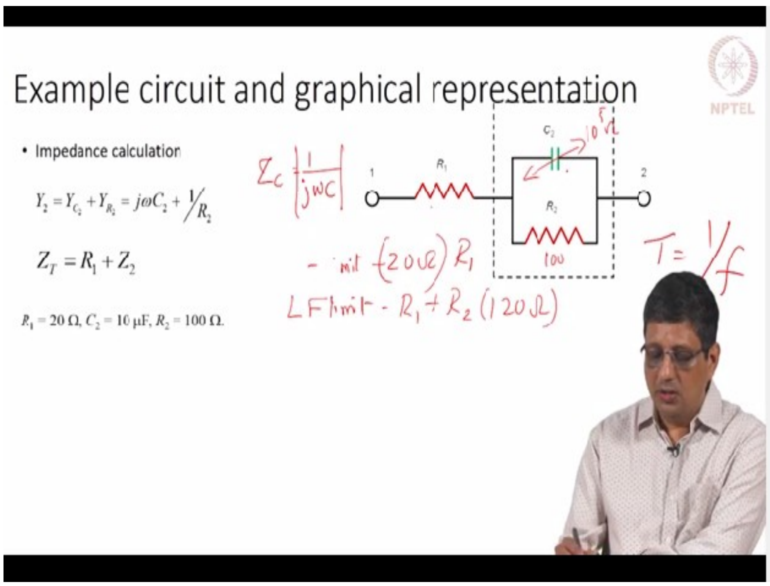
Electrochemical Impedance Spectroscopy
Prof. S. Ramanathan
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 04

Graphical Representation of Data (Complex Plane, Bode)

(Refer Slide Time: 00:13)



There is a little more complex system where you have 1 resistor in series with another box. That box contains 1 capacitor in parallel with the resistor. I am taking up this circuit because this can be used to model a very simple electrochemical reaction under certain assumptions. We assume mass transfer is very fast. We assume the reaction is very simple, straightforward, one-step reaction.

We assume that the other side has good reference electrode. Therefore, impedance is zero. R_1 represents the solution. C_2 represents the double layer capacitance and R_2 represents the reaction. Sometimes this circuit is called Randle circuit. Sometimes mass transfer resistance is also added and that can also be called as Randle circuit. Later we will explain about how to relate kinetics to this circuit. Right now, I want to calculate the impedance for this circuit. I want to call the left side as 1, the right side as 2. The admittance of the elements in the box is going to be, admittance of capacitance and admittance of resistance. So I will call this as $j\omega C_2 + \frac{1}{R_2}$. Sum of these will give me the admittance of the box. I will call total impedance as Z_{total}, it is going to be R_1+Z_2, Z_2 is going to be inverse of the admittance. So I want to take up some example numbers.

$R_1=20\Omega$, $C_2=10\mu F$, $R_2=100\Omega$

These are reasonable numbers for an electrochemical system. For 0.5 cm^2 electrodes, this is reasonable. $20\mu F/cm^2$ is considered normal for a simple electrode. 100Ω is one example of a resistance coming from the reaction. If I take this, I have to tell this is the frequency, tell me the impedance. So now we come to the impedance spectroscopy. We are looking at electrochemical system. We are measuring the impedance. Impedance is a coupled quantity or a pair quantity. It has magnitude and phase, a real and imaginary part. They are not exactly unrelated. It is not like if I give one frequency, I get a real part and imaginary part and I get the phase and magnitude. But these are not completely unrelated. We will see that again later.

Everyone is familiar with what is called spectroscopy. For example, in UV visible spectroscopy, we usually measure absorbance as a function of wavelength. Some of you might have done FTIR, which is Fourier-transform infrared spectroscopy. There, you would get absorbance or transmittance as the function of wave number. Wave number is inverse of wavelength. You can also plot it as a function of frequency. Frequency and wavelengths are related. So if you measure a particular quantity as a function of wavelength or as a function of wave number, as a function of frequency, we call it as a spectrum.

Here, we normally represent it as a function of frequency, f. Sometimes we will represent as a function of angular frequency, ω. But most of the time, you will see it as function of frequency. So we take an electrochemical system which means usually a 3 electrode system. In case of batteries, in case of fuel cells, you may not be able to introduce a reference electrode. So because of those practical difficulties, we will use a 2 electrode system. But we normally mean to use a 3 electrode system.

So when we use an electrochemical system, measure the impedance as a function of frequency, the set of data we obtain is called electrochemical impedance spectrum. Now when you get impedance spectrum, you can visualize I have 1 column of frequency and I get 2 columns of data; it may be real or imaginary. It may be phase and magnitude. I can plot it in different ways. Before we go there, I want to look at above mentioned circuit.

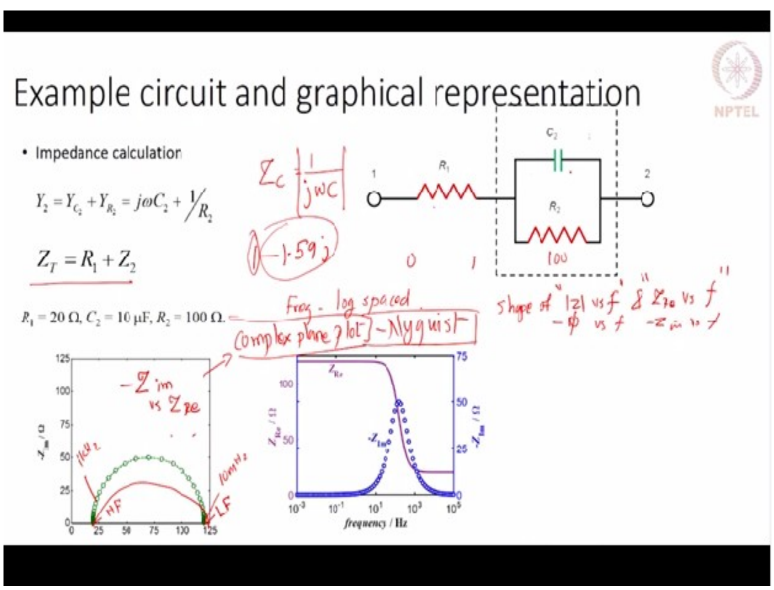
Let us think what we expect to see when the frequency is very high or when the frequency is very low. Typically, we use 30 kHz, 100 kHz, 1 MHz at the high frequency in an electrochemical impedance spectrum. Low frequency depends on how long we are willing to wait, how good the system is. We will at least go till 100 mHz. if the system is good, if you can wait for long time, we will go to 10 mHz. We can go to even 1 mHz. The best instrument say they can take data up to 10 µHz. However you also have to think why it takes long time for us to measure at low frequency? If I say 1 mHz, that means it takes 1000 seconds for 1 cycle to complete. I need at least 1 cycle data to get some idea of what the impedance is. The period is inverse of the frequency. So when I go to low frequency, the period becomes much longer. So we have to wait for longer time. In electrical impedance spectrum, people will normally work with 100 Hz, 1 kHz or they will go to megahertz and gigahertz. In EIS, we normally go to lower and lower frequency because lot of information is present only at low frequencies. So we want to go to as low as possible within the time constraint. Now we have an idea of what is meant by high and low frequency data. High means at least 10 kHz or 100 kHz range. Low means at least 1 Hz or lower than 1 Hz. So if I go to high frequency limit, what happens?

Whether it is high frequency or low frequency, the resistance (R_1) has the same impedance at all frequencies. It is R. Here it is 20 Ω. The impedance of the capacitor (C_2) is going to be, $Z_c = \frac{1}{j\omega C}$. C is a fixed number here. When I increase ω, this capacitance is going to be zero which means very small value of impedance. So this will act as a short circuit. So if C_2 gives very little impedance here, the resistor (R_2) offers a fixed resistance, i.e. R_2 offers 100 Ω in this case. If the magnitude of the impedance of the capacitor becomes much lower than 100 Ω, (if it becomes for example 0.1 Ω), current comes here, all the current will pass through this (capacitor, and not through the resistor R_2). Almost no current will pass through this (resistor R_2). So all the current will pass through this (C_2) and this 0.1 Ω can be neglected compared to the 20Ω of R_1 and the 100 Ω of R_2.

So I will see only 20 Ω of resistance, 20 + a small number. So at the high frequency limit, we will get R_1 (20 Ω). It will be a real number because C_2 will be almost 0. R_2 does not even play any role because it is blocking the current completely. So at high frequency, I should expect to see 20 Ω as the total impedance of this circuit. Now I will like you to guess what we will see at low frequencies? When I say low frequency, let us say 1 Hz or 0.1 Hz.

At this level, what will happen to the impedance of the capacitor? When ω is very small, Z_c is going to be large. That means C_2 is basically going to block. At low frequency, it is not going to be offering any pathway for current to go through. All the current has to go through R_2. Let us say ω is in the order of 10^{-1}. C_2 is 10^{-5} because it is 10 µF, that means 10^{-5} F. ω is in the range of 0.1. So impedance through C_2 is going to give 10^5Ω or something of that magnitude. So no current is going to go through it. Current is going to go through R_2 only. Therefore, the low frequency limit is going to be R_1+R_2, that means for this example, it is going to be 120 Ω.

(Refer Slide Time: 08:12)



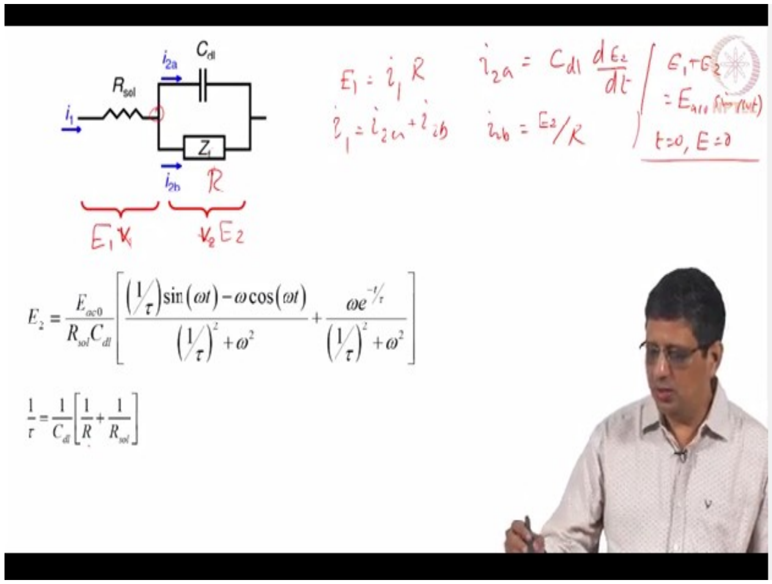
Now we can use this formula and calculate the impedance. One way of plotting the impedance is to plot $-Z_{imaginary}$ versus Z_{real}. The abscissa is Z_{real}, the ordinate is $-Z_{imaginary}$. If you look at the previous calculation where we had a resistor and capacitor in series, we got values say 1-1.59j. That means the real value is positive, imaginary value is negative. In most of the time, especially at high frequency and middle frequency data, middle meaning like 10 Hz or so, we are going to get data, with positive value for the real value and negative value for the imaginary value of the impedance. So usually it is plotted as $-Z_{imaginary}$ versus Z_{real}. At high frequency data, we saw that the total impedance is coming to 20 Ω. The low frequency data is coming to about 120 Ω. And these are going to be the mid frequencies (refer plot in the video).

Another point which I want to note is the frequencies. In UV visible spectroscopy, you would measure from 200 or 300 nm at the lower limit to 700 or 800 at the upper limit. It is going to be every 0.1 nm depending on the specification we give. It will be in linear scale, which means it will start at 400, 401, and so on. Here in EIS, it is usually done in log scale in geometric series. So if you take 1 frequency, I normally will not measure at 1 Hz, 2 Hz, 3 Hz, 4 Hz, and 5 Hz and so on because if you want to go to 10^5, I will have to take so many data points and it is probably not worth it. Instead, I will take 1, multiply it by 1.2, and multiply by 1.2 again. It is going to be 1.44 and so on. So I will reach 10. Then again if you multiply, it will go in geometric series. That means I can cover from 1 to 10 in for example 7 intervals or 6 intervals. So I can say 7 frequencies per decade or 6 frequencies per decade. If I say 1, 2, 4, 8 and 10, next it is going to be 10, 20, 40, 80 and 100. So it is going to go in that way and usually we do not like to take it in harmonics, which means I do not want to take an integer multiple of the base frequency. There are some reasons for that. Right now I am not discussing that. We want to take it as 1, then a fractional number and so on with 5 frequencies, 6 frequencies or 7 frequencies per decade. If you have more frequencies per decade, it is better. It takes longer time, but you will have more resolution.

Normally when you plot (Z_{real} vs $-Z_{imaginary}$), and want to mention the frequencies, you will have to mark at some points which shows 10 mHz, 10 Hz,1 kHz etc. Few points we have to give. Otherwise nobody knows what frequency corresponds to which data. Another point to note is the axis have to be in equal scale. If you take 0 to 25, whatever length we have in the x axis, say 2 cm, y axis also should give me the same number (2 cm). In many publications, it is not done correctly. It will be 0 to 20 Ω in y-axis and 0 to 200 Ω with the x-axis. It will distort the figure. In the current figure, we can see a clean semicircle. The capacitor in the present circuit is an ideal capacitor. Many times the data will actually come like this (refer video). it will be a semicircle which is pushed down. That means this cannot be represented by a simple capacitor. It needs to be represented by a different element. All this information will come only when you plot it in equal scale. The plot is called complex plane plot. This is the correct terminology when we use a 3 electrode system and measure the impedance. When you use a 2 electrode system, you can call it as Nyquist plot. Often, you will see that this is called as Nyquist plot in many journals. But the correct terminology for a 3 electrode system is to say complex plane plot.

The data can also be plotted in another format called Bode plot. In these plots, you can represent the data as a function of frequency. Now look at figure (refer video). The scale is from 10^{-3} to 100 kHz and is given in log scale. So frequency is in the log scale and pink colour line represents the magnitude of the impedance. The round blue colour points are minus of the phase value given in radian. You can represent it in radians or degrees. Magnitude is given in Ω. Sometimes this is plotted in linear scale as well. This representation is called Bode plot. And you can see at high frequency, it settles at 20 Ω. At low frequency, it settles at 120 Ω. It is also clear that it settles around 10 Hz (refer video). So I may not need to take data beyond this. For this system, beyond this, data does not tell much except that it is more or less constant value. For some other system, it may change. This is one way of representing Bode plot. Another way is to use the real and imaginary, here it is actually -imaginary that we want to plot as a function of frequency. If we look at |Z| versus frequency or Z_{re} versus frequency, they appear to be same here pattern wise. Likewise, if I look at -phase versus frequency or $-Z_{imaginary}$ versus frequency, they appear to be somewhat similar; it starts at 0 at the low frequency, ends at 0 and shows the peak. But if we have more complex system, they will not necessarily look the same. In the particular example which we took, it appears to be the same. I want you to keep in mind that if you plot absolute value of Z versus frequency, and -phase versus frequency to represent an electrochemical system, unless you actually calculate and plot, you will not know what it is for real and imaginary.

(Refer Slide Time: 14:45)



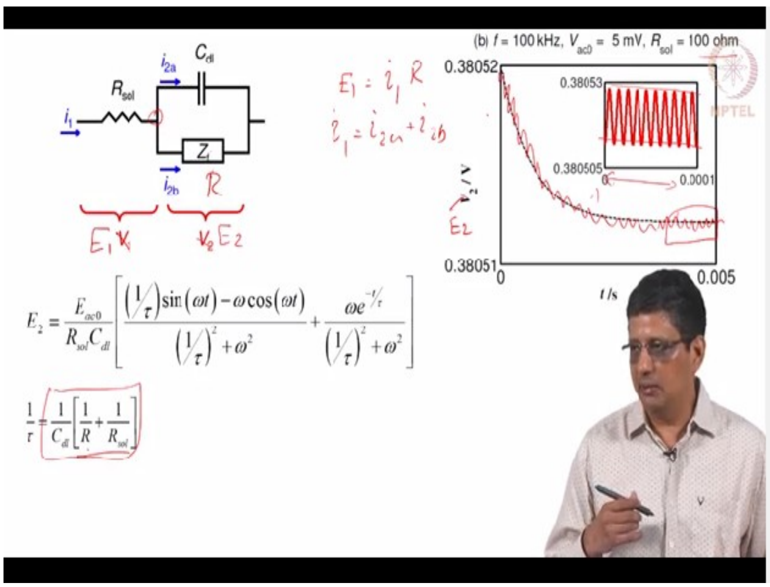
We have done the previous calculation using complex plane notation. If you take the previous circuit and let us say that potential across 1st part is E_1 and 2nd part as E_2. The 1st resistor is represented as R_1. C_1 is the double layer capacitance. Z_f is called faradaic impedance which says it is an electrochemical process. Any process where you have an electron transfer is called faradaic process. That can be represented by a simple resistor. We can write the equation for E_2 and solve (refer the above slide). Now, let's not go to that detail. I will just tell you that it is possible to get a similar expression for E_2 which means you know you can calculate E_1 and then calculate the current. In order to get E_2, if you calculate, you would get a time constant which depends on the double layer capacitance as well as the faradaic impedance and the solution resistance.

Previously, we just looked at one R and one C in series. You have one more R here (faradaic impedance) and that is going to come into the term which represents τ. Now the expression is somewhat similar to what you have seen before. Here you have E_{ac0}, $R_{solution}$ and C_{dl}. Previously, τ was relatively simple expression, but now it is a little more complex expression. You have a sine, you have a cosine and you also have a transient term (refer above slide).

You have tried the differential equation. You will have to say E_1 is given by $i_1 \times R$. Now i_1 is going to be $i_{2a}+i_{2b}$ because any current that comes to this point (1st part marked with red circle in the slide) has to either go as 2a or as 2b.You can calculate i2a using the potential drop across here

(E_2). So $\frac{dE_2}{dt}\times Cdl$ will give you i2a. Potential drop across here (E_2) divided by the resistor will give i2b. So if you use these equations, you can eliminate the remaining terms and E_1+E_2 has to be equal to E_{ac0} sinωt which is the applied voltage. You can write a differential equation in E_2 and like what we have done previously, we can solve and get the expression for E_2. You will have to use the initial condition as, at time t=0, applied voltage is 0. So my claim is if you do this, you will get this lengthy expression with a τ value related to R and $R_{solution}$ and C_{dl}.

(Refer Slide Time: 17:18)



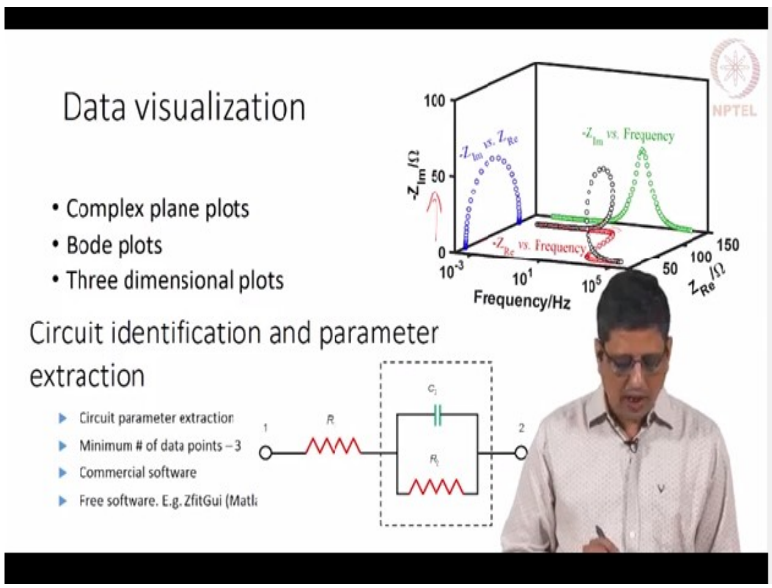
$$E_2 = \frac{E_{ac0}}{R_{sol}C_{dl}}\left[\frac{\left(\frac{1}{\tau}\right)\sin(\omega t)-\omega\cos(\omega t)}{\left(\frac{1}{\tau}\right)^2+\omega^2}+\frac{\omega e^{-t/\tau}}{\left(\frac{1}{\tau}\right)^2+\omega^2}\right]$$

$$\frac{1}{\tau}=\frac{1}{C_{dl}}\left[\frac{1}{R}+\frac{1}{R_{sol}}\right]$$

Now if we do this and then I want to plot this, I want you to see it takes more than 1 cycle for it to settle (Refer to video to fully understand this paragraph). This is done at an example of 100 kHz at 5 mVs and 1 Ω of $R_{solution}$ and certain values of C_{dl} and R, E_2 given as V_2 here, oscillates and settles after sometime. (It means you cannot just say, wait for 5 cycles). It usually settles after some time. So you have to say wait for 2 seconds, wait for 3 seconds, wait for 1 millisecond, some number there. So this goes from 0 to 0.1 millisecond, almost around at that point it settles. So it comes to steady periodic motion after certain time here. Now suppose you are changing the resistance to 100 Ω, for the same system. This is 5 millisecond, it settles after 3 or 4 milliseconds. Previously, it settled much below 0.1 millisecond. Here (with 100 Ω resistance) it settles after 3 or 4 milliseconds. It means here i am showing only the average value.

There are oscillations, goes like this and then because it is harder to see, I have not drawn that there (refer video). I have just drawn the periodically average values. In the very beginning, when I go from 0 to 0.1 millisecond, it looks like it is steady periodic except that there is a slight slant here. I have to really measure it for long time to know how long it takes to settle. And if I plot it here, it will be steady periodic. So when the resistance is higher, value of $\frac{1}{C_{dl}}\left(\frac{1}{R}+\frac{1}{R_{sol}}\right)$ will be low. If this value is lower, τ value is going to be higher. Time constant is larger means it takes longer time to settle.

(Refer Slide Time: 18:52)



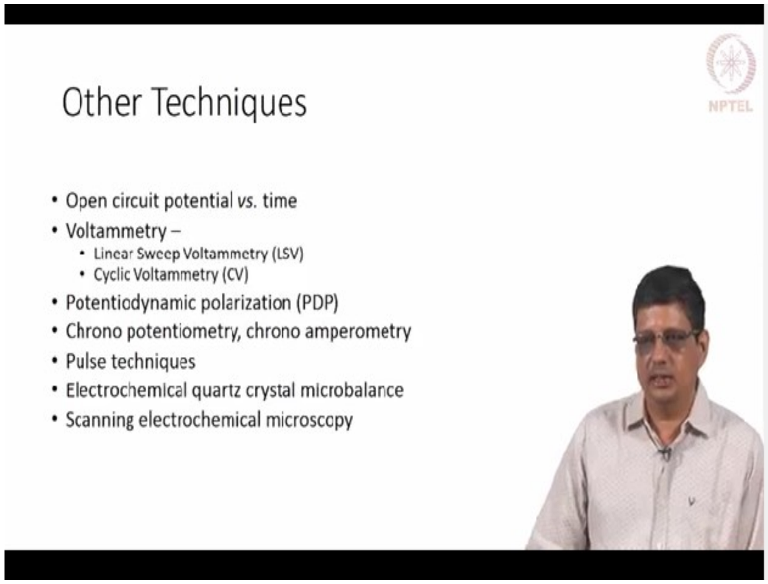
Another way to visualize this data is to plot it in what we call as 3D plot. Frequency is in the x axis here (refer slide or video), real is in the y axis and $-Z_{imaginary}$ is in the z axis. The scale has to be adjusted so that it looks somewhat equal scale. You may not be always able to do that. And the frequency is in the log scale. But if you are able to put it there, you can see this goes like a loop (refer slide or video). So if you visualize, it starts at a faraway point and then it comes towards us and then settles. You can also see how the imaginary will look like. So we can see Bode plot in one part which is $-Z_{imaginary}$ vs. frequency and other part of the Bode plot is Z_{real} versus frequency, and there is complex plane plot as well. This is fine when you plot only one set of data.

If you do experiments and you want to plot at condition 1, at condition 2, condition 3 etc. then you will have 3 sets of data, you can plot them but you cannot really see any difference. It is just going to be completely mixed up. Now which format is the better format?; complex plane format, Bode plot with magnitude and phase or Bode plot with real and imaginary. There is no one answer for this.

What we do is to plot in all 3 formats. And usually we have an idea of what system we are looking at, what is the phenomenon we are studying and then we analyse the data. Usually you will have to compare more than one set of data. We look at the data and see which format brings out the point very clearly. You cannot just say I will plot only in Bode format or complex plane format and do the analysis. You have to plot in all the 3 formats and analyse the data.

So far what we have done is, we have taken a circuit, taken numbers for those values and then calculated the impedance. What we normally do in real life is, we perform experiments, get data and then find a circuit or a reaction that will be suitable for the current system. Reaction is the next level. First level is to know what circuit can be used to represent or model this data. Here we will say we will use this circuit (refer slide or video). You can use other sets of circuits to model this exact same data. But let us say this is a good circuit for the current data. Next is to find the information of R_1, R_2 and C_2 and the best fit for this data. It is similar like in the case say; I have a set of data, I want to fit it to linear equation, y=a+bx and find the best values of a and b. If it does not fit, we may try a quadratic equation. If you have a physical understanding, you may try different sets of equations based on what you think is the correct model. So there are couple of aspects to this. One is to identify the correct circuit. Second is to extract the parameter values from this. Likewise, we should be able to identify the correct reaction and extract the kinetic parameters from that. This is the second level. So if you want to extract parameters from this, I will have to extract 3 elements. For example, if I want to fit this data to a linear equation, y=a+bx; you want to get a and b from this and you need minimum 2 points or 2 pairs. If you want to fit it to a quadratic equation, I need minimum of 3. Although it is better to have many more points to do linear regression. But if it gives you one point, you can get infinite number of solutions for any linear equation. Likewise, as absolute minimum; if i need 3 elements, I need 3 points. But typically, we want to use 50 to 60 points at the minimum. You have commercial software to do this part. It is not that difficult for a simple circuit. For a little more complex circuit, you will have to give correct initial values; otherwise, it will not converge.

(Refer Slide Time: 23:16)



The next part deals with other techniques.