram is a series combination of a resistor  $R_1$ , an inductor  $L_1$ , and a resistor  $R_2$ . The bottom diagram is a parallel combination of a resistor  $R_2$  and a series combination of a capacitor  $C_1$  and a resistor  $R_1$ .

Below the diagrams, it cites: 'Fletcher, S. (1964). Tables of Degenerate Equivalent-Circuit Analysis of Electrochemical Systems. *Journal of the Electrochemical Society*, 111(7), 1823-1826.'

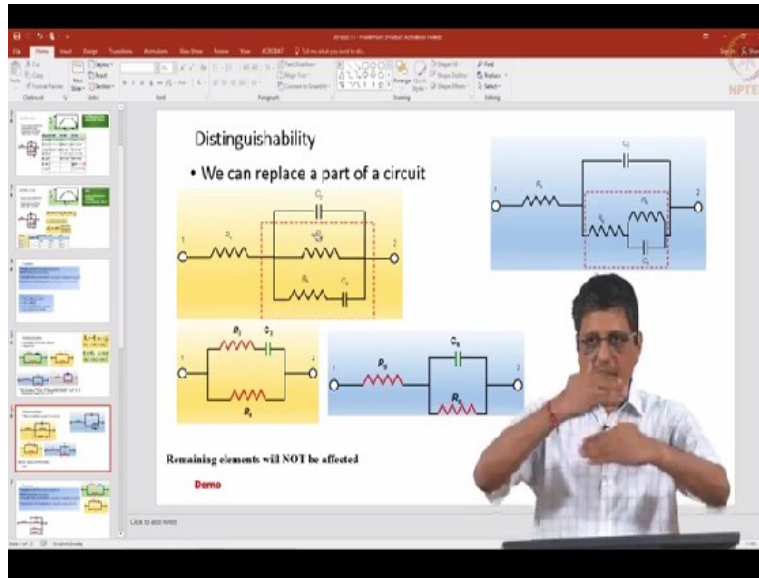
On the right side of the slide, several mathematical formulas are displayed:

- $R_1 = -R_2$
- $C_1 = L_1 / R_1^2$
- $R_2^{-1} + (R_1)^{-1}$
- $L_1 = -C_1 R_2^2$
- $R_1^{-1} + (R_2)^{-1}$

In this case, I will have to take the circuit. I have to take the bottom 2 which is CR which are on the negative region. And I have to take this resistance which is just below the capacitor. what I have is the following.

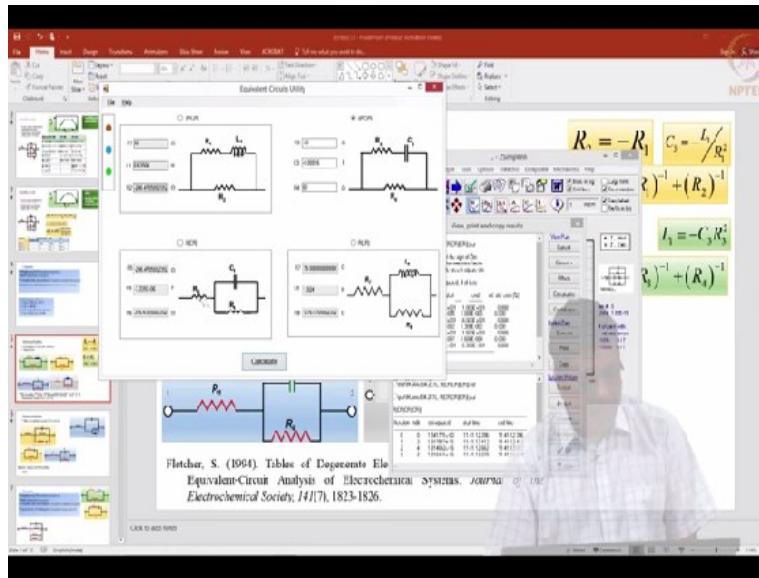
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Imagine you have a capacitor, below that a resistor, below that you have an RC, below that you have an RC. I can swap them. It does not matter. That last RC and bring it up. Now look at this. I can look at the resistance and the RC here and take that as 1 box and replace that box with either a Ladder circuit or an inductor. Inductor in this form which is RCR, so I can take this resistance in parallel with resistor and capacitor. Resistance in parallel to resistor and capacitor and replace it any of these 3. what I will do is to replace with  $R_1 L_1 R_2$ . So, if you go there, software tells me this resistance is 80  $\Omega$ . The one which is single resistance is 80  $\Omega$ . This capacitor is  $1.6 \times 10^{-4}$  and the resistor is -63. I will go here. Here I know the value. I can calculate the equivalent one for all other. I will select this is what I know. These are the things I want to calculate. Here this resistance  $R_4$  is 80  $\Omega$ . This resistor and capacitor, I will look carefully, this resistor is -63 and this capacitor is  $-1.6 \times 10^{-4}$ .

**(Refer Slide Time: 38:31)**



If I give -63, 1.6e-4 and 80, ask it to calculate (refer video, 39:20), it calculates and gives me 63 for R1, 0.63 for L1 and -296. For this I have used -299, probably because I used slightly different values here. now I know if I give -63, -0.00016 and 80, it fits. That means I can give an LR circuit with these values. I can replace it with a circuit like this with correspondingly negative value for resistance, capacitance, etc. if you can fit it with one model, you can fit with an equivalent model. What does it mean physically that I have not explained it yet? But previously when we fitted with LR, it did not fit well. We cannot say we should add one more CR or LR. We should see if it can fit better with an equivalent circuit.

What happens is in this case, the initial guesses made by the software for the LR circuit is not that good. It went to a local minimum. And there is no way you would know that you need a negative value on the resistance. Because data seems to be in the positive side. But when you fit with capacitor and resistor with negative values, every other element has positive value, it fits well. And the initial guesses made by the software are good enough for that. Worst case sometimes you will have to go and try on your own with various values. Then you will see what value will work. And at some limit, you will say no it does not, this circuit is not good. We have to go to next circuit. But here, because the capacitor-resistor based circuit fitted well, you can calculate the equivalent values for the inductor and resistor based circuit and you can tell I need a negative value and then it will fit.

We will continue with this example. Main point is you cannot just fit it to the one circuit and if does not fit well, you cannot assume that this is the best possible. You may have to do extra work in some cases.

**(Refer Slide Time: 41:16)**

Previous class	Today
<ul style="list-style-type: none"><li>• EEC fit</li><li>• Initial values</li><li>• Distinguishability</li></ul>	<ul style="list-style-type: none"><li>• EEC fit<ul style="list-style-type: none"><li>• Distinguishability</li><li>• Element value <math>\rightarrow</math> Physical phenomena</li></ul></li><li>• RMA<ul style="list-style-type: none"><li>• Simple Reaction</li><li>• Two step reaction</li></ul></li></ul>

In the earlier class, we had seen some examples of fitting circuits, fitting the elemental values, resistance capacitance from the data. We also saw that the initial values are important. And I think we also saw that some circuits, we cannot distinguish between them. They are identical.

I want to spend little more time on that and also more information on whether you can get physical interpretation from the circuit element values. It is not always possible. In some cases, it is possible. we saw that if you have 4 circuits that are given here, they are identical. They are degenerate, meaning as long as they allow positive and negative values, you can exchange the inductance and capacitance.

Even if you say I will keep only positive values, you can keep capacitance but arrange them in different way. And this is relatively simpler circuit, meaning it has 3 elements but you can have similar degenerate circuits with more elements. And the exact equivalence relationship between this resistance values.

**(Refer Slide Time: 42:19)**

### Distinguishability

- We can replace a part of a circuit

Demo

Now if I look at this (refer video, 42:22). You do not have to take only that circuit and replace. You can take that component out of a larger circuit and replace that. For example, I can take this circuit that is given here in this square box and replace that with a circuit which is rearranged in this manner. that means I can take that circuit here and replace it with circuit here. I do not have to change the value of  $R_1C_2$  but I do have to change the value of  $R_2R_3C_3$  here with the corresponding values here.

**(Refer Slide Time: 42:58)**

### Examples

- Simple circuit fit (Randel01, Maxwell 01)
- With inductors (Maxwell 02)
- Complex data set analysis (Maxwell 03, Ex NegRes.Ind. Loop.00)
- Importance of initial guess (Maxwell 04, using LR and CR)

Likewise, if I have a much larger circuit (refer video, 43:01). Look at this Maxwell circuit with resistance, 1 Maxwell pair, second Maxwell pair here. I can replace 1 2 3 with new resistance, resistance, and inductance, that means this will be a new number. This is going to be a different

number. This will be an inductor in fact. Next, I can take the new value here and that is in parallel with this. Essentially, I am shifting the resistance and inductance down and move this up.

That means I am going to get a circuit which looks like this. This is a new value here. Originally it was resistance and capacitance. Now I have modified into resistance and inductance. But I am going to push this value,  $R_3C_3$  as they are up and then this is going to be the resistance and inductance which we calculated now. These 3 are new calculated values. Now I can take these 3 values and replace 1 2 3, with a resistance, resistance and inductance.

That means it is going to be new resistance again and a resistance and an inductance. That means I can take a Maxwell circuit with 2 Maxwell elements of resistance capacitance and systematically replace them with resistance inductance. you do not need a separate formula for this type of circuit. You just have to do it in sequence.