

Solar Photovoltaics: Fundamental Technology and Applications
Prof. Soumitra Satapathi
Department of Physics
Indian Institute of Technology – Roorkee

Lecture - 40
Impedance Spectroscopy

Welcome everyone to our Solar Photovoltaics course. Today we are having the 8th week and today is our 5th lecture which is the final lecture. So in this week we have been discussing about the different characterization systems or some of the common technology which we need to know in the context of the solar cell. We have discussed about the vacuum technology which is very, very important.

We have discussed about the imaging technology and then the another thing which is very popularly used nowadays to measure the electrical parameters of the solar cell is the Impedance Spectroscopy. In today's lecture, we learn about impedance spectroscopy.

(Refer Slide Time: 01:07)

Definition of Resistance and Impedance

- Resistance is the ability of a circuit element to resist the flow of electrical current.
- Ohm's law defines resistance in terms of the ratio between voltage, E, and current, I.

$$R = \frac{E}{I}$$

$$Z = a + ib$$
$$|Z| = \sqrt{a^2 + b^2}$$

- While this is a well known relationship, its use is limited to only one circuit element -- the ideal resistor.
- An ideal resistor has several simplifying properties:
- It follows Ohm's Law at all current and voltage levels.
- Its resistance value is independent of frequency.
- AC current and voltage signals through a resistor are in phase with each other.

$$\Phi = \tan^{-1} \frac{b}{a}$$

Now the resistance is the ability of a circuit element to resist the flow of electrical current. We all know that what is the resistance is there. Now Ohm's law defines resistance in terms of the ratio between the voltage E and current I. I know that you know usually you assign the voltage as a V, but let us consider the voltage V has a later E. So the resistance according to the Ohm's law R is E/V E/I which you know as V/I so instead of V I have written E so E/I.

While this is a well known relation its use is limited only one circuit element the ideal

resistor. Now let us say when we are talking about this Ohm's law about the resistance so basically that corresponds to only the ideal resistance, but what happens if I have a capacitance. What happens if I have an inductance then obviously this E/I relation will not hold an ideal resistor has several simplifying properties.

It follows Ohm's law at all current and voltage levels. Its resistance value is independent of frequency. AC and voltage signals through a resistor are in phase with each other. Now obviously I mean at all current and voltage level the Ohm's law is valid, but what will happen let us consider your voltage is a complex quantity. What will happen let us consider your current is a complex quantity

Have you ever thought about that if you have a complex voltage and a complex current then will the resistance will be a complex resistance, yes. In that case you cannot call the resistance as a resistance we call it as a impedance, but before doing that let us look at what do you mean by the complex number I am sure that all of us have some basic introduction to the complex algebra and we know that a complex number can be represented as the sum of a real part and an imaginary part. So this is the real part and this is the imaginary part.

And we also have learnt or probably some of us know that we can find out the magnitude of this complex number which is called the mod of complex number and it is represented by this $|z|$ sign by putting the z between this 2 lines and this is $= \sqrt{a^2 + b^2}$. And then another quantity in terms of the complex number is of hedge. So basically we can say that the phase of the z if we call as a ϕ which is the phase of the z .

So that is $\tan^{-1} b/a$. Now whenever we define a complex number this $|z|$ quantity is very important its absolute value or its magnitude or modulus and its phase. So this magnitude $|z|$ and the value of phase ϕ that defines a location or coordinates in the complex plane. Now when you are talking about the current as a complex number and when you are talking about the voltage as a complex number then obviously the resistance also becomes a complex number. So then we do not call it as a resistance, but we give a separate name called impedance.

(Refer Slide Time: 04:31)

Real World

- Circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance. In its place we use impedance, which is a more general circuit parameter.
- Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above.
- Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell.

In real world circuit element that exhibit much more complex behavior. So I mean have you seen a electric circuit a very sophisticated electrical circuit which is made only of the resistor no. We have like different resistance, we have capacitance, we have inductance, we have ionic components so many different things. So this element forces us to abandon the simple concept of resistance.

In its place we use impedance which is a more general circuit parameter like resistance impedance is a measure of the ability of the circuit to resist the flow of electrical current so the definition is same. Impedance as the name suggest it impedes something, it prohibits the flow of something, flow of what electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above.

Electrochemical impedance is usually measured by applying a small AC potential to an electrochemical cell and measuring the current through the cell. So when you talk about the electrochemical impedance we apply a very small value of the AC potential and then we measure the corresponding AC current in the cell and that gives us the electrochemical impedance.

(Refer Slide Time: 05:52)

Real World

- Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).
- Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. Linearity is described in more detail in a following section. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC circuit AC current signal containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions a Fourier series. Electrochemical impedance is normally measured using a small excitation signal which is done so that the cell's response is pseudo linear.

Linearity is described in more detail in a next session. In a linear of pseudo linear system, the current response to a sinusoidal potential will be sinusoid at the same frequency, but shifted in a phase. So basically why we prefer linear system because a linear system or pseudo linear system for let us say if we apply a sinusoidal voltage so in the output we will also get a sinusoidal signal only there will be phase shift is there.

It is not that I apply a sinusoidal signal and I am getting a triangular signal at the output. So that is the linear signal so basically it restores the shape or the information of the signal.

(Refer Slide Time: 06:59)

Introduction: Impedance Spectroscopy

- Impedance Spectroscopy measures the impedance of a system to an applied voltage

$$Z(\omega) = E(\omega) / I(\omega)$$

- Since Z changes with applied signal frequency, Z must be measured as a function of frequency and resistance of sample evaluated.
- It is known as AC Impedance Spectroscopy Or Complex Impedance Spectroscopy and also as Electrochemical Impedance Spectroscopy (when applied to electrochemical systems)

Okay inductance or this impedance spectroscopy measures the impedance of a system to the applied voltage. So as I said that is a function of the frequency now we are applying a voltage the potential which is a function of the frequency is a function of omega and the current also become an AC current which is a function of the frequency it contains the excitation frequency as well as it is harmonics.

So that is why the impedance is also a function of the omega. Since Z changes with the applied signal frequency Z must be measured as a function of frequency and resistance of sample evaluated. So let us say I have an unknown sample I want to measure the impedance of that sample. So since the impedance depends upon the frequency so impedance should be measure as a function of the frequency.

So I will do a frequency sweep and I will measure the corresponding impedance at each and every frequency. It is known as the AC impedance spectroscopy. This technique is known as the AC impedance spectroscopy or complex impedance spectroscopy and also known as the electrochemical impedance spectroscopy when applied to electrochemical system. Now there is another important thing is here.

Nowadays we can also do the impedance spectroscopy in the absence of the light or also in the presence of the light, even in the presence of the light we can modulate the intensity of the light which is the intensity modulated impedance spectroscopy.

(Refer Slide Time: 08:23)

Principle

- Electrochemical impedance is normally measured using a small excitation signal.

$$E(t) = E_0 \exp(i\omega t)$$

$$I(t) = I_0 \exp(i\omega t - i\phi)$$

Impedance,

$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0 (\cos \phi + i \sin \phi)$$

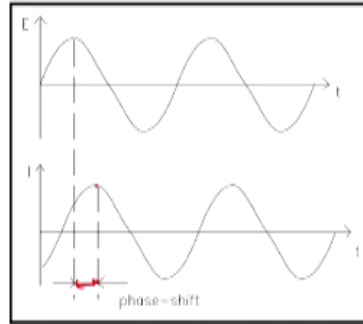


Figure 1. Sinusoidal Current Response in a Linear System

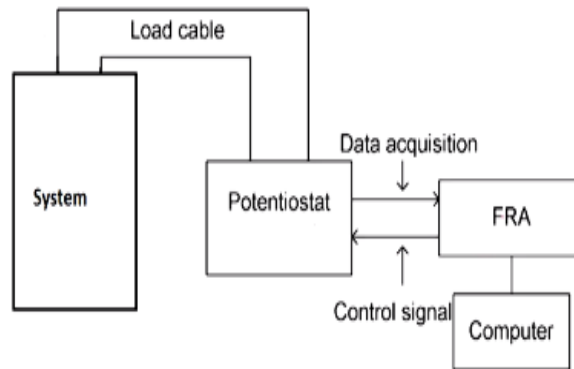
Now electrochemical impedance is normally measured using a small excitation signal. Now as a excitation signal we are giving $E(t)$ is $E_0 \exp(i\omega t)$ where ω is the frequency of the signal and E_0 is the basic amplitude. So I plot E versus t here and you can see that this is a sinusoid. So the corresponding current will be $I(t)$ is $I_0 \exp(i\omega t - i\phi)$ and there will be phase shift so $-i\phi$.

So it contains the frequency of the excitation and there will be a phase shift, but still it is a sinusoid. So the corresponding current will be a sinusoid, but there is a phase shift. You see that (09:03) if you look they are displaced. Now the top position is here, but here it is here. So there is a phase shift happening here right. So what will be the impedance? By definition we know impedance is E/I .

So it will be we can also write impedance as $Z_0 \exp(i\phi)$ that is amplitude and the phase part so that is basically the ratio of $E(t)/I(t)$. So basically it is $E_0 \exp(i\omega t) / I_0 \exp(i\omega t - i\phi)$ and $Z_0 \exp(i\phi)$ you can write it as $Z_0 \cos \phi + i \sin \phi$ because E to the power $i\phi$ we can write as $\cos \phi + i \sin \phi$. So basically there is a real part is there and then there is an imaginary part is there.

(Refer Slide Time: 09:45)

Instrumentation



Block diagram for a EIS measurement of an Electrochemical System

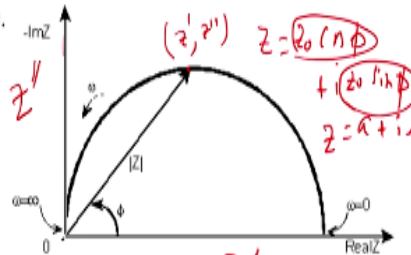
The conventional instrument system here what we have there is a system which is connected to a load cable to a potentiostat where you can the potentiostat is used to apply the AC voltage here and for the data requisitions we use a control signal which is connected to a computer along with a FRA and block diagram here of the EIS measurement system of an electrochemical system.

(Refer Slide Time: 10:10)

Data Representation: Nyquist

$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0 (\cos \phi + i \sin \phi)$$

- $Z(\omega)$ is composed of a real and an imaginary part.
- real part on the X axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot" (also Cole-Cole plot).



- Impedance is represented as a vector of length $|Z|$.
- Angle between this vector and the x-axis is the phase angle ϕ .

Now once we get the data so we represent the impedance data by 2 plot one is called the Nyquist plot another is called the bode plot. Now let us first see about the Nyquist plot. So the Z is the ratio of E/I which is $Z_0 \exp(i\phi)$ as you said that we can write it as $Z_0 \cos \phi + i \sin \phi$. $Z(\omega)$ is composed of a real and an imaginary part. Real part is on the X axis.

So here we put the real part and imaginary part we put it on the Y axis and the imaginary part on the X axis of the chart. So if we put the real part along the X axis and the imaginary part along the Y axis or you can write it as Z' and here you can write this as Z'' where Z' actually signifies the real part and Z'' signifies the imaginary part then this gap of this real part versus imaginary part that is called a Nyquist plot or also called Cole-Cole plot or Cole-Cole plot.

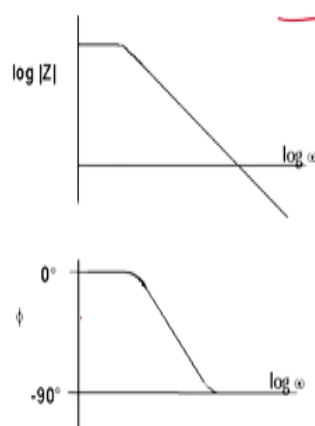
Impedance is represented as a vector of length Z obviously like let us say I have complex quantity $z = z_0 \cos \phi + i z_0 \sin \phi$. You compare it with $z = a + ib$. So this is the real part a and this is the imaginary part b . Now if I plot a diagram of the real and imaginary part. So I will get the location like this point which corresponds to Z' and Z'' so now if I connect it with the origin so we will get a line like this so this is a vector.

So this vector actually represents the complex impedance and the magnitude of this vector will give you the magnitude of this impedance and this vector whatever the angle is subtended to the X axis that gives you the phase of this vector so that gives you the phase of the impedance. And now you see that the frequency that we are sweeping from a low frequency to a high frequency. So towards the Y axis we get a high frequency value.

And as we go further and further way from the origin we get a low frequency value. So impedance is represented as a vector of length (Z) (12:31) angle between this vector and the X axis is the phase angle which is represented by ϕ .

(Refer Slide Time: 12:39)

Data Representation: Bode plot



The impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|Z| = Z_0$) and phase-shift on the y-axis.

There is another representation of the impedance spectroscopy called Bode plot. So in Bode plot the impedance is plotted as a function of the frequency of the phase angle is also plotted as the function of the frequency because in impedance spectroscopy basically we are changing the frequency. So the impedance is plotted with log frequency on the x axis and both the absolute value of the impedance mode Z which is Z_0 and phase shift on the y axis.

So in the x axis we can put the log of omega the frequency and the y axis we can put log of mode Z or Z_0 which is the amplitude or we can put the phase ϕ which varies between 0 to 90 degree. So this kind of data where you plot the amplitude versus frequency or the phase versus frequency that is called the Bode's plot or Bode plot. So now this was the ideal case, but what will happen in a real system.

(Refer Slide Time: 13:32)

Impedance Spectroscopy plot of real systems

- Deviate from ideal behavior due to :
- Distorted semicircles may arise due to
 - Overlap of semicircles with various time constants
- Depressed semicircles may arise due to
 - Electrolyte is not homogeneous
 - Distributed microscopic properties of the electrolyte
- Slanted or curved spikes may arise due to
 - Unevenness of electrode/electrolyte interfaces
 - Charge transfer across the electrode/electrolyte interface, diffusion of species in the electrolyte or electrode
- This deviation is explained in terms of a new circuit parameter called constant phase parameter

The real system there is a deviation from the ideal case as is always. So we get a distorted semicircles and this distorted semicircles may arise due to the overlap of semicircles with various time constants. Now this radius of this semicircle that gives the time constants on the circuit. Depressed semicircle may arise due to the electrolyte is not homogenous or distributed microscopic properties of the electrolyte.

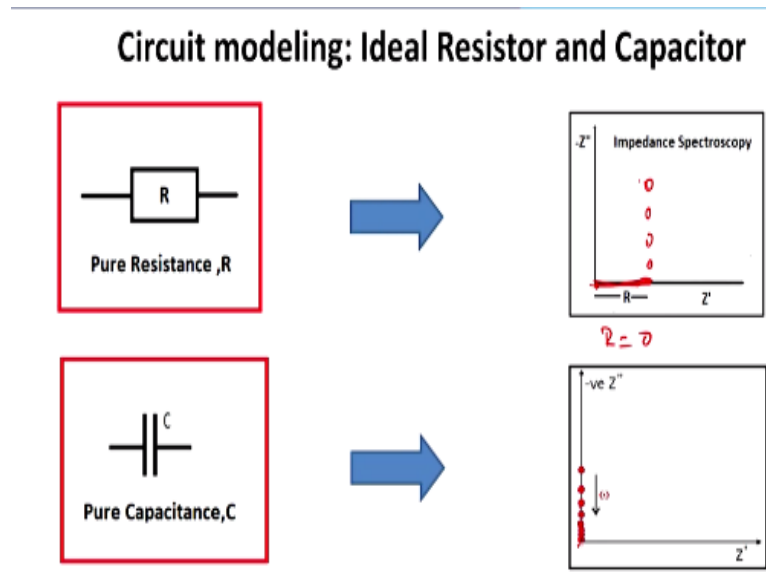
Slanted or curved spikes may arise due to the unevenness of electrodes electrolyte interface or charge transfer across the electrode or electrolyte interface. Diffusion of species in the electrolyte or electrode. This deviation is explained in terms of a new circuit parameter called constant phase parameter. So there can be deviation from the real circuit and that is called constant phase parameter and constant phase parameter can be due to the different reasons.

Now one important thing to mention here that so by impedance spectroscopy we can analyze the circuit. So when we have talked about the solar cell you remember that we have discussed about the equivalent circuit. So we said that any kind of solar cell can be represented by an equivalent circuit. Now once we have an equivalent circuit so we can use that equivalent circuit to model and feed the corresponding impedance.

So that means for any kind of solar cell if we do an impedance spectroscopy data and if we consider an equivalent circuit for that and if we feed that using that impedance circuit so we can get the corresponding electrical parameters for the devices. So by corresponding electrical parameters I mean the series resistance, the sun resistance, the capacitance, double layer capacitance or any ion diffusion or Warburg impedance.

So all of this different parameters which is actually the performance parameters of the solar cell that can be extracted just by analyzing the impedance data. So that is why impedance spectroscopy is a very powerful tool in the photovoltaics.

(Refer Slide Time: 15:27)

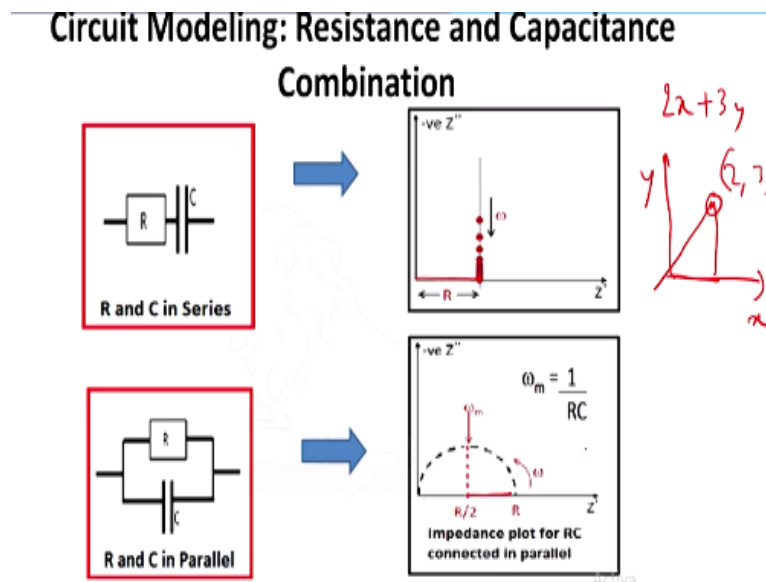


Now let us talk about the circuit modeling for an ideal resistor and capacitor. You see that if I have a ideal resistor like this it is a pure resistance. So then the impedance spectroscopy data if I plot Z' versus Z'' so it is just a dot on the real x axis and this value of this is a value of the resistance. It was a 100 ohm so that means this length is 100 ohm and if you have a pure capacitance like this which is a pure capacitance 100 microfarad capacitance.

For example, let us say. If I plot it in the Z' versus Z'' so it will look like a solid dotted solid gap. So it is again a straight line along the y axis, but it represents by the solid circles. Now what will happen if I put together both in a R and C . So I will have both this point which is shifted along the x axis and both this point. Okay let me ask one question so obviously from this figure we can see that this R has a definite value.

Now if R is 0 then this will be at this point. So when I am talking about the capacitance here pure capacitance so we consider $R=0$. Now similarly if we have a capacitance value of 0 then basically it is a simple dot. So if I have both resistance and capacitance then I have to come from the origin along this distance and then also I have to go along the y axis to represent both R and the C . So that is why in a real RC circuit.

(Refer Slide Time: 17:07)



As we will see in the next slide in this slide a real resistance and capacitance combination you can see a shift along the x axis and shift along the y axis and that is very obvious. Let us say I like to plot something like $2x+3y$. So what I will do I will plot along the x axis and I will also plot the y axis I will go 2 units along the x axis and then I will go the 3 unit along the y axis and I will get this point which is a coordinate of 2, 3 and which actually represents a vector $2x+3y$. If I add a unit vector to this, I will get a vector.

Now similarly the resistance and capacitance combination can be represented by a displacement along the x axis and the y axis. Now the question is the resistance and the capacitance can be combined in 2 different possible ways. It can be either in series or it can be in parallel. So if the resistance and capacitance are connected in series our previous

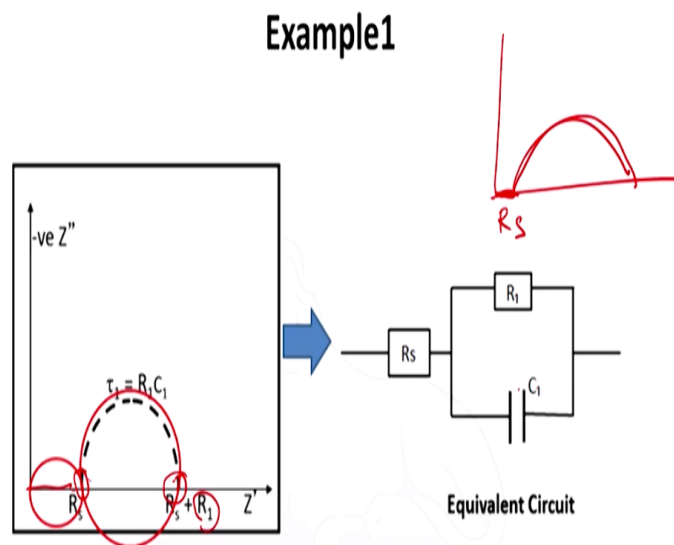
example 100 ohm resistance, 100 microfarad capacitance.

But now they are connected in series. So what will be corresponding impedance gap looks like. So the resistance has been shifted along the x axis 100 ohm and then the capacitance along the y axis. This is for the series circuit. It can also be connected as a parallel here you see the resistance is connected in parallel to the capacitance. So in this case what you will see that the impedance plot for the RC connected in the parallel that will give us like this kind of semicircular look.

And then this diameter of this semicircle is R or this part is R/2 and here the value of the capacitance is shown here and this value of omega changes at this point the value of omega is maximum and that maximum value of the omega gives the time constant of the circuit and that is 1/RC. So if it is a series resistance on capacitance it is only a point and then going up as a straight line.

And if you see a semicircle that means resistance and capacitance are connected in a parallel where the time constant is 1/RC.

(Refer Slide Time: 19:25)



Okay let us take an example so I have this kind of impedance gap this is my x axis, this is my y axis this is the Z prime this is the Z double prime right. So what I have seen that I have a curve like this semicircle it does not start from here, but it has shifted and started from here. So what does it mean so as we know it intersects along the x axis and the intersection point is actually a point of resistance.

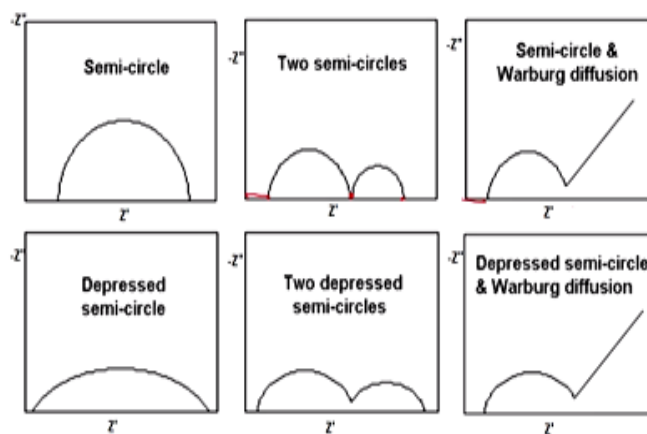
So that means it has a finite resistance at here and it has a finite resistance at here and also it has a time constant there is a capacitance value and the time constant is $R_1 C_1$. So basically so here this R_1 this value of the R_1 this resistance and the capacitance they are connected in parallel. So if the resistance and capacitance is connected in parallel then you will get a this kind of circuit.

Now in addition to that you have a resistance which is connected in series that is why this displacement along the x axis that is why this displacement along the x axis. So there is a displacement by the amount of R_s along the x axis and then there is a parallel combination of the resistance and the capacitance. So if we draw the equivalent circuit it will be a resistance R_s which is connected in series with resistance R_1 and capacitance C_1 which is connected in parallel with each other.

So by doing some simple analysis you can starting from an impedance data you can draw the corresponding equivalent circuit or if the equivalent circuit is given you can find out the corresponding impedance data.

(Refer Slide Time: 20:59)

Typical Plots for Some Electrochemical Systems



Typical Nyquist plots for electrochemical systems

Some typical plots for some electrochemical system is shown here like which you will see experimentally when you do the impedance spectroscopy for solar cell you can see a semi circle, but you already know that what does it mean right. So this R_s this is $R_s + R_1$ and the time constant (τ) (21:17) is $R_1 C_1$. So basically this is a series resistance which is connected or is resistant which is connected in a series to a parallel resistance and capacitance where the

last resistance and capacitance they are connected in parallel with each other.

It can be 2 semi circle, but the diameter of the semi circle is different right. So that means the value of the resistance is different. So that means we have one resistance here another resistance R1 here another resistance R2 here and the value of R1 and R2 is not same and we have also 2 different capacitance C1 and C2. Now you look here there is a semi circle in addition to that there is a spike is here.

So the semi circle means so there is a resistance here and there is a capacitance is there so if this semi circle touches along the x axis I know that there is another resistance component R1 is there, but instead of touching it is going up along the y axis. So this part comes due to the ion diffusion and that is called the Warburg diffusion. So if you see a semicircle with this kind of spike.

So then there are the resistance capacitance along with the ion diffusion or the Warburg diffusion component in the circuit. Now the semi circle can be depressed like this so that means so the y axis has been put under the stress here so this is depressed semi circle. It can have 2 depressed semi circles with different diameters. It can also have a depressed semi circle with a Warburg diffusion coefficients.

So these are the common typical impedance picture you will see while analyzing the data. Sometimes the impedance data can be very complex and once needs to consider a various kind of circuit model to get a best fitting. Now the electrochemical elements or what are the different contributions of the electrochemical cell when you measure the electrochemical impedance are the following.

(Refer Slide Time: 23:06)

Electrochemical elements

1. Electrolyte resistance (uncompensated resistance) (R_s, R_u)
2. Double layer capacitance (C_{dl})
3. Warburg impedance (related to diffusion) (W)
4. Charge transfer resistance (R_{ct})
5. Constant phase element (Q)

One is the electrolyte resistance. So in a electrochemical cell we use electrolyte. So electrolyte can also provide the resistance and that is usually called an uncompensated resistance so that is represented by R_s or R_u then there can be double layer capacitance C_{dl} . There can be Warburg impedance related to the diffusion which is represented by W . Charge transfer resistance R_{ct} or constant phase element Q .

So these are the different components. So whenever we model the circuit we have to keep in mind all of this factor. We have to consider about the electrolyte resistance, we have to consider about the double layer capacitance, we have to consider about the Warburg impedance, we have to consider about the charge transfer resistance also we have to consider about the constant phase element.

(Refer Slide Time: 23:51)

Electrolyte Resistance

- Resistance of an ionic solution. R_s, R_u
- It depends on :
 - (1) ionic concentration ✓
 - (2) type of ions ✓
 - (3) temperature ✓
 - (4) the geometry of the area in which current is carried. ✓
- In a bounded area with area A and length l carrying a uniform current the resistance is defined as:
$$R = \rho \frac{l}{A}$$

So what is electrolyte resistance so resistance of an ionic solution. So for example when you talked about the dye-sensitized solar cell we have seen that we have used iodine trichloride as a liquid electrolyte. So iodine trichloride liquid electrolyte that stays in a ionic form. So the resistance provided by this ions they are the ionic resistance. It depends upon the ion concentration.

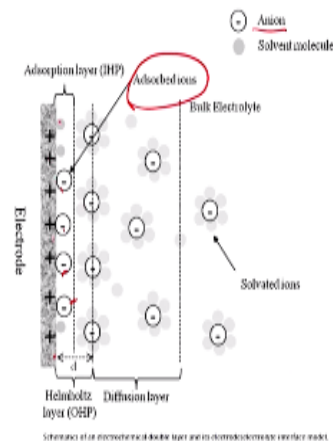
It depends what type of ions are there, is it a (()) (24:16) it depends upon the temperature of the system and it depends upon the geometry of the area in which current is carried. So basically a knowledge or R_s or R_U the electrolyte resistance can tell you about the ionic concentration. It can tell you about the types of ions, it can tell you the temperature, it can even tell you the geometry of the area in which current is carried.

In a bounded area with area A and length l carrying a uniform current the resistance is defined as $R = \rho l / A$ where l is the length A is the area and ρ is the coefficient of resistance.

(Refer Slide Time: 24:55)

Double Layer Capacitance

- Ions from the solution "stick on" the electrode surface
- Charges of these ions separate the charges in electrodes
- Separation is very small (order of angstroms)



Now what is double layer capacitance you look at this graph schematic of an electrical double layer and its electrodes and electrolyte interface mode. So here I have an electrode and you can see that this electrode behaves like a adsorption layer. So there are positive charge which lies at the electrode and just on the electrode there are negative charge is there and negative charge are what they are adsorbed ions.

So this negative charge are adsorbed ions, electrode is positively charged so there are positive charge here and then there are adsorbed ions are there. Okay but in addition to that there are

solvated ions are also there in the system. So this negative these are anion and the gray circle they are the solvent molecules. Now you see that this solvent anion they are being encircle with the solid molecules.

Now what will happen over the time the solvent molecules along with the solvent anions they can also come in the vicinity to this adsorbed ions. Okay so this distance from the electrode to the layer of the one layer this is the adsorption layer and then there is one more layer is there so that layer is called the Helmholtz layer. Beyond the Helmholtz layer we have the diffusion layer.

In this area there is a free diffusion of the ion is happening, but at this area once you come to the dotted boundary these electrons are attracted by the electrode here. So these are not the ions which is adsorbed on the electrode surface, but they stays to the vicinity of the electrode, but they cannot go outside the electrode also. So this 2 different kinds of ions or the 2 different layers of the ions can give rise to the 2 different capacitors.

And that is called the double layer capacitance and this distance is the Helmholtz layer beyond the Helmholtz layer you have a diffusion layer. So ions from the solution stick on the electrode surface so ions from the solution can stick on the electrode surface as you can see it here. Charges of this ion separate the charges is electrodes so since there is a charge is there in this ions so they can separate the charges in the electrode

So that is why they will pull only the positive charge close to them and separation is very small order of angstroms.

(Refer Slide Time: 27:07)

Charge Transfer Resistance (R_{ct})

- Electrode reaction is composed of :
 - (i) Charge transfer ✓
 - (ii) Adsorption/desorption ✓
 - (iii) Mass Transport ✓
 - Charge transfer may occur between the electroactive species and electrode
 - If no electron transfer, R_{ct} becomes very large
 - If there is an electron transfer reaction, R_{ct} becomes smaller
 - It connects in parallel with the double layer capacitance C
-

The third part in this case is the charge transfer resistance R_{ct} . Now the electrode reaction is composed of charge transfer adsorption or desorption or mass transport. Now let us say I have an electrode which I dipped in a ionic solution now what are the phenomena can happen. Ions can come and sit on the electrode or if there are ions already seated on the electrode they can go outside the electrode so that is called adsorption or desorption.

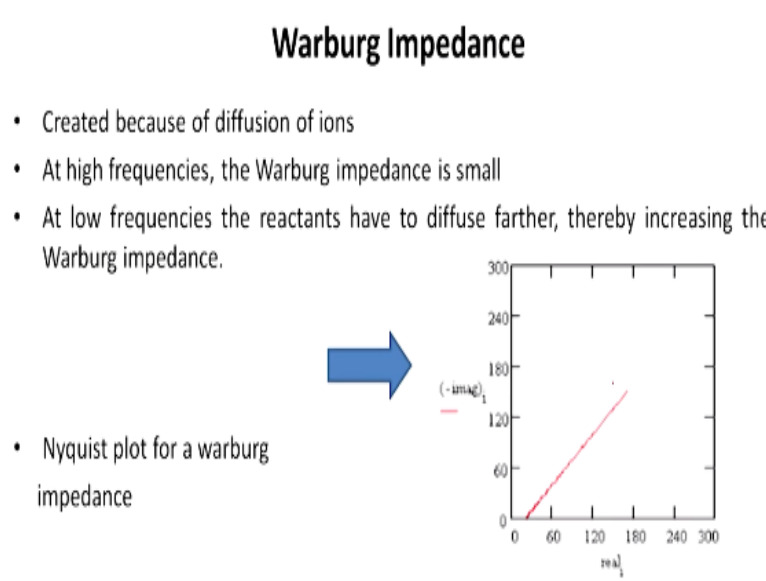
And then the electrode can transfer the charge to the ions that is the called the charge transfer or there can be a mass transfer also. So there are this 3 different phenomena can happen. We have already seen what is the adsorption and desorption. Now we look about the charge transfer. Charge transfer may occur between the electroactive species and electrode. So for example if I take a platinum electrode.

And then if I dip that electrode in some kind of charge electrolyte solutions so then there can be charge transfer between the electrode and the electroactive species. If no electron transfer R_{ct} becomes very large. So if there is no electron transfer between the electrode if there is no physical electron transfer between the electrode and the electroactive solution then the value of R_{ct} is very large. If there is an electron transfer reaction R_{ct} becomes smaller.

So for a electron transfer reaction charge transfer resistance value will be smaller and if there will be no charge transfer reaction then the R_{ct} value will be larger. It connects in parallel with the double layer capacitance C. So the charge transfer resistance or R_{ct} that is connected in the parallel with the Cdl or double layer. So whenever we have a electrode electrolyte interface will have a double layer capacitance and we will have some possibility of the charge

transfer resistance.

(Refer Slide Time: 29:02)



One more important thing is the Warburg impedance. Now this Warburg impedance that is created because of the diffusion of ion. Now the ion can diffuse inside the solvent in the system. So because of the diffusion of the ion this Warburg impedance or the spike things comes. At high frequencies the Warburg impedance is small so where is that you will get the high frequency towards the origin there the Warburg diffusion component is small.

At low frequency the reactants have to diffuse farther thereby increasing the Warburg impedance. So as we know what is impedance? Impedance is it is the obstacle the electrons or ions will feel. Now when the frequency is high so that means the number of vibration per unit time is very, very high. So then they will not feel that much impedance. So that is why the value of the impedance is small.

The ions whatever ion is a massive let us say it is considered as a massive charge particles, but when the frequencies value is low and it has to be diffused farther thereby the value of the Warburg impedance increase. So the Warburg impedance is represented by this kind of spike or the straight line. Nyquist plot for a Warburg impedance.

(Refer Slide Time: 30:14)

Constant Phase Element

- In general CPE has the properties of R and C
- Mathematically impedance of a CPE is given by the Complex quantity:

$$Z_{\text{CPE}} = 1 / (Y_0(j\omega)^n) = Z_0(j\omega)^{-n}, \quad 0 \leq n \leq 1$$

$$Z = \frac{1}{(Y_0 j\omega)^n}$$

$n=0$

- When $n = 0$, Z is frequency independent and $Z_0 \Leftrightarrow R$, CPE \cong pure Resistance
- When $n = 1$, $Z = 1/j\omega Y_0$. Hence $Y_0 \Leftrightarrow C$, CPE \cong pure Capacitance

The last thing was in those electrochemical parameters constant phase element. In general, the constant phase element or if you take the first word CPE that has the properties of the resistance and capacitance R and C. So in general CPE has the properties of R and C. Mathematically, impedance of CPE is given by the complex quantity Z_{CPE} is $1/Y_0 j \omega$ to the power whole n which is Z_0 which is the absolute magnitude or the modulus of the impedance times $j \omega$ which is the complex number $j \omega$.

The frequency times $-n$ where the values of n runs between 0 and 1. When $n=0$ Z is the frequency independent and $Z_0 = R$ and CPE is the pure resistance, but when $n=1$ $Z=1/ j \omega Y_0$ and hence $Y_0=C$ CPE pure capacitance. So the constant phase element can be either pure resistance or it can be pure capacitance. For the values of n in this situation like $Z=1/Y_0 j \omega$ to the power whole n right.

If you put $n=0$ so what will happen this to the power 0 then there will be no frequency term it is 1. So basically what you will get that Z_0 is nothing but R that is a pure resistance and if the n value is 1 the Z will be $1/Y j \omega$. So what is that, that is nothing but the capacitance $1/\omega * Y_0$ so that is the pure capacitance. So for the other values of 0, n and 1 for the values of n between 0 and 1 there will be mixed combination of the resistance and capacitance.

(Refer Slide Time: 32:01)

Constant Phase Element

Constant Phase Element:

$$- Y_{CPE} = Y_0 \omega^n \{ \cos(n \pi/2) + j \sin(n \pi/2) \}$$

- $n = 1$ → Capacitance: $C = Y_0$
- $n = 1/2$ → Warburg: $\sigma = Y_0$
- $n = 0$ → Resistance: $R = 1/Y_0$
- $n = -1$ → Inductance: $L = 1/Y_0$

'Non-ideal capacitance', $n < 1$ (between 0.8 and 1)

So constant phase element Y_{CPE} that is $Y_0 \omega^n \cos n \pi/2 + j \sin n \pi/2$. Now for $n=1$ capacitance $C=Y_0$ for $n=0$ we have seen it is resistance $R=1/Y_0$, $1/Y_0$ is the resistance R . $n=1/2$ it is Warburg so $\sigma=Y_0$ and $n=-1$ it is inductance $L=1/Y_0$. So non ideal capacitance $n < 1$ between 0.1 and 1.

(Refer Slide Time: 32:33)

Applications of EIS

- Study corrosion of metals.
- Study adsorption and desorption to electrode surface
- Study the electrochemical synthesis of materials.
- Study the catalytic reaction kinetics.
- Study the ions mobility in energy storage devices such as batteries and super capacitors.

Now what are some of the application of EIS. First of all, it has been commonly used in metallurgy for the study of corrosion of metals. It has been used for the study of adsorption and desorption to electrode surface in electrochemical spectroscopy. It has used in the study of electrochemical synthesis of materials. It has used for the study of the catalytic reaction kinetics and also for the study the ion mobility in the energy storage device such as batteries and super capacitors.

And it has been extensively used to find the ion mobility, Warburg diffusion coefficient in perovskites solar cells and inorganic solar cells also. So the theory of the ion migration or the Warburg diffusion that comes by the possibility or when this impedance spectroscopy was done on the perovskites solar cell.

(Refer Slide Time: 33:21)

Limitations of EIS

- Many parameters to fit: sufficient amount of data is necessary
- Overlapping processes in the frequency-plane may not be separated
- In theory, an indefinite number of equivalent circuits can be used to explain a recorded spectrum

But there are some limitation also of this impedance spectroscopy may parameters do not fit like sufficient amount of data you always need to fit the parameter and since this is a fitting it can always generate errors. So depending upon like what is the equivalent circuit we are considering and how much the good is our fitting parameter that will give the reliability of the data.

Overlapping process in the frequency-plane may not be separated and in theory and indefinite number of equivalent circuits can be used to explain a recorded spectrum. So that means one can use n number of equivalent circuit there can be so many possibility to explain this spectrum so then there is like uniformity or (()) (34:04). Somebody can explain it in this way somebody can explain in other way.

But in most of the cases if we know some common spectrum and we know about the photophysics of the systems then we can correlate the photophysics with the impedance spectroscopy or in other way the impedance spectroscopy will give you an excellent overview about the electrical parameters and the interplay of the ions and the electrons in the advance solar cells like perovskites solar cell or perovskites silicon tandem solar cells.

Now this field is very, very vast there are lot of emerging techniques which is now associated with the impedance spectroscopy and it has been extensively used nowadays.

(Refer Slide Time: 34:46)

References

- Barsoukov, E.; Macdonald, J.R. ; Impedance Spectroscopy; Theory, Experiment, and Applications, 2nd ed. John Wiley & Sons, Inc. , 2005.
- Yuan, Xiao-Zi ; Song, C.; Wang, H.; Zhang, J. ; Electrochemical Impedance Spectroscopy in PEM Fuel Cells; Fundamentals and Applications; Springer;2010.
- Lvovich ,Vadim F.; Impedance Spectroscopy; Applications to Electrochemical and Dielectric Phenomena; John Wiley & Sons, Inc. ;2012.
- Orazem, M. E.; Tribollet, B.; Electrochemical Impedance Spectroscopy ;John Wiley & Sons, Inc;2008.

You can look lot of references for example some of this is given here one of them is impedance spectroscopy theory, experiment and application and then there are electrochemical impedance spectroscopy in PEM fuel cells fundamentals and application. Electrochemical impedance spectroscopy in PEM fuel cells fundamentals and application Springer, impedance spectroscopy application to electrochemical and dielectric phenomena by Wiley and electrochemical impedance spectroscopy by Wiley and Sons.

So there are lot of books are there and it is also worthwhile to mention that there are lot of excellent research papers are available in this area. So if you are really looking for working in the impedance spectroscopy for solar cell characterization then there are lot of research paper is there which explains how this impedance parameters of a solar cell can be analyzed to correlate its photophysical properties.

So far as far as the some advance characterization system is concerned we have discussed about some basics like vacuum technology which is very, very essential if somebody is working in the photovoltaics field. We have discussed about some advanced imaging technique like scanning electron microscopy which is also required to know to optimize the morphology of the film.

And then there is some advanced characterization techniques for the electrical parameters like

static and dynamic parameters of a solar cell to optimize the efficiency of a solar cell that is done by impedance spectroscopy that has also been discussed. Now there are several other advanced characterization techniques that are there. For example, if I like to study the morphology of a solar cell then in addition to the SEM one can do atomic force microscopy also.

Now in atomic force microscopy that comes in different combinations like it can be conductive atomic force microscopy and then there are Kelvin probe microscopy is there. So then there are like different varieties of this AFM technique is there then some people use the STM also. Similarly, if we talk about the photophysics so not only the impedance spectroscopy.

One can do a time resolved spectroscopy like TCSPC Time-correlated single-photon counting where the time resolution is low to circumvent that there are like femtosecond time-resolved spectroscopy. So we can find out the transient absorption spectroscopy or photoluminescence spectroscopy by using femtosecond laser spectroscopy. So all of these things will give you the information about the defect states.

It will give you the information about the location of the defect states and various other information what kind of charge transport is happening in the systems and what is the reason for the recombination in the system where the recombination is happening etcetera. Similarly, like if somebody who wants to know more about the mobility of the system there are different methods like that.

For example, this SCLC method space charge limited current method the time of (()) (37:36) methods is there. Now in addition to that there are this solar cell parameter characterization unit like in solar cell you measure the current and voltage and fill factor. So you measure the JAC, VOC and fill factor. Now the standard multi meter which we used for measuring the current and voltage is not enough if you want to measure some sophisticated solar cell.

So there is a very standard system that is there is called solar simulator which mimics the sunlight by using an 1.5 filter along with some broadband (()) (38:09) light source and there which fills the voltage and we measure the currents and the instrument can generate the data of the quality factors that the fill factors value from where there we can calculate the efficiency and that is standard technique for measurement of the efficiency.

Again if we talk about the stability of the devices so then there is another instrument called humidity chamber where we allow the solar cell with a different humidity level, different like, you know, temperate level which is an environmental chamber. We allow the expedited aging of the system and we measure the aging of the system or the degradation or the stability of the system.

So in addition to that there are several other characterization units to the solar cell like pulse, laser based system, pulse PV based systems and then like as I have said that this conducting force microscopy, IR microscopy is there. So there are lot of advanced characterization systems are there, but these are some of the techniques which is essentially required if somebody wants to work in a solar cell.

So I guess we have learnt some concept and understanding about some characterization systems which is required for the solar cell or photovoltaics technologies. So with this we will conclude this course and I believe that you have enjoyed our whole course. Thank you very much for your attention throughout the semester.