Electrochemical Impedance Spectroscopy
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Lecture – 07
Type of Analyzers, Single and Multi-sine

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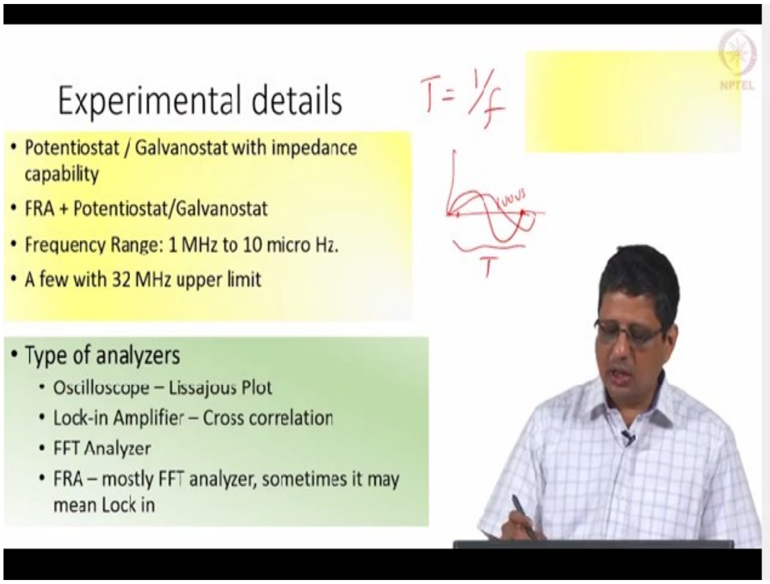

Experimental details

- Potentiostat / Galvanostat with impedance capability
- FRA + Potentiostat/Galvanostat
- Frequency Range: 1 MHz to 10 micro Hz.
- A few with 32 MHz upper limit

- Type of analyzers
  - Oscilloscope – Lissajous Plot
  - Lock-in Amplifier – Cross correlation
  - FFT Analyzer
  - FRA – mostly FFT analyzer, sometimes it may mean Lock in

Now we (can discuss experimental set ups in) details. Usually for the electrochemistry, you can get instruments, they host both potentiostat, galvanostat and the impedance capability in one instrument. So you can get workstations. You can get potentiostat and galvanostat separately as one equipment and what is called FRA or frequency response analyzer as another instrument and you can couple them together and then run these experiments, example: some of the Solartron company's products are like this. Solartron also sells one with the integrated facility. Normally you get frequency ranges of 1 MHz to 10 μHz. Right now, you can get few instruments with even higher 32 MHz as upper limit. Above certain kHz, may be 30, 50, 100 kilohertz, you do not really get useful data for normal electrochemical systems.

Pure electrical systems, you can get impedance analyzers for many megahertz and gigahertz, they are not going to be useful here. They will stop at few kilohertz at the lower end. In electrochemical system, you will get benefit mainly at the middle and low frequency. Middle here (means frequencies in the range of)10 Hz, 1 Hz, 100 Hz, low (means frequencies in the range of) 100 mHz, 0.1 Hz, less than that 1 mHz.

When you go to lower and lower frequency, what happens is, the period is going to be inverse of the frequency. That means if I draw a sine wave, it is going to take me certain amount of time to complete 1 sine wave. So if I measure at 1 mHz, I have to wait for 1000 seconds because 1/0.001 is going to give me 1000 seconds. I need to apply at least 1 cycle. It will actually start here. Does it have a phase difference or not? If you apply more cycles, it is better. But it is going to take longer time. Usually in the electrochemical system, you can go to low frequencies to get information, it takes long time, data tends to be noisy at low frequencies. So you want to have low frequency data, you have to wait for long time and still you may not be assured of a good quality data unless the system is well behaved.

So if you are going to get an instrument, if you get 1 MHz, it is good enough. if somebody says we can go up to 32 MHz, for liquid based electrochemical system, (and) you probably do not need that. It is not going to offer any benefit. There are different types of analyzers. One is called *oscilloscope*. I do not think it is being used now days, for this purpose.

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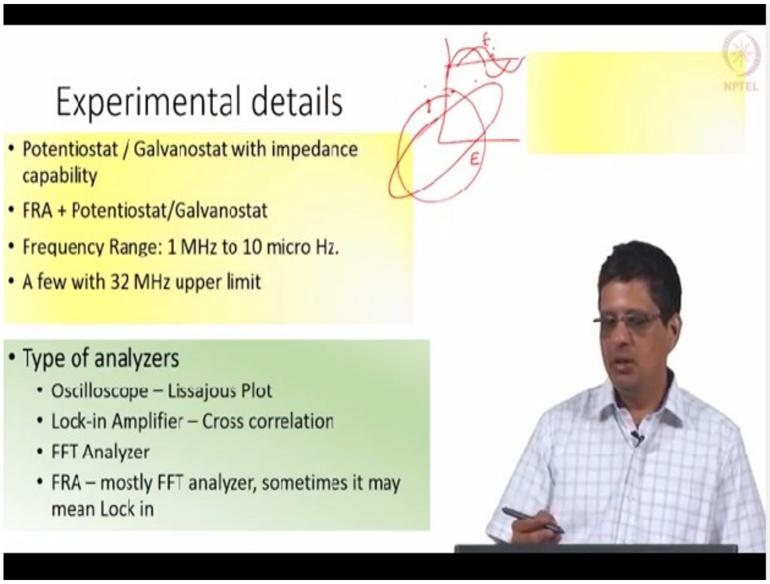

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In the oscilloscope, at a given frequency, you will apply a potential, sinusoidal potential; You will also get current, It may have a phase difference. And you would actually plot potential and current as a function of time. It may go like this, it may go like this and there will be a point which keeps moving in the oscilloscope, so you will trace that point, and from that you would find what is the phase, what is the magnitude?

So it is *i* versus *E* or *E* versus *i*, you can get the magnitude and phase of the impedance from that. You can also see whether the response is linear. What do I mean by that, we will see a little later. But it is slow. At each frequency, you have to monitor it, may be you can save that and take a printout and measure this value. Manually you will have to calculate the impedance, it is not used now adays.

Another type is called *lock-in amplifier*. It uses a technique called cross correlation. Again I will describe what that is a little later. And third is called *FFT analyzer*, Fast Fourier transform analyzer.

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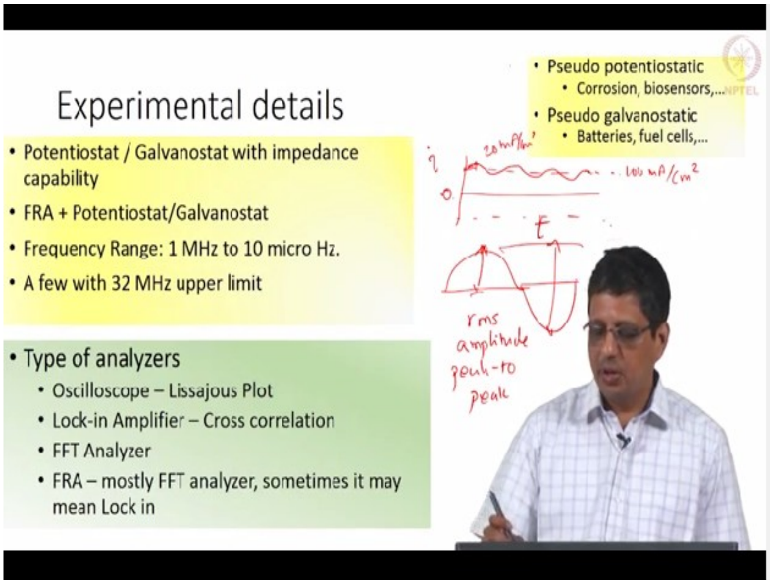

Experimental details

- Potentiostat / Galvanostat with impedance capability
- FRA + Potentiostat/Galvanostat
- Frequency Range: 1 MHz to 10 micro Hz.
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- Pseudo potentiostatic
  - Corrosion, biosensors,...
- Pseudo galvanostatic
  - Batteries, fuel cells,...

- Type of analyzers
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This term FRA is a *frequency response analyzer*, most of the times, it means *it is an FFT analyzer*, although I think sometimes it is being used for instrument which also use cross correlation. If you remember right, one of the vendor, Solectron uses cross correlation and call that equipment as an FRA, frequency response analyzer. And of course, most of the manufacturers will not even tell you how they actually analyze the data, and give you this result.

You click, you will get impedance, that is all they will tell. They will not show you how the current comes, I do not think many times they do not even record the current. They process it at the chip level and the chip gives you the impedance. It is saved here. You can run this in different modes. One is called potentiostatic and another is called galvanostatic.

The correct term is pseudopotentiostatic, because; let us say *this* is the potential, this is zero versus open circuit potential. I might superimpose 0.2 V with respect to, +0.2 V, -0.2 V, whichever. And then apply a sinusoidal wave on top of it. This is essentially saying [that] *it is more or less constant potential* of 0.2 V *with few mV of sinusoidal potential*. That is why we call it as *pseudo-potentiostatic*. This is usually used for studying in corrosion, biosensor, deposition, most of the processes. But in storage devices like batteries or fuel cells, energy devices, usually it is a constant DC current, you might say 100 $mAcm^{-2}$, on top of which we put 20 $mAcm^{-2}$, here by 20 $mA(cm^{-2})$, I means the amplitude of this. There are different ways of specifying: you can specify *rms* value, you can specify the *amplitude*, you can specify *peak to peak* (means from the maximum to the minimum). Amplitude is (measured) from *0 to the maximum*. *rms* is going to be amplitude/(approximately 1.4). [It is] *rms* means "root mean square" value. So when you choose data, [or] when you read papers [journal articles], watch this carefully. Some ~~(~~people denote as) 5 mV rms~~,~~(or) 20 mV peak to peak~~,~~ or as 10 mV amplitude. You will have to know how to interpret this or how to use that information. If you want to repeat an experiment, you want to conduct at the same condition, (then) you need to know what each of these terms mean.

See, the reason we conduct in galvanostatic mode in some cases and potentiostatic mode in some cases, is that *the impedance values of the batteries and fuel cells are very low*. When they are very low, then you specify potential, and say 10 mV potential oscillations, it will give rise to large currents. It may go beyond the instrument's capability.

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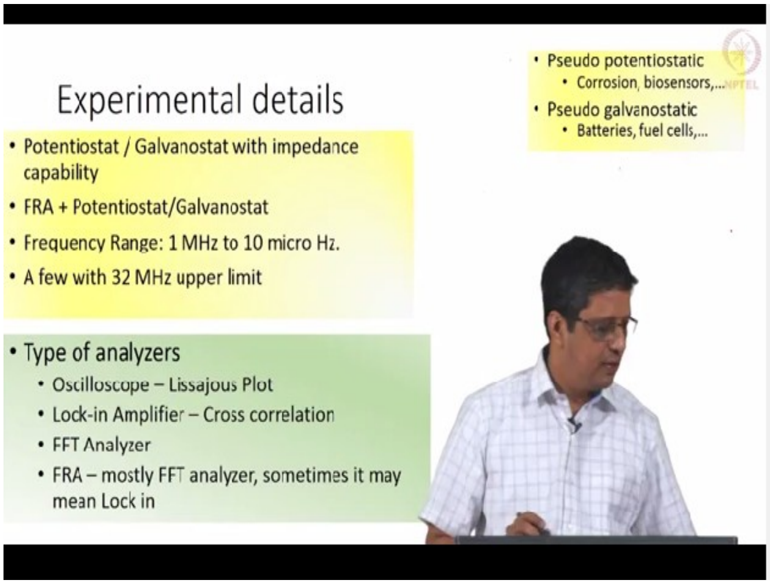

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So if I give 10 mV potential and let us say the magnitude of the impedance is 1 mΩ. the current that I get is going to be, [this many volts by ohms, would give me] 10 A current. On the other hand, instrument can give a constant current or a small oscillation in the current, it can measure the potential very accurately. So here if I give 100 mA current, that means 0.1, I would get 10^{-4}, that means 0.1 mV at the peak.

So it will actually be a sinusoidal potential with the maximum at 0.1 mV. It can measure it accurately. Those practical reasons which forces to use galvanostatic mode, it is not that in theory, you can use potentiostatic or galvanostatic mode, there is no problem. In practice because of the way the instrument works and because of the difficulties in achieving large current and measuring all this accurately, we use galvanostatic mode for batteries and fuel cells.

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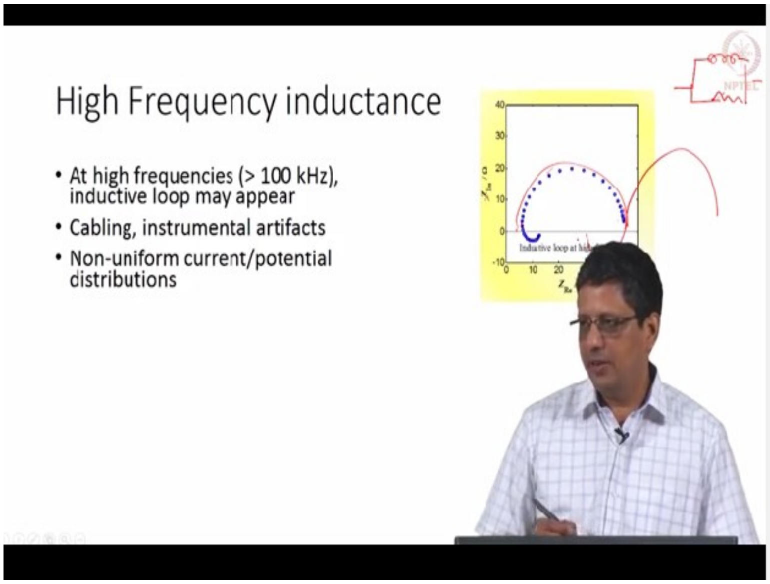

High Frequency inductance

- At high frequencies (> 100 kHz), inductive loop may appear
- Cabling, instrumental artifacts
- Non-uniform current/potential distributions

When you actually run an experiment, we would expect for example for very simple reaction, we would expect that it has a semicircle behaviour. It will show up as a semicircle. But many times, you will find inductive loop. Loop that comes like this in -Z imaginary versus Z real, if it comes as a semicircle, I would say it is a capacitive loop. A capacitor in parallel with resistance can give rise to this. If it gives two loops, I will say two capacitive loops are present. If it comes like this, I would say it is an inductive loop, because an inductor is parallel with the resistor can give rise to this type of behaviour.

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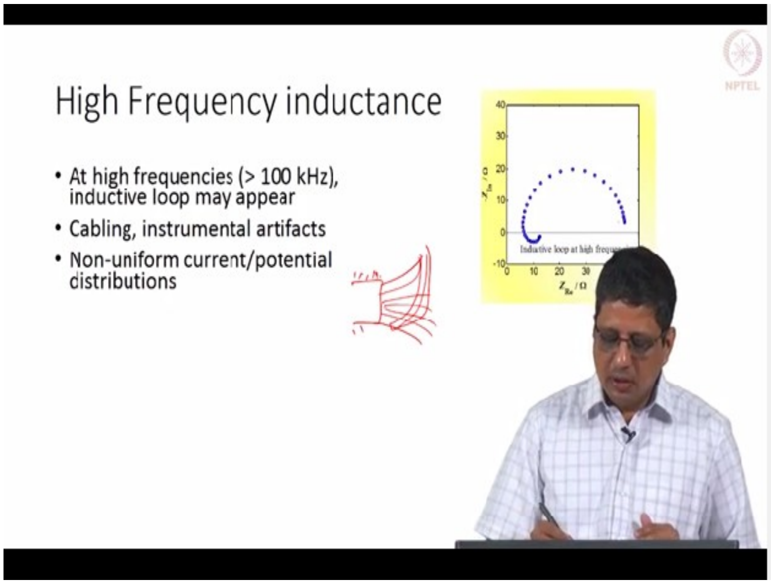

High Frequency inductance

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Now at high frequencies, you normally should not have anything except a constant value here. But you may get inductive loop and that may not be coming because of anything in the system, it may come because of the cables. If you have long cables running parallel, what an instrument measures is what is coming to the instrument, it may come, an artifact may come because two cables are having an inductance. It does not know it is not coming from the cell. So you want to have short cables. Sometimes even the electronics in the instruments can give you an artifact. That means it is not having an inductance but it gives you a measurement as if it is coming from an inductance. Sometimes in actual electrode itself, if you have an electrode like this, this is insulator. This is exposed to solution, If the (current) distribution is not uniform, you may have this problem.

If the reference electrode is placed at one end of this for example, and the electrode is large here, the working electrode is large. I have a reference electrode. Instead of, I want to bring it close, I bring it to this level because of the cell geometry I may be forced to do this. The current distribution here is not going to be uniform, potential distribution may not be uniform. This can also give rise to inductive loop. It does not mean you have a real electrochemical process or it does not mean you have a magnetic sum in the system. Easy way to avoid this is to start taking data at 30 kHz or lower values. Because you do not expect to say anything about the reaction at this kHz, use short cables.

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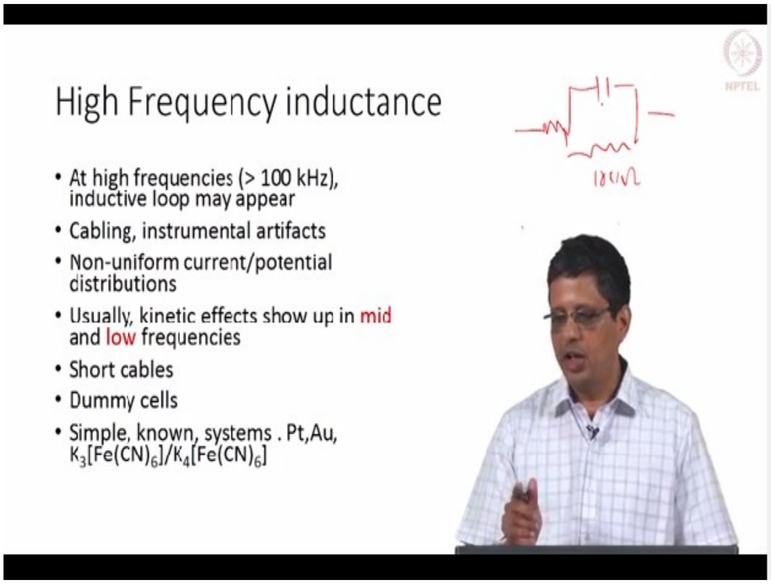

High Frequency inductance

- At high frequencies (> 100 kHz), inductive loop may appear
- Cabling, instrumental artifacts
- Non-uniform current/potential distributions
- Usually, kinetic effects show up in mid and low frequencies
- Short cables
- Dummy cells
- Simple, known, systems . Pt,Au, $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$

Usually the kinetic and mass transfer effect will show up at the middle and low frequencies. If you have doubt about the results, what you should do is first take a dummy cell. Dummy cell meaning it has a simple electrical circuit, these are actually resistors, physically may be 100 Ω, 1000 Ω. You can get them from the manufacturers themselves, electronic, the instrument manufacturer themselves. Run this and see whether you are getting what you are expecting to get there.

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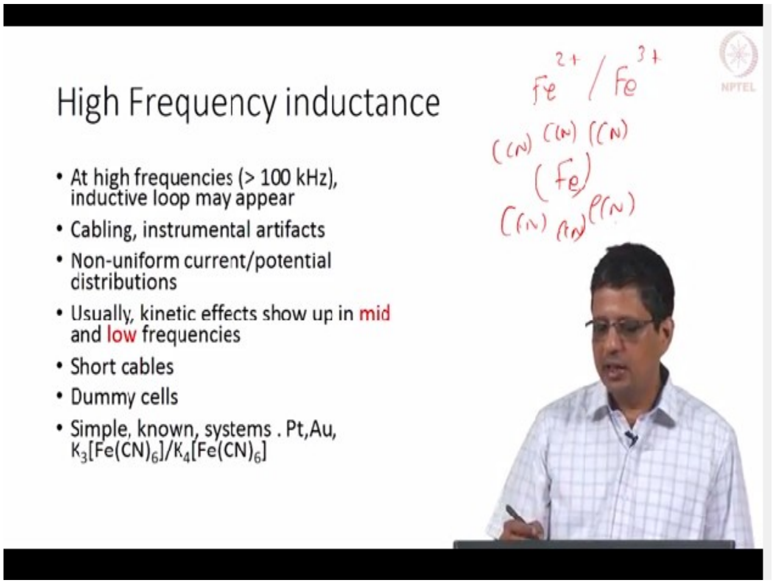

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If that works, next go to system where this is called potassium ferrocyanide and ferricyanide, many times it is referred to as Fe^{2+} and Fe^{3+}. Basically it has Fe, surrounded by six $(CN)^-$ molecules. So if you visualize, that it is surrounded in 3D in all directions by the cyanide and when it takes one electron or gives up an electron, this do not get reoriented. This is a large molecule, water hydration sheath is also not that important here. So it can take an electron or give an electron without much problem, without any reorientation. So it is called simple electron transfer reaction.

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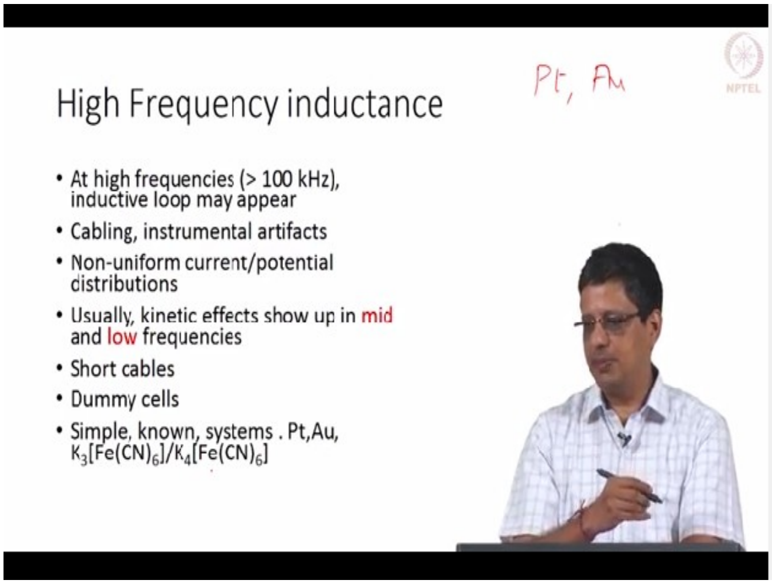

Pt, Au

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On the other hand, although we write other reactions for example we can write $Zn + 2e^- \rightarrow Zn$ metal. Zn^{2+} will have hydration sheath, that water has to go away before electron comes and it may not even happen in one shot, It may not happen 2 electrons will come at one shot and become metal. One electron may come, after sometime, it at this level is Zn^+ and then another electron comes.

So it is not necessarily going to be a very simple reaction. So if I want to study a simple reaction to make sure I understand this correctly my reference electrode is good, my cell geometry is good. Usually we would take platinum or gold electrode and conduct this reaction and see whether the impedance comes as expected. If it comes as expected, then we have confidence that the equipment is behaving correctly, cabling is proper, the reference electrode is working properly. So we study the actual system that we want to study. If this does not come correctly, we have to fix this instrumentation and cable before we go on to the actual experiments.

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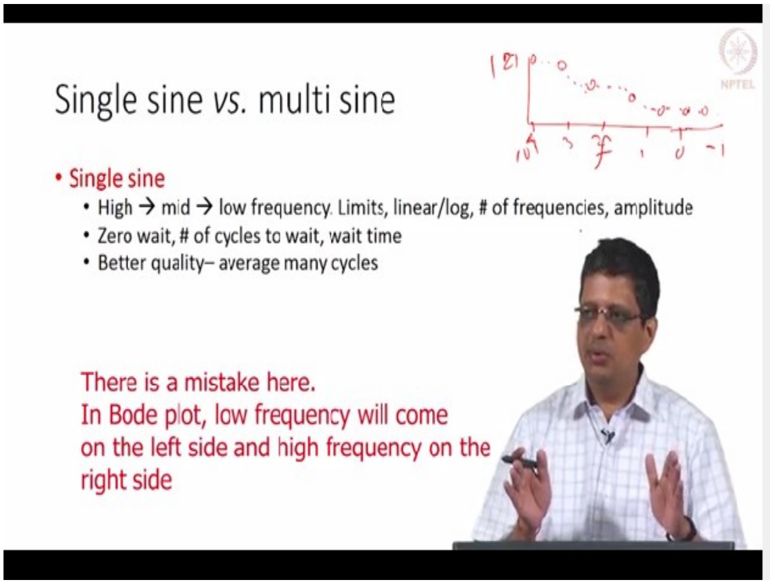

Single sine *vs.* multi sine

- Single sine
  - High → mid → low frequency. Limits, linear/log, # of frequencies, amplitude
  - Zero wait, # of cycles to wait, wait time
  - Better quality– average many cycles

There is a mistake here.
In Bode plot, low frequency will come on the left side and high frequency on the right side

You will (have) different choices; *single sine* and *multi sine*, sometimes called Fourier transform in the experimental setup, in the software. Normally you will start at the high frequency, if we say we want data from 10 kHz to 100 mHz, you will also have to specify how many data points are needed. These are usually in log space but different vendors or different manufacturers will have their own setup options. You will have to choose among them. You have to give the higher frequency limit and lower frequency limit. In some cases, you can choose linear scale or log scale, usually we will choose log scale. You can choose number of frequencies. Imagine that I have a Bode plot 10^4, may be 10^3. 10^2, 10^1, 10^0, 10^{-1} 1. This is 100 mHz, 1 Hz, 10 Hz, 100 Hz, 1000 Hz, 10,000 Hz.

We want to get data points like this. We do not want to get log space data but then it is going to take you longer time to get all the data. High frequency, it will not take that much time. Low frequency, it will take lot of time to measure data at each frequency. But then if one of the data is incorrect, it misbehaves, it just jumps up here, remaining data is clean, you will probably neglect this data and then say rest of the data; I am taking it as valid.

You have to tell the number of frequencies per decade or you have to tell the total number of frequencies. You want it to be reasonably large. if it is too large, it is going to take long time. If it is too small, you will have problem in interpreting the data or understanding the data, having confidence in the data. So there is a compromise. Amplitude, you have to specify depending on how the manufacturer say, is it rms, peak to peak, or the amplitude value. In some cases, you can also specify how long you have to wait, apply a sinusoidal potential and take data right away. We know that it has problem. In some cases, you will have zero wait time giving you reasonable result.

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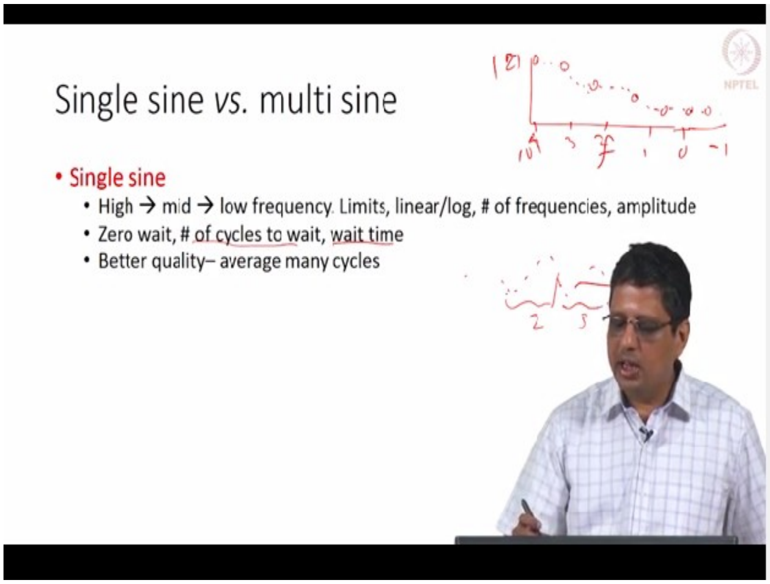

Single sine *vs.* multi sine

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Many times, we have seen, that it will come like this and then it will give steady periodic results. We want to be in this region and then look at the phase and magnitude of the current and then take the impedance. We do not know upfront, a priori we do not know where it is going to be, so you will have to guess. Some manufacturer will give you a choice of how many cycles to wait.

Some manufacturer will give you choice of how many seconds to wait. Many of these cases, you will have to run a trial, run few trials and then look at the data and then choose this. You may have to run at 2 seconds, 4 seconds, 10 seconds and then see which between 4 seconds and 10 seconds, there is no difference; 2 seconds and 4 seconds, there is a significant difference. You would say I have to wait at least 4 seconds to get stable periodic result.

So a priori, upfront I cannot tell you this is the correct number. It depends on your system. Sometimes even waiting for 1 second may be sufficient. Sometimes zero wait time may give you good enough data. zero wait time does not necessarily mean they will do 1 cycle and then get the result at the high frequency. At the high frequency, they may do more cycles. Some instruments will give you a choice of quality, data quality. They will not tell you what they really mean by that. They will not tell you how they judge, evaluate the quality and get the results. But they give you a choice. For example, in Princeton Applied Research, PAR, you will get a choice of 1, 2, 3, and 4 as the quality. (The value) 1 means poorer quality, 4 means-the best quality. If you say *best quality*, my guess is, one way of doing this is, I would (collect data for) more number of cycles and then do Fourier transform. Even if the phase value is little off, but when I do many cycles, hopefully I will get a better result; that is one way. It will take longer time. Another is to do 2 cycles, analyze the first cycle, analyze the second cycle, if they do not differ by more than a percentage, 5%, 10%, some (such) specification, then take that as good enough. If they differ, then you do one more and then compare number 2 and number 3 result. But have a cut-off, (e.g.) beyond four (cycles), I am not going to go (further) because at low frequency, it is going to take long time (to do that).

You cannot say it has to match within 2% from one cycle to another cycle, because if the system is poor, it will never (match and the data acquisition will never) end. But they (the manufacturer) will not tell you (all these details), they give you an indication that I will get, (or) you will get better quality data if you choose this option. (Internally, the software) it is probably using one of these (methods). In general, it will take longer time (to get better quality data). (If) At the same time they can give you the better quality data, why would anybody want a poor quality data? (i.e. if one can get better quality data in the same time required to get poorer quality data, why would anyone want to get poor quality data? You will have to wait longer to get better quality data, and that is why instrument manufacturers give you these choices). But these are the choices that you normally did in most of that commercial software.

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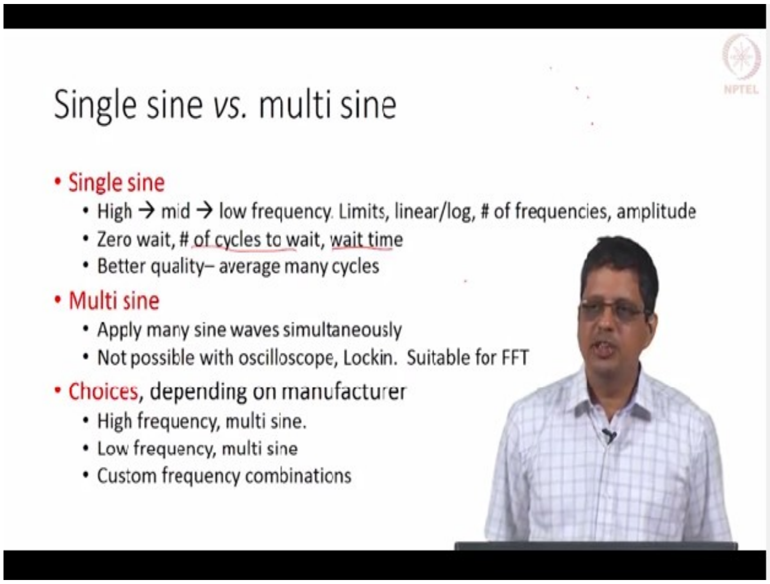

Single sine *vs.* multi sine

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  - Zero wait, # of cycles to wait, wait time
  - Better quality– average many cycles
- Multi sine
  - Apply many sine waves simultaneously
  - Not possible with oscilloscope, Lockin. Suitable for FFT
- Choices, depending on manufacturer
  - High frequency, multi sine.
  - Low frequency, multi sine
  - Custom frequency combinations

There is another technique called *multi sine*, where instead of applying one sine wave, you can combine multiple sine waves, apply them together. It will take you less time to get the set of data. So it is a shorter time. it is not possible to do this with oscilloscope or with the lock-in amplifier. You can do with FFT analysis. Some manufacturers will give you multi sine option at high frequencies. Some manufacturer will give you multi sine option at low frequencies. For example, CH instruments at low frequencies, it is at least the version we have, it is by default it is going to give only FFT. You do not have a choice of doing single sine and multi sine. High frequencies, if you want, you can do multi sine. In some manufacturers' case, they will say high frequency will have multi sine; low frequencies, you have a choice of doing multi sine or single sine.

Some instruments will give you the option of specifying the frequencies and applying, generating a multi sine and doing it. Other manufacturers will say, apply multi sine, you can say how many frequencies, but I will decide what are the amplitudes and phases of each of this frequency, sine waves. I will add them together, apply, get the result, do whatever analysis has to be done and give you the impedance at various frequencies.

So in some cases, you would get 1 to 100, one multi sine. 100 to 10,000 another multi sine. That is one type of choice. You can say 1 to 10,000, one multi sine. So variety of things are possible but usually my personal recommendation is not to use multi sine. But I want to go through the details and tell you why it is not a good thing. Before that, I want to show what is done in FFT analyzer which is the commonly used analyzer.

So I want you to understand what is FFT; FFT is a Fourier transform done for discrete points of data. You may be familiar with Fourier transform. You have a function, (here) we are looking at periodic functions only. You can have an integral to tell, to transfer it from time domain to frequency domain. But when we measure data, data acquisition uses what is called A to D, analog to digital.

It will take data at periodic intervals, for example, potential or current continuously but it will record data only at regular intervals, and that data is analyzed. So it comes with its own limitations. So we will continue tomorrow with what is done with FFT, what are the things one should know about FFT so that you can understand the results that you get from the instrument. We will stop here today.