Electrochemical Impedance Spectroscopy

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Lecture – 03

Time Domain Results

Now I want to give you an example where you can actually derive the values and you can get a better idea for a case where you have resistor and capacitor in series. This is one example.

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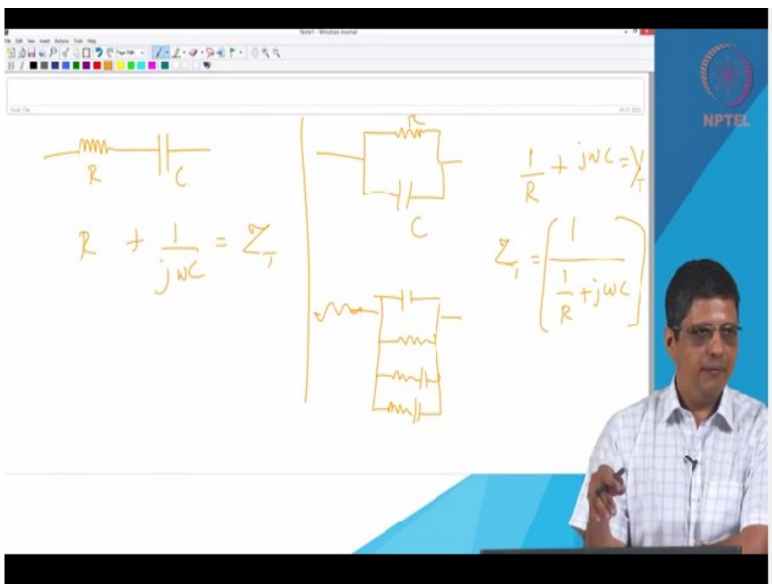

Another example is having resistor and capacitor in parallel. If you look at the second example, it is actually simpler to solve. Previously, I told that you can get the current across the capacitor by using the derivative, $C\frac{dE}{dt}$ will give you the current. From that we wrote that you can get the impedance as $\frac{1}{\omega C}$ for the magnitude. You can write the impedance as $\frac{1}{j\omega C}$. So out here, I can write $\frac{1}{R}+j\omega C$ as the net admittance. First admittance of the top element is $\frac{1}{R}$, admittance of the bottom element is $j\omega C$. I can write total impedance as $\frac{1}{R}+j\omega C$, (it is) easy to do here as long as we know what the impedance of each element is. Similarly, in the first example, I have to add the impedances (to get the net impedance) because they are in series.

Impedance of first element is given by R. Impedance of the second element is given by $\frac{1}{j\omega C}$; and this will tell us the total impedance. Similarly, you can have more complex structures. You can have structures where you have many resistances in series. You can have structures where you have 1 capacitance and 1 resistance in parallel, another resistance and capacitance in series in the same circuit. You can have one more resistance here. These are some of the examples you will see later. But it is possible to do it using this notation.

So I also want to show you how to use the differential equation and still get the same answer. Sometimes it can be lengthy. Derivation can be lengthy but you will get better understanding by going through that. Most of the time, we will just use the complex notation, add the impedances or add the admittances and get the value but you should be aware of actually what happens when you apply a potential or when you apply sinusoidal wave.

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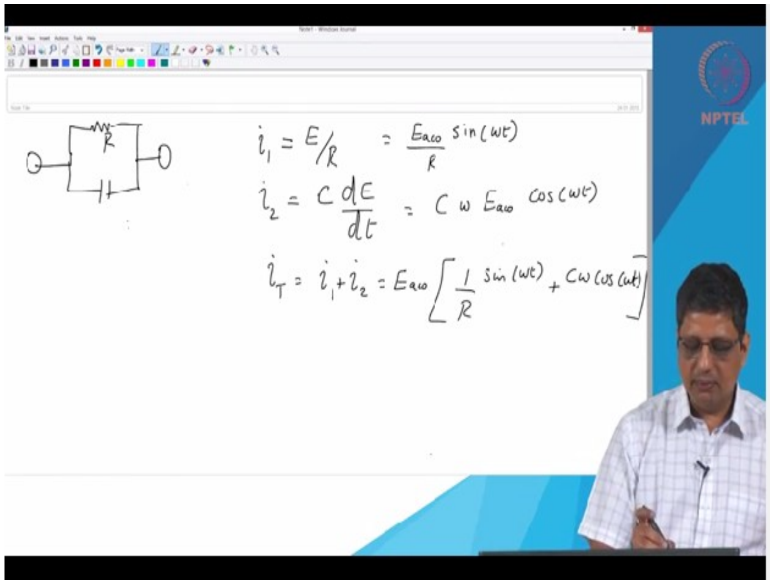

So first we will take the circuit where you have a resistor and a capacitor in parallel. Current through the top part, we will call it as i1 and that is going to be related to the potential applied across the 2 locations between which the resistor and capacitor are connected parallel; $i_1 = \frac{E}{R}$. It is an algebraic equation. Current through the bottom part is given by the differential equation; $i_2 = C\frac{dE}{dt}$. When you apply simple sinusoidal wave, we will write it as; $i_1 = \frac{E_{ac0}}{R}\sin(\omega t)$ and i_2 we will write it as; $C\omega E_{ac0}\cos(\omega t)$ we have seen this before.

And the total current is the sum of the current through the top branch and the current through the bottom branch. I am just taking the E_{ac0} outside this equation.

$$i_T = i_1 + i_2 = E_{ac0}\left(\frac{1}{R}\sin(\omega t) + C\omega\cos(\omega t)\right)$$

Now look at this, the magnitude of the impedance is going to be E_{ac0}/i_{ac0}. That is going to be

$$\frac{1}{R} + C\omega$$

. It is going to depend on ω. (This is) because the capacitor current depends on ω, (i.e. it depends on the frequency).

The magnitude of the impedance is also going to depend on the frequency. The phase is also going to be changing. Phase is not 90 °. Phase is not 0. It is going to be a combination of the current through the resistor and the current through the capacitor. So the phase value will change when we change ω. Phase value depends on the value of R, value of C and the value of frequency.

This is relatively easy to solve. Meaning, you can arrive at this total current and you can plot it for a given R, given C, given frequency. You can use Matlab or any programming language you are comfortable with and plot current as a function of time for a given AC potential. You change R, you change C, or you change ω, what is the effect. You can see it easily. And you can clearly see the phase will change when you change ω.

Normally in an electrical circuit, we are not thinking of changing the R value or C value. You see we apply different AC frequencies, we are going to get results and based on the results, we will interpret the system. Now let us look at the other system. It is going to be little lengthy derivation. But I think it will be worth it.

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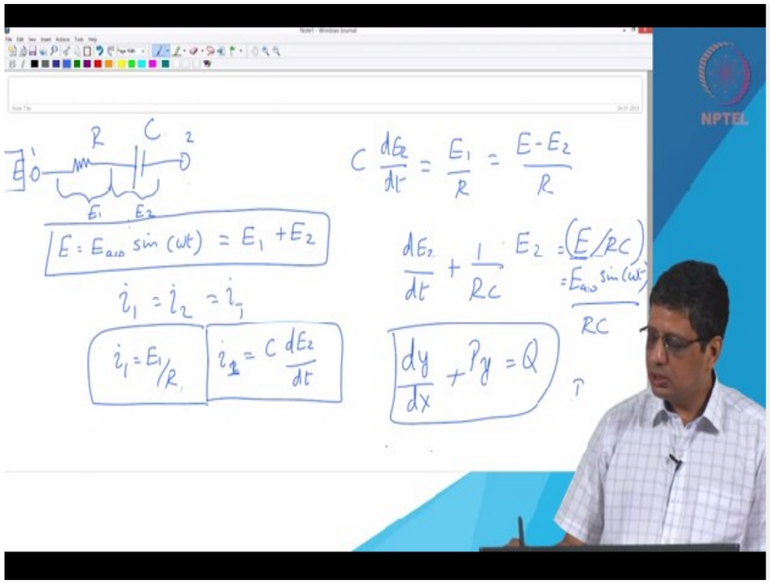

When you actually look at the circuit, it looks very simple and it is simple with R and C connected in series. Now I apply a potential across terminal 1 and terminal 2 and that is given by the value E. We will write it as E_{ac0} sin ωt. The potential drop across the resistor, we call it as E_1 and across the capacitor, we call as E_2 and we can write the total potential drop is going to be sum of E_1 and E_2, algebraic sum of E_1 and E_2.

$$E = E_{ac0}\sin\left(\omega t\right) = E_1 + E_2$$

Now the current through the resistor has to be the same as the current through the capacitor. Whatever current comes to resistor, it has to go through capacitor. So I will write $i_1=i_2$. And that has to be equal to the total current that we measure. We know the relationship between i_1 and E_1;

$$i_1 = \frac{E_1}{R_1}$$

and i_2 and E_2. Potential drop across the capacitor is E_2; therefore, it is going to have the equation;

$$i_2 = C\frac{dE_2}{dt}$$

. Out of these, we know E_{ac0}, we know ω, this is what we apply.

We know the resistance; we know the capacitance. What we want to know is, either i_1 or i_2. We do not know E_1 and E_2. We want to eliminate this. We have 3 equations. We have E_1, we have E_2, we have i_1, i_2. $i_1=i_2$; therefore, we can write this also as i_1. We want to eliminate E_1 and E_2 and get the value for i. Therefore, we can write i=a function of known values $E_{ac0\omega}$, R and C.

Now what I want to do here is to first get a value for E_2. I want to write $C\frac{dE_2}{dt}$. i_1 is same as i_2; therefore, I will write it as $\frac{E_1}{R}$. I will write it as $E-\frac{E_2}{R}$. I can rearrange it and get it as an equation $\frac{dE_2}{dt}+\frac{1}{RC}E_2=\frac{E_{ac0}sin(wt)}{RC}$; R and C are constants now.

On the right side, you have sin(ωt), it is a function of t. E_2, it is going to be a function of t. We have seen this equation before, where P and Q can be constants, R can be functions of x. In this case, our independent variable is t. Our dependent variable is instead of y, it is E_2 but when you have an equation like this, we use what is called integrating factor.

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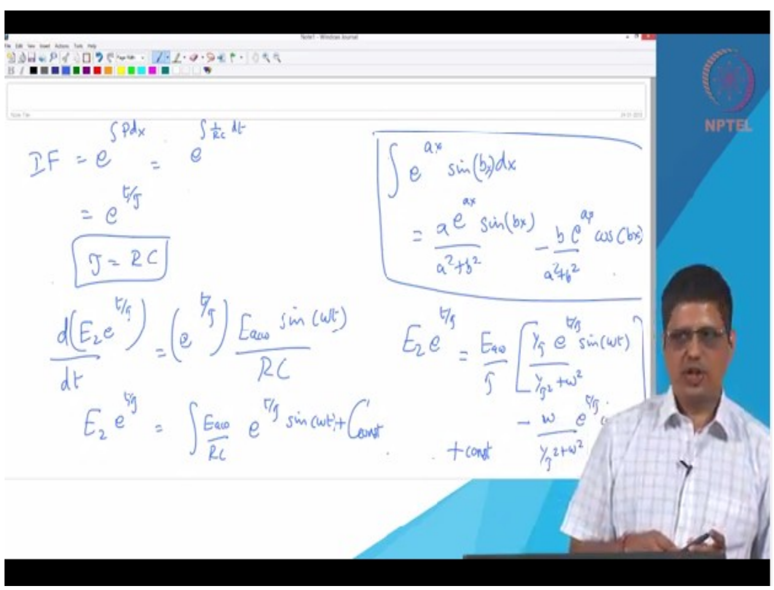

When we use integrating factor, we would write it as exponential. In this case, we will write it as, where we say at time constant τ, is a product of R and C. It has the units of time. We call it as time constant. We will write the integrating factor as e power t/τ. Basically I am expecting that we should be solving this equation and getting the answer for E_2. Once you get E_2, you can get E_1.

And once you get E_1, you can get the current value very easily. We should expect to get the same answer that we got by using the complex notation. If it is in series, we should get $R+\frac{1}{j\omega C}$. Effectively, whether you use this complex notation or whether you use the differential equation when we plot the current or when we plot the impedance, we should get the same answer.

If I use this, I will be able to write; combining together after multiplying by the integrating factor, you can write like this.

$$\frac{dE_2 e^{\frac{t}{\tau}}}{dt} = e^{\frac{t}{\tau}} \frac{E_{ac0}\sin(\omega t)}{RC}$$

So on the right side also multiply by the integrating factor. I can integrate this equation.

$$E_2 e^{\frac{t}{\tau}} = \int \frac{E_{ac0}}{RC} e^{\frac{t}{\tau}} \sin(\omega t) + C$$

C here is a constant, we will just write it as a constant. You can look at the equation of integrating

$$\int e^{ax} \sin(bx)\, dx$$

You can do integration by parts.

Right now just take it for granted that this equation will give you an answer like this.

$$\int e^{ax} \sin(bx)\, dx = \frac{ae^{ax}\sin(bx)}{a^2+b^2} - \frac{be^{ax}}{a^2+b^2}$$

That is, you are going to have factor of $\frac{a}{a^2+b^2}$ and $-b/(a^2+b^2)$ you are going to have the same integrant here. You are going to have $e^{ax}\cos(bx)\,dx$. This is after going through the derivation.

An easier way for you to check is to take a derivative of this expression and then verify that it actually matches with the integrant there.

Now for the equation here, I can use this expression and I would get the value as $E_2 e^{\frac{t}{\tau}}$. On the right side, I have a factor of $\frac{E_{ac0}}{\tau}$ which is same as RC and in addition, I have 1/τ as a, ω as b and on top of all this, I have an integration constant. It is a little lengthy but I do not think it is particularly difficult. What we will do is substitute for the initial condition at time t=0, potential is 0.

It is a sinusoidal wave, so E_{ac0} sinωt. Time t=0, sine is going to be 0. So it starts at 0, total potential is 0, potential across resistance is 0, potential across the capacitance is 0. With that initial condition, if you substitute here, we should be able to get the constant value. Then we should compare what we get here versus what we get in the complex number notation.

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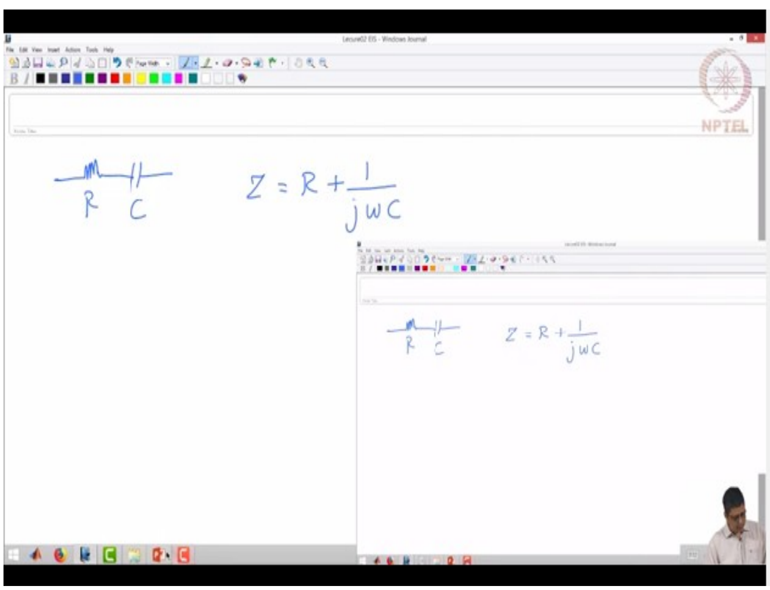

So yesterday, we were looking at this circuit where you have a resistance and capacitance in series and if you write in complex notation, you can easily write the impedance as impedance of resistor and the impedance of the capacitor, add them together, you will get the total impedance. We can write the equation for the current and we have gone through the derivation.

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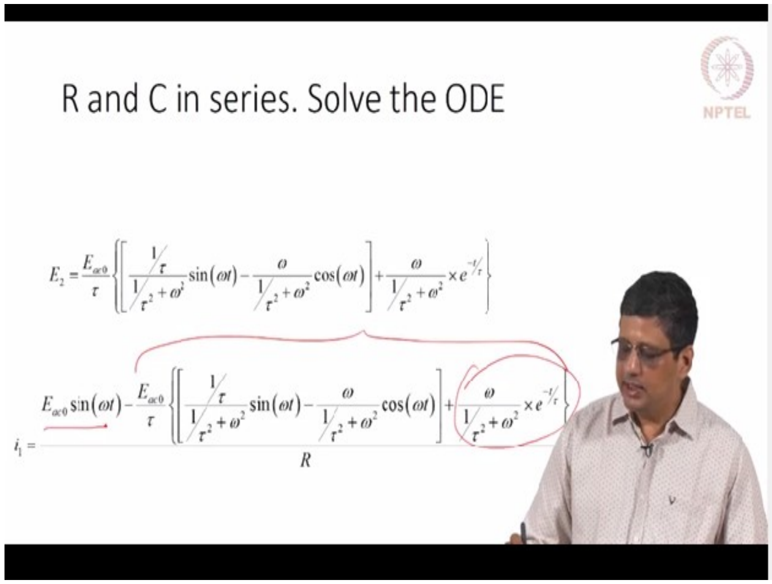

And we can get the potential across the capacitor as E_2, right. We will get a fairly lengthy expression. The point that I want you to note is that there is an exponential term. We know it is a resistor and capacitor in series. So we know the potential across the capacitor. We can calculate the potential across the resistor.

It is $E-E_2$ will give you E_1 and then divide by the resistance to get the current. So again you get an expression saying E here is the potential applied. This is the potential across the capacitor. The difference tells the potential across the resistor. Divide by the resistor value, you will get the current.

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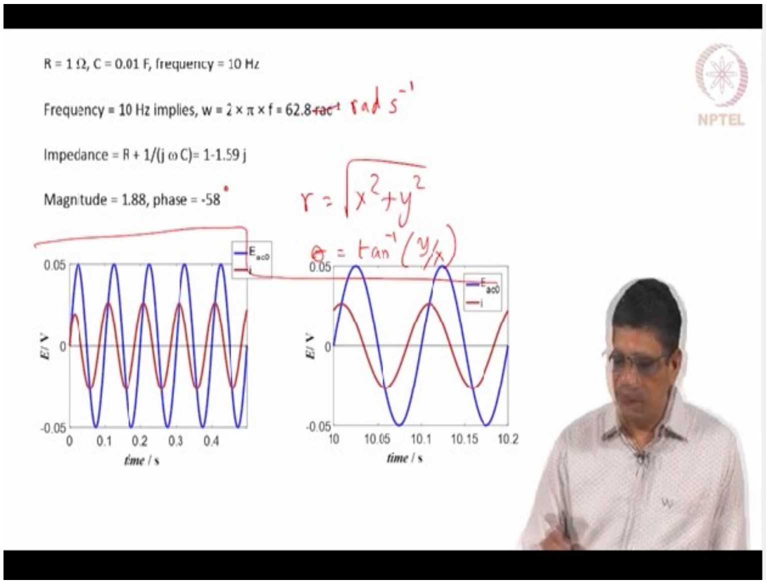

Now I want to give you an example. Let us say the resistance is 1 Ω. Capacitor is of 0.01 F. We apply a sinusoidal wave of 10 Hz frequency, that means in 1 second you will get 10 complete cycles. There are 2 ways of representing the frequency. F is the normal frequency, ω is called angular frequency and that is going to be 2π f and that is given in radian per second.

So if you multiply 2×3.14, whatever number of decimals, ×10, you will get about 63 radians per second. Impedance of course you can calculate as $R+\frac{1}{j\omega C}$, j being the imaginary number and you will get the value of 1-, and I truncated into 2 decimals. You will get 1.59 because you are going to get 1/j. Once you get 1/j, it is going to be –j. ωC; ω is about 60. C is about 0.01. So you are going to get 1.59. if I take the magnitude of this complex number; so if you visualize, you have the abscissa and ordinate. You got 1 on the x axis, 1.59 in the y axis. So it is going to look like a vector in this direction. The magnitude of that vector, you will calculate it as r;

$$r=\sqrt{x^2+y^2}$$

and you are going to calculate the angle as;

$$\theta = tan^{-1}\frac{y}{x}$$

You will get an angle of about 58 ° and amplitude of about 1.88.
Without solving the ODE, you can get this value. This is lot simpler than solving the ODE. But I want to show you what happens when you solve the ODE, the expression in the previous slide, I want to plot the potential in the blue colour line. The current, of course, it is not in voltage. It is going to be in amperes. Current, when you plot it, accounts for the exponential term also. That is you have all the 3 terms that we saw in the previous slide.

We can go back there. See you have one set of terms here and then an exponential term here. This exponential term will go towards 0 at longer time. So in the beginning, you have all the values of importance. Later, this is going to be negligible and the remaining terms will come into play. So when we plot the entire expression, what we get is current starts at 0, it goes up, down, up, down and so on.

The first cycle and the second cycle are not identical. Second to third, there is more or less same. And after that it appears to be pretty much the same. Also notice, although both potential and current start at 0, after sometime, there is a phase difference. We are not synchronised. I have plotted it for time duration of 10 s to 10.2 s. So at 10 Hz, that means 2 cycles are there. 0.1 s is 1 cycle.

You have 2 cycles of potential. Now look at the current value. It has a phase offset and that is stable. So this type of result is called steady periodic. That means it is not steady value. It is periodic. For 1 oscillation to next oscillation, it is not different. So after sometime, it achieves steady periodicity. In the beginning, there is some transient also. Later the transient becomes negligible.

That information does not come by looking at the complex plane notation and adding $R + \frac{1}{j\omega C}$. What you get in the complex plane notation is the steady periodic result. It does not tell you that there is going to be transient in the beginning. It does not also tell you how long it will take for it to stabilize. Here within a cycle, it stabilizes. Second to third cycle, there is not much difference.

But later, we will see example where it takes longer time to stabilize. It is not 1 cycle. You may have to wait for many cycles. Now how do you know that these 2 results are correct, that is I have a magnitude in phase based on one type of calculation. I have plotted current as a function of time using the ODE and they should give me the same result. At a very crude level, visually I want to see this.

This is 0.05, this is probably around half of this. So I can say magnitude of the impedance is going to be potential/current. It is going to be roughly 2. This is 1.88. So if you just eyeball, it looks okay. it does not look wrong. I want to look at the phase. Starting points of these 2 cycles are identical. It is going to be 0 ° phase difference. If the peak occurs at this location, it is going to be 90 °.

Peak in the red line occurs little after the blue line crosses 0. So it is between 0 to 90 °, 60 looks okay. This is the very superficial level of checking. At this level if it does not match, we have a problem. Slightly better way of checking is to actually go in and measure the magnitude or the maximum peak here. We know the maximum here, take the ratio, it has to be 1.88 or 1.87 whatever the number of decimals we have.

Similarly, find the exact time where this crosses 0 and you can calculate the phase. We know the period. Entire period is 360 °. The distance here in the time scale will tell us the difference. So we find this distance divide by the entire period, multiply by 360, should give us the phase difference and that should come to 58. Since the current comes before the potential, 58 here will become -58 ° for the impedance. That is a slightly better way of doing it.

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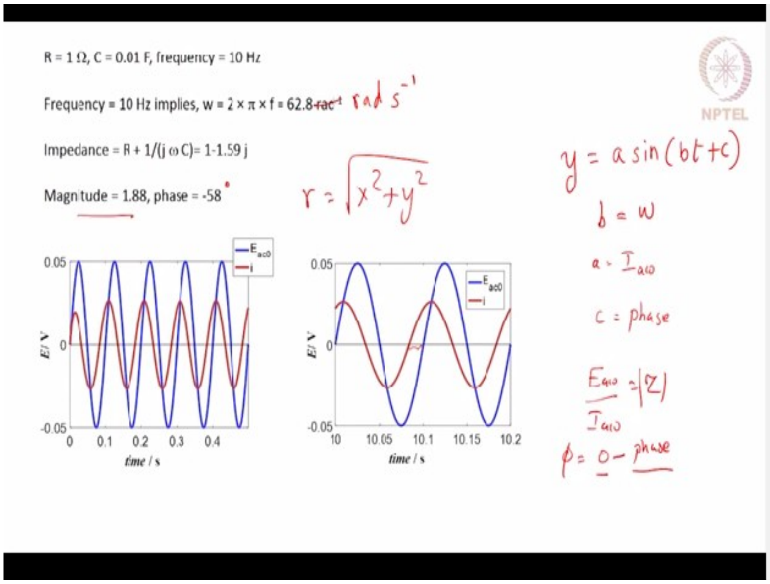

Even better way of doing it is to fit this curve to an equation saying $y = a\sin(bt + c)$. We have to verify that *b* comes out to be the same as ω. '*a*' here will be amplitude. And *c* here will give me the phase. I can take E_{ac0}/I_{ac0} to get the magnitude and check whether it is the same as 1.88. Phase of the potential is 0. Phase of the current is whatever we measure here and if I will take this equation and calculate the phase, I should get this as *0-phase*, (so it) should be -58 °. This is the third choice.

First is to just eyeball. The level you have to make sure it is not wrong. It does not tell you it is correct. It says it cannot be very wrong. Second level is to look at the actual locations where they are crossing and then do this. Third level is to fit it to this equation. And the fourth level is to take this current data and do what is called Fourier transform.

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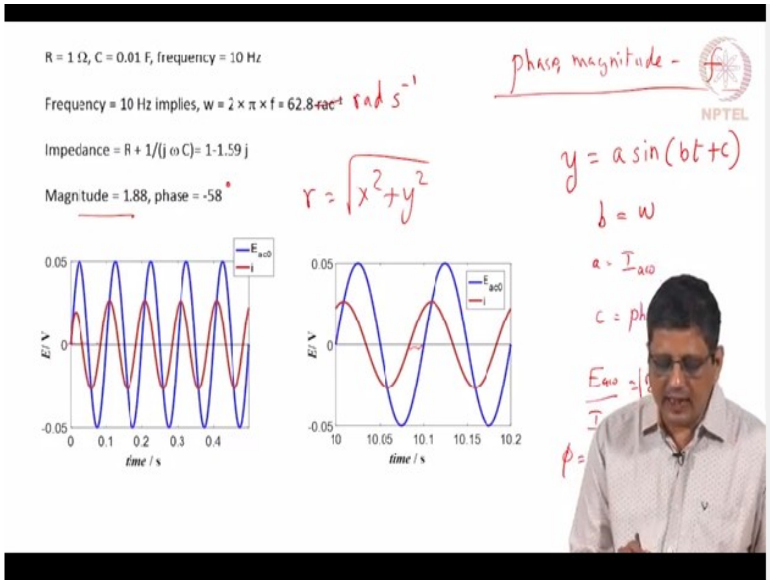

We will go into the details later but using Fourier transform, you can get the phase and the magnitude at a particular frequency. You may have a wave with multiple frequencies combined together. Even then you can use Fourier transform. There are certain ways of doing it so that you can get the data correctly. When I say do the Fourier transform, you are going to get numerical values here. You do not have data at all time. You will have data at certain time intervals.

So you have discrete data. It depends on the sampling frequency. In the actual experiment, it depends on the time we give in the ODE solution. So it is discrete data and pitfalls in using Fourier transform to extract the information. Right now we will not worry about it. We will say if you do Fourier transform, you can get the phase and magnitude at any given frequency and use that to compare with the magnitude and phase based on this.

So sometimes you will have to use the ODE to solve, to understand certain things. You also get to know one more point. If I take the first cycle and fit it to this equation or do Fourier transform, I will not get the correct values. I have to wait for some time and take the steady periodic results. That means when you do experiments, you will have to apply the cycle, wait for some time for the system to stabilize or for the response to stabilize and then take data, that data is going to be a good quality data.

You want to take it as fast as possible, it is not necessarily going to be good quality. Sometime you will have to compromise. If the system degrades over time, you will have to say fine, I know it is not good quality but I want to take it in the beginning itself. I want to take after sometime, etc. But you should be aware of what you are getting.