Electrochemical Impedance Spectroscopy
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Lecture – 16
Introduction to EEC, Choice of Circuits, Confidence Intervals, AIC

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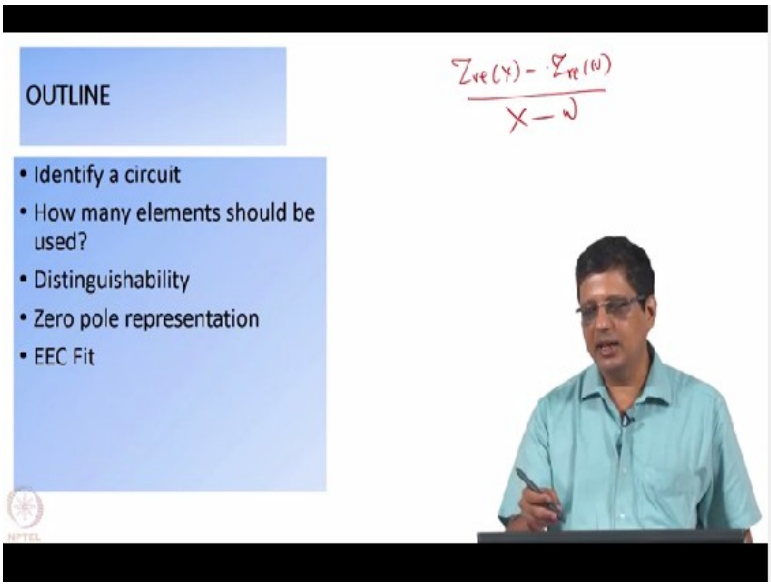

So we end up usually using either Professor Macdonald's software or Linear KKT. We have also developed our own software, but without any extrapolation and it does the trapezoidal integral. What you should probably do [to understand this idea well], is to write a program to calculate the real part and imaginary part from a given data set, for at least 1 point. That is [you have the equations for the integration], doing numerical integration, okay.

So, you will be able to understand what goes in there. And, (also understand) what are the challenges. (If you just take a) look at the formula, it appears easy; "Okay, I need to use the formula and get the result"; whereas (if you) actually use the formula, you (will) know whether there are any difficulties in using it, okay?. Then, you would know when somebody gives you a software, they have done some calculations, (and have handled) certain challenges [for example you may see a place where you get 0/0], okay?

So the equation looks like $\frac{Z_{\mathrm{Re}}(x) - Z_{\mathrm{Re}}(\omega)}{x - \omega}$. So, when x=ω, it will look like 0/0, right? But it is not (an essential) singularity, this singularity can be removed. And, it is not that difficult to work with, but I would like you to try evaluating the integral, [KKT integral], then you will really know "This is how it is done", " This is what we are getting out of it".

So next, I want to go through analysis. So what you have seen so far is "I want to validate the data. I do not worry whether I have to use 10 Voigt elements or 1 Voigt element, I just want to know whether the data is valid or not". Now I want to show you analysis where you can use circuits and say "This circuit can produce this spectrum. I can use the circuit to get some physical meaning out of this system", okay. Ultimately circuit is still an analogy, okay.

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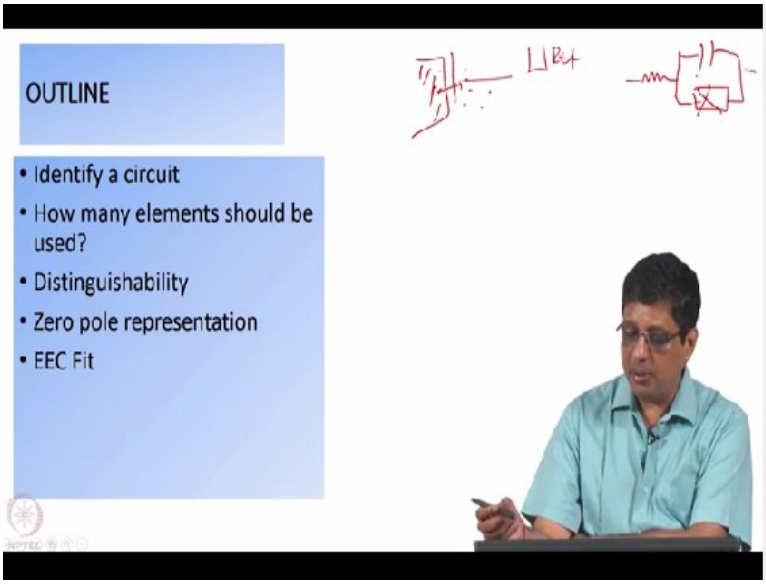

But earlier I have shown that you have an electrode, you have an electrolyte, you have a reference electrode here and you can represent the electrolyte using a simple resistor. This forms a double layer. I can represent that by a capacitor. If there are reactions here, I can represent that by some sort of impedance. It may be a simple resistor; it may be more complicated than that. And if there is absolutely no reaction happening, it is broken.

So this circuit can be used to evaluate. So, let us say, I have one situation where I get a spectrum that can be modelled by a circuit like this.

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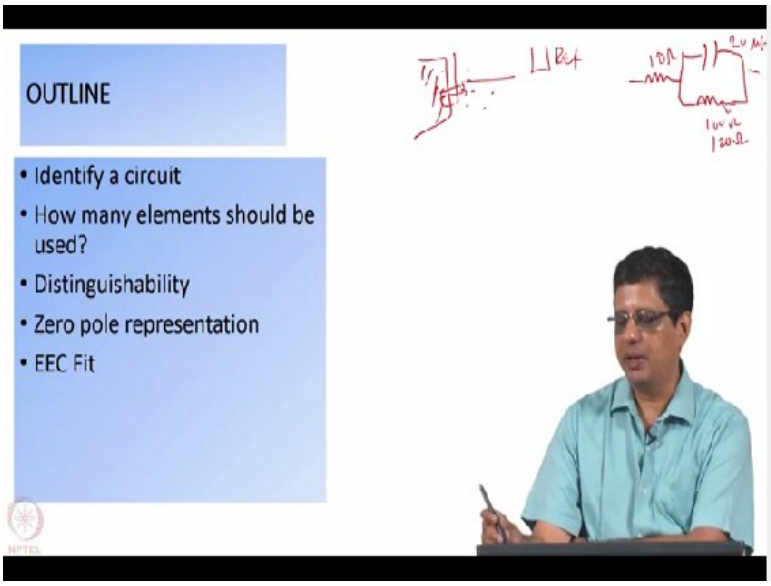

And I can fit it and get values for this. This may be 10 Ω, this may be 100 Ω, this may be 20 μF. (Under) more or less same (condition), I change the solution, or I add something to the solution; everything remains the same, except this 100 Ω becomes 120 Ω. So, now I can say "okay, because I added this chemical, this reaction has effectively slowed down". "Slowed down", "something has happened", the change in the elemental value, [I can think and say)]"okay, maybe this is consuming some of the reactant".

I have to come up with some interpretation based on what is happening in the system; what, [I think,] is happening in the system. And in order to do that, first we need to know which circuit is the correct circuit to use. We need to identify the, okay, "which is the correct circuit to use" and "how many elements should be used". Should we use 2 Voigt elements, 3 Voigt elements here. Do we need to use Voigt circuit?

Do we need to use Ladder circuit? Do we need to use something else?; That is one. Here I cannot keep adding 'n' number of elements, right? Then, sometimes it will fit well in one representation, (and) it may not fit well in another representation. And theoretically, if you know that these 2 are actually equivalent, you know that it (the problem of not fitting in one representation) is more of the software issue; (perhaps the) initial values in the software is the problem, NOT "the model is not fitting well in one case and it is fitting well in the other case". That means,… (let us say that)

I have 2 equations.

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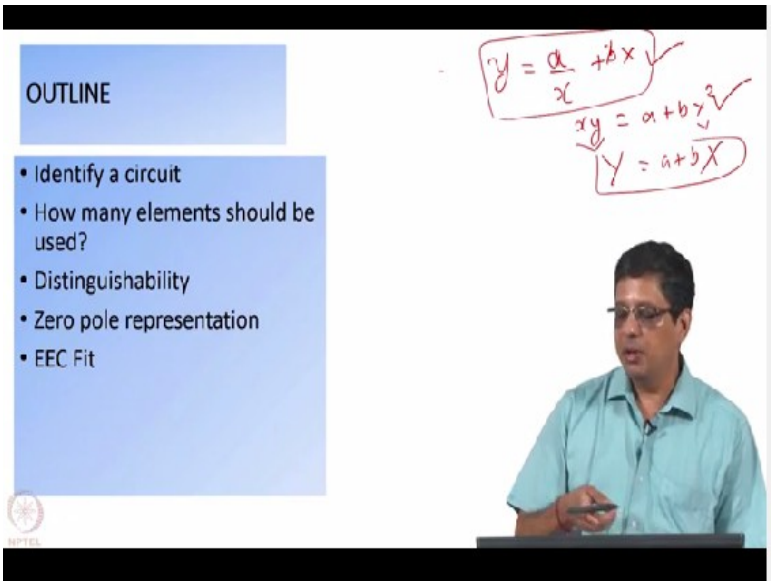

Imagine I have an equation which goes like ($y = \frac{a}{x} + bx$); this is one form. (Consider, $xy = a + bx^2$) It is another form (of the same equation). So if you give x and y data, I can create a new data called xy, I can create a new data called $x^2$and I can write it as y=a+bX (where $X = x^2$). I can fit it. If I use the first form, the software may not fit it well (and we may wrongly conclude that) "This is a poor representation". (But) that is not correct. It is just that, may be, the initial values are not correct and it is going to a local minimum and saying "it is not converging".

I cannot say "I can get the data to fit this (first) form well but it does not fit this (second form)". Because, we know that these 2 are equivalent. Likewise, in the circuit, you should know which one are equivalent. Can we, in theory, say that these 2 are the same? "Same" meaning the element values are of course different, but I cannot say that "it fits one of this correctly and does not fit the other one correctly", okay.

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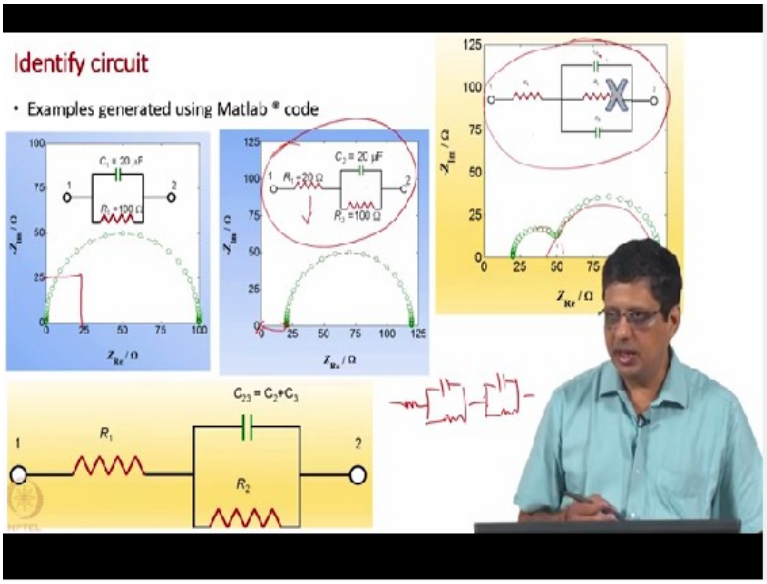

So I want to show you some examples. This data are of course generated using Matlab. You can use any language and get this. If it shows a semicircle, and you want to say "it is a semicircle" when these are equi-scaled, 25 Ω, 24 Ω in x and y direction. They have the same length. And it starts at 0 at the high frequency, you can represent this by 1 Voigt element. This case, I have generated it using this value, so I know I can fit it using these values.

If the value is offset, (high frequency value is offset), you will have to add a resistor to that; And this is usually what you will see, at least in the high frequency. This is going to start like this and come here, okay. For electrochemical system, this is what you would see. A semicircle with an offset. If I see 2 loops, this is 1 capacitive loop, this is another capacitive loop. I cannot add another capacitor in parallel because these 2 can be added together.

These 2 are basically elements in parallel, and can be represented by 1 capacitor. So this circuit is the same as this circuit. I need to add a pair here. A pair here means "a resistor and capacitor" to model this. So I originally have this circuit here to represent 1 semicircle, I can add 1 more like this; that is a possibility.

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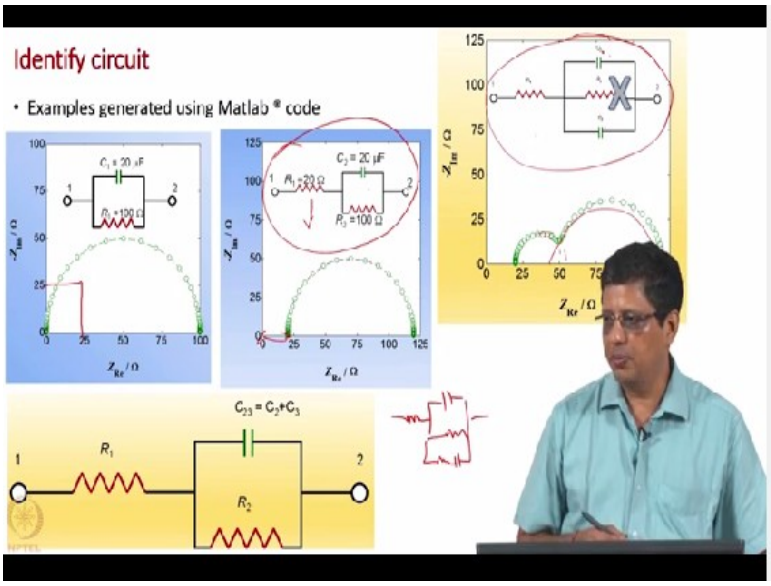

I can add 1 more as this; that is also a possibility. Of course, I can add in the Ladder format, I am not showing you here but all of this will give you data in this format.

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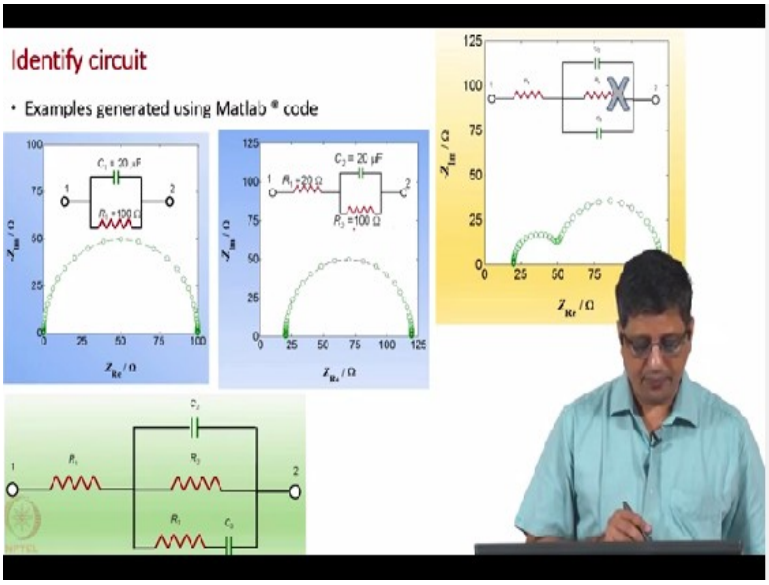

So all of this will be able to model this equally well. So I can choose a Maxwell representation and say "This works well. This will be able to fit the data".

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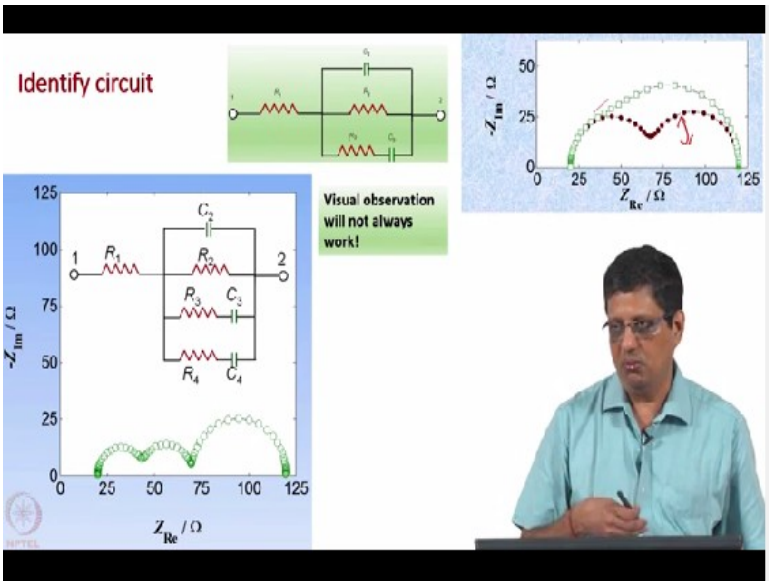

If I see 3 loops, I would say I can use C_2, R_2 and then 2 more RC pairs. Now, here I have shown you data where you have well separated loops and clean data. Visual observation will not always work, right. I have taken a circuit like this where I have C, R and then 1 Maxwell pair. Depending on the value of R_3, C_3 and R_2 and other parameters, I can get a loop like this which is shown in the brown colour.

I can get a loop like this which is shown in the green square. And out here if you look very carefully, it is not 1 loop, it is actually 2 loops. But visually when you look at it, you can say it looks like a distorted semicircle. So, you cannot arrive at the conclusion by visually looking at it. You can look at, this data and say "I cannot model it as 1 semicircle", that is clear. I need minimum of 2 semicircles to model this. But I may need more (than 2 time constants to model this). I will have to really look into that, okay.

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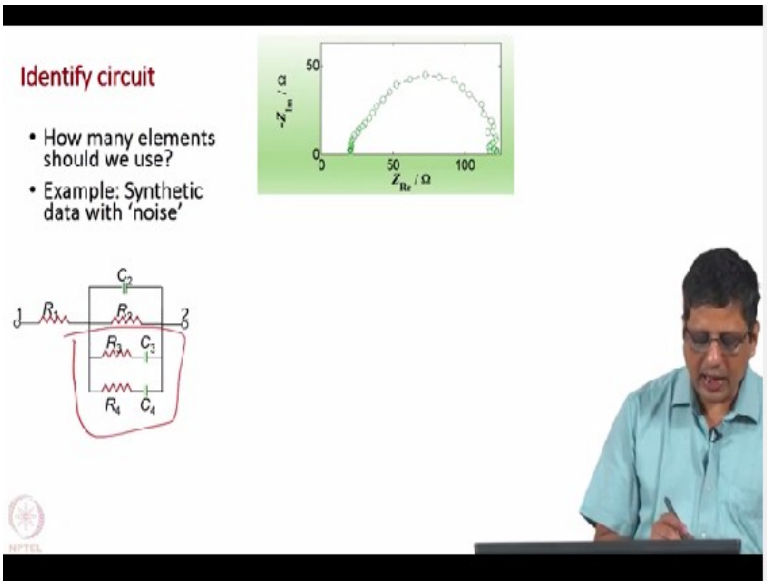

So "how many elements should we use", if you are given a data? So, what I have done is to synthesize data with some noise. This is a data synthesized with random noise added. So, you can see it is little ugly. I can take the circuit. Initially, I will model it only with R_1, C_2 and R_2. So 1 semicircle.

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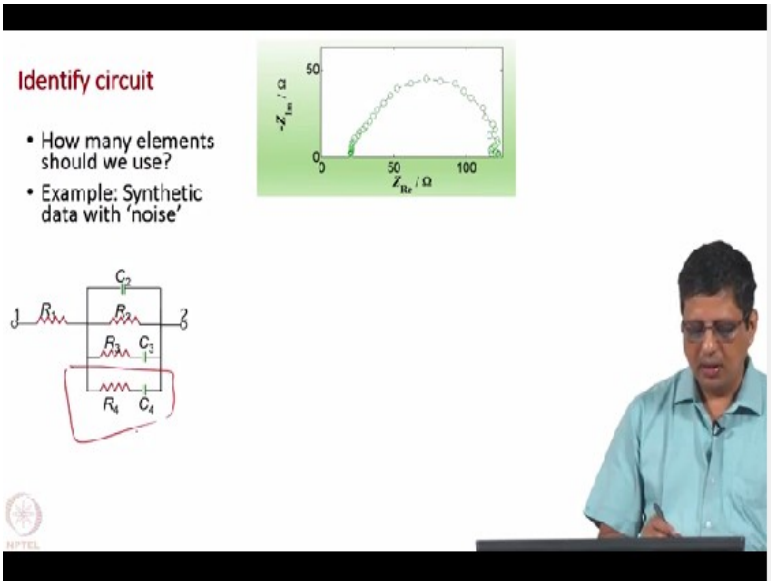

Next, I will add 1 more element and remove this. I will say I will add R_3 and C_3.

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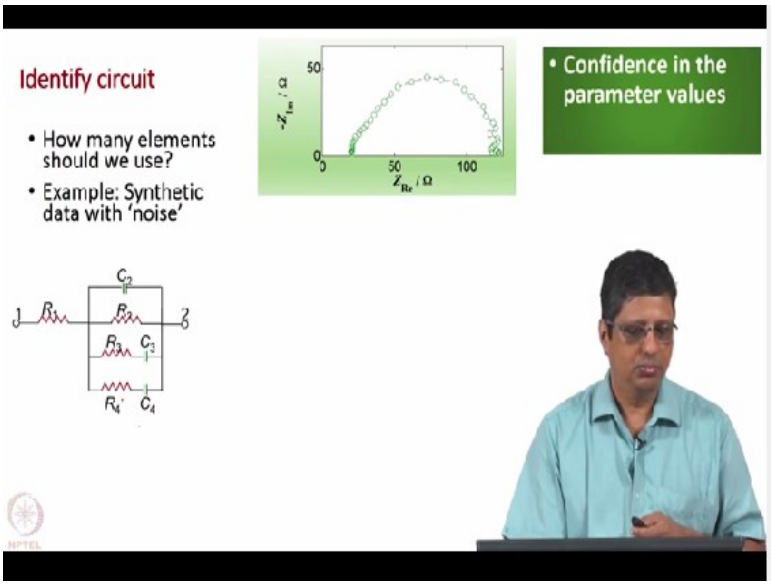

Next, I will say I will add R_4 and C_4 also. So when you use a software to get the values, a best fit values for R_1, C_2, R_2, C_3, R_3, etc.; when you go through this iteration, software give you the best fit parameter value and usually the commercial software will also give you the confidence in each of this parameters,.

I will see if I can do this now. Let me take a data. Anyone of the data. I do not know how this is, (i.e. I have not analyzed it before illustrating it here, I don't know how this data looks).

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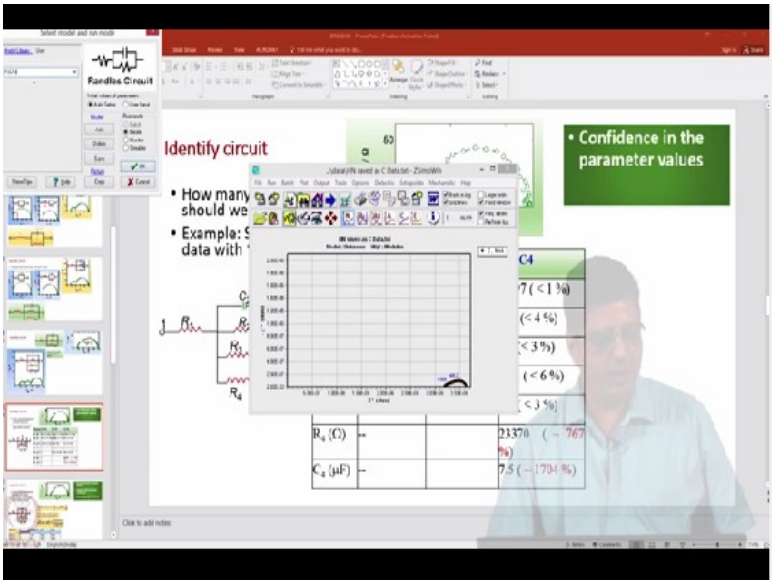

This is a Zsimpwin software. I have taken some data. I have not even gone through this before. I will fit it to a model and I will fit it to a simple model. And, each software will have its own way

of telling “how this is arranged in series” or “whether it is arranged in parallel”. So in this case, it is R(CR). If you go to another commercial software, they may have a different representation. They may have +/ in one of the software. (It) does not matter. You learn the syntax of that particular software (as required). It is fine.

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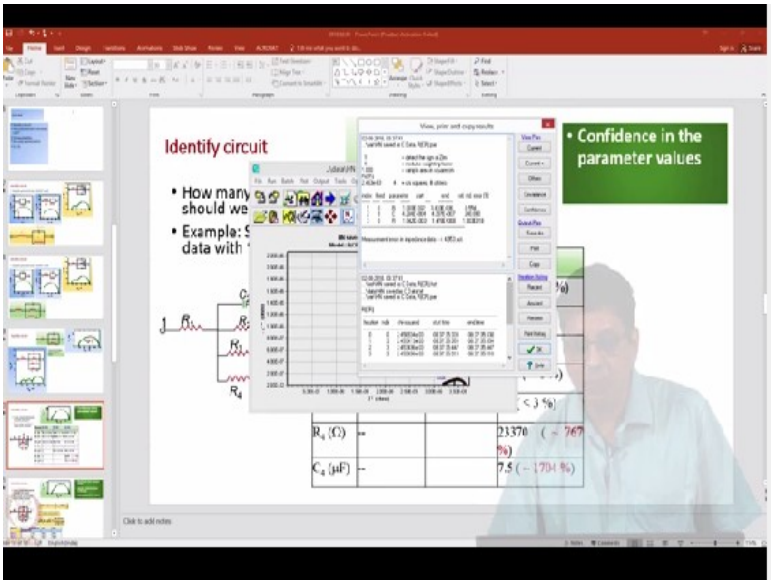

I do not expect (this model) to fit (the data) well, it will fit poorly. No problem. And in this case, I can see or view the results by clicking here. (The) thing I want you to note is this is the parameter value R, this is the final parameter, best fit parameter value C and R and relative standard error is less than 1% here. It is 240% here. It is 10^{18}, (it is) just way too high. It is a poor fit.

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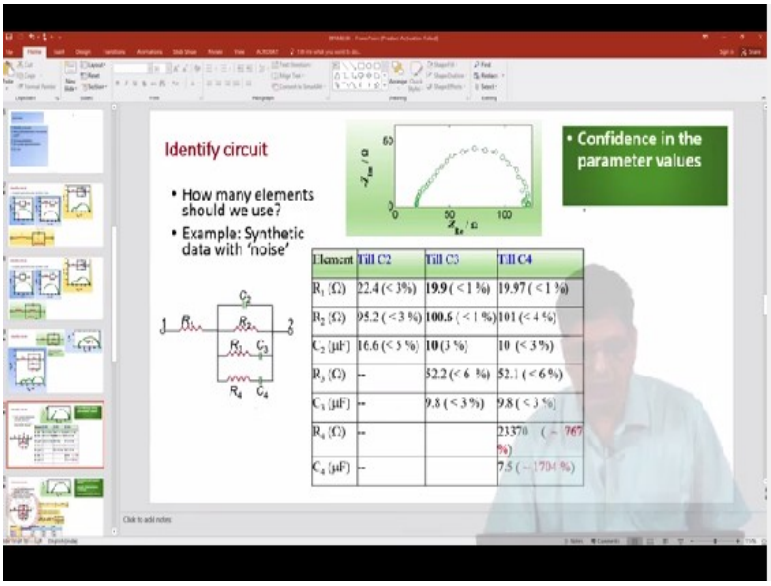

You can visually see, that is one (way to decide whether fit is good or not), but you should also be able to get the confidence interval values. And in this case, if I restrict it to R_2, C_2, , I get the values ; that I have a semicircle with only R_1 C_2, R_2 and I get 22 (Ω) , 95 (Ω), 16 (μF respectively). It will fit and you have reasonable confidence in this. It is less than 5%. Considering I have added noise, this is not too bad.

If I add 1 more, R_3, C_3, look at the confidence. It is good. 1% 1% 3 %, < 6% , < 3 % and I have actually generated using 20, 100, 10 (with appropriate units) and then if I remember it is 50 and 10. I have generated using a circuit which has R_1 C_2 R_2 R_3 and C_3. But I have added some noise.

Let us see what happens when I try fitting it with another Maxwell pair. Looks good, I get some values here and they have poor confidence. And look at the value, it is 23 kΩ which means this is going to be very high resistance. It is not really contributing to the current at all compared to the current passing through these values. So I should say probably I should stop at R_3, C_3. Here I should not just keep adding elements. This is one way of looking at it. There is another way. You have to look at the confidence interval.

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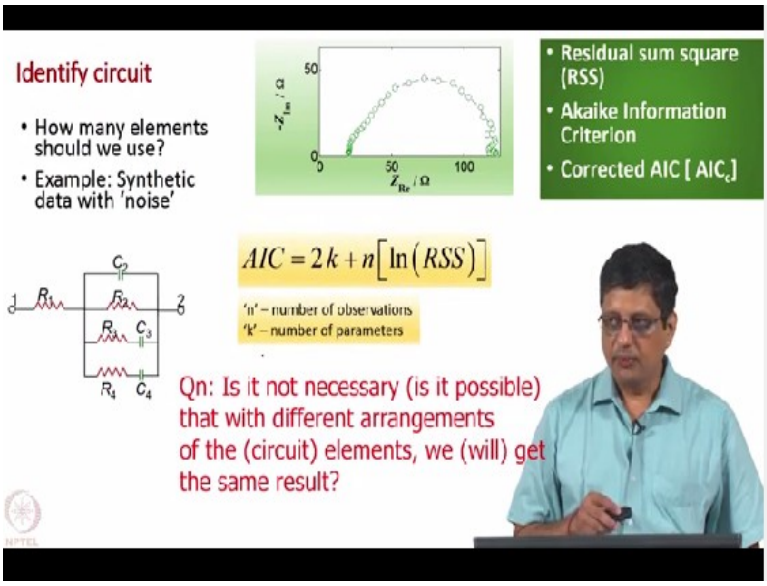

In addition,…. In addition, you have to look at the residual sum square; meaning, when you fit the model, you get the difference between the model and experiment in the real part and the imaginary part, square them; that is the residual, you square them and add them together, okay. **"Professor - student conversation starts"** Sir, is it not necessary that with different arrangements of the elements, we get the same result? **"Professor - student conversation ends."**

You will get the same result. But not by adding 1 Maxwell pair. That is R_1 C_2 R_2 will give you, let us say, a set of impedance. By adding R_3, C_3, I cannot get the same value.

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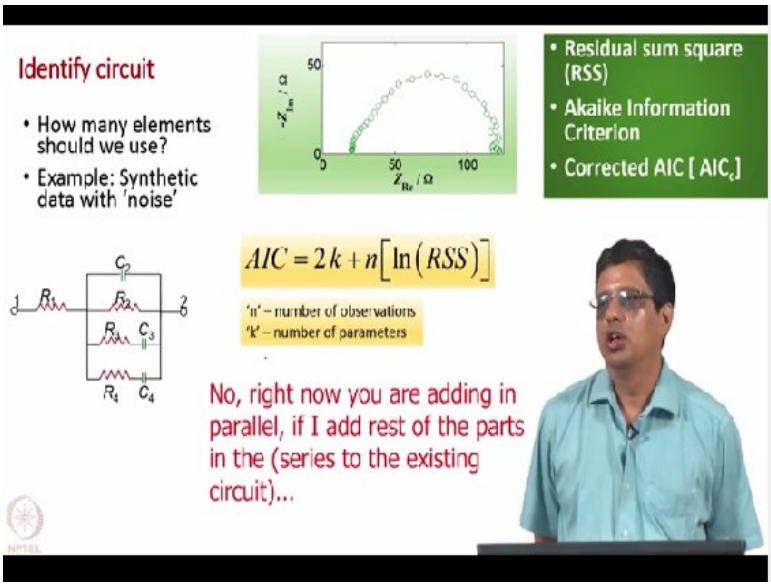

"Professor - student conversation starts" No, I am saying that right now you are adding in

parallel. Yes. If I add the rest of the parts in the. If you use a Voigt series. Yes. **"Professor - student conversation ends."** Or if you use a Ladder series. Ladder is not a representation. If you add in a different location in the circuit, that is what you are asking, right. Instead of this, can I add like this.

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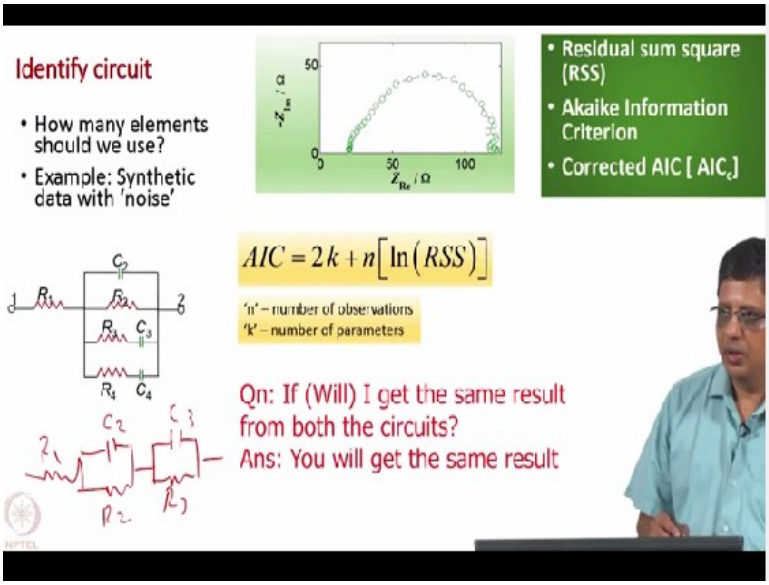

And call this as R_1 C_2 R_2 C_3 R_3. **"Professor - student conversation starts"** Yes, or it might get the result same from both the circuits. You will get the result same. **"Professor - student conversation ends."**

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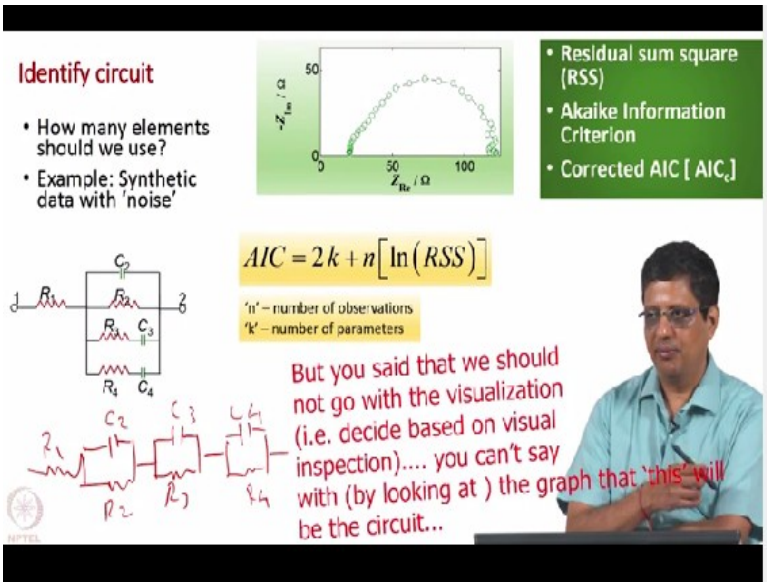

This circuit, if it fits well to this circuit, I can show you an identical fit, not approximately equal

or roughly equal, identical fit with this. Of course, the values of C_2 C_3 will be different. But these are equivalent. I will show you the example a little later. But physically "which circuit do you think represents your system better", meaning "physically can you interpret the results better?" **"Professor - student conversation starts"** But you said that we should not go with the visualization.

You cannot say with the graph that this will be the circuit. **"Professor - student conversation ends."** With the graph, you cannot tell how many pairs you need.

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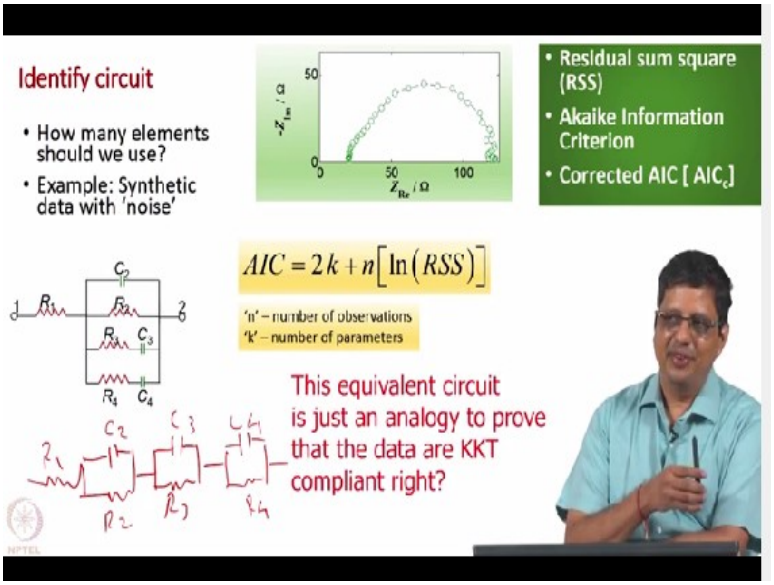

"Professor - student conversation starts" Sir, but this equivalent circuit is just an analogy to prove that the data is a KKT compliant. No, that part is over. So; **"Professor - student conversation ends."** Right now what we are doing is to fit it with circuit and see whether you can physically interpret the data.

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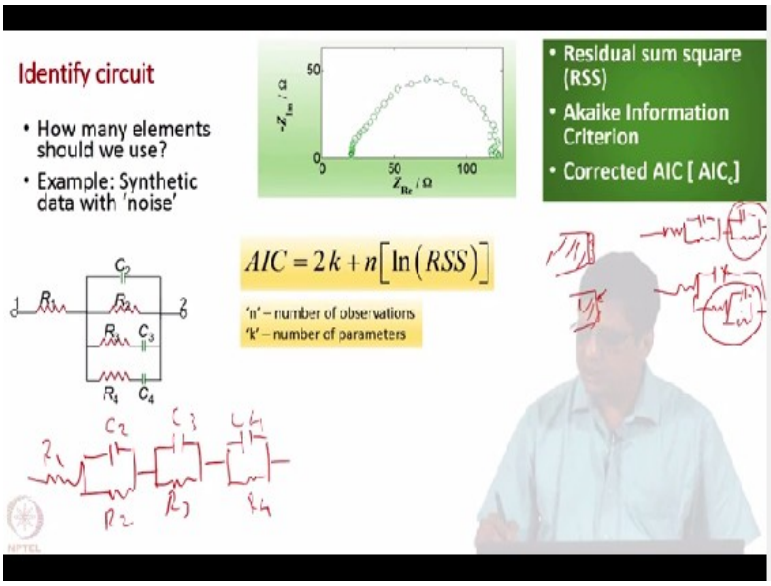

Meaning "If I have a metal here. I may have a thin film here", okay. And I might think "It is porous, reactants can go through it. It can react here". I might use a circuit saying this resistor, this and this, I can show like this and then say "Any change here is because of the change in film quality. I am doing different methods of synthesis" or whatever. That is one way of representing. I can look at another case where I get data from a reaction with no film, nothing.

Which case, it may be better to represent it by a Ladder circuit and assign, "it goes through an intermediate path"; that is "It, reactant, does not go to product directly. It goes through an intermediate stage". And what happens here is related to what happens to the intermediate. Although if it fits the circuit, it will fit this circuit also, okay. I will give you another example.

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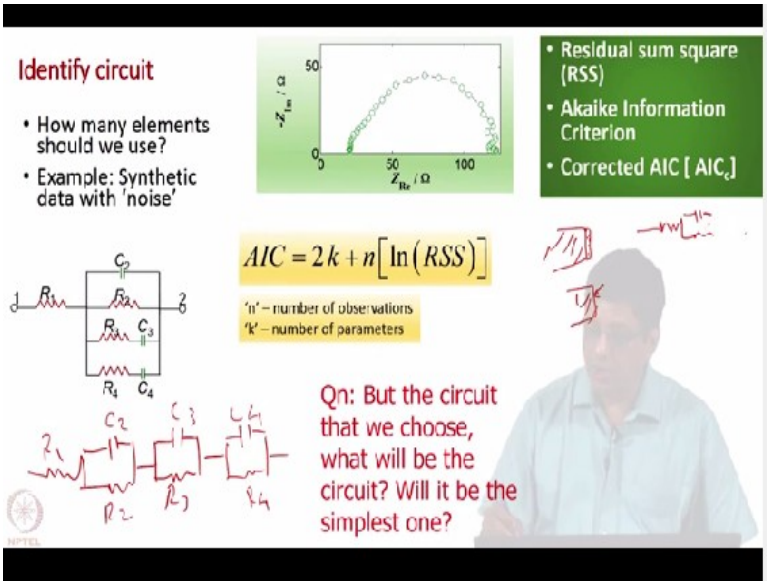

"Professor - student conversation starts" Sir, but the circuit that we choose is what will be that. It will be simplest one. **"Professor - student conversation ends."** No, first thing, you need to have some idea about your system. And then come up with the model of that. When I say visualize here, I mean "Think about the system and see which circuit is probably a good representation", okay.

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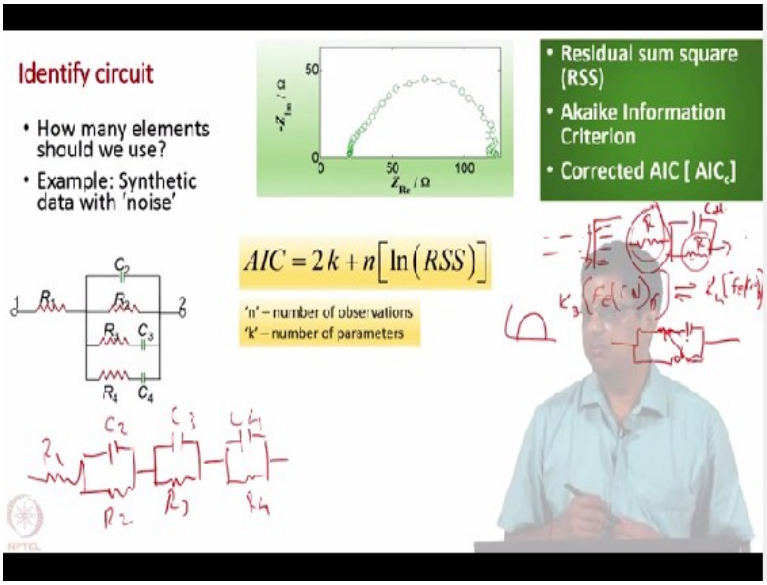

Now remember this, let us say this is electrolyte. This is an electrode. This is a double layer and we expect a very simple reaction to happen here. A standard redox reaction is the $K_3Fe[CN]_6$ to $K_4Fe[CN]_6$, okay with electron transfer. This case, I know that reaction can be represented by a simple resistor. So I can say this double layer capacitor, this is the resistor and this is the solution

resistance.

I have physical meaning assigned to this resistor. I have a physical meaning assigned to this, this represents the reaction and this represents the double layer capacitance and this would give me a semicircle here. The same semicircle can be modelled by another circuit. Whatever data you get from this, I can model by this, model with this.

But, I cannot assign solution resistance to this. I cannot assign reaction tone of this. It becomes more difficult to interpret this data. So when we choose a circuit, 2 or more circuits will fit the same data. Which circuit do we use? Depends on what is your understanding of the system. What do you think should be the correct representation of the system? You should be able to come with a logical explanation and say… Here, for example I would say "this will represent the solution resistance", "this will represent the reaction impedance"….

That is, reaction will not occur at a infinitely fast rate; it will occur at a finite rate and you can adjust that by adjusting the DC potential. So if I take this and adjust the DC potential, only this will change. Capacitance will not change. The resistance, solution resistance will not change. If we move the reference electrode away from this, only the solution resistance will change. So I can interpret it.

Here when I move the reference electrode from the working electrode, both will change. So just because the circuit can model this data, does not mean this is the appropriate circuit for that situation, physical situation. On the other hand, I can give you a board with a variable resistor here, a capacitance here and a resistor here. Now if I change the resistance, only this will change.

So you have to have some idea about the system. You cannot just take this data and say "this circuit fits it; therefore, I will interpret it…". It is like telling that I have a UV visible spectroscopy, I have done the experiment, "I got data at 400 nm or 450 nm. The absorbance is 0.3". Not good enough; you can get the same colour; at a particular wavelength, you can get the same absorbance, from different chemicals. You can get potassium dichromate; it will give you orange colour. I can give you orange dye, that will also give you orange colour, right? I cannot

tell anything about their system by just saying this "absorbance at this wavelength is so much". I need to have some idea. I may have a reacting system where the colour changes because of particular reason. I need to say "this chemical is consumed" or 'this chemical is produced'.

So, independent of all these, just by looking at the spectrum, all that you can tell is this is KKT compliant or it is not compliant without knowing what the origin of the data is. The rest interpretation you will necessarily have to have some idea about the system.

"Professor - student conversation starts" Sir. Yes, go ahead. But is it the right way to go with the software only. Meaning? Meaning in the software, we have this specified circuits. Yes. Okay, so if somehow we can find a new circuit, how we will confirm that this is the right way to go with this circuit?

You mean new element or new circuit? Both, complete circuit, I mean, we are making in the Ladder type of something. Yes. But if you find something else new, how will you. **"Professor - student conversation ends."** Most of the software will give you flexibility to add your own circuit, okay. Some software also give you flexibility to add your own element.

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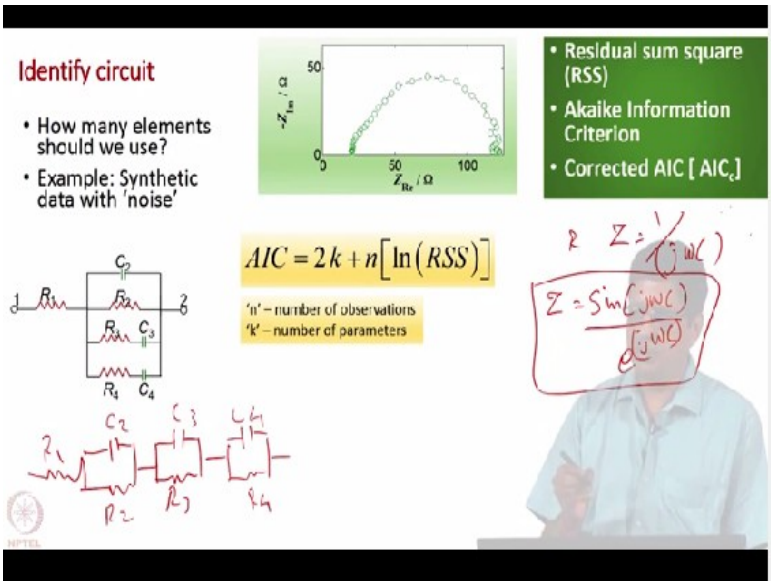

Meaning here R is a resistor. So at all frequencies, it is going to have 1 value. C is a capacitor for which the impedance is given by this. You can also say "I will come up with a new element, I have some understanding of this phenomenon; I will come up with a new element where the

impedance is given by, (I am just making up this story)… ". This is a new element. Physically, I can justify this. This is the impedance

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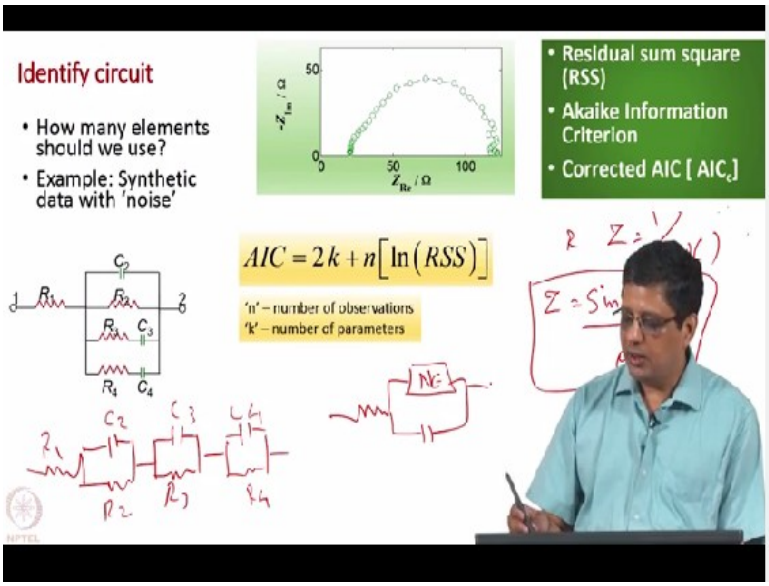

Some software at least will give you the flexibility to add this element and then say "This is the circuit, this is the new element and this is how I will interpret the data " and then ask it to fit it. If they do not give you, you have to write your own code to do the optimization, okay.

But you better have a good justification for coming up with any new element.

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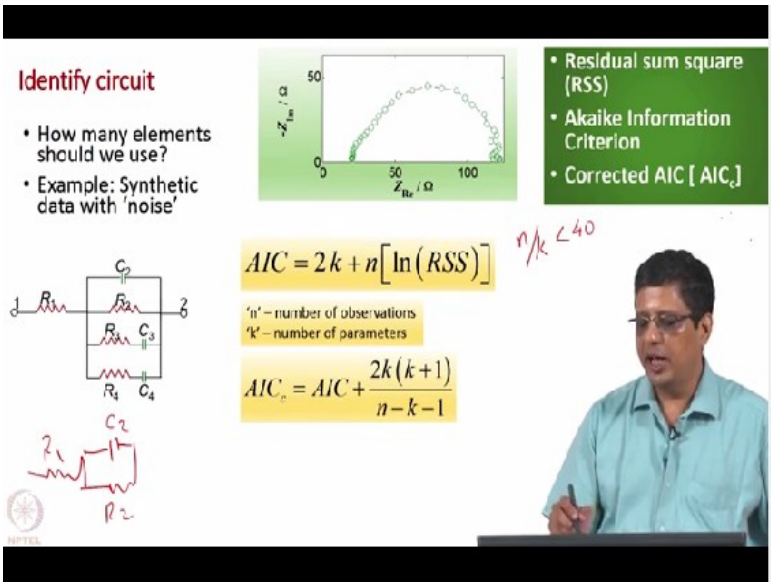

Most of these things have been analyzed well. I do not want to say "you cannot come up with a

new element"; but it is not trivial. You can add most elements, meaning, like "I can add one more pair of resistance and capacitance", that, all the software will allow you (to do that) anyway. Now whether you want to add or not; you really have to think about your system and see whether it is justifiable.

If it fits well with 4 Voigt elements, you can repeat the experiment, confirm, yes it can be fitted only with 4 Voigt elements, data does not fit with 3 Voigt elements or 2 Voigt elements. I need to come up with some interpretation to tell "why it need so many (Voigt elements)". I do not know if I am answering your question but, …okay.

Now whenever I add more pairs, usually my residuals will go down. I will fit it better, okay, but think about it. I have an equation, imagine a quadratic equation, cubic equation, a polynomial, I fit it to linear, I get a residual. I add one more, it becomes a quadratic equation. The residual decreases a lot. I add one more, residual decreases a little; probably not worth it. I cannot say "it keeps decreasing; therefore, I will keep adding more". So, there is a proper way to do this. 'n' is a number of data points and I keep adding more and more parameters, okay.

There is a criteria called Akaike information criterion and when the data points are less than 40; (Correction: Actually it is) NOT "data points are less than 40", n/k (should be less than 40). If I have a 50 data points, I have 2 parameters, (or) 3 parameters, (or) 4 parameters. When ~~it~~ (n/k) is less than 40, I need to use a slightly different formula. It is called corrected AIC, because ~~this~~ (regular AIC) has some assumptions which is suitable for large number of data points (and it is not correct to employ them for small data set). So I can calculate the residual sum square, multiply that by number of observations. This is sort of a penalty.

If I keep adding more and more 'k'…, ('n' remains constant anyway), the residual sum square will keep decreasing but at some point, the penalty for adding more parameters becomes too much. So, I cannot just say RSS keeps decreasing; therefore, I will keep adding more numbers. And this is a corrected formula which is usually what is applicable for us because impedance data set, normally you will have 40, 50, 60, 70 data points; (We usually do not have) 1000s of data points.

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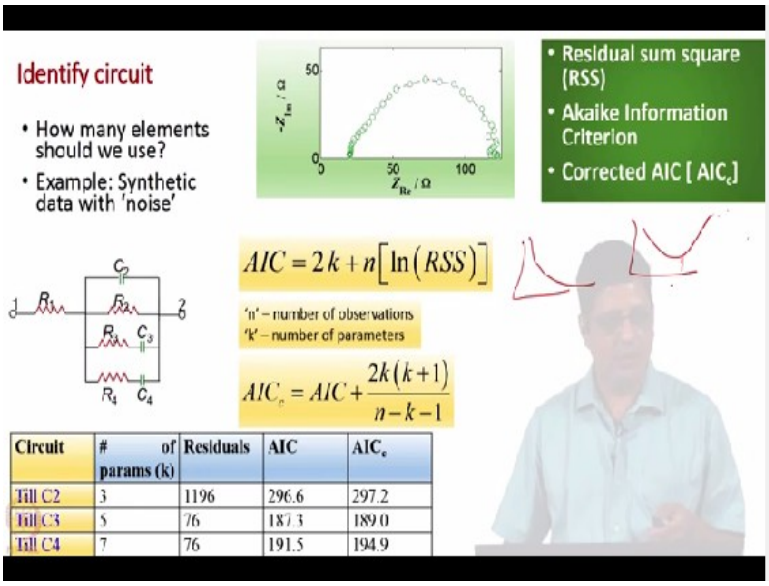

And if I use these, I want to show you here that if I use this at only until C_2, you have 3 parameters, R_1, C_2 and R_3. Residuals are large and you get some value for AIC. If I add 2 more, it becomes 5 parameters. There is a drastic decrease in residual and AIC is low. if I add 1 more pair, (you have to trust that I have done the calculation correctly, okay), the residuals are more or less the same.

But the AIC is increasing now. So if I look at the number of parameters versus residuals, it will decrease and remains flat. If I look at the AIC versus number of parameters, it will look like this and I have to choose something which is close to this. So that is looking at it in a statistical way and then saying that "Beyond this, I should not add more set of elements", okay.

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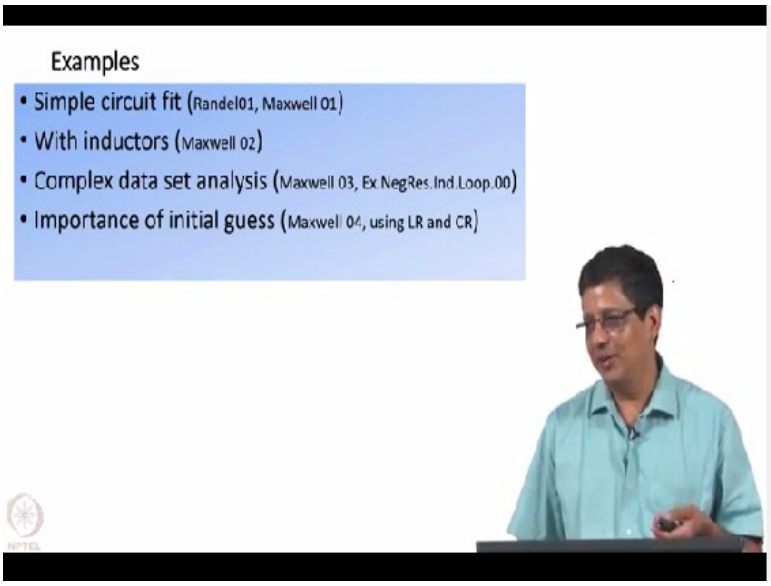

Tomorrow, we will look at examples where I will take the Zsimpwin software to model some data and show you some cases where it works well, some cases where it does not work well. And when it does not work well, what is the way to make it work well, okay. We will stop here today.