Electrochemical Impedance Spectroscopy
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Lecture – 06
Assignment 01

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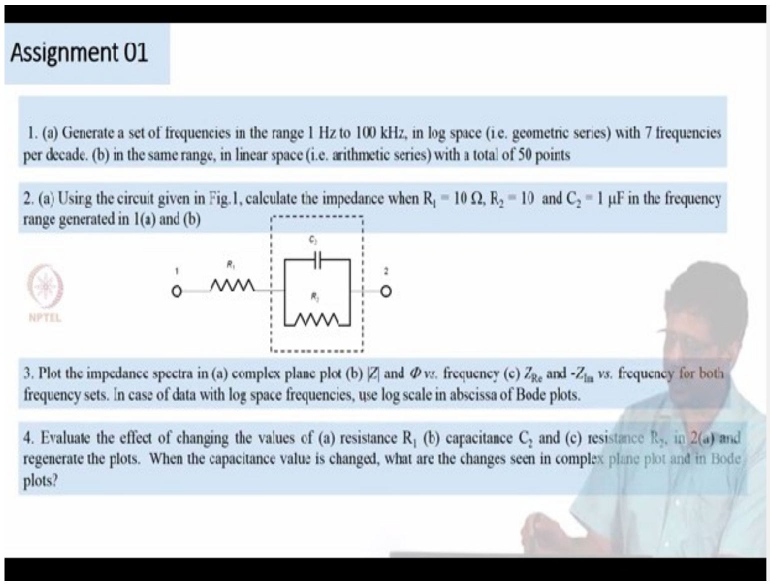

~~So~~ I want to describe the assignments. In this assignment, first I want you to generate a set of frequencies, in both log scale as well as in linear scale. The idea is this: if you have an electrical circuit and you measure impedance spectrum, then if the frequencies are in log scale, what would you see; and if the frequencies are in linear scale, what will we see. So for that I have split that into multiple questions.

First part is to just generate a log space or geometric series frequencies from a minimum value of 1 Hz to maximum of 100 KHz, and typically we give seven frequencies per decade, so I have given that number. At the minimum, you need five frequencies per decade, if you can get ten frequencies per decade, it is well and good. In the same range, if you use linear space, what would we get? And then in the second part of it, we take a simple circuit called Randles circuit. Here we are just going to say that it has resistance of 10 Ω in the R_1, and a capacitance of 1 μF. Typically, you will get 10 or 20 μFcm^{-2}. So if you have a very small electrode, 1 μF is a reasonable number. And then a second resistance, R_2, I had given it as 10 Ω. It is not written clearly here, it has to be 10 Ω. And if we generate a spectrum, using the set of frequencies that we got in the first part, what would we get?

We want to plot that, either in the complex plane plot or as Bode plot. In the Bode plot, you can plot magnitude as a function of frequency and φ or the phase as a function of frequency. That is one way, sometimes you can also plot real part as a function of frequency and imaginary part as a function of frequency, that has been shown in some publications. And whenever you use Bode plot, you should plot the frequencies in log scale.

Here, at least for the case where the frequency is generated or log space or geometric series, you have to plot them in log space and the linear frequencies you can plot in linear space or log space and see how that appears. The idea is for you to understand that if you use linear space, then many of the features will not be clear. But I would like you to try that and get that information or see that information.

When you span a frequency of 1 Hz to 100 kHz in logarithmic or geometric series, then you would have few frequencies in 1 to 10 Hz, few in 10 to 100, few in 100 to 1000, 1000 to 10000, 10000 to 100000. Whereas if you do in linear scale, most of them will appear only in the large frequencies and you will see very few in that below 100 Hz. And the example is from 1 Hz to 100 KHz.

Many times, you will have to take data from 1 mHz or sometimes (from) 100 μHz to few kHz. So, after plotting this, I also want you to see what happens if you change the resistance, R_1, from 10 Ω to 5 Ω or 20 Ω. What happens if you change the capacitance value, C_2 of 1 μF, we can make it 0.5 μF, 5 μF and then plot them again in the Bode plot, or in the complex plane plot.

So, "is there a difference between the one that is plotted now *vs.* the one which was plotted with the original set of values", which is 10 Ω and 1 μF? If you put both of them in the same plot, will you be able to tell the difference. What happens when you change the R_2? The idea is this: If you know that *whenever the resistance R_2 is changed, in Bode plot, it will appear like this*; *in complex plane plot, it will appear like this*; then, when you actually do the experiment, you might do it in one solution, (with) the same electrode you might change the solution composition; you might add a chemical or you might change the electrode surface and then redo the experiment. And when you compare, if you see certain change in the result, you should be able to think and say, “this most likely means that this resistance has changed” or “this capacitance has changed”. It will help you get an understanding of the physical phenomena, if you have this knowledge. So basically from the plots, can we get an idea of what has changed in the system? To get that (knowledge), I would like you to try this part.

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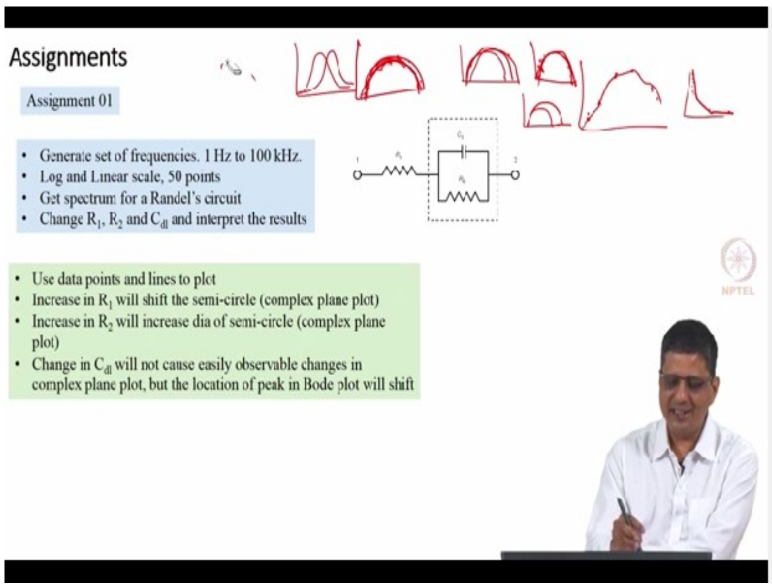

Let us quickly go through what the problems are, and what I expected to see. And *some of the mistakes that I observed in the answers* are discussed in this class, and *what you should do to correct them*. So the first set of assignment problems are here, I think 3 or 4 problems. I would ask you to generate set of frequencies in log scale, linear scale, set number of points and then use that frequency set to generate the spectrum, plot it in different formats, change the value of R_1 and R_2, change R_{sol} or polarization (resistance) and double layer capacitance and tell *what you see*, (and what your) interpretations (are).

So when you plot it, you should plot (with points). You can use lines, I do not mind (that), but if you do not use points, many times you will not see what is happening. So, (for example) in Bode plot, if there are many points here, and two points here, (using) line will not tell you anything. You will not be able to tell that *there are more points in one region*, and *there are very few points* *in other region*. (So, it is better to use points)

If you put points, you would be able to see (that). Finally, how you present when you realize what is happening; *finally how you present that* is different; meaning, if you are looking at data, you should know where the data lies, how they are placed, and then if you want to emphasize certain points, you will present it, first time it is better to put data points and lines, (i.e.) markers and lines. And if you look at complex plane plot, [what is commonly called as Nyquist plot], if you change the R_1, this entire circle will shift to the right in the complex plane plot. In the Bode plot, you will have pair of responses, like real and imaginary or phase and magnitude and they will move. In the phase (vs. frequency), you may not see much of a change. In the magnitude (vs. frequency), you will see that it shifted. If R_2 is changing instead of(…); In R_1 case, it is going to shift like this, but semicircle will not change.

If R_2 is changing, let us say it increases but R_1 remains the same, semicircle diameter will increase. Third, if you take a spectrum and change the C_{dl}, actually the points here (in complex plane plot) will move, but the circle diameter and if you just draw it as a line, that circle diameter will not change, circle location, (i.e.) center will not change. If you had taken data only up to this, if you had taken in a limited range, it may look like it is moving to the bottom, imaginary is decreasing; some of you have written like that, but that is not correct. Actually, if you watch very carefully, the point location at a given frequency will change. So, you will see that in some cases, the maximum will occur at some frequency. If you change the C_{dl}, that frequency will change, that means the point would move to the left or to the right or you can say it to the bottom on either side, does not matter. But all of this will trace the same semicircle; it will be moving in that semicircle. What happens is, let us say there are 100 points here. If you change the C_{dl}, some of them will get squeezed in one side but entire curve, [if you just look at it without looking specifically at the points but just overall curve], it will not change. And when you are comparing two or three cases, when you will compare their spectrum, the spectra you would usually just, look at the shape, look at that polarization resistance, solution resistance and you may not quickly observe this.

Whereas if you go to Bode plot, it will change [visibly, when C_{dl} is changed]. The location of the peak will change. Here [in complex plane plot], if you overlay two plots, you will think they are more or less identical. If I draw, for a given R_{sol}, given R_1, given R_2, if you change the value of C_{dl} a little and plot one as a continuous line, another as marker, you will think both are same, unless you are very careful in noting which frequency point lies where.

If you do the same thing in Bode plot, say for example one of them will be marker, one of them will be continuous line, you will know there is a difference. So if there is a change in C_{dl} and other parameters do not change, it is easy to see that in Bode plot. If there is a change in R_1 and R_2, it is easy to see that in complex plane plot. That is what I would expect you to tell; so it is not just, you can do this, you can get this, go step by step, show me the plot. [and then] I would like you to actually think about the meaning of those results. I can show you those values here, and I can show you right in the presentation that if you change C_{dl}, this is how it will come. One second you would see [but you are not likely to remember]. But if you do it [yourself as in this assignment], you would really see [and remember] what will happen when you get 2 sets of data.

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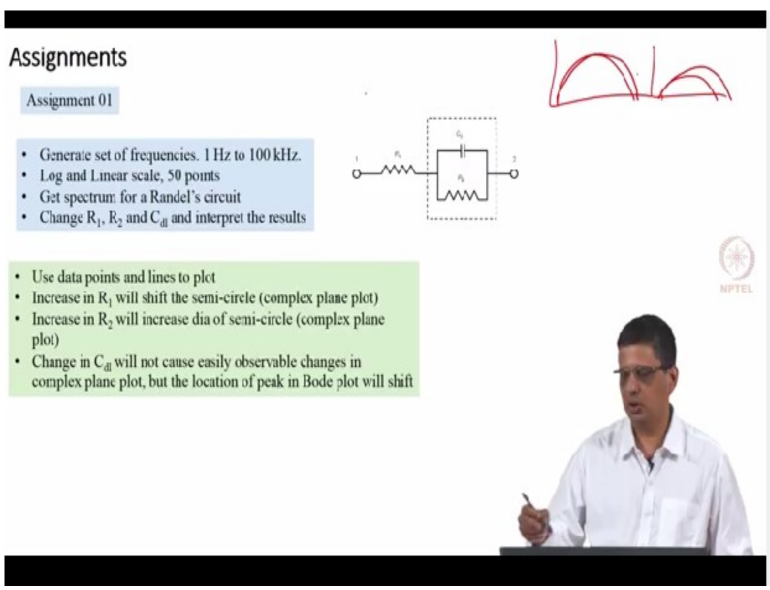

If you plot them together, you say *run it at one condition*, *you get the data like this*. You *run it with another condition*, *you get a data like this* ; within experimental error, they look the same. You may or may not realize [that] right away; whereas, if you run it in one condition, it looks like *this*, in another condition, it looks like *this*.[please refer to video]. You can say “yes, this is because there is change in R_2”.