Electrochemical Impedance Spectroscopy
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Lecture - 20
Assignment 04

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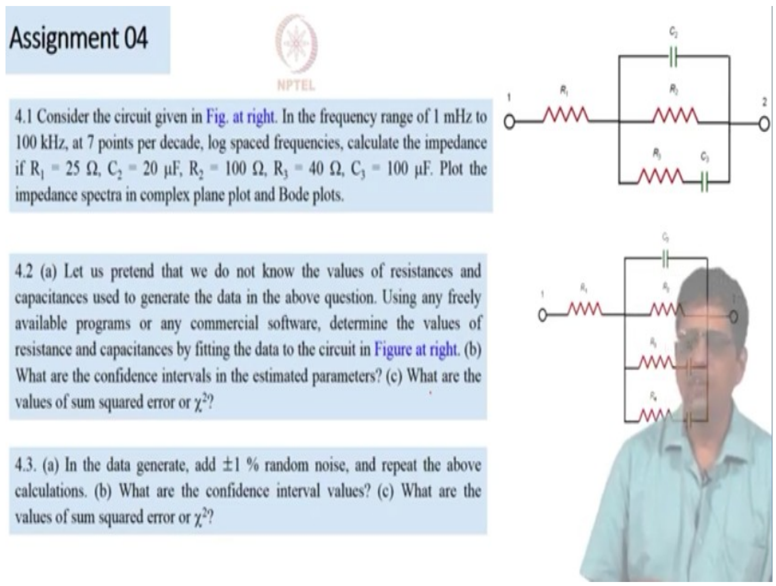

So in this ~~actually~~ assignment, I want you to learn about EEC and data fitting using EEC. ~~So~~ Here, I would like you to first look at the figure on the right. You have a circuit, R_1 here can be considered as a solution resistance, C_2 on the top can be considered as double way capacitance. It is a Maxwell circuit for the Faradaic reaction with R_2 here possibly representing polarization resistance and R_3, C_3 representing the Maxwell element.

So here I would like you to again generate a spectrum for a given frequency range, large phase frequencies for a set of values, reasonable values 25 Ω for solution resistance, 20 µF for double layer capacitance, polarization resistance is 100 Ω, and then the Maxwell elements, they have values of 40 Ω and 100 µF. So you can use this and generate the spectrum and plot it in complex plane plot as well as in Bode plot, this is the first part.

Next, let us see this is experimentally obtained data. It is a clean data no noise, but we do not know which circuit it is, or actually we will first say, we know what the circuit is. This is the circuit. Now I would like you to try and get the values of R_1, C_2, R_2, R_3, C_3, using any commercial software or free software. So basically we pretend that we do not know the values of R_1, R_2, etc., and then find this.

It is a clean data, you should not have any difficulty in getting these values. When you get these, you should also look at the confidence intervals in the data, in the best fit parameter values. For example, if R_1, you get the value of R_1, do you get it as 25 Ω ± 0 Ω, or is a 25 Ω ± 100 Ω, 25 Ω ± 5 Ω, all these things make a difference.

Similarly, what is the chi square value? In this case, you should actually get a zero error and within round of error, you should get within round of value, you should get chi square value, because it is a clean data. Now if I add 1% random values or random noise to this data, and redo this, I should actually get a confidence interval, which is nonzero that means it should be 25 Ω ± 2 ohm or some such number and similarly the chi square value should be little high. If I include 2% noise, if I include 5% noise, it is going to be more. So you get an idea of what type of value should I expect from this.

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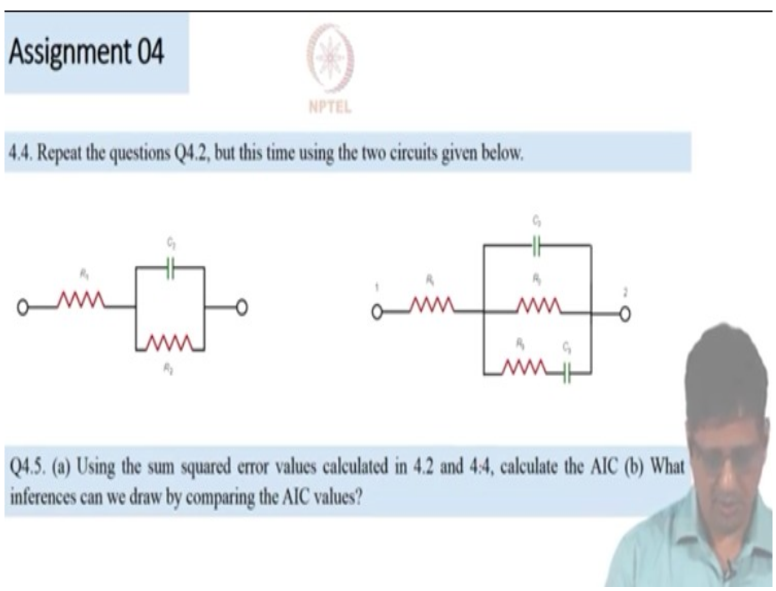

If I use a circuit with one more Maxwell element, it will fit well. So should I conclude that that circuit is a better circuit or that circuit is a good circuit? If I did not know that that circuit on the top is the appropriate circuit and if I have taken this circuit first and then fit it, what would I see, will I see good confidence interval for all these good, meaning tight confidence interval for all these parameters or will some of this parameters have a large confidence interval.

So that is something I would like you to check. Similarly, what is the value of chi square? Chi square can be low and still you might be over fitting. That is something I would like you to try. Then, what happens if I use a simpler circuit. So if I use Randle's circuit, it will fit poorly. That you can guess. What are the parameter values? What are the confidence intervals in the parameter values? That is something I would like you check. Chi square value will be poor, that means a large value, but that is also something I would like you to check and if I use the correct circuit, I should get a perfect fit, with very low chi square value. Now, if I add little bit of noise, how will it work? What will happen for the best fit parameter values, and chi square values for the standard circuit or for the correct circuit. Correct circuit here is the Maxwell circuit with one Maxwell element.

Then, if I over fit, that means, if I give a model with two Maxwell elements, I am adding more parameters. So chi square value comparison is not just the best way to do. It is one way, but it is not always going to tell you whether it is good or not. Confidence interval and parameter is something we should look at. In addition, you should also look at what is called a Akaike information criteria .

We have seen this in the class AIC. When increase in number of parameters, there is a penalty for this, although the chi square value will decrease or the sum square error will decrease and you add more parameters. There is a penalty for adding for more parameters and you can use this to identify, which circuit is the best circuit.

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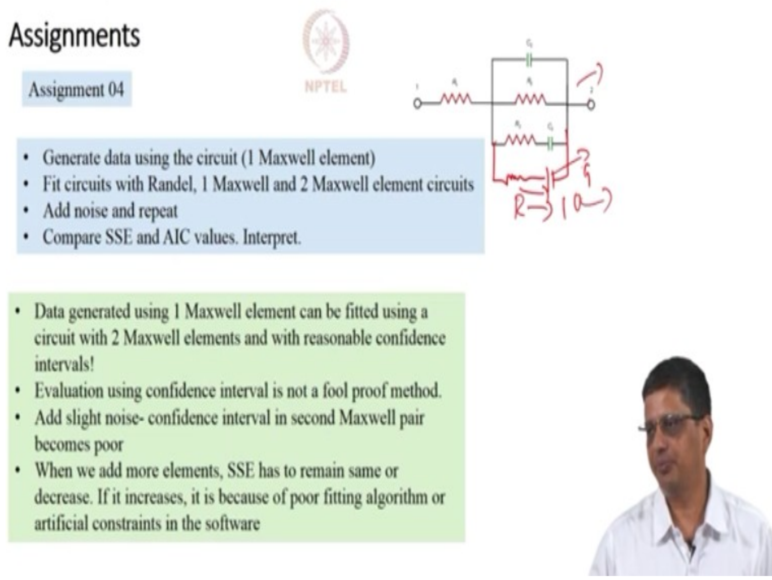

In the fourth question, I had given a circuit, where the Faradaic impedance is represented by one Maxwell element and I asked you to fit it to different circuits, one circuit without the Maxwell element, another circuits with actual Maxwell element, third circuit with an additional Maxwell element. This is one set of exercise. Then, add little bit of noise, and then do the same thing. Fit it one Maxwell element, two Maxwell elements and zero Maxwell element, which is basically the another circuit. And then compare the sum square error Akaike information criteria and then come to conclusion. I also asked you to calculate a confidence interval in the parameters. Usually, we expect if the confidence interval is poor, that may not be the best representation. Sometimes, you do not have a choice, you will have to use the parameter with poor confidence interval. So if you do it, depending on the software, you can generate data with one Maxwell element.

And you can fit it to another circuit with two Maxwell elements and it will fit, and it can give you reasonable confidence interval. What it means is, imagine this, this part alone. I have written it as R_3, C_3, let us call it as 100 Ω, 100 µF. I can get the same effect by using 200 Ω, 200 µFcorrect. I could be wrong, I have to check, maybe this is 50 µF we have to check.

But basically, this can be split into two. If I give you one resistance 100 Ω, I can take it as 50 Ω + 50 Ω or 20 Ω + 80 Ω. If I ask you to fit a circuit this, program may or may not realize that they are redundant. Depending on the algorithm used, it can split into this and it can probably go to some local minimum. It can fix a value here, fix a value here, fix meaning it will settle at some value and it will optimize and get you values here.

And they can be with moderate confidence interval, it is possible. Try with one element, if it does not work, try different initial values, if it does not work at all, you know, okay, I do need two elements, otherwise I cannot handle with one element. Generally, you want to look at confidence interval, if it is poorer, it is probably not a good idea to use it. If it is moderate, you cannot assume that it is the best one.

If you add noise, slight fluctuation, it will actually help you move away from the local minimum and you will find actually, experimental data will have some noise, that is there. You will find that it is possible to actually identify one pair of the elements will have poor confidence interval, one pair will have good confidence interval. So one Maxwell element is actually better circuit for that. Another thing is because of the way, the software uses its own constraints, sum square error, When I add more elements, I expect the sum square error to remain the same or it becomes less. I fit this, it models the data, there is some difference between the experimental data, experimental or simulated data and the model data here. If I add one more element, error has to go down, or at the worst case, it has to remain the same, but sometimes the software will give you a higher error. Reason is it does not set the R value to be infinity. It cannot set it to zero.

If I add R value here, it cannot set it zero, it will have an non-zero value. That is the constraint given by the programmer. It cannot set an infinite value here, it will set a large value here. So sometimes, what will happen is, the software will tell you, when you add more elements, error becomes little larger. Do not use a larger error and calculate the AIC. You have to say the error has to be at least as small as this.

If the error is as small as this, but you are going to add more parameters, obviously AIC is going to be higher. So watch for that also. Do not blindly get, assume that this is correct. That is hopefully what we learn from this assignment. Because what happens is, they will have an artificial constraint saying that the R there has to be minimum of some number or maximum can be 10^{20}. It cannot be infinity. They do not let it go to zero.

They do not let it go to negative unless you ask it to go to negative. If I ask you to go to negative, again it would not go to zero, it will go to non-zero value with a minimum and maximum in the numbers. So what happens is let us say, this is the best circuit. We generate data, this is the best circuit, I do this, if $R = \infty$, that is a good circuit. Now by adding, I should not get a higher error, I should get lower sum square error

But max this can be set to 10^9, there will be some constraint in the software. It does not set to infinity or at least one switch we normally use do not. Then some current will still go through this. It will deviate slightly from the perfect fit. If it can be set infinity, it works well. If this capacitance can be set to zero, it works well. This cannot be set to zero, this cannot be set to ∞. It does not work as well. That means, there will be some current going through this.

That means the model impedance will be slightly different from the perfect value. I can get some square error of zero from this. I may get larger than zero here. Any of you tried that you add elements, and the sum square is such that slightly higher, chi square value will be slightly higher.