**Physics of Renewable Energy Systems**
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Lecture - 51
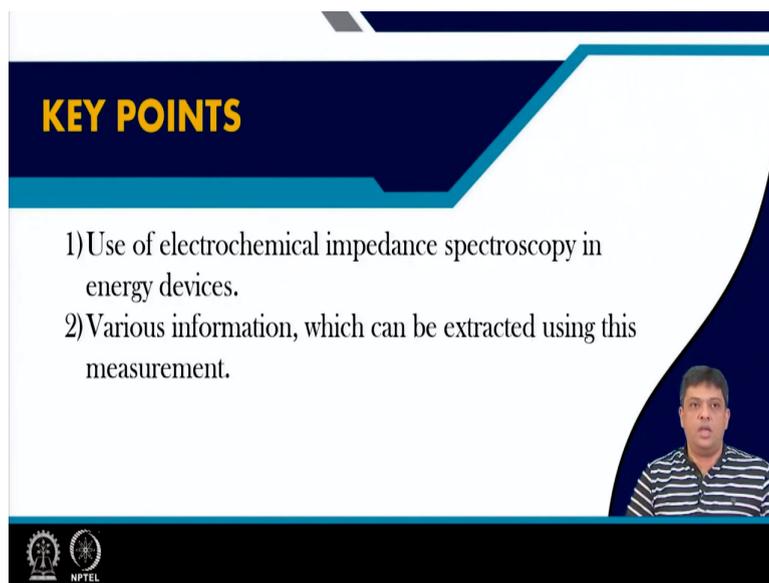**Electrochemical Impedance Spectroscopy**

Welcome again, let us start our discussion on the next characterization tool that is extensively used in electrochemical systems and few other applications which have been discussed in this course, and that technique is called Electrochemical Impedance Spectroscopy. In today's lecture, we will give you the basics of impedance spectroscopy.

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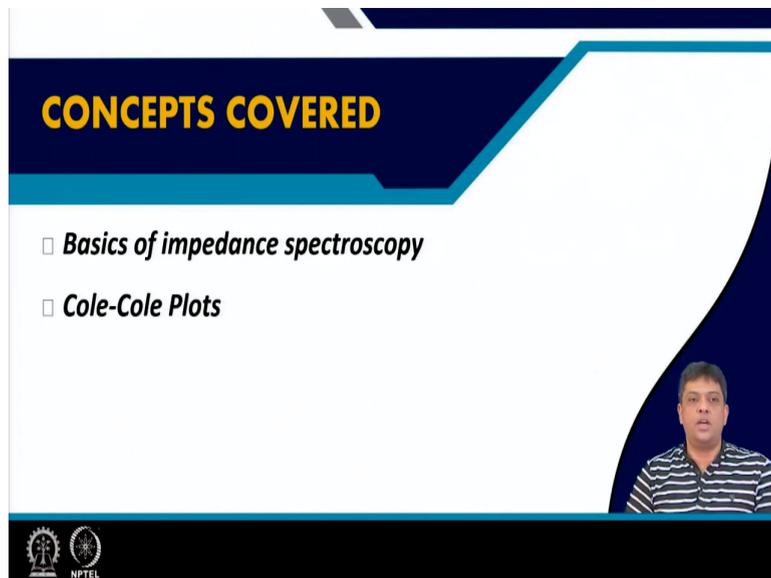
You may have heard about the term cole-cole plots. So, what are these cole-cole plots and how do we reach to these cole-cole plots would also be discussed today.

And then you will be able to clearly understand the importance of electrochemical impedance spectroscopy many times also called as EIS the importance of EIS in energy devices and characterization of these energy devices. And, you will also be able to understand the range of parameters which can be determined by performing the experiments that are utilizing the concepts of EIS.
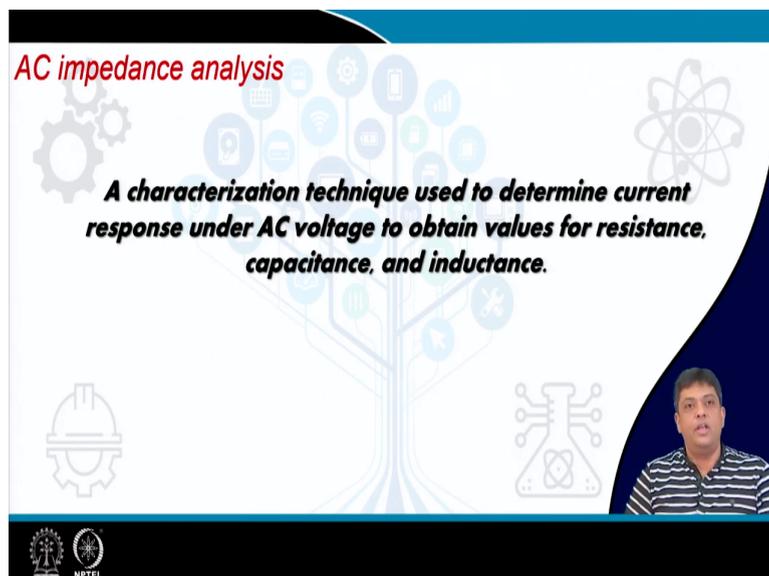
How do we actually define AC impedance analysis? This is a technique which is used to determine current response under AC voltage. What do we mean? We mean that we are going to find out the changes in current as a function of applied AC voltage and this technique can

be used to obtain values. Values of what? The components such as the resistance capacitance and inductance. So, this technique will be giving you the values of resistance capacitance and inductance which are associated with a given circuit or a device.

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What have we understood, right from our school days, if you have voltage then the current lags by 90 degrees. So, if you have a voltage then the current lags it by 90 degrees. Which means that there is a phase difference which exists between voltage and current. Suppose, we write the voltage, variation in voltage be sinusoidal in nature.

So, you write V_t is equal to V_m sine omega t, V_m is the maximum voltage, which you are looking at, omega is the angular frequency. The corresponding current would be It is equal to I_m, sine omega t minus theta, because you have the change in the phase. So, you are lagging. So, therefore, current lags by 90 degrees.

The amplitude of the AC voltage and current is written as V_t is equal to V_m exponential j omega t and it is equal to I_m exponential j omega t minus theta this is the way you write the amplitude of the AC voltage. How do you define impedance? V by I and if you talk about the magnitude of the impedance then you take the modulus and that is V_m by I_m, but from this curve, it is very clear that your impedance will have the real part and the imaginary parts.

So, Z would be equal to Z dash plus I Z double dash or j double dash, whichever notation you would like to use. So, you have two things real part and imaginary part of the impedance the

real part which you see is the resistance and the imaginary part actually is associated with the reactance and this reactance includes the contribution from the capacitance and the inductance that is the capacitive effects and inductive effects are leading to the appearance of the reactance. So, real part imaginary part both these factors have to be carefully examined.

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Figure: Complex plane plot of impedance
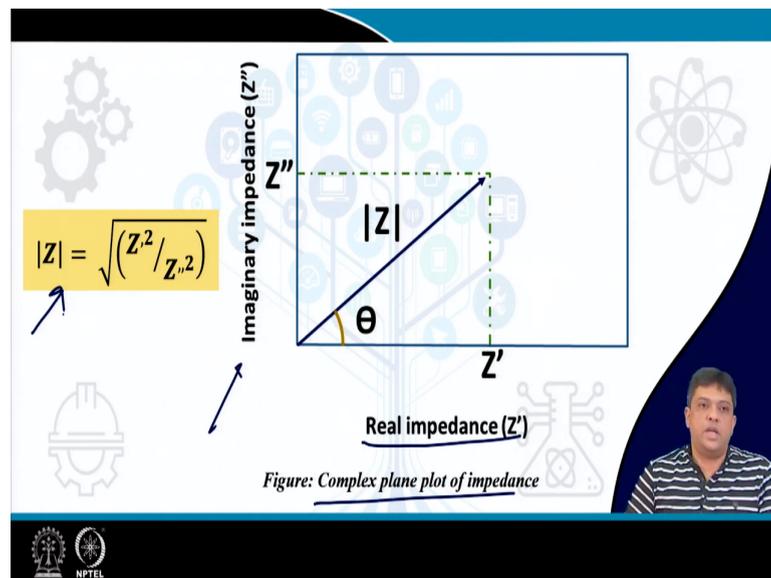
You can plot the real part and the imaginary part and you get the complex plane of the impedance and from there, you can clearly see that Z double, the amplitude would be equal to under root Z dash square by Z double dash square. So, you will get in a complex plane. You can plot the impedance.

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If you do not consider capacitance then how do you relate charge with voltage you have Q is equal to C V, we have already defined the value of V and the way V is defined is. What? Vt is equal to VM sine omega t, then use this definition here and what will you get, Q is equal to C. V_m sine omega t. What is current? Current is dQ by dT. So, you will get It is equal to I omega, I_m cos omega t.

So, you can plot the out of phase component and in phase component, so you can, in the linear part you get the amplitude and then you get the phase this is what you can clearly see, that, if you go from DC to AC side, you go to omega very high frequencies, then what you obtain and if you go to Dc side, then what you obtain. And, then as you go on going from low frequency to high frequency side, what happens? So, this is what you are going to see, the points of R_e and R_f will become clear in the next few slides.
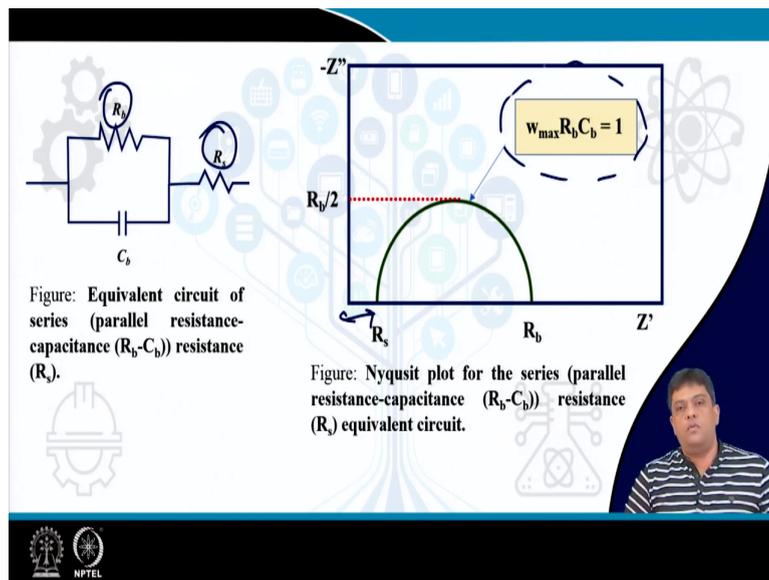
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Figure: Equivalent circuit of capacitance + (resistance – capacitance)

For neglectable values of Cb, the circuit exhibits characteristics similar to a Rb–Ce equivalent circuit.
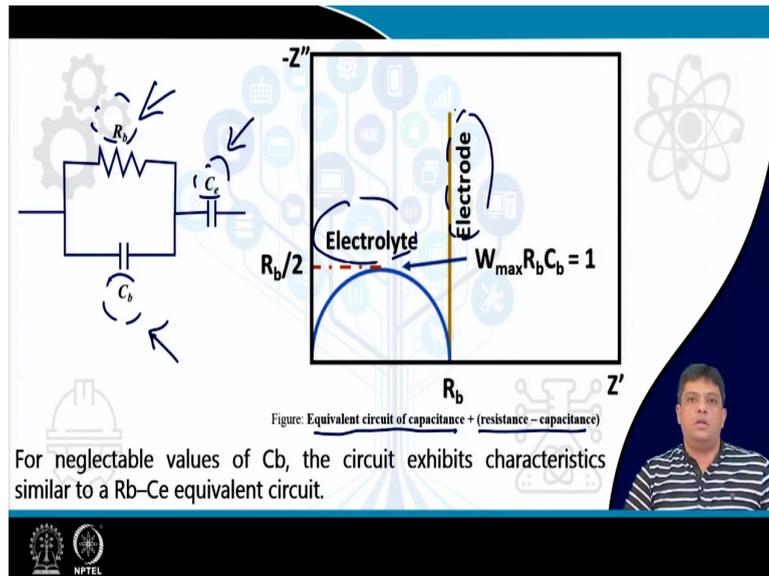
Now, if you look into any system which we have discussed in now, then what you will see that they can be represented as a equivalent circuit. So, you have R_b, C_b and C_e. So, you have the double layer capacitances. The capacitance is like the IR drop of the electrolyte very stains the interfacial resistances and then you have the capacitor effect.
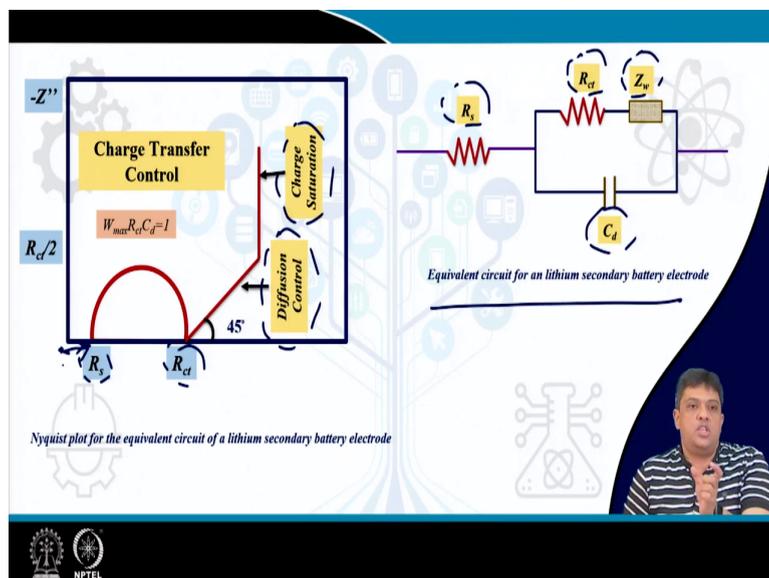
So, you have the effect and if you plot this curve, then this is given by the equal and circuit of the capacitance and resistance minus capacitance effect. So, you get contributions from electrolyte and electrode So, you get two components which are given. So, omega max Rb, C_b is equal to 1, then you are getting the value for the electrolyte resistance.

Figure: Equivalent circuit of series (parallel resistance-capacitance (R_b-C_b)) resistance (R_s).

Figure: Nyqusit plot for the series (parallel resistance-capacitance (R_b-C_b)) resistance (R_s) equivalent circuit.

Similarly, you can draw for any other parallel resistance effect. So, under earlier case we had R_b, C_b, C_e, here we have R_b, C_b R_s, and then you can see that there is a shift in the point you get the semicircle. So, again you can get the value of omega max and from there you can see what is the value of R_b, C_b.

Nyquist plot for the equivalent circuit of a lithium secondary battery electrode

Equivalent circuit for an lithium secondary battery electrode

Hence, if you look into a lithium-ion battery, which is secondary battery then it can be given us a series for instance, a charge transfer instance is there then you have the impedance and you have the capacity. So, you have the, the capacity which is of the battery. So, what you

obtained then you perform the measurements you will get various nature. The linear curve is coming in from the charge saturation.

The one which is increasing at 45 degrees, then that is coming in from the diffusion control and you have the values of our R_{ct} and R_s and this gives you the internal resistance. So, you have the internal resistance because of which you see the semi-circle is not going to 0, so there is a IR drop. So, that is giving you the IR drop.

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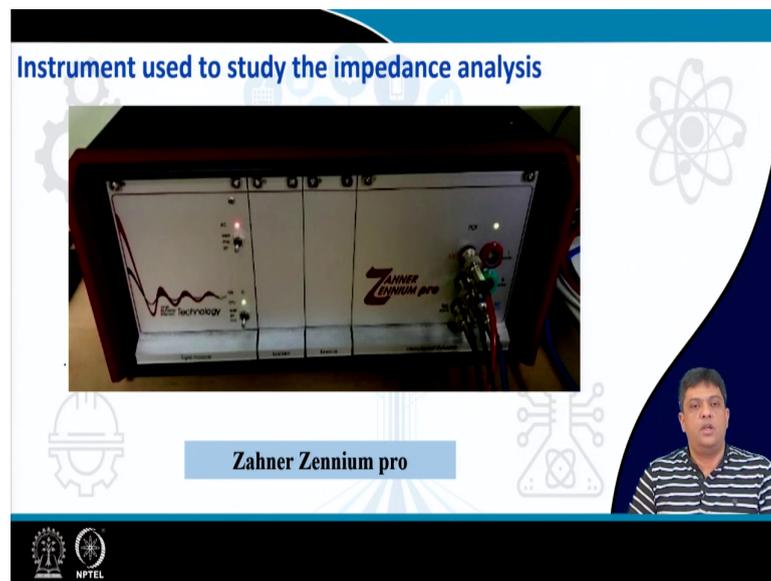
This is the instrument which is typically used to measure impedance of super capacitors or batteries. And so, what are you going to have you are going to have? A signal generator and you have to have the way to monitor the change in the current.

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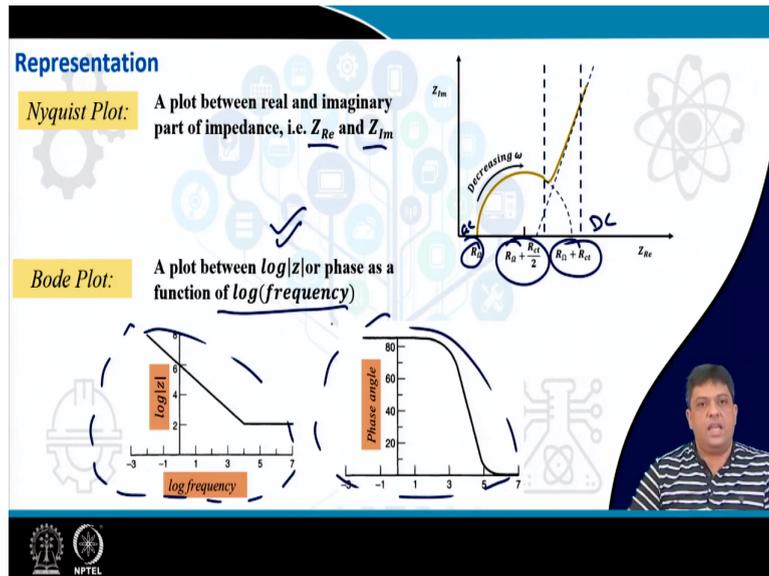
By that, what will you get? You will have the Nyquist plot. The Nyquist plot will give you what? It is a plot between the real part and the imaginary part of the impedance and this is your DC side and this is your AC side. So, what you obtain is the variation in the real and imaginary parts of the impedance and then from by plotting you can get information about the various factors.

So, if you take the intercept in the real side of the impedance plot what are you getting you will get the resistive contributions and if you take the intercept on the imaginary part side of the Z then you are talking about in terms of the inductive and capacitive effects which are there. Other ways which can be plotted is the, the Bode plots. And those are what? The variation of log Z or phase as a function of log of frequency and then you can get different information of phase angle and the change in the phase angle.

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Formulation of the theory:
- According to Stern model electric double layer is formed at the electrode-electrolyte interface.
- Consider, the electric double layer is equivalent to the parallel plate capacitor.
- Take the system as RC circuit.
- At any time, the sum of the voltages, E_R and E_C, across the resistor and the capacitor, respectively, must be equal to the applied voltage; hence:

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$
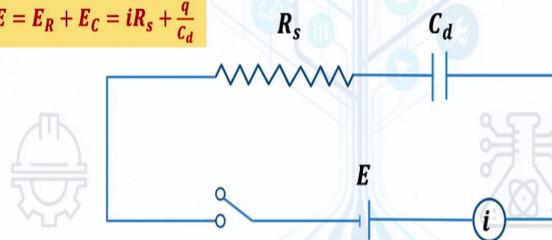
So, how have we reached to this point that we would like to use EIS for characterizing batteries or super capacitors in the Stern model which was used to explain the electric double layer formation at the electrode, electrolyte interface we have seen how you can model the formation of the same and because of this double layer formation even though the distance between these two parallel rays of charges is very small, you could still consider the electric double layer as equivalent to the parallel plate capacitor.

Now, you have the series instance and then you can consider the overall circuit as an RC circuit and once I have an RC circuit, I can easily analyze the circuit what will be the total voltage this will be the voltage which will be across the E_R and E_C that is the sum of the voltages appearing across the resistance R_S and the CD that is the capacitor and that would be equal to the value of E. So, E is equal to E_R plus EC that is equal to iR_s plus q by Cd. This is simple.

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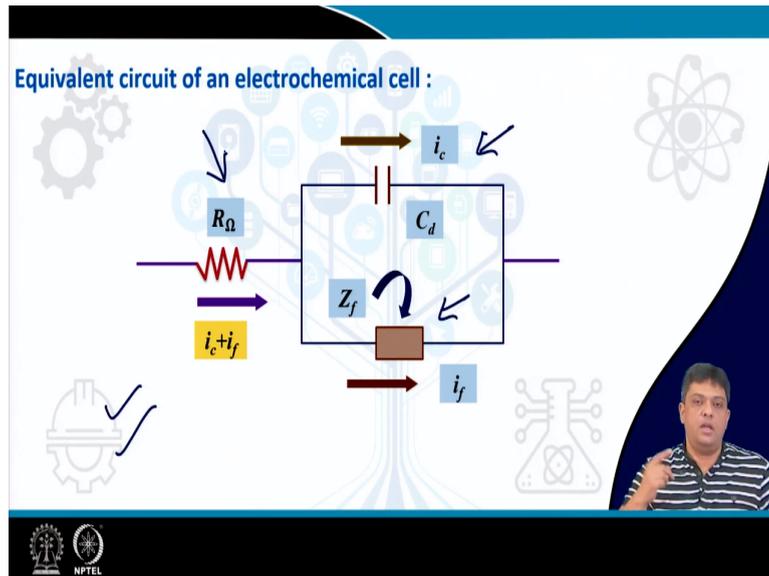
So, now we have the RC circuit and we know what is an equivalent circuit. So, for an electrochemical cell, you have a typical equivalent circuit which looks like this. You have the impedance which comes into picture the double layer formation and that leads to the capacity or the capacitance which you calculate and you have the capacitance associated with double layer formation and then you have the resistance which is coming in to the picture.

So, you have a resistance and then the impedance coming in from the capacitive and the double layer formations.

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What will happen in this equivalent circuit? All the current must pass through the solution resistance. So, now, you have the flow of ions, solvated ion. So, what is happening the current must pass through the solution resistance therefore, R omega is inserted as an series element to the, to whole circuit, so that you are able to represent this effect of current passing through the solution resistance. Now, you have faradic processes.

What happens in faradic processes? You have changes in the electrode potential, you have reduction processes, you have oxidation processes, electrode is given, electrode is taken. So, there is a much more complex picture which needs to be considered and this also introduces the complexities that you will have to take into consideration, the frequency effects. But, in general what you do that you take this factor into account and then define the effect using the general impedance term Z_f.

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Variation of total impedance

In reference to the equivalent circuit mentioned in the previous slide, the total impedance of the cell can be expressed as series combination of R_B and C_B.

The real part of the impedance:

$$Z_{Re} = R_B = R_\Omega + \frac{R_s}{A^2 + B^2}$$

The imaginary part of the impedance:

$$Z_{Im} = \frac{1}{\omega C_B} = \frac{B^2/\omega C_d + A/\omega C_s}{A^2 + B^2}$$

where, $A = (C_d/C_s) + 1$ and $B = \omega R_s C_d$

Substituting R_s and C_s value,

$$Z_{Re} = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/3}}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2(R_{ct} + \sigma\omega^{-1/2})^2}$$

$$Z_{Im} = \frac{\omega C_d(R_{ct} + \sigma\omega^{-1/2})^2 + \sigma\omega^{-1/2}(\omega^{1/2}C_d\sigma + 1)}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2(R_{ct} + \sigma\omega^{-1/2})^2}$$

With reference to the equivalent circuit, what happens? The total impedance of the cell can then be expressed as a series combination of R_B and C_B, you can write the real and the imaginary part of this where constants A and B are defined as A is equal to C_d by C_s plus 1 and B is equal to omega R_s C_d substituting these values of R_s and C_s you can then obtain the values of Z real and Z imaginary. So, you can get us complex equation and then you can get the real and the imaginary parts.
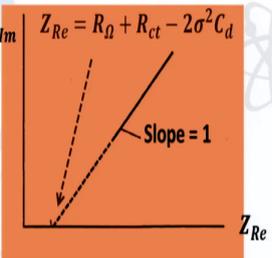
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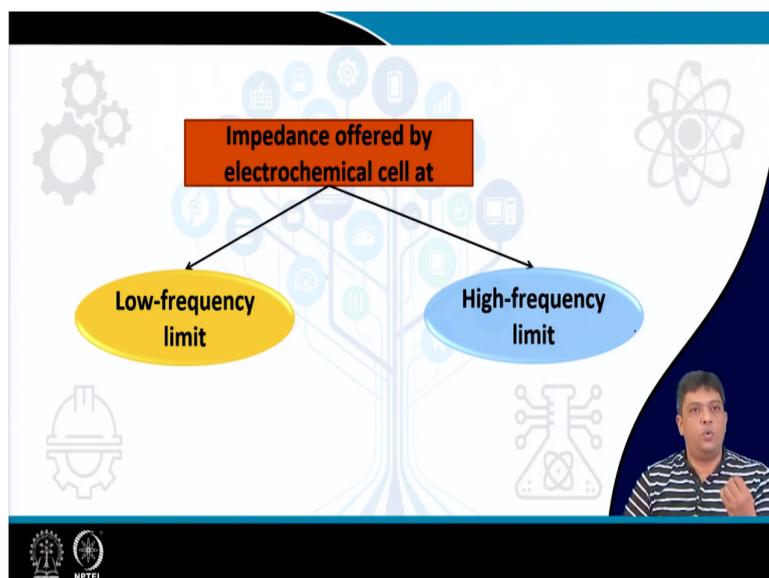
Once you have obtained that you can plot it as a function of changing voltage. So, you have two regions, one is low frequency limit and the high frequency limit. So, you go from DC to AC.

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And at low frequencies omega tends to 0 that is you are talking about DC and the real part is given by R omega plus R_{ct} plus sigma omega raise to power of half and you can also write the impedance of the imaginary part. If you combine these two together, you can write the Z imaginary is equal to what is equal to Z real part minus R omega minus R_{ct} plus 2 sigma square C_d, this is for a electrochemical systems. So, I have now obtained the value of real part and the imaginary part and the relation between the two.

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Low-frequency limit :

> Where, σ is quantitatively predictable from the constants of the experiment, like temperature, concentration of the reacting elements, Faraday constant etc.

> Thus, the plot of Z_{Im} vs. Z_{re} should be linear at low-frequency limit and have unit slope, as shown in the figure.

> So, the frequency dependence in this regime comes only from Warburg impedance terms (Z_w), as R_Ω and R_{ct} is constant.

And you can see that sigma is predictable from various constants of experiments like temperature, concentration of the reactants, Faraday constant etc. And when you are talking in the low frequency limit, the plot of imaginary versus real part of the impedance should be linear and have a unit slope as was discussed in the earlier figure.

Now, in this region, the frequency dependence also comes in from the warmup impedance term that is Z_w and the terms R omega and, the charge transfer resistance R_{ct}, so, you have Warburg impedance and sometimes you will also hear terms like Warburg capacitance, if you talking about the super capacitors or any kind of devices like the ones which we have mentioned.

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High-frequency limit :

➤ At very high frequencies, the Warburg impedance becomes unimportant in relation to R_{ct}. The equivalent circuit is shown in the Figure.
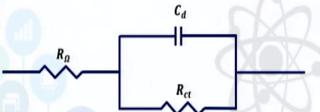
$$Z = R_\Omega - j\left(\frac{R_{ct}}{R_{ct}C_d\omega - j}\right)$$

The different components:

$$Z_{Re} = R_\Omega + \frac{R_{ct}}{1 + \omega^2 C_d^2 R_{ct}^2}$$

$$Z_{Im} = \frac{\omega C_d R_{ct}^2}{1 + \omega^2 C_d^2 R_{ct}^2}$$

➤ At high-frequency limit the relation between real and imaginary part of the impedance for any electrochemical system can be written as:
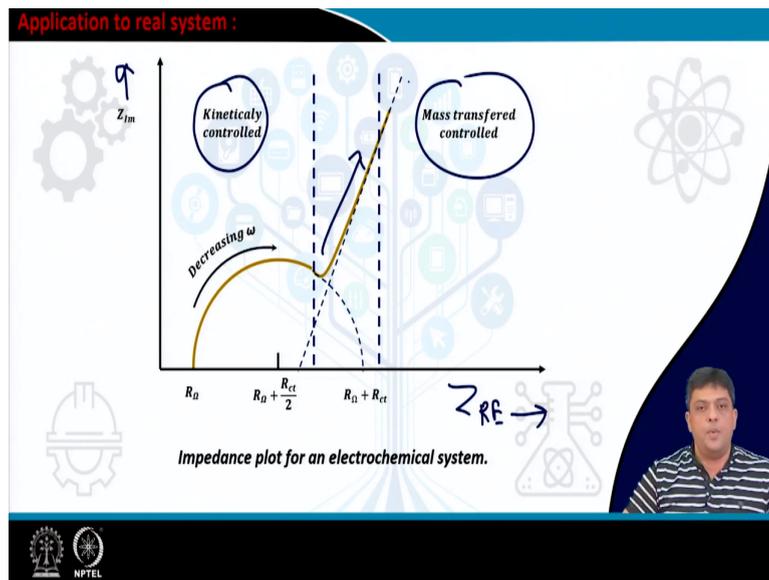
$$\left(Z_{Re} - R_\Omega - \frac{R_{ct}}{2}\right)^2 + (Z_{Im})^2 = \left(\frac{R_{ct}}{2}\right)^2$$

Similarly, you can analyze and you can determine the real and the imaginary parts in the high frequency limits.

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Impedance plot for an electrochemical system.

And what you then do you plot both the curves, because now you have the equations you can determine both the values and then you plot a curve versus Z imaginary versus Z real. So, you plot the curves and we have already seen what happens in the high frequency region then you have the increase in the system one is the diffusion control other is kinetically control and the final region is the mass transferred control processes which come into picture.

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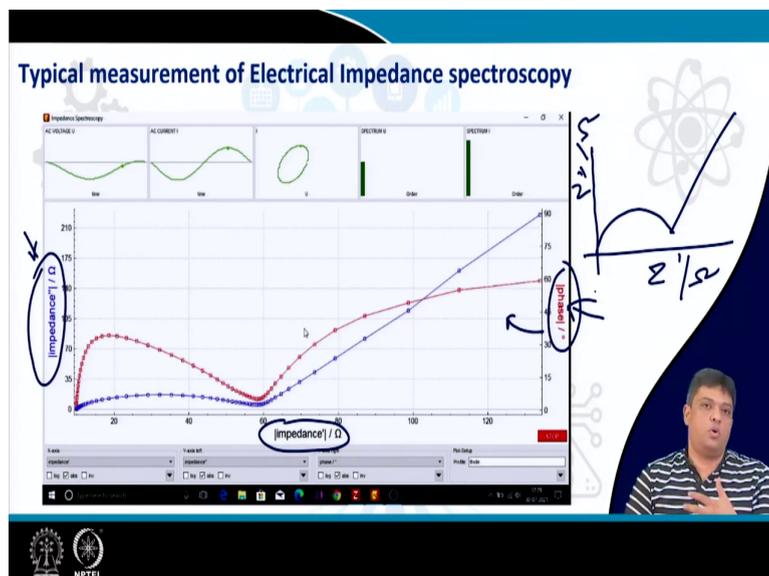
So, this is what happens in the real experiment. So, we have been showing you how you perform the experiment. So, you take the sample, make the electrodes and you put it in the cell then you apply what type of measurement you want.

So, you would like to perform the impedance spectroscopy when you start the measurement, you can clearly see that we have defined the range we have decided define the frequency range, we have defined how many times you would like to perform the measurement, all the parameters are defined and then you start the measurement it will go on changing the frequency and you can clearly see one side you are getting impedance and the other side you are getting the change in the phase.

So, there are two axis and real impedance versus the imaginary part of the impedance is given by the blue curve and the red curve gives you the changes in the phase associated. So, if I know the changes in the phase, then I can immediately write the total impedance of the system and from there I can extract.

So, you can clearly see what you can see that you have a curve and then it is rising this is what you see for the Z double prime versus Z prime plot, ohm, the unit ohm. So, you have the real and imaginary part curve and you can clearly see what happens. So, this is the way you obtain the data.

And from there, we have already seen what is a relationship between impedance the real part of it and the imaginary part of the impedance and how they are related and then you can get the change in the phase and then you can write the complete impedance of the system. And from there you can extract information about the kinetically control processes, the mass controlled processes or the diffusion controlled processes.

So, if you are talking about diffusion-controlled processes, then you are talking about capacity and you are then talking about the capacitances or the capacitive nature of the system.
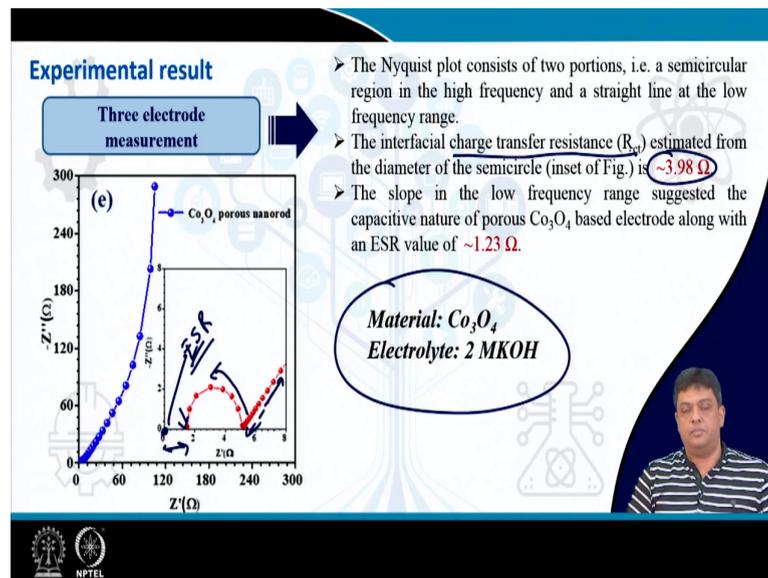
This is what you have obtained and if you see for example, like we are discussed for cobalt oxide. So, if you go back and see the previous lecture, where we talked about cobalt oxide. So, this is a typical impedance analysis you can clearly see that the curve is shifted and this gives you your value of the ESR the equivalent series resistance, so, this is an intrinsic resistance which is associated with the electrode or the electrode fill which you have used to characterize the impedance variation or your used to perform the experiment.

So, this fill which was utilizing 80 percent of cobalt oxide, 10 percent of activated carbon, 10 percent of polymer and electrolyte was two molar KOH, then you had the capacitive nature you had the capacitive nature, but obviously, there was changes in the impedance from low to high frequency size and then the curve was not starting at the origin that is 00 it was shifted and that is the shift gives you the magnitude of the ESR the equivalent series resistance.

Similarly, you could obtain the charge transfer resistance R_{CT}, which is approximately four ohms in this case. What would you like to see? You would like to see a device which has very low values of ESR because then your joule heating and the resistive losses would be minimize and device will have higher cycling stability and a longer lifetime.
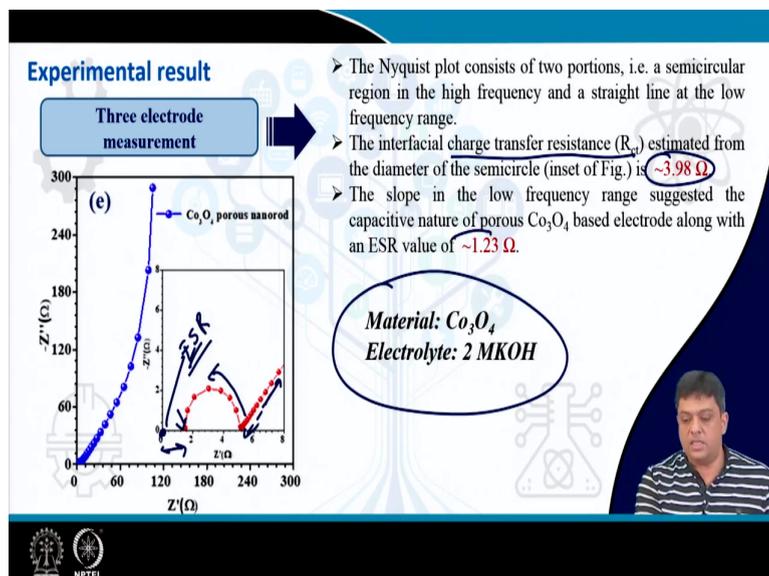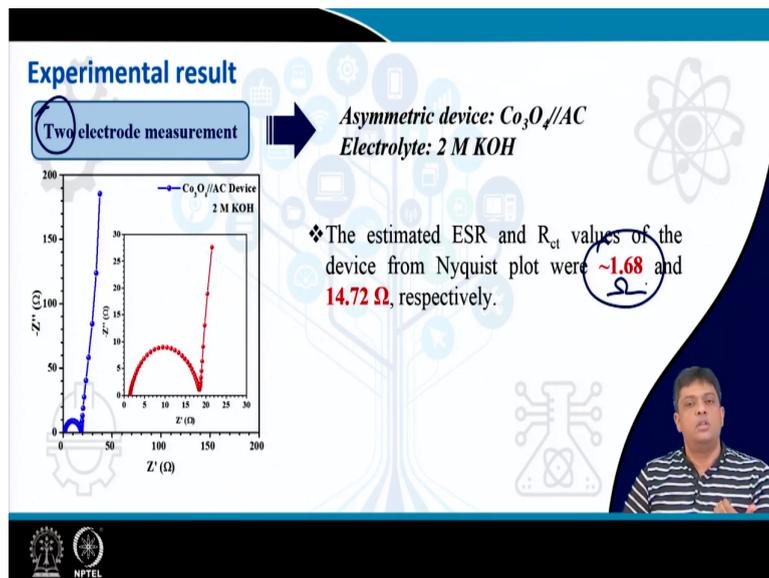
You could see that was cobalt oxide and simply which was in three electrode you can also characterize the device in two electrode that is a full cell. Now, I have taken and made the full cell device. So, for three electrode, what did you get?

You had an ESR of 1.23 ohms, whereas for the other case, what have you obtained, you can clearly see that the ESR values have gone up from 1.23 to 1.68 ohms and that is nearly 30 percent or slightly more increase in the ESR value and that can happen because now you have the full cell, you are talking about loss at the other electrode as well as the losses coming in

because of the casing the spring and other factors where you can see appearance of the resistance.

So, when you go from two electrode, sorry, three electrodes to, actually repeat from the word when. So, when you go from three electrode to two electrode systems, mostly you will see that there is an increase in the ESR values and they are very easy to estimate and if you see an increase which is very much higher than what was observed in the three electrode configuration, then you need to relook at the fabrication strategy of a device and then you may have to modify it, so, that you can bring down the ESR values as near to the one which you opt in using a three electrode measurement.

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There are other measurements which are performed using this concept and hence, this technique can be used to monitor corrosion effects because, if you are continuously monitoring and there is corrosion then the resistance is changing or you have formation of layered oxides or oxides or you have removal of elements.

And then, because of this the resistive contribution from various layers change and hence, that will manifest itself in the whole pool plots that is the Z double prime versus Z plot. You can characterize the porous electrodes. They are also used to characterize semiconductor electrolyte junctions, the state of the charge of batteries, the catalytic reactions, the adsorption

desorption at the electrode surfaces, the ion mobility in energy storage devices and bio sensor applications. These are a few of the applications of EIS technique.

There are many more techniques and this technique is extremely powerful specifically, in systems where any kind of change in resistance capacitance or inductance is taking place and you can monitor these changes quite easily and accurately.

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So, it is highly accurate. So, non-destructive measurement, so, you get the sample pack. Easy to operate, the concepts are easy, what we have studied from our school days actually we are using those formulations and making the use of the theory and designing the experiment. The problem is sometimes the initial capital cost is quite high because the instruments which are there and mostly used, they are quite expensive, but, other than that, it is easy to operate. And you must have some knowledge about the complex data analysis and then only you will be able to extract all the information that is available in the EIS spectrum.
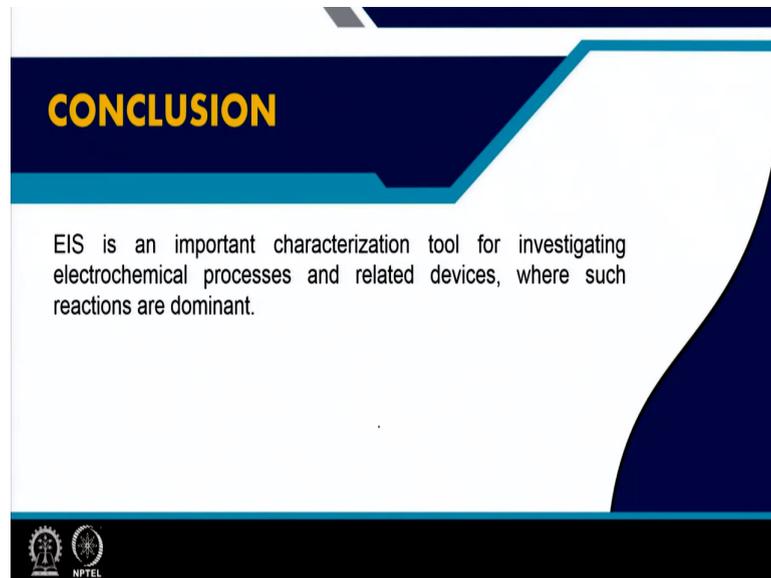
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These are the major references from which we have used the curves or the figures have been used.

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And I hope I have been able to tell you the importance of the EIS technique for investigating the electrochemical processes and many other related devices which have been discussed in this course. And in the next lecture, I will talk to you about few more experimental techniques, which are used to characterize the materials or few other devices that have been discussed in this course. And those techniques are your SEM, TEM, XPS that is Scanning Electrode Microscope, Transmission Electrode Microscope and X Ray Photo Spectroscopy. Thank you very much.