Electrochemical Impedance Spectroscopy
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Lecture – 02
Rate Constant, Concept of Impedance, Z of Electrical Elements, Differential Impedance

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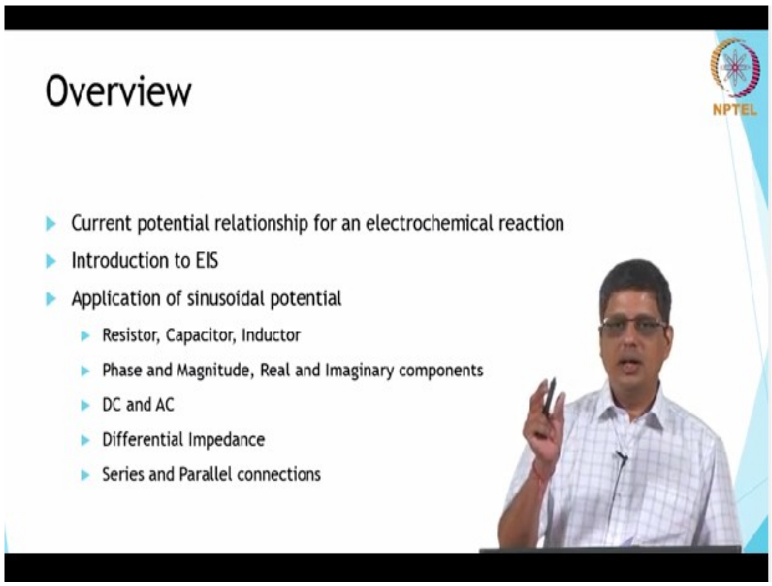

So what we find in the previous class was that we have an electrode, the electrolyte interface and when you have a metal immersed in solution, it forms what is called double layer and you have a potential drop across the double layer. When you want to measure the potential, you can measure it only across two electrodes. You cannot measure the potential drop across a single electrode.

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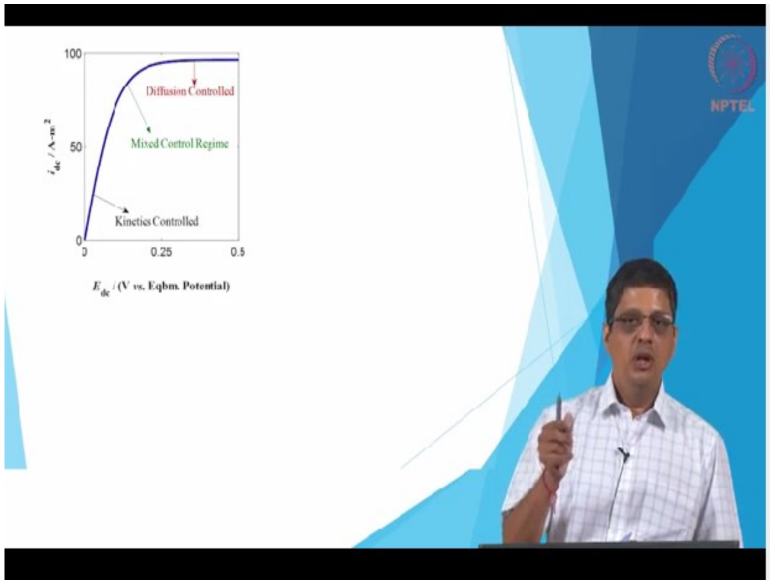

and whenever we want to measure the potential or whenever we want to control the potential, we want to make sure that the changes in the potential occur at the working electrode: the electrode of our interest. Which means the second electrode has to be an electrode where the potential drop does not change. So, we have a special electrodes called *reference electrodes*. We use the reference electrodes and the working electrode and the reference electrode should offer low resistance or low impedance, and in addition, that should not change in the potential. So whenever current comes through, we need to collect the current in the third electrode called counter electrode. So normally we use the three-electrode cell for the electrochemical studies. We also saw that we use supporting electrolyte to minimize the resistance of the solution called, solution resistance. And at that level I think we left it saying that we have to consider cases where you have flow, mass transfer effects, we have to consider the case where the potential changes the rate constant. So if I give you an example of how the electrochemical current changes with potential, you visualize this situation. You have a metal on one side, you have a solution on the other side, the reactant species comes from the solution, diffuses, comes to the metal, reacts, the products that are formed, it may be solid formed on this or it may be diffusing out in the solution phase.

So it has to diffuse, come in, react and then go out. If I give low potential, then the reaction will be slow. Diffusion will be faster compared to this, so the net reaction rate is controlled by the kinetics. If I give large potential, reaction rate will be very fast. When you have a fast reaction, mass transfer becomes the rate limiting step. That means you consume the reactant A, then the reactant A concentration at the interface becomes very low. The product concentration will become very high. Diffusion from the boundary layer becomes the rate limiting step. Beyond the boundary layer, we assume everything is well mixed. If you look at the current, the current will be low at the low overpotential. And in this region, we call it as kinetic control. When you go to very high potential, it is going to be diffusion control. And in between where diffusion and kinetic play a significant role, we call it as mixed control regime.

Later when we (describe) the impedance with diffusion effect, I will also show you how you can derive this expression for this current.

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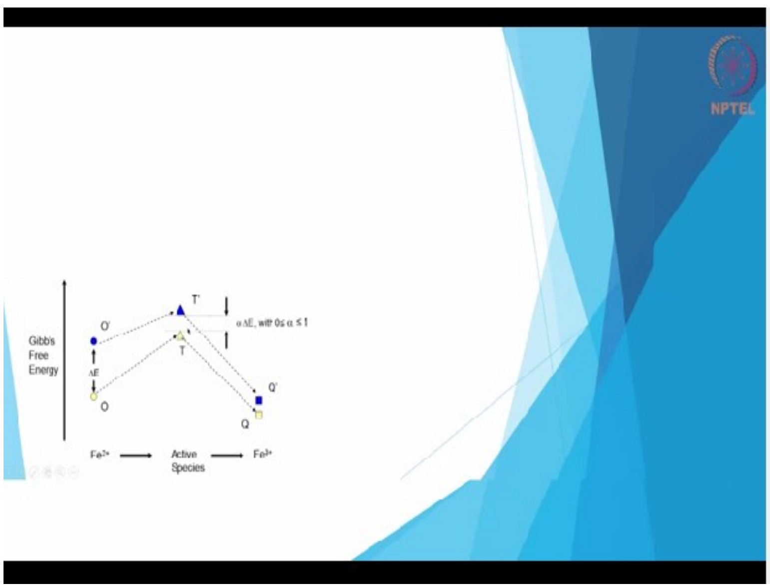

Now how does the potential change the rate constant? When we change the potential, we apply for example, 0.1 V with respect to the equilibrium potential or with respect to the open circuit potential. Not all the 0.1 V will go in helping the reaction go faster. If you have a reaction where Fe^{2+} gets oxidized to Fe^{3+}, it does not happen in one step. Normally we believe that it goes through a transition state, it goes to an excited state and from that it goes to the final step. So if I show this example, O is the reactant state, Q is the product state and the transition state is given by T and when I do not apply any potential, O-T-Q is the pathway, and the y axis is for the Gibb's free energy. If you apply the potential, ΔE, the transition state does not remain at the original place, it also shifts. At the higher potential, transition state also moves, the products Gibb's free energy state also moves. So what happens is, they do not move to the same extent. So they move to a lesser level and that is given by a fraction called α, it is called charge transfer coefficient. It lies between 0 to 1. This case, T will not move to T'. In the sense T and T' will be the same. The worst case, all the ΔE will be superimposed here. Now when I change the potential, this has to go from O' to T' and then come to the product of Q'.

So previously when I did not apply any potential, it has to go from O to T and then to Q. It needed to climb an activation hill. Now it needs to climb a different activation hill. So the rate constant is related to ΔG. Rate constant is given as exponential of ΔG. Now I change the ΔG. Previously it was T - O. Now it is T'- O'. And how much is the change, how much is the difference now is controlled by the value of α.

So if α = 1, we do not have any benefit. If α = 0, you get the maximum benefit. Because now it has to climb lot smaller hill. Typically, α is going to be between 0 to 1. And normally, we do not know the value of α So the standard value, that is commonly taken is 0.5.

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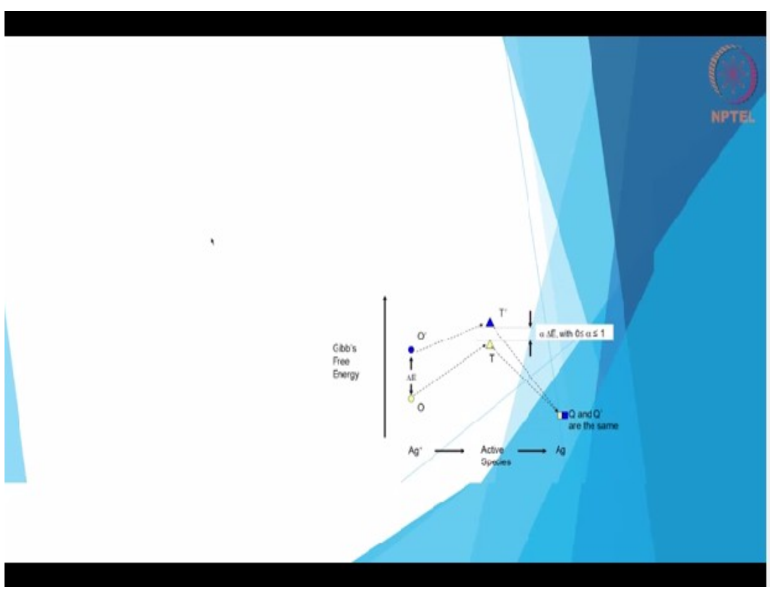

To understand what happens in the little easier way, you can look at this scenario where Ag^+ deposits from the solution onto the electrode. The electrode is held at ground potential, that it is at zero potential. So Q and Q' are the same for this electrode. In the solution, Ag^+ is solvated, it is in the solution and by applying different potential, I can change that Gibb's free energy level of this, and only fraction of it goes to the transition state. Therefore, you get part of it specially taking the rate constant that is part of it is going to help increase the rate constant. This part is going to remain the same and when you write the equation for this, you will find that rate constant is exponentially related to the potential. So first part is that mass transfer plays a role and we have to consider that in most of the cases. We can control the boundary layer thickness by changing the flow rate by rotating the electrode.

Next is the *rate constant*, kinetics can be controlled by changing the *potential*. And it is not linear, it is *exponentially related*.

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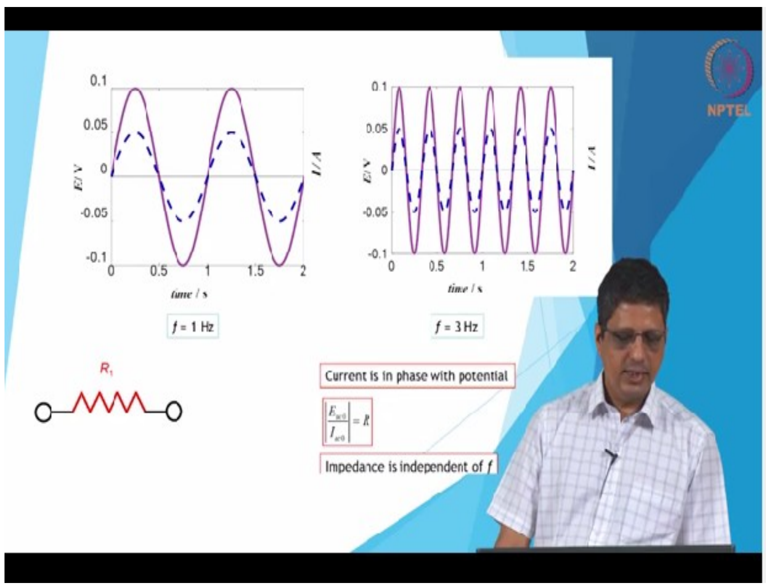

Now we will move on to the concept of impedance. You are all familiar with resistor. You have a resistor; you can apply a sinusoidal wave of frequency. In this example, we have seen sinusoidal wave of 1 Hz. The potential here is given by the violet colour line and the current, it is on the right axis, I have not given numbers for that, the magnitude is represented by the maximum or peak value.

First point to notice is that when the potential starts at zero, current also starts at zero. When the potential is maximum, current is at maximum. That is current follows the potential without any phase difference, they are in sync. If you change the frequency from 1 Hz to 3 Hz or any other number, in 1 second in this example, we will have 3 cycles completed. The current value does not change. If you look at the peak value here and the peak value here, at 1 Hz and 3 Hz, peak values are the same. The current is still in phase with the potential. So, for a resistor, the current is always in phase with the potential. The phase difference is 0. The current value does not depend on the frequency. I also want to show you what happens when you have a capacitor. We also want to see what happens when you have an inductor.

These are electrical elements and later, we will see what happens when we have electrochemical reaction. So in this, current is in phase with potential and you can get the magnitude of E_{ac0}/I_{ac0}, that gives you the resistance and this is also called the impedance of the resistor and that is independent of the frequency. We will move on to the next example where you have a capacitor.

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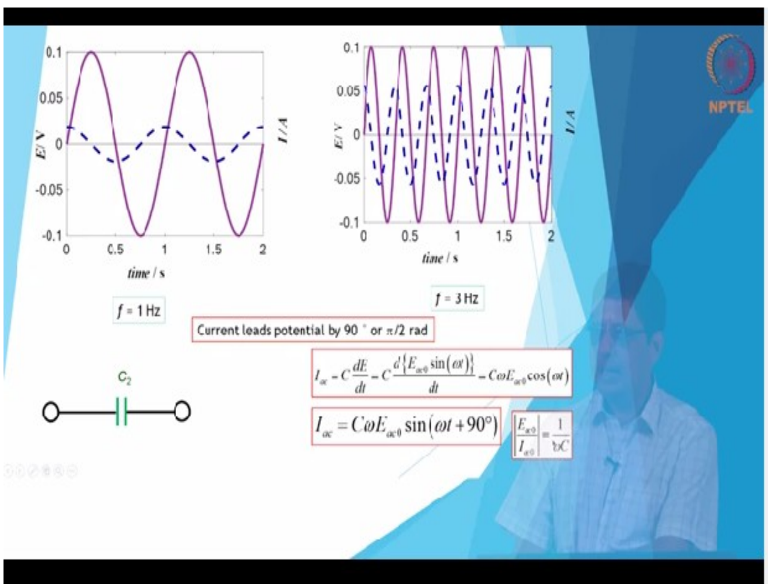

Again the potential is given in violet colour and the current is given in the dashed line, blue colour line. First point to notice is that there is a phase difference. The current starts at zero here and the potential is at zero V here. So the current comes actually before the potential. If I take this as a sinusoidal wave, starting here, it goes up and completes a cycle. Potential starts here, so current actually leads the potential, it comes before the potential. This is after we apply few cycles. this is how it will come. When I start giving the potential here, the current will not start here. Current will also start at zero. But then it will stabilize within a cycle. And afterwards, when I look at the second, third, fourth cycle, starting as time t = 0 at the beginning of the second cycle or the third cycle and then draw the potential, this is how the potential will look like and this is how the current will look like.

So current will have a phase offset. Second, look at the magnitude here, i t is at certain value. If we change the frequency, this is what I would see. I increase the frequency, it goes from 1 Hz to 3 Hz; Within a second, I have 3 cycles, potential cycles. Now I still have 90 ° offset or π/2 radians offset. You have 2π radians for 360 °. So 90 ° will correspond to π/2 radians.

You also see that the magnitude here is smaller compared to the magnitude here. These are drawn at the same scale, although I have not given you the numbers. So at higher frequency, you get more current for the same potential. So the peak potential is 0.1 V here, peak potential is 0. 1 V here. Current value is a low value here compared to high value here. So the first point to note is that current leads the potential by 90 °.

The relationship between the current and the potential for a capacitor is given by the differential equation. So, *ac* current is given by C, it is the capacitance, multiplied by the derivative of potential with respect to time. And because it is a sinusoidal wave, you can write the expression. C is the capacitance that will not change for a given capacitor. But whenever you change the frequency, I will get a different current magnitude.

Because when you take the derivative, you are going to get the ω out and then sine will become cosine. Sine becomes cosine, you can write cosine as sine with 90 ° offset. So this shows the relationship between current and potential. This equation gives you for a capacitor, how this impedance can be calculated. If I want to calculate the magnitude of the impedance, I have to take it as potential/current, and the absolute value is given by the bars here.

I can take the ratio of E_{ac0}/I_{ac0}. The phase difference is 90 °, that comes here. Current actually leads this. But the impedance (magnitude) is given by 1/(ωC). So whenever the ω value increases, [ω is called the angular frequency], whenever the frequency increases, impedance will decrease. So for the same current magnitude, you will get more current. Higher frequency, it is easier to pass through the capacitor. (At) Infinite frequency, it will offer zero impedance.

So normally resistance is something where we say, potential divided by the current will give you the resistance. Impedance is something where you have a potential divided by the current but you also have to know the phase. So it has magnitude and a phase. In case of resistor, the phase is zero. In case of capacitor or in case of an inductor or in general for a reaction, you will have to expect that the phase may or may not be zero.

So sometimes impedance is called as the *generalized resistance* or it is also called as the *vector ratio of potential to current*, sometimes it is referred to as *transfer function*. You give potential, you can calculate the current, these two are related by a transfer function. So there are different ways of expressing (impedance).

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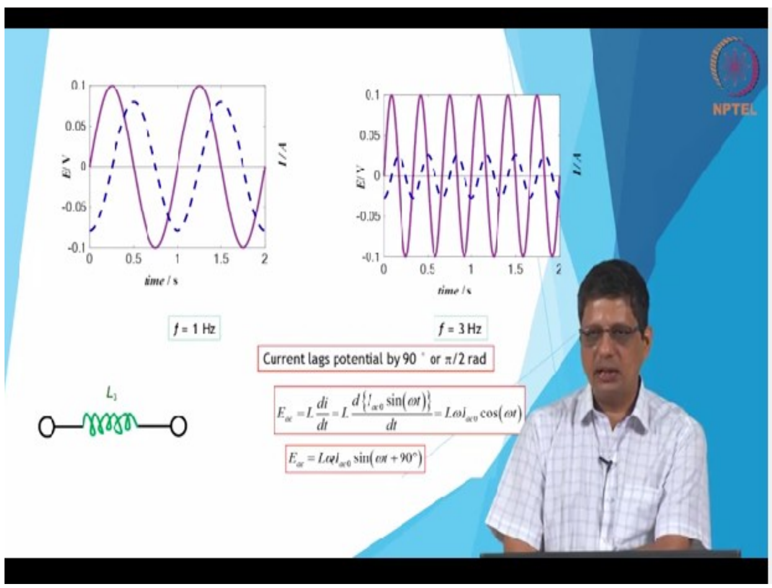

And the third example is for an inductor. For an inductor, there is a phase offset but it lags behind the potential. Current lags behind the potential. So potential starts here, it goes up and comes down and completes the cycle. For the inductor, the current starts with a π/2 radians or one-quarter of a cycle later. So it lags by 90 °. It is similar to capacitor except that it lags here compared to the capacitor in which it leads.

And for 1 Hz, it has certain magnitude. If we apply 3 Hz, the magnitude here actually is lower. So for an inductor, if you go to higher and higher frequency, you will get less amount of current. So here the phase lags by 90 ° or -π/2 is the phase difference. And the relation between potential and current is given by the differential equation where L is the inductance, that is a constant for a given inductor. If you want to find the current, you have to integrate it. Right now, we can just get the relationship between potential and current by taking the derivative of the current with respect to potential, sorry with respect to time, and again you can write the cosine as sin(ωt+90 °), except that now the current lags. You can find the magnitude of E/I and that is going to be ωL. If I take the equation, rearrange it, so that I get $\frac{E}{I}$, I will get ωLsin(ωt+90 °).

Phase difference comes here and then the remaining part is the impedance. So here what it means is for a given inductance, if I ask to, this is the capacitor, what is the impedance? You will have to ask me what is the frequency of the wave that you are applying, then I can tell you what the impedance is. If it is a resistor, this is 10 Ω, the impedance is 10 Ω. If it is inductor, I have to tell you the inductance, if it is a capacitor, I will have to tell you the capacitance. In addition, you also have to be given the frequency.

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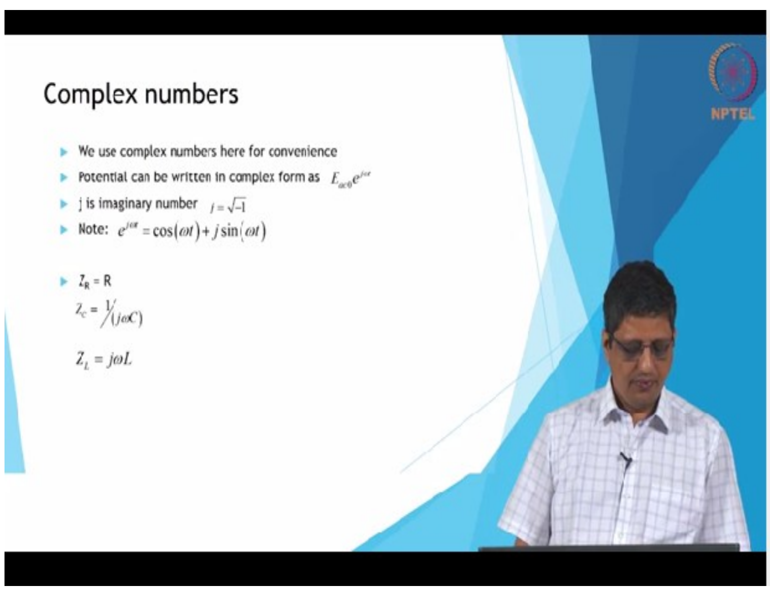

Now we usually represent impedance as a complex number. See we saw the current has a magnitude and phase. If you take the vector ratio of potential to current, that also has a magnitude and phase. Magnitude of the potential divided by the magnitude of the current will tell magnitude of the impedance. Phase of the potential which is usually zero because we are applying the potential, we say at time = 0, it just starts; therefore, phase is zero.

Phase of the potential minus the phase of the current will tell us the phase of the impedance. Now we have 2 quantities. One is the magnitude, it can vary from zero to any number, any positive number. Another is phase which can vary from 0 to 360 ° which means we can represent this in polar coordinates. We can also represent this in Cartesian coordinates. We can write it as real + imaginary.

Now do not think because it has an imaginary number, there is something unreal about this. It is just the convenient way of representing phase and magnitude in one number. One number here means complex number. So we can call it as one number. We can also call it as pair of numbers, real part and imaginary part. We can also say it has a magnitude and phase. So *we use complex number for convenience*, not because the imaginary part of impedance is somehow unreal.

Potential, we can write it in the complex form as $E_{ac0}e^{(j\omega t)}$ where j is given as square root of -1. It is an imaginary number and normally *i* is reserved for current density in the electrochemical impedance spectroscopy; *i* is reserved for current in the electrical circuit, so we do not want to use *i* for square root of -1. [In normal complex numbers mathematics], you would use *i* for imaginary number, but not in this course.

Here we use *j*, of course, sometimes you will have confusion when someone uses *j* for current density. So, in this course, we are just going to keep *i* for current density or current if it is an electrical circuit, and *j* for square root of -1. Now $e^{i\theta}$ or $e^{j\omega t}$, you can represent it, you can write it as cos(ωt) + j sin(ωt). You are familiar with what is called De Moivre’s theorem.

So it is possible to write it as sine and cosine. Sometimes, it is convenient to use it as an exponential, sometimes it is easy to use it as sine and cosine; whichever way is convenient we will use it that way. Likewise, sometimes we will use polar coordinate, sometimes we will use cartesian coordinate. When you have a complex number, if you want to add or subtract, it is easier to do it as a real + imaginary.

If you want to multiply or divide, polar coordinates is easier to handle. So we will just use whatever is convenient to us. Z is normally used for impedance. So Z here refers to impedance of a resistor and that is given by R. Impedance of a capacitor, we would write it as 1/(jωC). 1/(ωC) is the magnitude, 1/*j* tells [1/j is $\frac{1}{\sqrt{-1}}$, that is going to be -*j*, that really tells that] the current is leading by 90 °, that means impedance is going to have [a phase of] -90°.

Now if you visualize in the complex plane, you will write it as *x* axis here, *y* axis here. This is the real part; this is the imaginary part. -*j* means, it is -90 °, +*j* means it is going to be above this real axis, it is going to be +90 °. So impedance is given by 1/(jωC), impedance of a inductor is given by (jωL). This is just another way of saying the impedance has a magnitude of ωL and it is going to lag by 90 ° if current is going to lag by 90 °, impedance is going to have +90 °. Since impedance is potential divided by current for the magnitude, the phase of impedance is potential phase - current phase.

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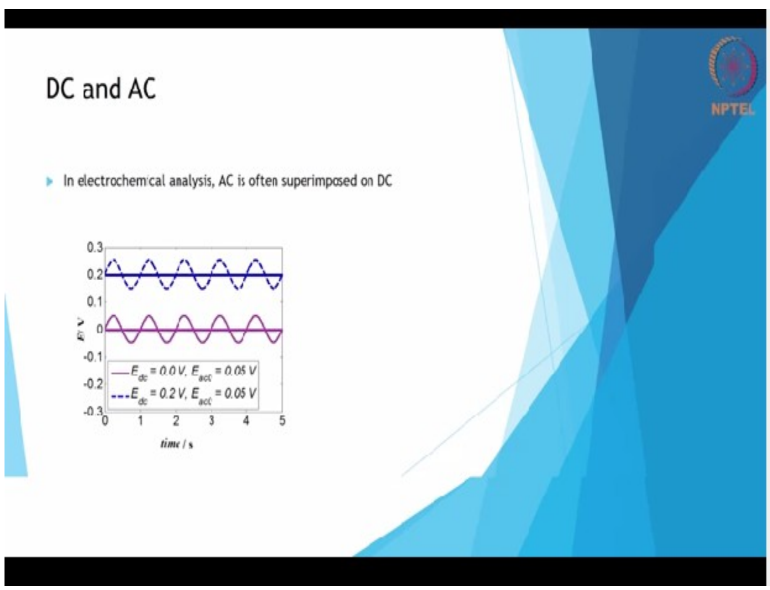

In actual electrochemical impedance measurement, many times we superimpose an *ac* on top of *dc*. Many times we will just use an *ac*. Many time meaning, depending on the type of experiments you are conducting and what you want to measure, you may superimpose an *ac* on top of *dc*. If you look at the violet colour line, it is just an *ac* with zero *dc* bias. If you look at the blue dashed line, it has a 0.2 dc and 50 mV of ac superimposed on it at particular frequency. 1 cycle, 2 cycle, 3 cycle, 4 cycle, 5 cycles in 5 seconds, so 1 Hz frequency. And you will not get the same impedance value. In a simple electrical circuit, it will not show any difference. When you have an electrochemical reactions, when you superimpose a *dc* and *ac*,[i.e. *ac* on top of *dc*], you will get a different impedance.

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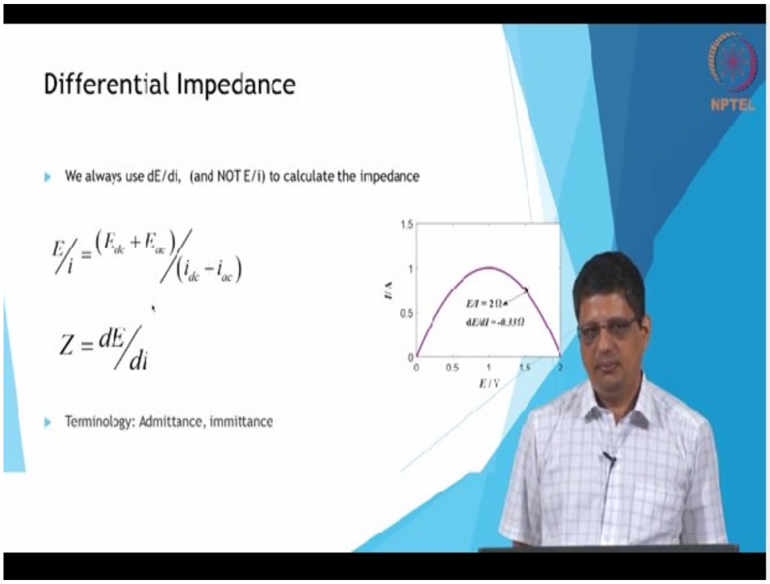

Now another point is very important, which I want you to note is that when you use the equipment and measure the impedance, what you measure is actually '*differential impedance'*. Differential impedance means, it is dE/di. It is not E/i. And there is a difference. I will show you with an example here. Let us not worry about what type of reaction will give us this type of curve. Let us just say current versus potential, if I draw, it is going to go like this and come down.

It is going to increase up to 1 V and then it is going to decrease. When you have a metal immersed in a liquid, when you apply potential, it may form a passivation on top of it. So when you go to higher and higher potential, it may form a passivating layer which means the current will decrease after sometime. Low potential, it may not cover the surface, passivation layer may not cover the surface, you may get higher current as you increase the potential. But beyond a limit, it can decrease. So it is not an unrealistic example. If you take the value of E/i, E here is in 1.5 V. It is on x axis and i is, let us say 0.75, you are going to get 2 Ω. If you take the dE/di, the slope here is going to be di/dE, correct? dE/di, I am going to get a value of -0.33. First point to notice, it is negative, and then the value is different from the E/i value that we got before; because the slope at a particular location is not going to be equal to the value at that location. Slope is different and the value is different. And what we measure experimentally is dE/di, it is not E/i, which means you should not be surprised to see negative values of impedance. We will elaborate more on it when we show example reactions where we show that if this type of reaction for these kinetic parameter values, you will get negative impedance and this is the physical meaning of this.

So if I measure E/i, I will have to write $E_{dc} + E_{ac}$ because here I will take a DC potential of 1.5 and on top of it, we will superimpose an AC and we will have a current which has a DC value and an AC value. But we are not going to look at E/i, we will only look at E_{ac}/i_{ac} and there are other terms used: one is *admittance* which is basically inverse of impedance. Impedance is denoted by Z, admittance is usually denoted by Y and some papers, usually the older ones will use a term called *immittance*, that is a common terminology for both impedance and admittance. So this way we are measuring immittance unless they really tell you what exactly they measure, it can be either impedance or admittance.

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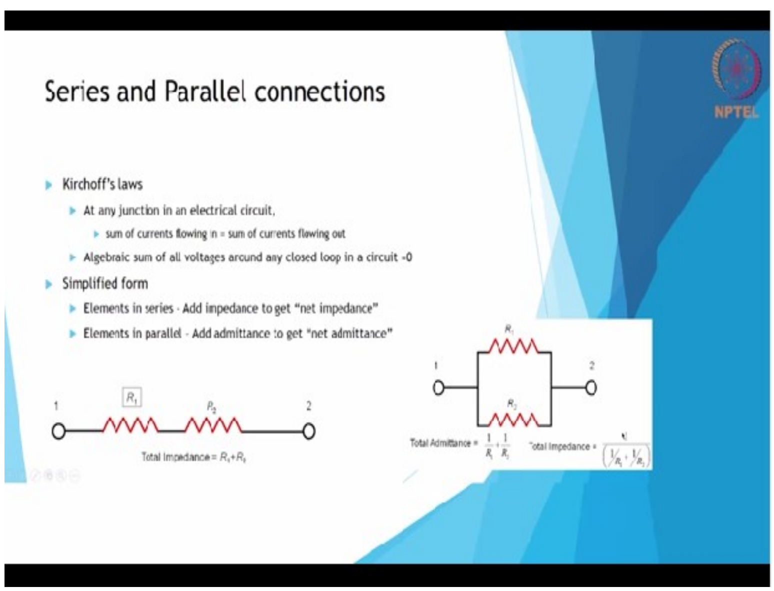

Next when you connect 2 elements in series or parallel or any other way, we want to be able to calculate the impedance, for the entire set. The more general laws are called *Kirchhoff's laws*. If you look at any junction, sum of the current that flows in must be equal to the sum of the current that flow out. Normally, if you just look at 2 elements, simple cases, whatever comes in has to go out.

Second, if you take a close circuit, closed loop, and I take their potential, algebraic sum, means if you are going from A to B and then B to A, that has to have zero potential. So that algebraic sum of all potentials around any closed loop is zero. That means if you go from A to B this way or this way, I should have the same potential. If you go from A to B in this way, B to A is going to have the negative value, it has to be equal in magnitude opposite in sign.

Now most of the time, we will look only at elements in either in series or in parallel. Although these laws can be applied even in much more complex situations, we will look at cases where they are in series or in parallel. If you have 2 elements in series, in this example, I have R_1 and R_2. The total impendence, I measure between the location 1 and location 2, that is going to be the sum of the impedances here.

If I put two elements in parallel, R_1 and R_2, the admittance has to be added to get the total admittance. So admittance of R_1 is going to be $1/R_1$. Admittance of the second element is going to be $1/R_2$. Sum of this will give us the total admittance, total impedance is going to be inverse of the net admittance.