Electrochemical Energy Storage
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Module - 02
Definitions and measuring methods
Lecture - 09
Impedance Spectroscopy Measurement and Analyses

Welcome to my course Electrochemical Energy Storage and this is module number 2, where I am talking about the Definitions and measuring methods pertinent to lithium and batteries and this is lecture number 9, where I will be talking on Impedance Spectroscopy Measurement and its Analysis.

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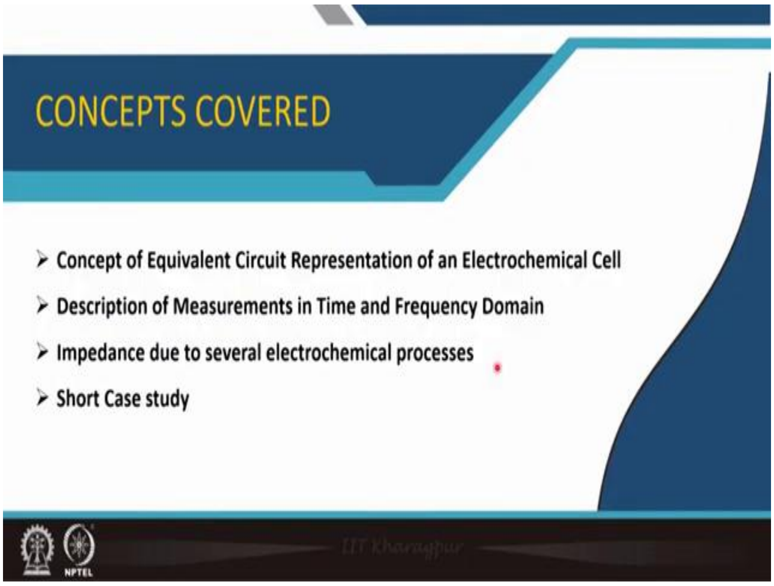

CONCEPTS COVERED

- Concept of Equivalent Circuit Representation of an Electrochemical Cell
- Description of Measurements in Time and Frequency Domain
- Impedance due to several electrochemical processes
- Short Case study

So, first I will define the concept of equivalent circuit presentation of an electrochemical cell then subsequently we will talk about description of measurement in both time domain and frequency domain. Then third I will introduce impedance due to several electrochemical process, what are the typical impedance and then I will show a short case study to further illustrate these concepts, which I will cover in this lecture.

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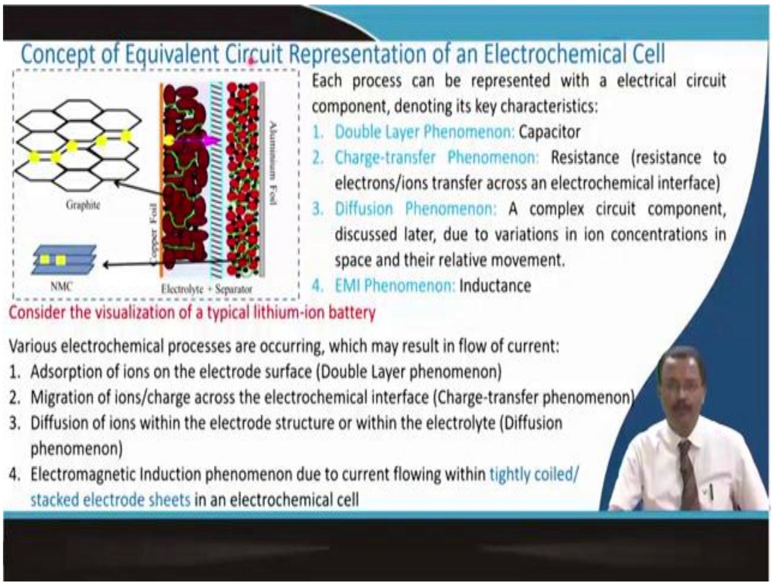

Concept of Equivalent Circuit Representation of an Electrochemical Cell

Each process can be represented with a electrical circuit component, denoting its key characteristics:

1. Double Layer Phenomenon: Capacitor
2. Charge-transfer Phenomenon: Resistance (resistance to electrons/ions transfer across an electrochemical interface)
3. Diffusion Phenomenon: A complex circuit component, discussed later, due to variations in ion concentrations in space and their relative movement.
4. EMI Phenomenon: Inductance

Consider the visualization of a typical lithium-ion battery

Various electrochemical processes are occurring, which may result in flow of current:

1. Adsorption of ions on the electrode surface (Double Layer phenomenon)
2. Migration of ions/charge across the electrochemical interface (Charge-transfer phenomenon)
3. Diffusion of ions within the electrode structure or within the electrolyte (Diffusion phenomenon)
4. Electromagnetic Induction phenomenon due to current flowing within tightly coiled/ stacked electrode sheets in an electrochemical cell

Now, let us start with the concept of equivalent circuit representation of an electrochemical cell. By this time you can understand that in case of a rechargeable lithium ion battery we have a negative electrode usually graphite is used which is having a layer structure.

And a positive electrode is used which is basically lithium nickel manganese cobalt; one-third, one-third, one-third or slightly different composition involving this ratio where the total amount of nickel manganese cobalt always is 1. So, this is basically li MO 2 kind of structure is a layered material.

Now, you have the construction where you have separator in between which is soaked with electrolyte then in one end you have the cathode material which is coated on aluminum foil. Other end you have anode material or the negative electrode which is basically graphite which is coated on the copper foil. Now, each process can be represented with an electric circuit denoting the key characteristics.

So, electric circuit equivalent of each of this I will try to introduce. The first one is a double layer phenomena, which is like a capacitor. You have anion or cation that is adsorbing on the electrode surface. Then there is a change transfer phenomena involved resistance to electron or ion transfer across the electrochemical interface while I was talking the electrochemical potential already I introduce this concepts to you. Then there is a diffusion phenomena this is a complete circuit component.

It is difficult to actually compile it in a electrical circuit equivalent that I will discuss later due to basically two problem one is the ion concentration in space and also their relative movement and there is another less considered phenomena which is EMI phenomena and this is related to the inductance.

So, you consider the visualization of a typical lithium ion battery. Various electrochemical process are occurring which may result in flow of current. So, it is no more a equilibrium process.

Adsorption of ions on the electrode surface, this is a double layer phenomena I mentioned. Migration of ion or charge into the electrochemical interface, this is a charge transfer phenomena.

Then diffusion of ions within the electrode structure or within the electrolyte that is a diffusion phenomena. And electromagnetic induction phenomena which just I introduced this is due to current flowing within a tightly coiled stacked electrode in the electrochemical cell.

When I will talk about the construction of the cylindrical battery or the stacked battery like (Refer Time: 05:08) cell then this will be clear to you.

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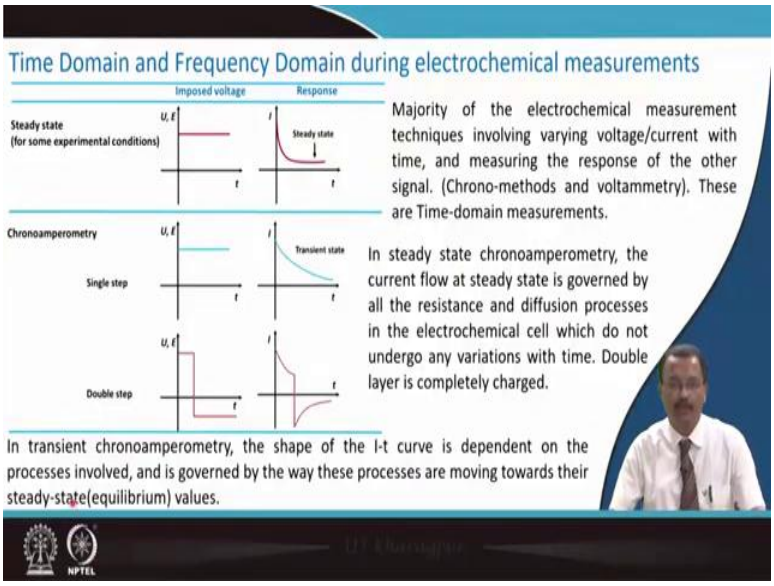

Time Domain and Frequency Domain during electrochemical measurements

Majority of the electrochemical measurement techniques involving varying voltage/current with time, and measuring the response of the other signal. (Chrono-methods and voltammetry). These are Time-domain measurements.

In steady state chronoamperometry, the current flow at steady state is governed by all the resistance and diffusion processes in the electrochemical cell which do not undergo any variations with time. Double layer is completely charged.

In transient chronoamperometry, the shape of the I-t curve is dependent on the processes involved, and is governed by the way these processes are moving towards their steady-state(equilibrium) values.

So, this already I have introduced, majority of the electrochemical measurement techniques that involved the varying voltage or current with time. So, it is a time dependent signal and measure the response of other signal. So, if you are applying voltage measuring current or applying current measuring voltage, so, accordingly you have a chrono-method and voltammetry.

These are all time domain measurement. In steady state if you consider chronoamperometry current flow is steady that is governed by all resistance and also the diffusion process that I was talking about, which do not undergo any variation with time.

So, double layer is completely charged for example, but in transient chronoamperometry the shape of the I versus t curve is dependent on the process that is involved and it is governed by the way these processes are moving towards the equilibrium condition that is a steady state condition..

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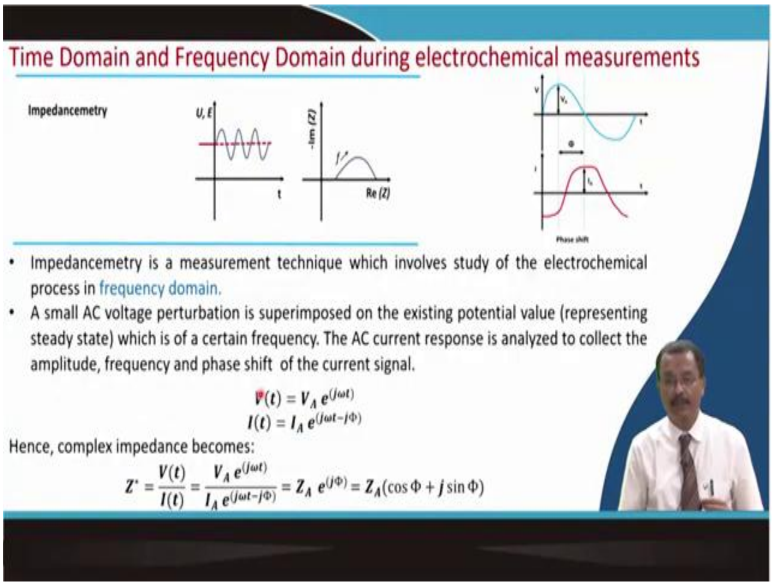

Time Domain and Frequency Domain during electrochemical measurements

Impedancemetry

- Impedancemetry is a measurement technique which involves study of the electrochemical process in frequency domain.
- A small AC voltage perturbation is superimposed on the existing potential value (representing steady state) which is of a certain frequency. The AC current response is analyzed to collect the amplitude, frequency and phase shift of the current signal.

$$V(t) = V_A\, e^{(j\omega t)}$$
$$I(t) = I_A\, e^{(j\omega t - j\Phi)}$$

Hence, complex impedance becomes:

$$Z^{*} = \frac{V(t)}{I(t)} = \frac{V_A\, e^{(j\omega t)}}{I_A\, e^{(j\omega t - j\Phi)}} = Z_A\, e^{(j\Phi)} = Z_A(\cos\Phi + j\sin\Phi)$$

So, this time domain measurements sometimes it is not very fruitful. If you convert the time domain to frequency domain then this electrical electrochemical measurements are more prominent and this also I defined in one of my earlier lecture it is called impedancemetry, where you can see that the red line is a specific state of charge of the battery. It could be half charge or half discharge or full charge.

So, this is the state of the charge and then in that situation we are applying a sinusoidal voltage of small amplitude and variable frequency. So, the frequency you can vary from kilo hertz usually from hertz to 100 kilohertz not more than that otherwise inductive effect will come into play. And then eventually you measure the variation of current.

So, voltage and current in this particular system they are not in phase as you can see there is a phase lag. So, based on this measurement we can define a spectroscopy and which we call a, impedance spectroscopy. So, by definition impedancemetry is a measurement technique that involves the study of electrochemical process in frequency domain not in time domain.

So, as I said a small AC voltage perturbation is superimposed on the existing potential value. So, existing potential value the state of charge or state of discharge which is at a certain frequency you can apply. And AC current response that is analyzed to collect the amplitude frequency and phase shift data of the current signal that is measured.

So, V the voltage that is given by this and current is separated by this phase. So, this phase angle is defined here. So, from the complex impedance that is V by t it is something like resistance in AC field. So, this is given by this. So, V A by I A is Z A, and this is nothing but exponential of j phi. So, this is you can expand the Euler equation Z A cos phi plus j sin phi.

$$\boldsymbol{V(t) = V_A\, e^{(j\omega t)}}$$

$$\boldsymbol{I(t) = I_A\, e^{(j\omega t - j\Phi)}}$$

$$\boldsymbol{Z^* = \frac{V(t)}{I(t)} = \frac{V_A\, e^{(j\omega t)}}{I_A\, e^{(j\omega t - j\Phi)}} = Z_A\, e^{(j\Phi)} = Z_A}(\cos \Phi + \boldsymbol{j} \sin \Phi)$$

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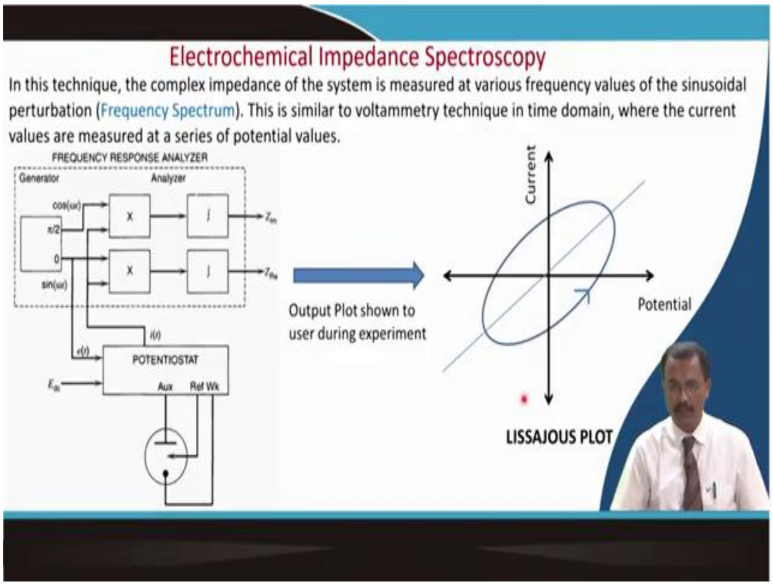

Electrochemical Impedance Spectroscopy

In this technique, the complex impedance of the system is measured at various frequency values of the sinusoidal perturbation (Frequency Spectrum). This is similar to voltammetry technique in time domain, where the current values are measured at a series of potential values.

During electrochemical impedance spectroscopy ideally you should have a counter electrode. Here I have mentioned a, auxiliary electrode then there is a provision for a reference electrode if you wish to put. If not then this reference electrode and the counter electrode they are short circuited the provision is there in the equipment and then you have your sample this working electrode.

So, you are your material is in a standard Ec dc condition and then you are applying the potential as a function of time and then measuring the current as a function of time, so to give it ultimately transform into the frequency domain. So, if frequency response analyzer that is use potential stat Galvano stat system usually equipped with this which is having a generator which can change the phase in accordance.

And this is the analyzer and finally, you get the current output and from that current output you can eventually measure the value of impedance in its complex plane in imaginary and real term. So, for a normal solid insulator you can have various possibilities and this change in possibilities, if you plot current versus potential in a oscilloscope you feed the data.

So, you get a Lissajousfigure. Sometimes it is an ellipse elliptical kind of thing sometimes it is a circle sometimes straight line depending on the relative condition between the voltage and current and associated frequency.

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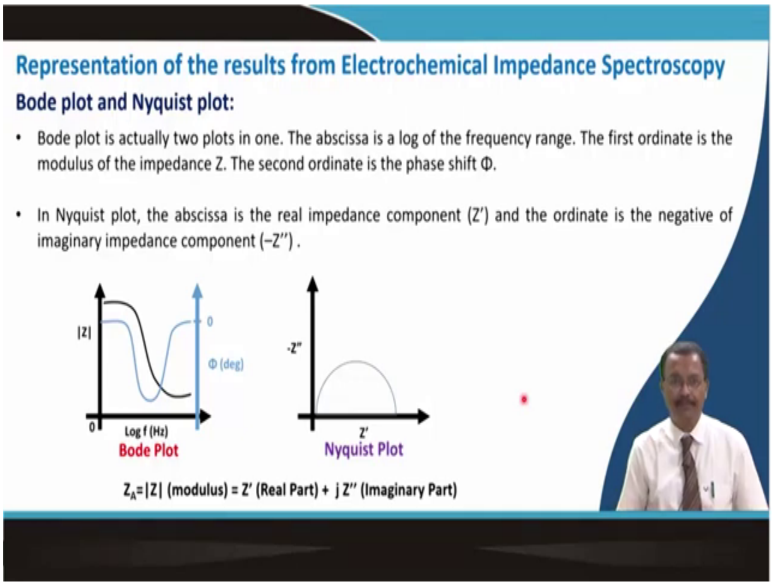

Representation of the results from Electrochemical Impedance Spectroscopy

Bode plot and Nyquist plot:

- Bode plot is actually two plots in one. The abscissa is a log of the frequency range. The first ordinate is the modulus of the impedance Z. The second ordinate is the phase shift Φ.
- In Nyquist plot, the abscissa is the real impedance component (Z′) and the ordinate is the negative of imaginary impedance component (−Z″) .

$Z_A = |Z|$ (modulus) = Z′ (Real Part) + j Z″ (Imaginary Part)

So, the representation is down done of this impedance spectroscopy either in terms of a Bode plot or a Nyquist plot. Bode plot is actually two plots in one. The abscissa is the log of frequency and the first ordinate is the modulus of the impedance Z as I said Z is an, complex number. So, this is the modulus of the impedance and the second ordinate is usually the phase shift.

You can see the phase shift here. And you can work it out that if you have a complex impedance you can have a real part and an imaginary part. You can always get the modulus of the value of Z and then you can make the Bode plot because frequency you know and phi you are measuring as well.

In case of Nyquist plot the abscissa is the real component of the complex impedance. So, this is Z prime and ordinate is the negative of the imaginary impedance component. So, for a normal RC circuit you get if you do the impedancemetry, then you get a circle like this. So, here I have shown the modulus is equal to real part plus imaginary part and from a series of data you can estimate this value.

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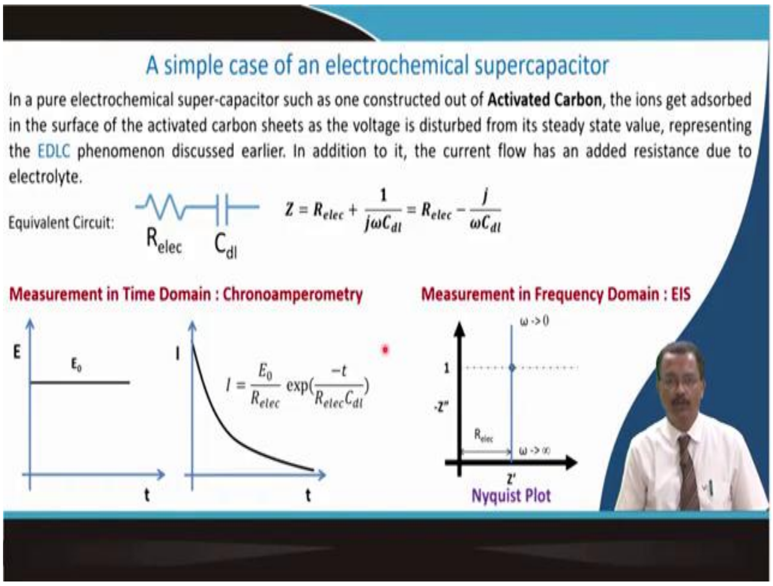

A simple case of an electrochemical supercapacitor

In a pure electrochemical super-capacitor such as one constructed out of **Activated Carbon**, the ions get adsorbed in the surface of the activated carbon sheets as the voltage is disturbed from its steady state value, representing the EDLC phenomenon discussed earlier. In addition to it, the current flow has an added resistance due to electrolyte.

Equivalent Circuit: R_{elec} C_{dl} $Z = R_{elec} + \frac{1}{j\omega C_{dl}} = R_{elec} - \frac{j}{\omega C_{dl}}$

Measurement in Time Domain : Chronoamperometry

$I = \frac{E_0}{R_{elec}} \exp(\frac{-t}{R_{elec}C_{dl}})$

Measurement in Frequency Domain : EIS

Nyquist Plot

So, if I consider a simple electrochemical capacitor, it is having a pure electrochemical say super capacitor, which I already explained that this is constructed out of a activated carbon. So, ions get absorbed on the surface of the activated carbon sheets as a voltage is disturbed from the steady state value that represents the electric double layer capacitor which already I described in one of my earlier lectures.

In addition to it the current also flows that has an added resistance due to the electrolyte because electrolyte is not something which is a super conductor. So, it has its own internal resistance. So, you can modulate that you have a resister part, which is connected in series with double layer capacity.

And then you talk about the impedance. So, resistance will come this resistance of the electrolyte part and for a capacitor the resistic part is given by 1 by j, j is nothing but root over of minus one and the frequencies concerned and capacity double layer capacitance. So, you just multiply it with j j in both sides. So, this comes like this.

$$Z = R_{elec} + \frac{1}{j\omega C_{dl}} = R_{elec} - \frac{j}{\omega C_{dl}}$$

So, in the time domain measurement already you have seen that it is almost a constant DC kind of voltage that is there and you are applying a perturbation of AC frequency and the current will assume this. I leave it on you to see the exponential kind of decay of the current from higher secondary conception you can do that, but if you now convert it to the frequency domain then you will get a straight line here.

$$I = \frac{E_0}{R_{elec}} \exp(\frac{-t}{R_{elec}C_{dl}})$$

And this part will actually tell you what is the electrolyte resistance and frequency this part will be at higher frequency and this part will be positive at this particular frequency. So, it will be a basically straight line, where it will have a single value of Z prime and Z double prime will change.

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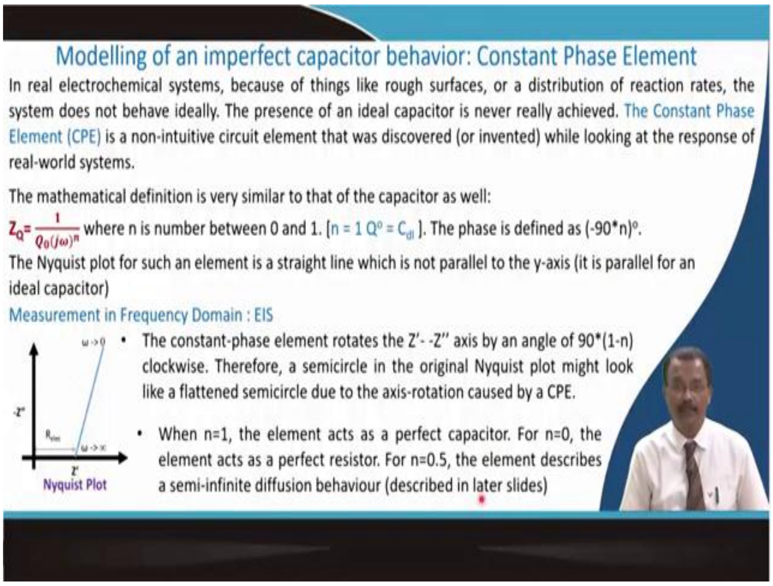

Modelling of an imperfect capacitor behavior: Constant Phase Element

In real electrochemical systems, because of things like rough surfaces, or a distribution of reaction rates, the system does not behave ideally. The presence of an ideal capacitor is never really achieved. The Constant Phase Element (CPE) is a non-intuitive circuit element that was discovered (or invented) while looking at the response of real-world systems.

The mathematical definition is very similar to that of the capacitor as well:

$Z_Q = \frac{1}{Q_0(j\omega)^n}$ where n is number between 0 and 1. [n = 1 $Q^0 = C_{dl}$]. The phase is defined as (-90*n)°.

The Nyquist plot for such an element is a straight line which is not parallel to the y-axis (it is parallel for an ideal capacitor)

Measurement in Frequency Domain : EIS

- The constant-phase element rotates the Z'- -Z'' axis by an angle of 90*(1-n) clockwise. Therefore, a semicircle in the original Nyquist plot might look like a flattened semicircle due to the axis-rotation caused by a CPE.
- When n=1, the element acts as a perfect capacitor. For n=0, the element acts as a perfect resistor. For n=0.5, the element describes a semi-infinite diffusion behaviour (described in later slides)

Now, in real electrochemical system because of various parameters like the surface is rough, the rate of reaction is distributed it is not single rate constant this does not behave like a real capacity. So, the presence of a ideal capacitor is replaced by a constant phase element which is abbreviated as CPE.

This is in a non intuitive circuit element that is invented while looking at the response in the real world electrochemical impedance graph. And the mathematical definition is very similar to the capacity. So, this impedance is 1 by Q 0 Z omega and this n term is there. So, n is the number between 0 and 1. So, n equal to 1 then Q 0 is C dl this thing. The phase is defined as something like minus 90 into the value of n.

$\mathbf{Z_Q} = \frac{1}{Q_0(j\omega)^n}$ where n is number between 0 and 1. [n = 1 $Q^o = C_{dl}$]. The phase is defined as $(-90{*}n)^o$.

So, the Nyquist plot of such element is a straight line like the earlier one, but it is not parallel to the ordinate. So, measurement in frequency domain of EIS, the constant phase element that rotates this Z prime and Z double prime axis by this angle what I mention 90 degree into 1 minus n in the clockwise pattern.

Therefore a semicircle which I showed for the RC circuit that might look a bit flattened semi circle due to the axis rotation because of this constant phase element. So, when n is actually 1 then element acts like a perfect capacitor, for n is equal to 0 the element acts like a perfect resistor and when n is 0.5 the element describes a semi infinite diffusion behaviour. So, in later slide we will talk about this.

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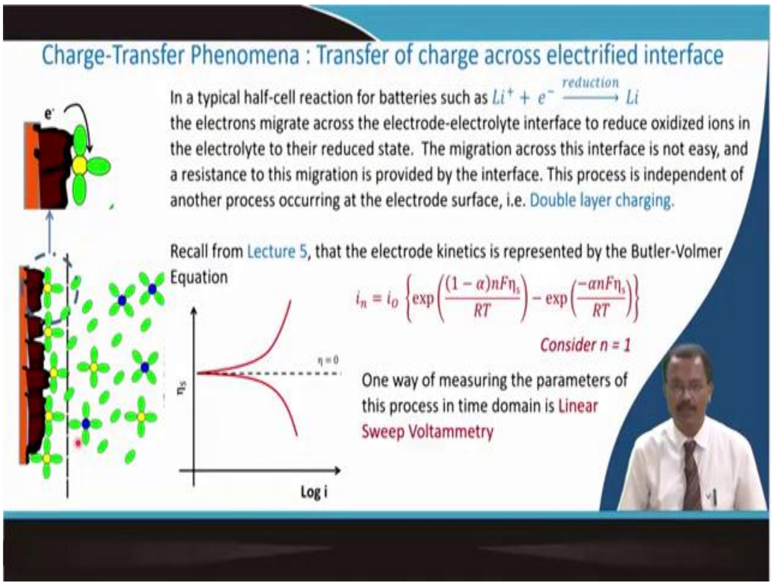

Charge-Transfer Phenomena : Transfer of charge across electrified interface

In a typical half-cell reaction for batteries such as $Li^+ + e^- \xrightarrow{reduction} Li$ the electrons migrate across the electrode-electrolyte interface to reduce oxidized ions in the electrolyte to their reduced state. The migration across this interface is not easy, and a resistance to this migration is provided by the interface. This process is independent of another process occurring at the electrode surface, i.e. Double layer charging.

Recall from Lecture 5, that the electrode kinetics is represented by the Butler-Volmer Equation

$$i_n = i_0 \left\{ \exp\left(\frac{(1-\alpha)nF\eta_s}{RT}\right) - \exp\left(\frac{-\alpha nF\eta_s}{RT}\right) \right\}$$

Consider n = 1

One way of measuring the parameters of this process in time domain is Linear Sweep Voltammetry

Again we come back to the charge transfer phenomena and already I defined the transfer of charge across the electrified interface. So, in a typical half cell reaction that I have shown that lithium ion that is taking electron that is getting reduced and forming lithium. The electron migrates along with the electrode electrolyte interface to reduce the oxidized ion in the electrolyte to the reduced state.

Now, this migration in the interface is not easy and there is a resistance involved. This resistance to the, this migration is provided by the interface and this process is independent of another process that is occurring at this interface this is called double layer charging.

So, in the last lecture we talked about the electrode kinetics that is represented by this Butler Volmer equation. So, here this n value while I derive it I consider this n is equal to 1 so, you can consider n equal to 1. So, this is another way you can basically plot the Tafel equation where you can see the linearity this log I versus this plot is not being maintained particularly at the higher current limit.

$$i_n = i_O \left\{ \exp\left(\frac{(1-\alpha)nF\eta s}{RT}\right) - \exp\left(\frac{-\alpha nF\eta s}{RT}\right) \right\}$$

So, one way of measuring the parameter of this process in time domain is the so called linear sweep voltammetry, which also I have explained in one of my earlier lectures.

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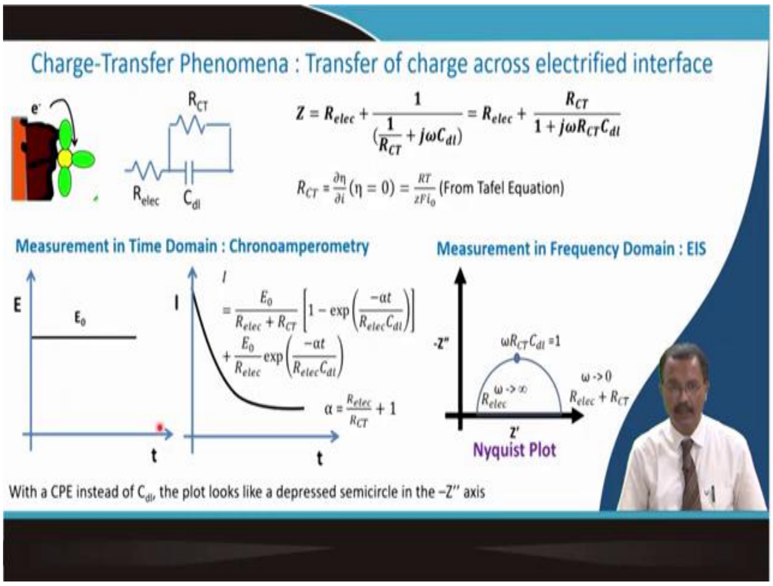

Charge-Transfer Phenomena : Transfer of charge across electrified interface

$$Z = R_{elec} + \frac{1}{(\frac{1}{R_{CT}} + j\omega C_{dl})} = R_{elec} + \frac{R_{CT}}{1 + j\omega R_{CT} C_{dl}}$$

$$R_{CT} = \frac{\partial\eta}{\partial i}(\eta = 0) = \frac{RT}{zFi_0} \text{ (From Tafel Equation)}$$

Measurement in Time Domain : Chronoamperometry

$$I = \frac{E_0}{R_{elec} + R_{CT}}\left[1 - \exp\left(\frac{-\alpha t}{R_{elec}C_{dl}}\right)\right] + \frac{E_0}{R_{elec}}\exp\left(\frac{-\alpha t}{R_{elec}C_{dl}}\right)$$

$$\alpha = \frac{R_{elec}}{R_{CT}} + 1$$

Measurement in Frequency Domain : EIS

Nyquist Plot

With a CPE instead of C_{dl}, the plot looks like a depressed semicircle in the –Z″ axis

Now, I will consider the charge transfer across a, electrified interface. You remember we talked about when electrochemical potential I mentioned that that now it is a transfer of charge across the electrified a charged interface. So, then your impedance you can construct it from the electrolyte and this two.

$$\boldsymbol{Z = R_{elec} + \frac{1}{(\frac{1}{R_{CT}} + j\omega C_{dl})} = R_{elec} + \frac{R_{CT}}{1 + j\omega R_{CT} C_{dl}}}$$

$R_{CT} = \frac{\partial \eta}{\partial i}(\eta = 0) = \frac{RT}{zFi_0}$ (From Tafel Equation)

One is this charge transfer resistance is also introduced here and this is the simplified form. So, from Tafel equation I already defined this RT Z F 0 is when this value of over potential is almost 0 and that is related to this charge transfer resistance. So, that is almost an equilibrium process over potential is very close to 0. Now, this transient a bit change because I put this relation again how the current decays and this part actually does not go to 0.

$$I = \frac{E_0}{R_{elec} + R_{CT}} \left[1 - \exp\left(\frac{-\alpha t}{R_{elec} C_{dl}}\right)\right] + \frac{E_0}{R_{elec}} \exp\left(\frac{-\alpha t}{R_{elec} C_{dl}}\right)$$

$\alpha = \frac{R_{elec}}{R_{CT}} + 1$

Unlike the other case where this charged transfer situation was not there. So, this is a time domain plot and if you do the impedance plot in the frequency domain between Z double prime and Z prime which we call Nyquist plot. Then a semi almost semi circle you will get, but depending on the CT you can have slight depressed semicircle where this maxima point; here the value of this omega; that means, related to frequency as you know omega is equal to 2 pi F.

And this is the charge transfer resistance and this is the double layer capacitance that is equal to 1 and RC is the time constant that is involved. So, that is also defined as tau. So, omega tau is equal to 1 and higher frequency you will get in this side and relatively lower frequency will get in the other side.

So, this part is the resistance of the electrolyte that you are getting that also I have defined and the diameter from here to here this is electrolyte plus charge transfer resistance.

So, depending on this frequency, frequency I have not defined, but certainly this is at low frequency range. You can estimate if from this kind of circuit is assumed where this charge transfer resistance and the double layer capacitance they are connected in parallel you get from the Nyquist plot you can have this value extracted right.

So, what you will have to do? You will have to construct a correct kind of equivalent circuit and then from your measured data you will have to simulate according to the circuit. So, you need to know that if this is my ideal circuit and it is completely matching with my experimental value.

Then all these individual component what is the electrolytic resistance, what is the charge transfer resistance, what is the double layer capacitance everything I can get out of my impedance spectroscopy measurement and relevant analysis.

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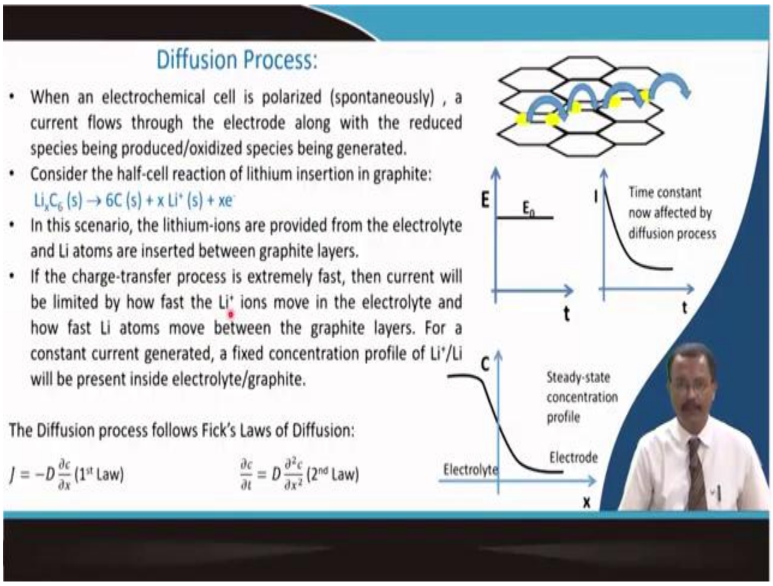

Diffusion Process:

- When an electrochemical cell is polarized (spontaneously) , a current flows through the electrode along with the reduced species being produced/oxidized species being generated.
- Consider the half-cell reaction of lithium insertion in graphite:
  $Li_xC_6\ (s) \rightarrow 6C\ (s) + x\ Li^+\ (s) + xe^-$
- In this scenario, the lithium-ions are provided from the electrolyte and Li atoms are inserted between graphite layers.
- If the charge-transfer process is extremely fast, then current will be limited by how fast the Li^+ ions move in the electrolyte and how fast Li atoms move between the graphite layers. For a constant current generated, a fixed concentration profile of Li^+/Li will be present inside electrolyte/graphite.

The Diffusion process follows Fick's Laws of Diffusion:

$J = -D\frac{\partial c}{\partial x}$ (1st Law)

$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$ (2nd Law)

Now, we will talk about the diffusion process. When a electrochemical cell is polarized a current flows through the electrode along with the reduced species being produced or oxidized species being generated right. So, if you consider this half cell reaction when this is the discharged state, so, lithium is going into the electrolyte. So, lithium ions are provided from the electrolyte because initially it goes through the electrolyte and lithium ions are inserted between graphite layer.

So, that case if it is there actually this is the reverse part. So, the charge transfer process is extremely fast. The current will be limited by how fast lithium is moving in the electrolyte and how fast lithium ions move between the graphite layers.

For a constant current generated at a fixed concentration profile of lithium ion versus lithium will be present inside the electrolyte and graphite interface. So, the time domain spectra that is something like this where lithium is basically getting diffuse inside the graphite layer.

So, one can have a steady state concentration profile inside the electrode you can see the electrode part there is a concentration difference. So, from here the diffusion starts in electrolyte it has sufficient concentration.

So, this diffusion process it follows either Fick's first law the atomic flux or ionic flux is diffusion coefficient and concentration gradient or the second law where del c by del t, this is varies with del 2 c by del x square gradient.

$J = -D\frac{\partial c}{\partial x}$ (1st Law)

$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$ (2nd Law)

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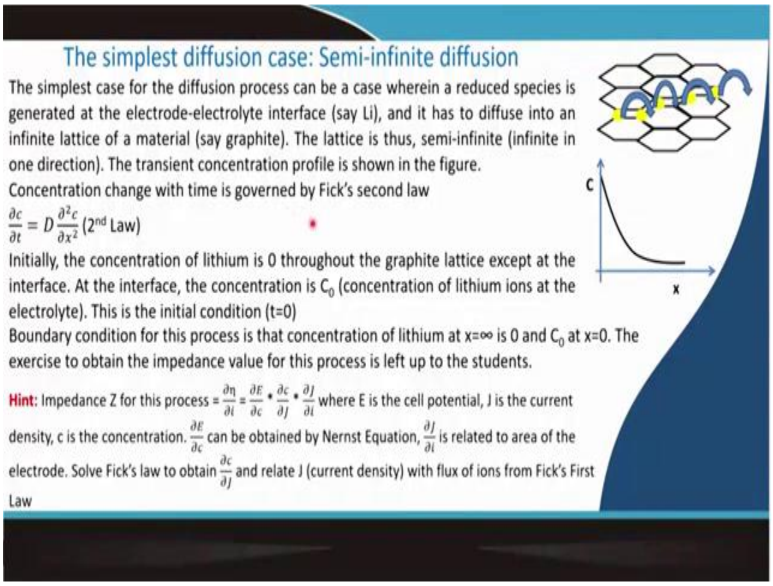

The simplest diffusion case: Semi-infinite diffusion

The simplest case for the diffusion process can be a case wherein a reduced species is generated at the electrode-electrolyte interface (say Li), and it has to diffuse into an infinite lattice of a material (say graphite). The lattice is thus, semi-infinite (infinite in one direction). The transient concentration profile is shown in the figure.

Concentration change with time is governed by Fick's second law

$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$ (2nd Law)

Initially, the concentration of lithium is 0 throughout the graphite lattice except at the interface. At the interface, the concentration is C_0 (concentration of lithium ions at the electrolyte). This is the initial condition (t=0)

Boundary condition for this process is that concentration of lithium at $x=\infty$ is 0 and C_0 at $x=0$. The exercise to obtain the impedance value for this process is left up to the students.

Hint: Impedance Z for this process $= \frac{\partial \eta}{\partial i} = \frac{\partial E}{\partial c} \cdot \frac{\partial c}{\partial J} \cdot \frac{\partial J}{\partial i}$ where E is the cell potential, J is the current density, c is the concentration. $\frac{\partial E}{\partial c}$ can be obtained by Nernst Equation, $\frac{\partial J}{\partial i}$ is related to area of the electrode. Solve Fick's law to obtain $\frac{\partial c}{\partial J}$ and relate J (current density) with flux of ions from Fick's First Law

So, let us consider the simplest case of diffusion that is the case where a reduced species is generated at the electrode and electrolyte interface say that is lithium and it has to diffuse into the infinite lattice say in the graphite. So, lithium plus is coming from the positive electrode part and transporting through the electrolyte at the interface.

It is getting reduced from li plus to metallic lithium and then it is going inside the graphite. And here you can consider that the source of lithium inside the graphite is almost negligible and then it is progressively the diffusion will take place.

So, the concentration change with time this is governed by the Fick's second law. Initially the concentration of lithium as I said is 0 throughout the graphite lattice except at the interface at the interface concentration is C 0, concentration of lithium ion at the electrolyte it is same like this.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \text{ (2}^{\text{nd}}\text{ Law)}$$

This is the initial condition at t equal to 0 last view slide I have shown it boundary condition you can apply for this process concentration of lithium when x is infinite is 0 and C 0 at x equal to 0 from the concentration. And now this is the exercise for you to obtain the impedance value of this process and try to solve this problem.

As a hint the impedance of this process is del eta by del i and that is del E by del c into del c by del J into del J by del i. So, E is a small, potential J is the current density, c the concentration and this one this term you can obtain from Nernst equation, the voltage that you get out of the concentration difference and this part del J del i is related to the area of the electrode.

$$\frac{\partial \eta}{\partial i} = \frac{\partial E}{\partial c} * \frac{\partial c}{\partial J} * \frac{\partial J}{\partial i}$$

Now, you solve the Fick's law to obtain del c by del J and relate the current density with flux of ions from the Fick's first law. If you do that then you can obtain the impedance value of this process and this is a bit complicated, but if you understand the way I have introduced the concept I think and with some knowledge of diffusion I think it will not be very problematic to solve you the impedance value.

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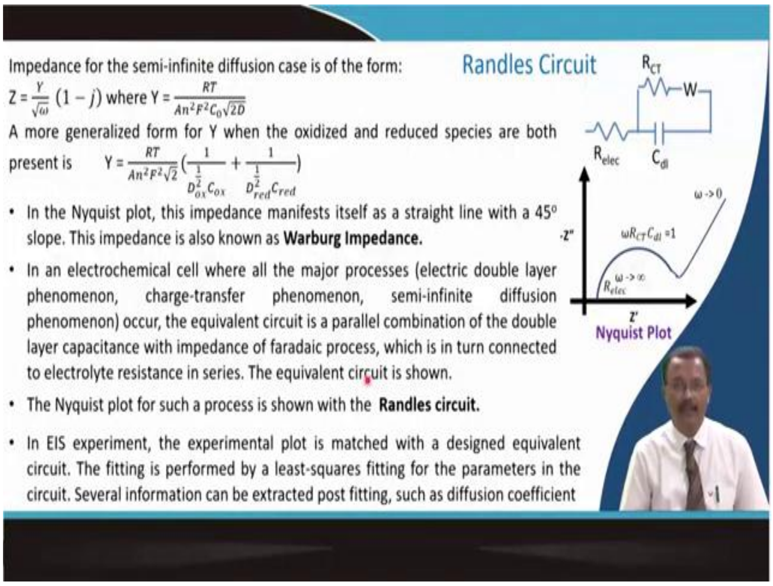

Impedance for the semi-infinite diffusion case is of the form:

$Z = \frac{Y}{\sqrt{\omega}}(1-j)$ where $Y = \frac{RT}{An^2F^2C_0\sqrt{2D}}$

A more generalized form for Y when the oxidized and reduced species are both present is $Y = \frac{RT}{An^2F^2\sqrt{2}}\left(\frac{1}{D_{ox}^{\frac{1}{2}}C_{ox}} + \frac{1}{D_{red}^{\frac{1}{2}}C_{red}}\right)$

- In the Nyquist plot, this impedance manifests itself as a straight line with a 45° slope. This impedance is also known as **Warburg Impedance.**
- In an electrochemical cell where all the major processes (electric double layer phenomenon, charge-transfer phenomenon, semi-infinite diffusion phenomenon) occur, the equivalent circuit is a parallel combination of the double layer capacitance with impedance of faradaic process, which is in turn connected to electrolyte resistance in series. The equivalent circuit is shown.
- The Nyquist plot for such a process is shown with the **Randles circuit.**
- In EIS experiment, the experimental plot is matched with a designed equivalent circuit. The fitting is performed by a least-squares fitting for the parameters in the circuit. Several information can be extracted post fitting, such as diffusion coefficient

So, impedance of a semi infinite diffusion case usually takes the form like this one and if it is more generalized then it takes the form of this one. Again this needs a little bit work out to do following the standard complex algebra theory. So, the Randle circuit for this kind of situation, where semi infinite diffusion case is operative. Here you can see that instead of only this electrolyte and R CT and double layer capacitor we have introduced an additional term, which is in series with R R CT value the charge transfer value.

Z = $\frac{Y}{\sqrt{\omega}}\ (1-j)$ where Y = $\frac{RT}{An^2F^2C_0\sqrt{2D}}$

Y = $\frac{RT}{An^2F^2\sqrt{2}}\left(\frac{1}{D_{ox}^{\frac{1}{2}}C_{ox}} + \frac{1}{D_{red}^{\frac{1}{2}}C_{red}}\right)$ [Generalized form]

And if you see the corresponding impedance graph this will introduce a tail at lower frequency because of this. So, the Nyquist plot the impedance manifests itself as a straight line. Usually this angle is 45 degree slope and this impedance is also known as Warburg impedance.

In an electrochemical cell where all the major process electric double layer phenomena, charge transfer phenomena, semi infinite diffusion phenomena occur, equivalent circuit is a parallel combination of the double layer capacitance with impedance of a Faradaic process which is in turn connected to the electrolyte resistance in series. This is the equivalent circuit that is shown.

Nyquist plot of this process with this type of Randle circuit is shown also here. In this electrochemical impedance spectroscopy experiment the experimental plot is matched with a designed equivalent circuit. So, you can in the software you can design this kind of circuit according to your understanding on the physical phenomena and then match with your experimental value and then the software itself gives all kinds of parameters which is of our relevance including the diffusion coefficient.

So, one such plot will give you electrolyte resistance then charge transfer resistance double layer capacitance and not only that from this Warburg impedance you can also estimate the diffusion coefficient. I will show certain practical data on this, but certainly this has made our life quite simpler because a software like ZSimpWin you can construct this circuit physically and it will do all the calculation and simulate the data according to the circuit and you just match it.

So, it is just like a black box, but if you understand the process and if you work it out that what will be its impedance value and in reals real part and imaginary part and then construct the circuit although it is very very tedious I think your understanding will be quite good.

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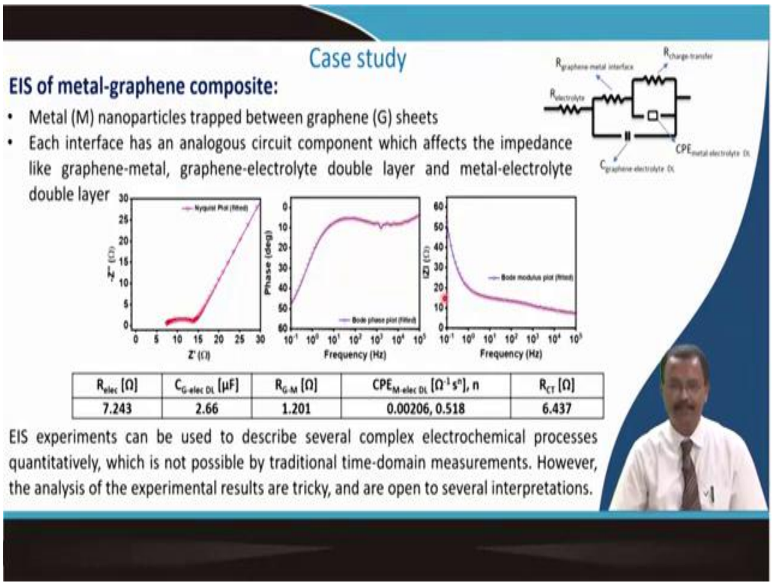

Case study

EIS of metal-graphene composite:

- Metal (M) nanoparticles trapped between graphene (G) sheets
- Each interface has an analogous circuit component which affects the impedance like graphene-metal, graphene-electrolyte double layer and metal-electrolyte double layer

R_{elec} [Ω]	$C_{G\text{-}elec\ DL}$ [μF]	$R_{G\text{-}M}$ [Ω]	$CPE_{M\text{-}elec\ DL}$ [$\Omega^{-1} s^{n}$], n	R_{CT} [Ω]
7.243	2.66	1.201	0.00206, 0.518	6.437

EIS experiments can be used to describe several complex electrochemical processes quantitatively, which is not possible by traditional time-domain measurements. However, the analysis of the experimental results are tricky, and are open to several interpretations.

So, this is the case study that I wanted to show. Metal nanoparticle trapped between a graphene layer sheet. So, this is the Randle circuit that we construct it. You can see electrolyte is there then graphene metal interface is this resistor then the charged transfer resistance is here, then the CPE value instead of CDL we put it here, and graphene electrolyte double layer that also a capacitor. This is a quite complicated circuit at this stage for you to understand, but it works well.

So, each interface has analogous circuit component which affects the impedance like graphene metal, graphene electrolyte double layer, metal electrolyte double layer and then we could get the experimental plot which is the symbol. And we could also get the phase versus frequency plot.

And we also get the Bode plot and then we fit it along with this circuit. And you can see it is a perfect match almost a perfect match although this is the experiment that was done in our laboratory. And then I can calculate the electrochemical resistance. I can calculate the C G electrolyte double layer graphene electrolyte double layer.

I can calculate the graphene and metal this resistance this value graphene and metal interface. I can although also estimate the constant felt constant phase element values; here including the n and you see here n is 0.518. I mentioned it should be between 0 to 1 and charge transfer resistance.

So, this EIS experiment can be used to describe several complex electrochemical process quantitatively which is not otherwise possible by traditional time domain kind of measurements. However, this analysis of the experimental results as I said they are quite tricky and they are open to several interpretation and how well you can define your Rendle circuit that will prove your case.

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REFERENCES

- **C. Glaize and S. Genies,** Lithium batteries and electrochemical storage systems, Chapter – 2 pp 48 – 62 Wiley (2013) (Study materials)
- M.E. Ozarem and B. Tribollet, Electrochemical impedance spectroscopy, Wiley (2008)
- Application notes by Gamry and Metrohm

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So, these are the references for general impedance related thing. You should go to this book as your study material. And this is an excellent book by Ozarem, which talks about Electrochemical Impedance Spectroscopy, it is a Wiley book and Application notes by several Gamry and Metrohm their site that you can study.

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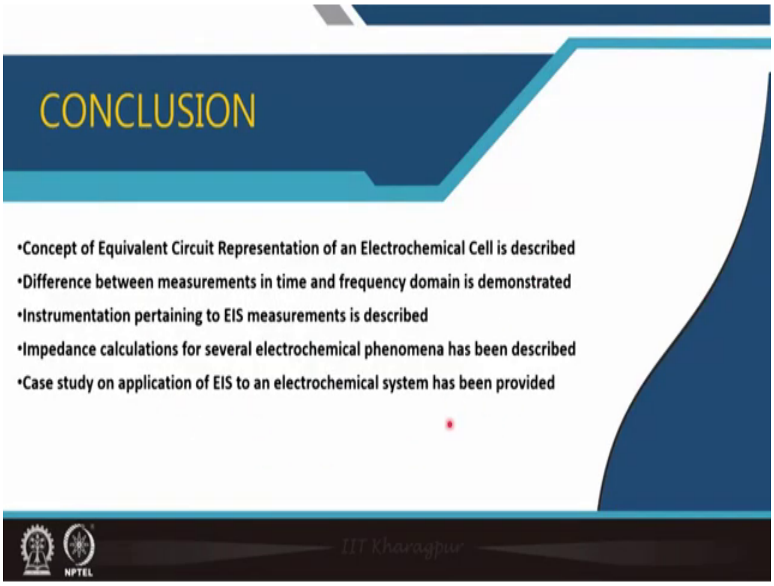

CONCLUSION

- Concept of Equivalent Circuit Representation of an Electrochemical Cell is described
- Difference between measurements in time and frequency domain is demonstrated
- Instrumentation pertaining to EIS measurements is described
- Impedance calculations for several electrochemical phenomena has been described
- Case study on application of EIS to an electrochemical system has been provided

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So, concept of equivalent circuit representation of electrochemical cell we have described. Then difference between measurements in time and frequency domain that we have demonstrated. And instrumentation which is pertinent to EIS measurement that is described.

Then impedance calculation for several electrochemical phenomena that also has been described and one simple case study on the application of EIS to the electrochemical system has been provided.

Thank you for your attention.