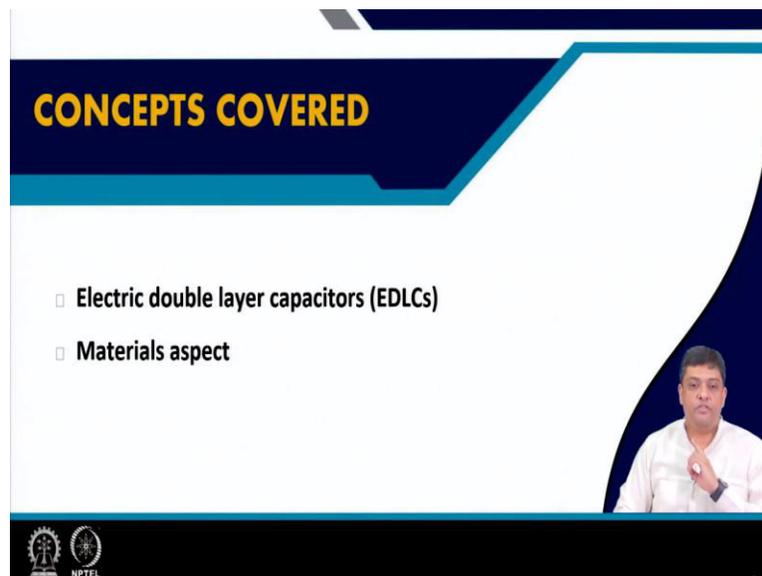


Physics of Renewable Energy Systems
Professor Amreesh Chandra
Department of Physics
Indian Institute of Technology Kharagpur
Lecture 31
Electric Double Layer Capacitors (EDLCs)

Welcome again. In the previous two lectures I gave you quite detailed introduction about the topics which we are going to cover in this module be it be concept of double layer formation, be it the concept of pseudocapacitors and I had also spent significant amount of time in explaining to you the way the word supercapacitor was actually coined.

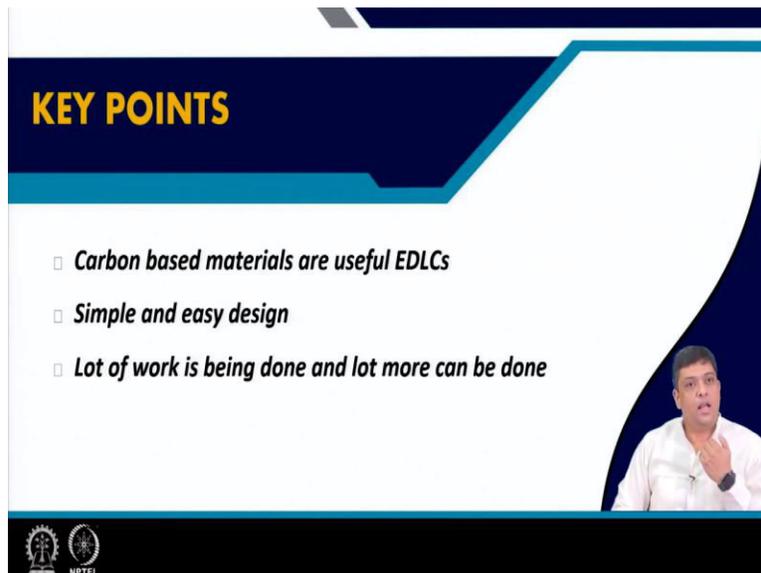
We had also given you the classification of supercapacitors and two main classifications are either as electric double layer type supercapacitors or pseudocapacitors. So, let us today start with our discussion on one of these supercapacitors that is electric double layer type supercapacitors.

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So, the main concept which we will cover today we will be dealing with the explanation of formation of the double layer in the kind of supercapacitors which we will be discussing today. How the materials aspect coming into the picture and how they will contribute in the future to make these devices even more useful to us?

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KEY POINTS

- *Carbon based materials are useful EDLCs*
- *Simple and easy design*
- *Lot of work is being done and lot more can be done*

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You will find that carbon-based materials would be extremely useful for EDLC's. These EDLC's that is electric double layer capacitors are quite simple to understand and the design of these EDLC's is also very simple. There is lot of work being done and you can also contribute appreciably and significantly to improve the performance of these devices even further.

So, in the previous module, if you remember at the end, we had discussed about this synthesis of carbon structures using various kind of bio-wastes and that strategy could help in reducing the impact of bio-waste on the local environment or we could use agri-wastes and then convert into carbon particles which could be used in lithium-ion batteries.

Similar types of carbon structures are also useful for these devices. So, today you will see that the idea which I proposed earlier that if you like to make an industry which is going to make carbon nanoparticles from agri-waste or bio-waste, then they are also going to be extremely useful for another energy storage device that is supercapacitor.

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1) The electrochemistry of double layer formation involves:

- a) *Electrostatic energies* ✓
- b) *Molecular or ionic distribution of the ions and solvent molecules in the high interfacial field.* ✓

If one considers a charge electrode surface and the interfaces in the double layers, the electric field can attain very high values; $\sim 10^7 \text{ V cm}^{-1}$.

Similar picture is obtained in the solvation shells of the ions.

The formation of double layer describes the condition of two array layers of opposite charges, separated by a small distance, and facing each other.

This is very similar to parallel plate type conventional capacitors.

The slide features a background with faint icons of a lightbulb, a gear, and a network. A small video inset in the bottom right shows a man in a white shirt speaking. The NPTEL logo is visible in the bottom left corner.

Now, the moment I say there is a double layer formation in a system which is using an electrolyte. Then what am I indicating I am possibly indicating that the electrochemistry of the double layer formation is involving electrostatic energies obviously two parallel arrays of charges and molecular or ionic distribution of ions and solvent molecules in high interfacial field. These are the two concepts which are possibly going to come into picture.

If you consider a charged electrode surface and the interfaces in the double layers, the electric field can actually obtain very high values these are similar to what are obtained in the solvation shells of the ions. And because of this field the formation of the double layer describes the condition of two arrays, two arrays means at both the electrodes.

But if I consider one electrode side then you have two array layers of opposite charges separated by a distance and facing each other. So, you have two array layers of opposite charges separated by a distance and facing each other. This is what we are indicating when we are talking about double layer formation and the moment I look into this picture, this looks to be very similar to a parallel plate type conventional capacitor.

Here the only difference is that d is very small at the negative charge if I am talking about the positive charge on the electrode is in the electrolyte side and this is on the electrode surface.

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Electrical double layer capacitors (EDLCs)

Electrolyte
Positive electrode
Negative electrode
Load resistance
Electric field

This supercapacitor is based on the principle of formation of the electric double-layer at the interface between the electrode and the electrolyte.

This high value is obtained in double layer capacitor because:

- the situation is very different in double layer because no bulk dielectric in the normal sense is present.
- only the water of hydration of the ions and the monolayer film of adsorbed solvent water at the electrode interface constitutes the dielectric of the double layer capacitance.

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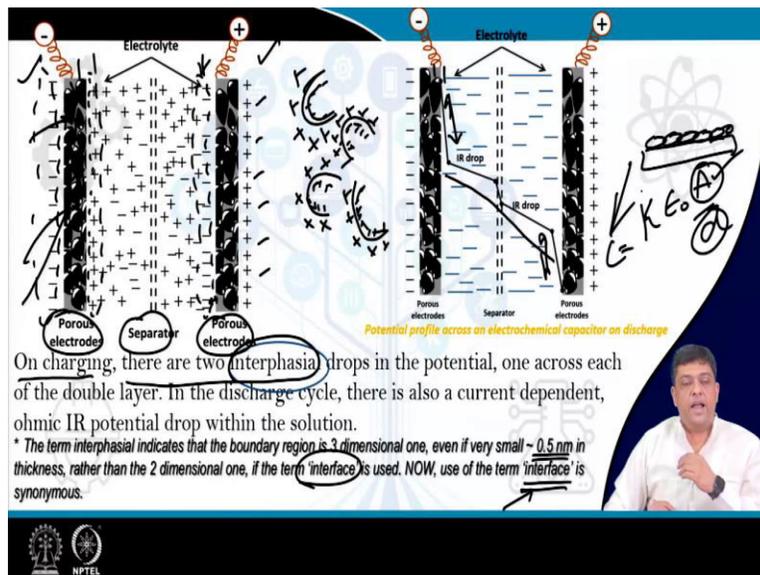
So, what is an electrical double layer capacitor or electric double layer capacitor this supercapacitor is based on the principle of formation of the electric double layer at the interface between the electrode and the electrolyte, this is what I have just spoken. The high value comes in because the situation is slightly different as just stated what is the major difference, there is no bulk dielectric in the normal sense this dielectric is actually replaced by an electrolyte.

In addition to that, only the water of hydration of the ions and the mono layer film of absorbed solvent water at the electrodes interface constitutes the dielectric of the double layer capacitance. So, what are we seeing? We have an electrode surface. Now, if you have an electrode surface, then you can had some absorption of the water on this surface.

So, you have not absorbed water layer on this surface. In addition, if you have positive charge on this surface, then you have a counter layer which is made up of the negative charges coming in from the ions in the electrolyte or you can say the solvated ions if you consider the true picture. So, you have the solvent in ions and the adsorbed layer which is on the surface of the electrode.

So, the layer which is formed by the either the cation or the anion which counters the charge on the electrode, the total in between these two layers that is the only dielectric which you consider and because it is happening at a very short distance the distance becomes extremely small.

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So, what are we talking about? Let us, explain once again. So, on charging, there are two interfacial drops, I have just used and encircled this word interphasia. This spelling is not wrong. I will just tell you what it means. So, when you charge there is a drop in the potential one across the double layer. In the discharge cycle what happens there is also a current dependent on ohmic IR potential drop within the solution.

So, you if you charge then you have let us say positive charges then what is happening you have the counter negative charges stabilizing in front of the positive electrode and on the other side you have the opposite picture and on top if what we had seen, we had also said that on the electrode surface you can have some absorb water. This is what you see.

Please note that the term interphasia indicates that the boundary region is three dimensional one, even if it is very small of the order of 0.5 nanometres in thickness. And it is not a two dimensional where the term interface is used. So, if you are talking about two dimensional pictures, then you talk about interface where if you talk about the three dimensional picture, then the word interphasia is more appropriate.

But, in today's understanding or the way people use this term interface has become synonymous to interface. So, if but, the true picture would have been interphasia if you are talking about three dimensional picture. But interface is mostly used today. So, I hope it is clear to you how the

charges are forming. So, you have a separator, you have the porous electrode and you have the counter electrode which is also porous electrode in this case.

Both are made using carbon and you can see that you have pores in these structures, so that if I have the materials then charges can form on each surface and then you will see that the double layer formation is taking place. So, you have let us say a double layer formation here, here, here, here and here. So, this is why you use nanomaterials it gives you the area which is much larger and accessible for the electrolyte iron that is the aqueous media to intercalate.

So, the electrolyte can move in and then you can have the formation of layers and if you have the area which is much larger where this layers are forming, then you have increased the value of A and in the equation $K \epsilon_0 n A / d$ which is equal to C, A has increased the value of d is already in the nanometre range you are talking about separation at the interface the d is already quite small. So, the value of C will go up.

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What will be electric field across this double layer?

We know, whenever there is separation of electric charges, electric fields arise.

We have already discussed earlier the Coulomb's law and Poisson's equation.

So, consider a plane metal electrode interface at 1 V across an ideally polarizable electrode double layer. Then the field E would be:

$$E = [1.0 / (3.8 \times 10^{-9})] \text{ V cm}^{-1}$$

for a double layer thickness of 3.8Å {this value corresponds to the distance of closest approach* of simple hydrated cations eg. Na⁺}

**In reality, the thickness depends on the ionic radius of the ion and thickness of its time averaged hydration or solvation shell.*

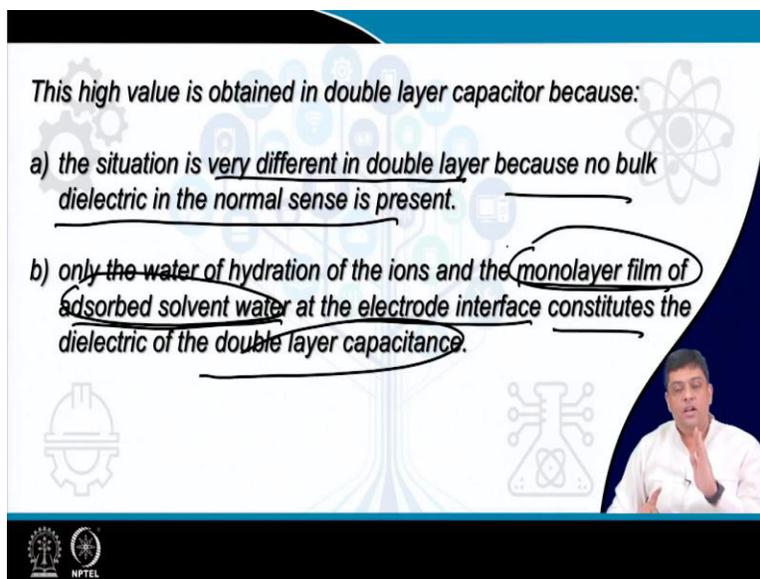
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Just to explain why we mentioned the electric field across this double layer can have very high values. We know that whenever there is a separation of electric charges electric field arises the first lecture of this module we had started with the discussion on Coulomb's law and then the field induced that is why we started from there. We have also discussed Poisson's equation.

So, if you consider a plane metal electrode interface, at one word across an ideally polarizable electrode, double layer. So, electrode which can be polarized then the field is 1 divided by 3.8 into 10 raise to the power of 8 volts per centimetre. What is this 3.8? This value corresponds to the distance of closest approach of simple hydrated cations such as sodium. So, this is the distance of closest approach for $N + 2$ for an electrode which is at 1 volt.

So, that is a near as it can reach. So, you have 3.8 angstrom separation if you can calculate, you will find that the electric field would be extremely high. In reality, the thickness depends on ionic radius of the ion and the thickness of its time average hydration or solvation shell. So, what happens as a function of time and then how do you obtain the solvated and then you have to consider the solvation shell and that is the value which will come into picture here.

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This high value is obtained in double layer capacitor because:

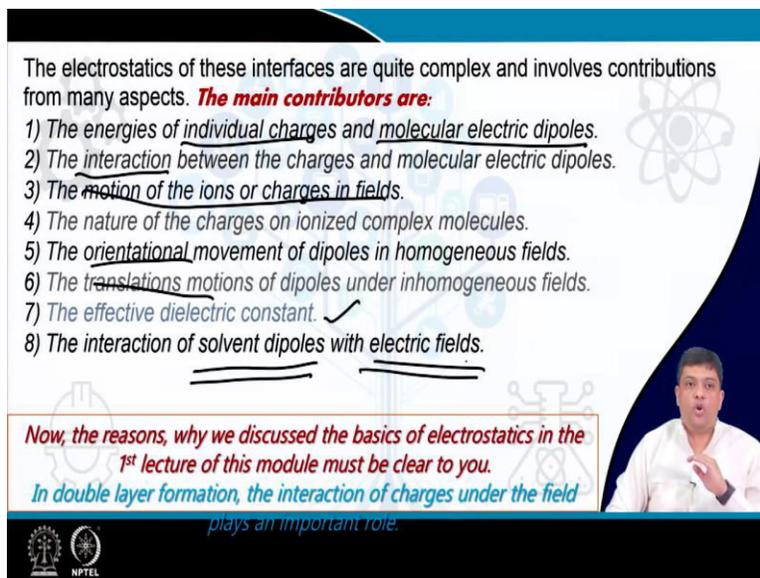
- a) the situation is very different in double layer because no bulk dielectric in the normal sense is present.
- b) only the water of hydration of the ions and the monolayer film of adsorbed solvent water at the electrode interface constitutes the dielectric of the double layer capacitance.

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Hence, the values which you obtain are extremely high because, you see you are dividing 1 by 3.8 into 10 raise to power of 8. So, of the order of 10 raised to power of 7 per centimetre. Clearly the situation is very different in double layer because no bulk dielectric is used. And we are only considering the water of hydration of the ions or the monolayer film of absorbed solvent water at the electrode interface along with the absorb solvent, water and monolayer film which will constitute the dielectric.

Hence, d is small A is extremely large and this type of systems are called as electric double layer capacitors. So, double layer you saw what is the formation explain using the concepts of capacitors or the physics of capacitors and you have also seen why you have such high electric fields. So, electric charges separated and the whole concept very similar to capacitors and therefore, they are called as electric double layer capacitors.

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The electrostatics of these interfaces are quite complex and involves contributions from many aspects. **The main contributors are:**

- 1) The energies of individual charges and molecular electric dipoles.
- 2) The interaction between the charges and molecular electric dipoles.
- 3) The motion of the ions or charges in fields.
- 4) The nature of the charges on ionized complex molecules.
- 5) The orientational movement of dipoles in homogeneous fields.
- 6) The translations motions of dipoles under inhomogeneous fields.
- 7) The effective dielectric constant. ✓
- 8) The interaction of solvent dipoles with electric fields.

Now, the reasons, why we discussed the basics of electrostatics in the 1st lecture of this module must be clear to you.

In double layer formation, the interaction of charges under the field plays an important role.

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The electrostatics of these interfaces are quite complex and they actually involve many more contributors. If you look into what can be the major contributors, you will be immediately answering to my question and those would be you will have to consider individual charges and molecular electric dipoles.

Now, if you have charges and molecular electric dipoles and how are they interacting between each other or what is the interaction between them as of now, you have considered that there is a static layer but you are talking about formation of a layer in a liquid media or an aqueous media where there is Brownian motion.

So, you have motion of the ions and hence how do you form the static layer or is the layer continuously having some motion and it is more dynamic in nature rather than being static in nature. So, the motion of ions or charges in fields as well as a function of orientation or translational motions of the dipoles.

And what will be the effective dielectric constant you will take you will take the water and then use its dielectric constant or you will use the combination of the deposited monolayer of the film along with the of that of the electrolyte, which we are using. So, there are various complex pictures which come into picture and along with that the solvent dipoles itself can interact with the electric fields and then lead to the change in the overall capacitance value which you are obtaining.

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Advantages of EDLCs

1. Deliver capacitance in Farad order. ✓
2. Using high surface area materials, high capacitance value can be easily achieved. ✓
3. No need of special charging circuits to control charging and discharge.
4. Overcharging do not hamper the life time for the device.

Other advantages will be discussed a bit later.

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Even if these are detrimental or they can limit the maximum value which you can obtain still compared to conventional capacitors, the EDLC's will be able to deliver capacitances which are very high maybe in orders of farads or few 100 of farads. The advantage is being driven by the fact that they are using high surface area materials and therefore, you are having circuits or devices which do not need special charging circuits to control the charging or the discharging rates.

And because you are talking about layer formation in the electrolyte electrode interface, then the overcharging do not hamper the lifetime of the device and they can have very high life that is cycling stability can be of the order of a few 100, 1000s. So, they can be used over 100000 or more cycles and we will see as we go along what are the other advantages.

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Disadvantages of EDLC

1. The life span is limited depending on the choice of electrolyte used in the device.
2. Operation window is limited in the case of aqueous electrolyte based EDL capacitor.
3. Electrolyte leakage. ✓
4. High internal resistance and associated IR drop.

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But there are disadvantages the value can change by the choice of electrolyte, the operational window is limited because you are using aqueous electrolyte if you use water based electrolytes and you are looking at operational window of 1.2 volts plus minus because that is where water dissociates and then the electrolyte becomes unstable.

If you are unable to seal these kinds of devices carefully then because you are talking about aqueous electrolytes, they can have the problem of leakage out of the device and along with this the high internal residence what we saw during the charging or the discharging cycle, you saw that there is an IR drop specifically during the discharge cycle you have the IR drop which is very prominent and that can reduce the achievable specific capacitance values.

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Some important properties of EDLC

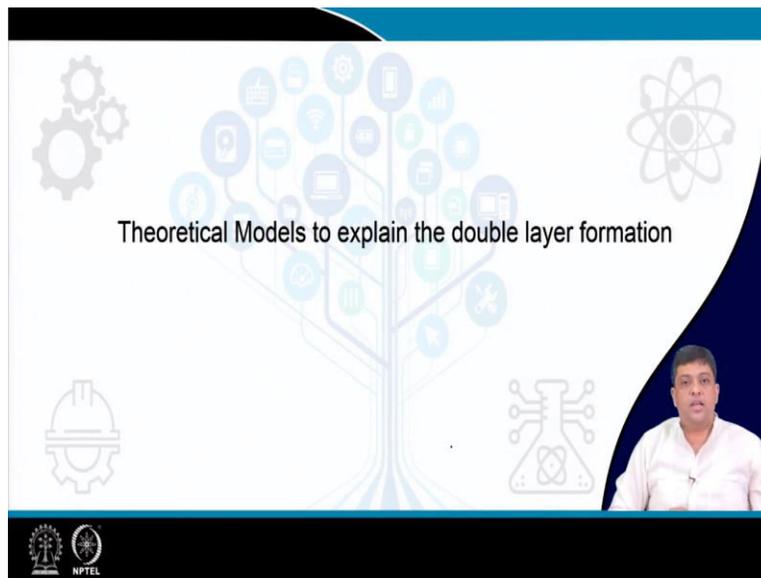
Property	Value
Temperature range	-25 to +70 °C ✓
Electrode material	Activated charcoal ✓
Electrolyte fluid	Aqueous electrolyte, organic electrolyte ✓
Storage mechanism	Electric double layer formation ✓
Pollution	No or minimum ✓
Cycle number	>100,000 times ✓
Capacity per unit volume	1-100 F ✓



But, if I have to talk about a stable carbon based EDLC then the typical temperature range it can operate is between let us say minus 20 to plus 70 degrees, if you go below 0 degrees, then you have to talk about electrolytes which are actually not going to freeze. So, it is about the electrolyte choice when you go below room temperature or you go towards the freezing temperature for water.

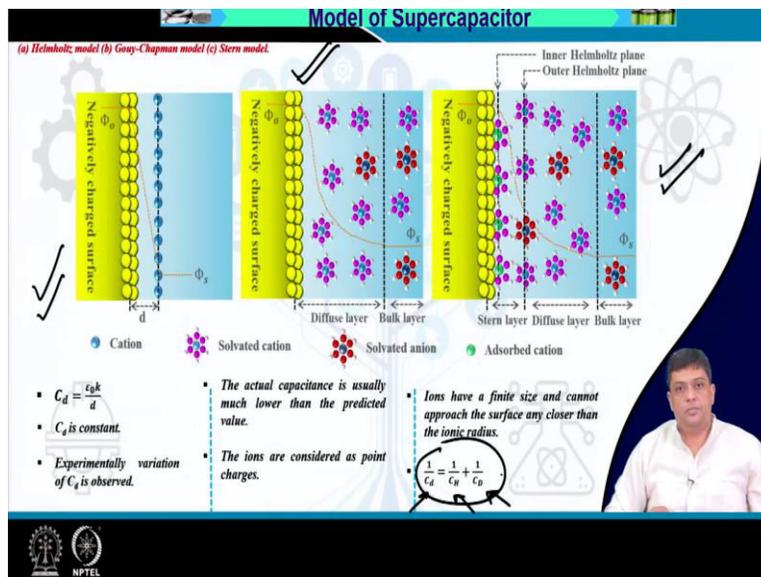
Hence, you can use aqueous or organic electrolytes and both these electrolytes will lead to the formation of double layer and you can get very high values once form the environmental impacts are quite minimal and if you want to use them for large number of cycles that can easily be obtained let us say 100,000 times or more and the EDLC's which are available in the market are in the range of one to 100 farads.

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Now, these are the concept which we explained let us see how mathematically the same was described.

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So, they are of various models which were used and which have been proposed. The first one is your Helmholtz model picture. The second one is your Gouy Chapman model and the third one is your Stern model. So, let us start and discuss each one of them.

So, that you also get a idea about the theory behind the way you obtain the final capacitance that is $1/C_d$, where a C_d can be your observed specific capacitance or the capacitance which is equal to $1/C_H$ and $1/C_{\text{capital D}}$, where $1/C_{\text{capital D}}$ can be the capacitance the diffusion layer and C_H is the capacitance in the Stern layer.

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Helmholtz Model

This is the First and basic model to explain Electric Double Layer formation in a supercapacitor.

Assumptions:

- Charge separation at the metallic electrode and electrolyte interface
- There is a charge separation at the interface
- All the ions are at a separation of 'd'
- Infinite diffusion rate

The diagram shows a yellow vertical bar on the left labeled "NEUTRICALLY CHARGED SURFACE". To its right, a blue vertical bar represents the electrolyte. A double-headed arrow between the surface and the electrolyte indicates a separation distance 'd'. A small circle with a plus sign is shown near the interface. The text "Helmholtz Model" is written at the bottom left of the diagram area. The slide also features a small inset video of a man in a white shirt in the bottom right corner and logos for NPTEL at the bottom left.

So, The Helmholtz model was the first and the basic model which was used to explain the electric double layer formation. What are we describing you are describing that you have an electrode surface which is charged on this surface you can have absorbed water molecules from the aqueous electrolyte and then you have the counter ions which are there to balance the charges which are stabilizing on the charged electrode surface.

So, one layer is forming in the electron and the other charged layer is in the electrolyte. This was proposed by Helmholtz basic assumption was that the charge separation at the metallic electrode or you can say the electron and the electrolyte interface was means you had two layers which were forming at the interface and these two layers were separated by a distance d along with that, you have an infinite diffusion rate. So, this is what you were believing. So, you had two potentials which were stabilizing and you had the infinite diffusion rate.

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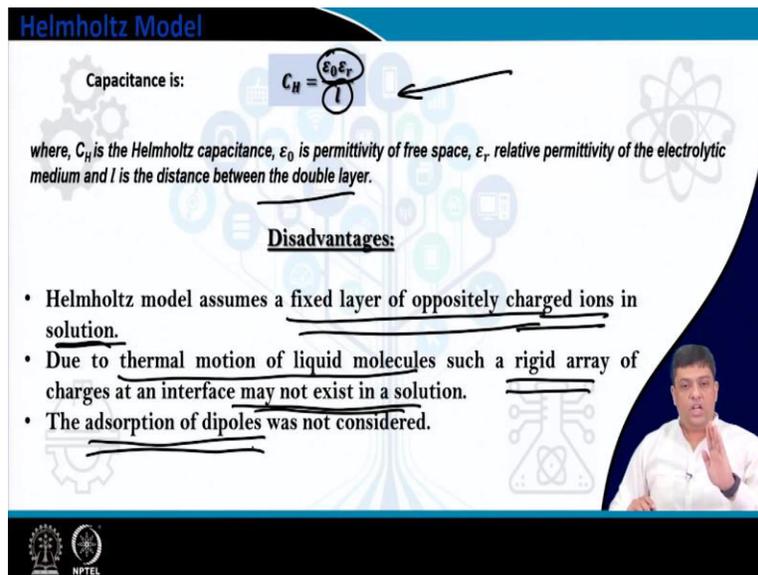
Helmholtz Model

Capacitance is: $C_H = \frac{\epsilon_0 \epsilon_r}{l}$

where, C_H is the Helmholtz capacitance, ϵ_0 is permittivity of free space, ϵ_r relative permittivity of the electrolytic medium and l is the distance between the double layer.

Disadvantages:

- Helmholtz model assumes a fixed layer of oppositely charged ions in solution.
- Due to thermal motion of liquid molecules such a rigid array of charges at an interface may not exist in a solution.
- The adsorption of dipoles was not considered.

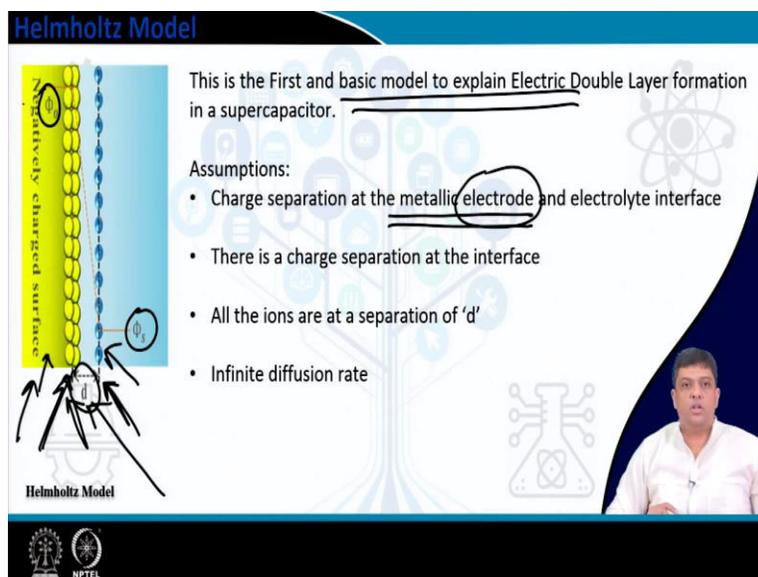


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Assumptions:

- Charge separation at the metallic electrode and electrolyte interface
- There is a charge separation at the interface
- All the ions are at a separation of 'd'
- Infinite diffusion rate



The capacitors was basically given by epsilon naught epsilon r by l where CH is the Helmholtz capacitance epsilon 0 is the permittivity of free space epsilon r is the relative permittivity of the electromagnetic medium and l is the distance between the layer. So, very similar to what you had seen in the case of conventional capacitance.

But there came the first disadvantage it assumed a fixed layer of oppositely charged ions in the solution fixed layer. So, if I go back you see this is a fixed layer we are talking about and that is

not correct. You are talking about a fluid and motion of ions in the fluid we have seen we are talking about the flow of these ions which are undergoing Brownian motion.

So, how do you get fixed layers along with that, you have thermal motion and getting rigid arrays at the interface would be quite difficult. And the third point which was not considered was the absorption of the dipoles they were just not considered.

Then, this was actually able to explain up to certain facts, but the moment you started talking about getting a specific capacitance at very high scan rates or discharge rates, then you were unable to explain the observed data. But initial model was good enough to tell why the specific capacitance actually increases, so very simple model.

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Gouy-Chapman Model
Gouy-Chapman proposed a more complicated model to explain EDL behaviour.

Assumptions:

- Introduction of a potential dependent parameter in the model.
- The thermal motions of ions near charges surface was considered.
- Introduction of a diffused double layer.
- It was considered that the concentration of oppositely charged ions decreases with distance from the surface.

The diagram illustrates a negatively charged surface (yellow spheres) with a potential Φ_0 . It shows a diffuse layer of ions (purple and red spheres) and a bulk region. The potential in the bulk is Φ_b . The diagram is labeled "Gouy-Chapman Model".

This limitation was removed by Gouy-Chapman which considered a slightly modified picture and then they introduce certain new concepts. What was proposed by them that there is a potential dependent parameter, there is a potential dependent parameter. The thermal motion of ions near the charges surfaces was considered.

So, you see that there is no static layer, but they are randomly slightly distorted from a layer if you may say so, then they are not exactly at one layer but they are showing some kind of motion but if you draw a locus of these charges then these charges would be the layer, which will be countering the charge which is formed in the electrode layer.

And this would be forming the double layer even though you can turn them as a diffused double layer. Why? Because you had a continuously reducing potential which was not linear but it was nonlinear before you could reach the bulk of the material. And it was considered that the concentration of the oppositely charged ions decreased with the distance from the surface.

So, you when you move away from the diffuse layer and you reach the bulk layer, you are actually able to go to the normal electrolyte condition where the overall condition is charge neutral the condition was only getting modified near the charged surface. So, two opposite pictures, one static charges one potential dependent parameters and with a diffused double layer.

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Gouy-Chapman Model

Solving the Boltzmann distribution of the ions using Poisson's electrostatic law and associated boundary conditions, the capacitance value for the diffuse layer could be expressed as:

$$C_D = \left(\frac{2Z^2 e^2 C_0 \epsilon_r \epsilon_0}{k_B T} \right)^{1/2} \cosh\left(\frac{ZeV}{2k_B T}\right)$$

where, Z, e, C₀, k_B, T and V denote ionic charge, electronic charge, bulk concentration of ionic species, Boltzmann constant, temperature, and the applied potential, respectively.

Disadvantages:

- This model also considered the charge as point charges.
- Overestimated the ionic concentration close to the charge surface.
- Failed in the case of multivalent ions to explain the charge concentration.

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So, solving the Boltzmann distribution of ions using the Poisson's electrostatic law one could show that the capacitance of diffuse layer was given by the equation given in this slide. But, there were some immediate consequences and which were evident disadvantages this model also considered the charges as point charges.

It overestimated the ionic concentration close to the charge surface and it failed to explain the condition if you have multivalent ions. So, if you have conditions were are multivalent ions then the formation of the charge layers could not be explained.

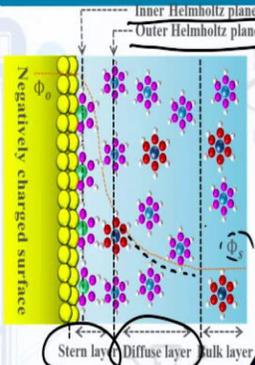
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Stern Model

Stern combined the propositions of the earlier two mentioned models.

Assumptions:

- The double layer was divided in two parts.
- A Stern layer and a Outer diffused layer
- Stern layer was then divided into two parts:
a) IHL and b) OHL.



The diagram illustrates the Stern Model of the double layer. It shows a negatively charged surface (yellow spheres) on the left. The potential is labeled as ϕ_0 . The Stern layer is divided into the Inner Helmholtz plane (IHL) and the Outer Helmholtz plane (OHL). The diffuse layer is shown as a region where the potential decreases from ϕ_0 to ϕ . The bulk layer is the region where the potential is constant at ϕ . The diagram also shows the distribution of ions (red and purple spheres) in the Stern and diffuse layers.

Then came the contribution from Stern and very simple Stern model actually combines the propositions of both the earlier models. It states that the double layer has two parts what is that a Stern layer and a diffuse layer the Stern layer is having two components the inner Helmholtz layer and the outer Helmholtz plane and the diffuse layer is the one where there is a continuous reduction in the field before you reach the field ϕ , which is that in the bulk of the solution. So, you considered static charges as well as the diffusion parameters.

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IHP and OHP

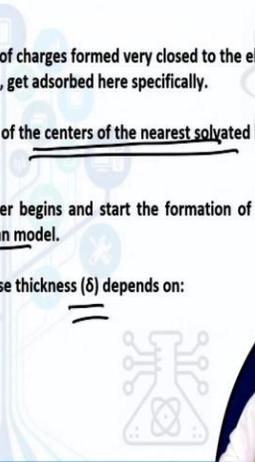
Inner Helmholtz plane/layer (IHP/IHL) is the surface of charges formed very closed to the electrode surface. It is considered that the ions, with finite size, get adsorbed here specifically.

Outer Helmholtz plane/layer (OHP/OHL) is the locus of the centers of the nearest solvated ion next to inner Helmholtz plane.

Beyond the outer Helmholtz plane, the diffuse layer begins and start the formation of double-layer, similar to what was proposed in Gouy-Chapman model.

This field extends to the bulk of the electrolyte, whose thickness (δ) depends on:

1. Ionic charge ✓
2. Electronic charge ✓
3. Temperature ✓
4. Ionic concentration ✓
5. Dielectric constant of electrolyte ✓



The diagram illustrates the Stern Model of the double layer. It shows a negatively charged surface (yellow spheres) on the left. The potential is labeled as ϕ_0 . The Stern layer is divided into the Inner Helmholtz plane (IHL) and the Outer Helmholtz plane (OHL). The diffuse layer is shown as a region where the potential decreases from ϕ_0 to ϕ . The bulk layer is the region where the potential is constant at ϕ . The diagram also shows the distribution of ions (red and purple spheres) in the Stern and diffuse layers.

What is the inner Helmholtz plane or layer is the surface of charges formed very close to the electrode surface similar to the model given by Helmholtz it is considered that the ions with finite size get absorbed here specifically. So, ions gets absorbed. The outer Helmholtz plane is the locus of these centres of the nearest solvated ions. So, now, you are not considering the point charges, but you are considering the solvated ions.

So, if I consider let us say the electrolyte potassium hydroxide KOH then solvated ion K plus surrounded by the water molecule. So, solvated ions were considered. Beyond the Helmholtz plain the diffuse layer similar to what was proposed by Gouy-Chapman appears and then only you reach the condition where the bulks solution condition is obtained.

This field which we are talking about the condition of diffuse layer extend to the bulk of the electrolyte, whose thickness actually depends on the ionic charge the electronic charge the temperature, the ionic concentration and the dielectric concentration of the electrolyte or dielectric constant of the electrolyte.

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The slide is titled "Treatment of the diffuse layer". It contains two bullet points: "❖ To understand the diffuse layer ion distribution" and "❖ To estimate its dependence on surface charge density". Below these is a yellow box labeled "Approach:" with a downward arrow pointing to a grey box containing "✓ Poisson's electrostatic equation" and "✓ Boltzmann distribution law". The slide also features a small video inset of a man in a white shirt in the bottom right corner and logos for IIT Bombay and NPTEL at the bottom left.

So, to understand the diffuse layer distribution we will have to have certain points in our mind that what are we going to take into consideration we are going to take into consideration the static charge is the diffuse part of the layer and then combine the final capacitance absorbing both these layers to obtain the final specific capacitors or the capacitors of the double layer. So,

we will use the Poisson's electrostatic equation and Boltzmann distribution law to obtain the mathematical equations.

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Treatment of the diffuse layer

Let ψ_r is the potential at a distance r from the electrode surface.
Then, the concentration of cation (c_+) and anion (c_-) at that distance can be expressed as:

$$c_{\pm,r} = c_{\pm}^0 \exp\left[-\frac{z_{\pm}e\psi_r}{kT}\right] \quad \text{--- (1)}$$

where, c_{\pm}^0 , z_{\pm} represent the bulk average stoichiometric concentration and charge numbers of cations, anions, respectively.

The space charge density ρ at a distance r can be expressed as:

$$\rho_r = z_+ e c_+^0 \exp\left[-\frac{z_+ e \psi_r}{kT}\right] + z_- e c_-^0 \exp\left[-\frac{z_- e \psi_r}{kT}\right] \quad \text{--- (2)}$$

One-dimensional electrostatic distribution of ions using Poisson's equation:

$$\frac{\partial}{\partial r} \left(\epsilon_r \frac{\partial \psi_r}{\partial r} \right) = -4\pi \rho_r$$

Substituting the value of ρ_r

$$\frac{\partial}{\partial r} \left(\epsilon_r \frac{\partial \psi_r}{\partial r} \right) = -4\pi \sum c_{\pm}^0 z_{\pm} \exp\left[-\frac{z_{\pm} e \psi_r}{kT}\right]$$

Using the identity

$$2 \frac{\partial^2 \psi_r}{\partial r^2} = \frac{\partial}{\partial r^2} \left(\frac{\partial \psi_r}{\partial r} \right)^2$$

$$\frac{\partial \psi_r}{\partial r} = \pm \left[\frac{8\pi kT}{\epsilon} \sum_{\pm} c_{\pm}^0 \exp\left[-\frac{z_{\pm} e (\psi_r - \psi_s)}{kT}\right] - 1 \right]^{1/2}$$

So, if you consider the concentration of cations and anions at a given distance then you can write at this concentration can be related with a potential which is ψ_r at a distance r from the electrode then the concentration of the cation or the anion can be given by the relation given in equation number 1 on this slide. Where C_0 represents the average stoichiometric concentration and z_+ or z_- represent the charge number of cations or anion respectively.

Now, once I have obtained the concentration, we can talk about the space charge density at a given distance r and that is given by equation number 2 in this slide. So, now, I have obtained the space charge density I have also obtained the concentration. Using the one dimensional electrostatic distribution of ions given by Poisson's equation we can write $\epsilon_0 \frac{d^2 \psi}{dr^2} = -\rho$.

So, we have obtained the value of ρ from this equation substituting the value of ρ which we have obtained earlier in this equation we can reach to a condition which is given in the last equation by remembering the identity that $\frac{d}{dr} \left(\frac{d\psi}{dr} \right)^2 = 2 \frac{d\psi}{dr} \frac{d^2 \psi}{dr^2}$. So, we can get a relation how your potential is going to change as a function of distance. This is what we are saying. This one comes in from the constant of integration. So, now, we have actually obtained a relationship between the two terms.

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Boundary condition: $\frac{\partial \psi_r}{\partial r} \rightarrow 0$
 $r \rightarrow \infty$
 $\psi_r \rightarrow \psi_s$

The equation mentioned in the previous slide arises by incorporating these boundary conditions.

Now, assuming Gauss's relation:

$$\left(\frac{\partial \psi_r}{\partial r} \right)_a = -4\pi q_M / \epsilon_a$$

It can be applied near the electrode surface bearing the charge density q_M , at a closest approach a , ϵ_a is the local value of the dielectric constant

In that region, taking the mean value of ϵ_a as $\bar{\epsilon}$

And knowing that they are by $\frac{d\psi}{dr} \rightarrow 0$, if you are talking going towards the solution side ψ_r is equal to ψ_s . Use this relation you will get the Gauss's relation which is given by the $\left(\frac{d\psi}{dr} \right)_a = -4\pi q_M / \epsilon_a$ where what is it you are getting the charge density is given by q_M at a closest approach distance of a ϵ_a is the local value of the dielectric constant. If you take the average value of the dielectric constant then let us say we write by $\bar{\epsilon}$. So, now we are going to replace ϵ_a by $\bar{\epsilon}$ and then we will see what happens.

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In that region, taking the mean value of ϵ_a as $\bar{\epsilon}$
 Moreover, solvent dipole orientation at the electrode surface will lead to condition, which will mean that a lower value of $\bar{\epsilon}$ in the region $r = a$ than further away from the electrode.

With these assumptions, q_M is obtained as:

$$q_M = \left(\frac{kT\bar{\epsilon}}{2\pi} \sum_{\pm} c_{\pm} \left\{ \exp \left[\frac{ze(\psi_a - \psi_s)_{\pm}}{kT} \right] - 1 \right\} \right)^{1/2} \rightarrow (1)$$

For symmetrical electrode, $|z_{\pm}| = z_+ = |z_-| = z$, and $c_{\pm} = c_+ = c_- = c$

Therefore,

$$q_M = \left(\frac{kTc\bar{\epsilon}}{\pi} \right)^{1/2} \sinh \left[\frac{ze(\psi_a - \psi_s)}{2kT} \right]$$

With the condition that the solvent dipole orientation at the electrode surface will lead to the condition what does it mean that permission of the double layer which means, that a lower value of absolute in the region r is equal to a then further away from the electrode. So, with this assumption what is the value of q_M you will obtain is given by equation number 1 in this slide.

For symmetrical electrodes that mean both the sides you have the same electrodes you have z plus minus is equal to z plus that is equal to z minus that is equal to z and z c z plus minus is equal to c plus is equal to c minus that is equal to c .

Hence, what do you get you get the relation for q_M . It is very clear that q_M also depends on temperature and the type of the ions you are going to use because that will define the fields and the kind of electrolyte you will use because that will define the dielectric constant. So, you must remember that you have parameters which will define the value of q_M .

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Capacitance of the diffuse part of the double layer

The overall potential difference between metal and the solution can be expressed as addition of two parts.
 $\phi_M - \psi_1$ and $\psi_1 - \psi_s$ where, ψ_1 is the mean potential at $r = a$

This contribution depends on q_M so that $\frac{\partial(\phi_M - \psi_s)}{\partial q_M} = \frac{\partial(\phi_M - \psi_1)}{\partial q_M} + \frac{\partial(\psi_1 - \psi_s)}{\partial q_M}$ ①

This equation can be written as: $\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$ ②
 C_1 is the Helmholtz compact layer capacity, and C_2 is diffuse layer capacity

Proceeding further: $C = \frac{C_1(z^2 e^2 \bar{c} \bar{\epsilon} / 2\pi kT)^{1/2} \cosh[ze(\psi_1 - \psi_s) / 2kT]}{C_1 + (z^2 e^2 \bar{c} \bar{\epsilon} / 2\pi kT)^{1/2} \cosh[ze(\psi_1 - \psi_s) / 2kT]}$ ③

If you have the value of q_M , you can clearly see that you can obtain the conditions for the overall potential difference and you will find that, you can write the final capacitance value in the way which is written in equation 3 of this slide. It is clear from this equation that there are various parameters which will contribute in the value c , which is a combination of capacitance in the Helmholtz layer or the Stern layer and the diffuse layer.

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Capacitance of the diffuse part of the double layer

Considering point charges, as described by Gouy, ψ_a becomes identical with ϕ_M , the potential of the metal with respect to the solution

$$\frac{\partial q_M}{\partial(\psi_a - \psi_s)} = \left(\frac{z^2 e^2 \bar{c} \bar{\epsilon}}{2\pi kT} \right)^{1/2} \cosh \left[\frac{ze(\psi_a - \psi_s)}{2kT} \right]$$

This may be identified with the differential double layer capacity C .

But, this relation had a major discrepancy because of the:

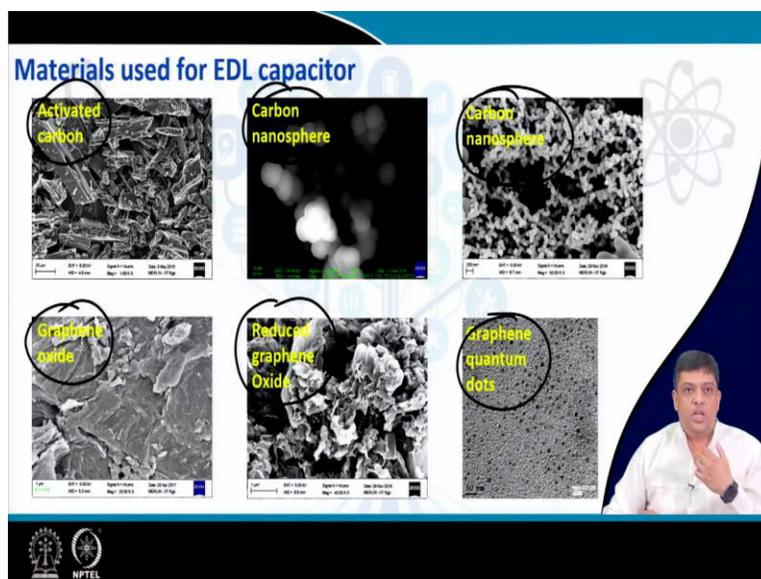
- ❖ The assumption of point charge ✓
- ❖ Continuous ionic charge distribution upto electrode surface

Considering the point charges for example, in the Gouy Chapman model, you have ψ_a becomes identical with ϕ_M the potential of a metal with respect to the solution and you will

find that if you take the derivative, you can obtain the relation of variation of $\frac{dq}{d\psi}$ minus ψ .

So, this may be identified with the differential double layer capacity this way is this you can also talk about that differential double layer capacities. But this relation had a major discrepancy that it assumed a point charge and continuous ionic distribution which was removed in the subsequent models and the most accepted model is the one given by the Stern postulates.

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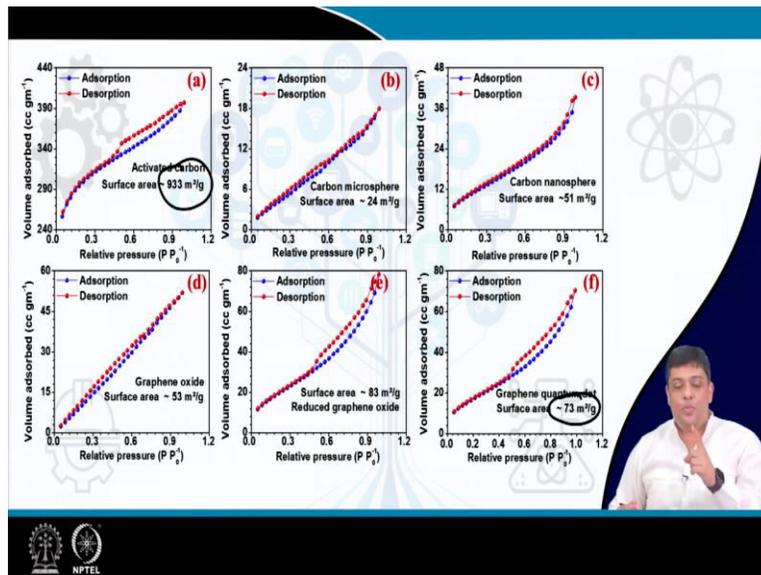


If you look into the discussion today, you see that we have been focusing on the use of different materials carbon based materials, but do you only have one type of carbon? No, you have

carbons of various types. And if you choose different types of carbons, you will get different kinds of values from these kinds of supercapacitors and these are the pictures which we have seen earlier also when we are talking about lithium-ion batteries.

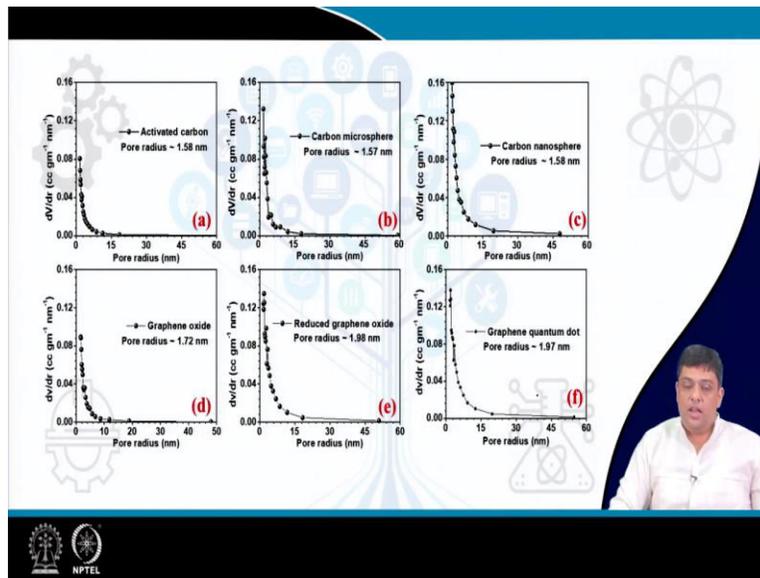
So, we had talked about activated carbon carbon nano spheres, carbon nano and carbon micro spheres, graphene quantum dots reduce oxide or graphene oxide. So, you have different kind of carbon structures which can be obtained.

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They have different surface areas you can have right from 933 meter square per gram to 73 meter square per gram. So, you can see now that you have materials with different surface area and if you have different surface area what will change the specific capacitance obtained using those materials will surely change because the value of a is changing.

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We will see that they also have different pore radius and how do we estimate these values, we have a dedicated module number 11 and 12 which we will be discussing on characterization techniques and there we will talk in detail about the way you estimate the pore size the pore volume the pore radius and how these impact the electrochemical performance of the energy storage device.

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Pores of the material

Porosity is an important property for the EDL type supercapacitor.

- ✓ Over all increases the surface area of the materials
- ✓ Depending the pore size, capacitance will be decided for material.
- ✓ Higher pore size means that larger ions can be accommodated within the material

The diagram illustrates the structure of a porous carbon layer. It shows a current collector on the left, a porous carbon layer in the middle, and an electric double layer on the right. The porous carbon layer consists of carbon particles and an electrolyte solution channel. A magnified view of a carbon particle shows an inaccessible inner-pore. Labels include: Current collector, Porous carbon layer, Electric double layer, Electrolyte solution channel, Carbon particle, and Inaccessible inner-pore.

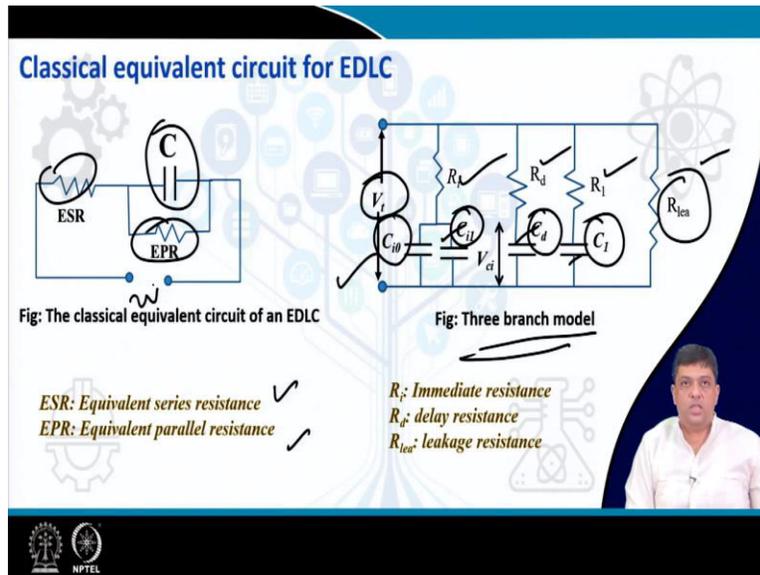
Figure: Pores of the material

A small inset image of a person is visible in the bottom right corner of the slide.

But let me just very briefly give you what these pores are as we have seen these pictures these are the voids between two particles and depending upon the pore size the capacitance will be

decided why because depending upon the pore size the electrolytes would be able to intercalate or move out and if you more electrolytes are able to access the material surface then you have higher magnitude of double layer which will be considered and hence the capacitance will go up.

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How do you look into the electrical side of these EDLC's. So, if you consider the classical equivalent circuit of the double layer what you are seeing you are simply seeing the equivalent series resistance and then you have two resistance in combination with a capacitor circuit.

But in reality if you take the three branch model what you have, you will consider the capacitances at the first layer and then you have the diffuse layer and then the final capacitance which of the devices you will consider and then the load or the leakage resistance which you will also consider. So, you have the three resistance which you will consider along with that the capacitances which you will consider and that is what the voltage you will be obtaining.

So, depending upon the equivalent circuitry which you want to draw the EDLC's can be broken down into a combination of RC circuits and then you can find out the voltage which you will be obtaining from these devices.

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Calculation of specific capacitance from CV

Capacitance of a supercapacitor $C = \frac{dq}{dv}$

Current flowing through the circuit $I = \frac{dq}{dt}$

Combining the equation,

$$C = \frac{\int I dt}{dv}$$

Scan rate applied to the capacitor,

$$S = \frac{dv}{dt}$$

So, the formula can be rearranged as

$$C = \frac{1}{vS} \int_{-v}^{+v} I(v) dv$$

Mass specific capacitance, $C_s = \frac{C}{m}$

$$\therefore C = \frac{1}{m v S} \int_{-v}^{+v} I(v) dv$$


EDL capacitance from CV profiles

Y

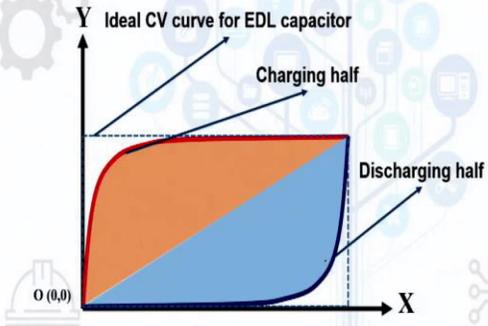
Ideal CV curve for EDL capacitor

Charging half

Discharging half

X

O (0,0)



Calculation of specific capacitance from CD

Capacitance of a supercapacitor $C = \frac{dq}{dv}$

Current flowing through the circuit $I = \frac{dq}{dt}$

Combining the equation, $dq = \int I dt$

Total charge accumulated at the electrode, $dq = I \Delta t$

Voltage developed at the electrode excluding the voltage drop, $dv = V - IR$

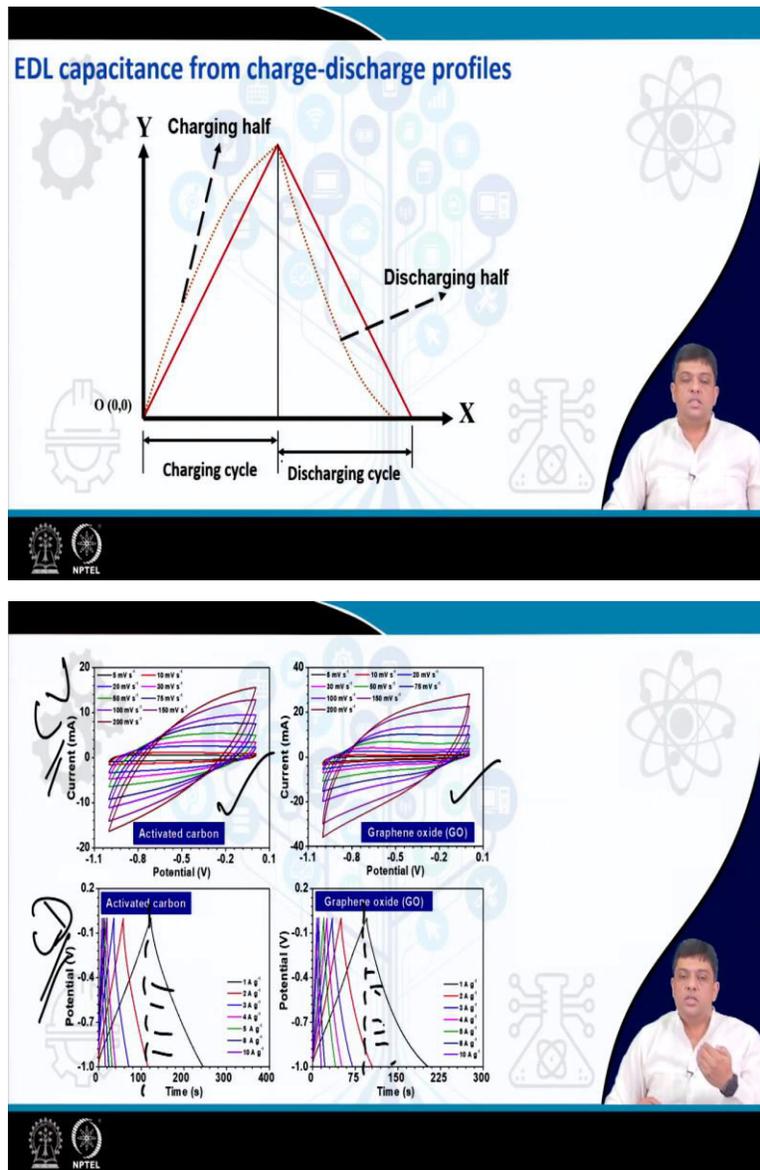
Mass specific capacitance, $C_s = \frac{Q}{m}$

$C_s = \frac{I}{m} \frac{dt}{V - IR}$

To calculate the specific capacitance, you have two kinds of techniques one is called the cyclic voltammetry and the other is charge discharge and these are the typical formulas which are used and how they are obtained to extract the value of C, we will be spending dedicated lectures on these characterization tools.

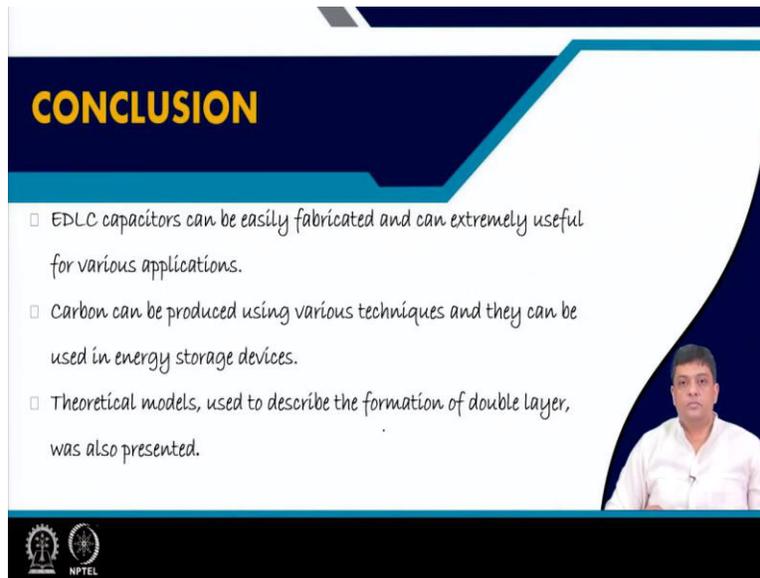
So, I am not spending time now, because we will spend dedicated lecture on CV and CD where you will be able to understand more in detail, but these are the two techniques which are used to extract the value of the specific capacitance C_s , why C_s ? We are writing specific capacitors because we are dividing the capacitance by the mass. So, then, we are talking about the specific capacitance.

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And we will see what does these curves look like but if you look into our typical capacitor fabricated using an activated carbon or a graphene oxide, this is the CV curve and this is the CD curve which you have and by using the discharge side of this cycle, I can estimate the specific capacity of the device. So, this is what you do experimentally and you will understand each and every step of performing this experiment when we take the lecture on CV and CD.

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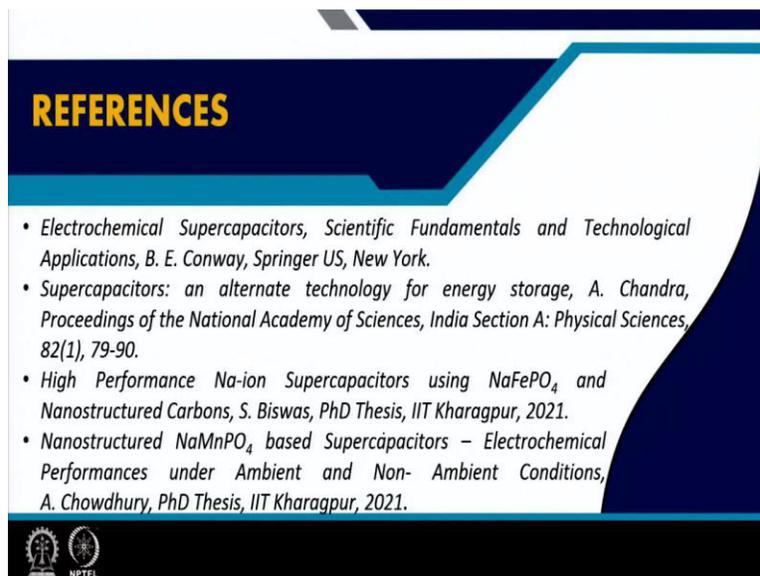
CONCLUSION

- EDLC capacitors can be easily fabricated and can be extremely useful for various applications.
- Carbon can be produced using various techniques and they can be used in energy storage devices.
- Theoretical models, used to describe the formation of double layer, was also presented.

The slide features a dark blue header with the word 'CONCLUSION' in yellow. Below the header, there are three bullet points in a light blue font. On the right side of the slide, there is a small video inset showing a man in a white shirt speaking. At the bottom left, there are logos for IIT Kharagpur and NPTEL.

But, I hope that after hearing today's lecture, you have understood the theoretical models which are able to explain the formation of double layer the formation of double layer in electric double layer capacitors and have also understood that these kinds of supercapacitors are fabricated mostly by using carbon base electrodes and they can deliver extremely high capacitance values.

(Refer Slide Time: 51:22)



REFERENCES

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- *Supercapacitors: an alternate technology for energy storage*, A. Chandra, *Proceedings of the National Academy of Sciences, India Section A: Physical Sciences*, 82(1), 79-90.
- *High Performance Na-ion Supercapacitors using NaFePO₄ and Nanostructured Carbons*, S. Biswas, PhD Thesis, IIT Kharagpur, 2021.
- *Nanostructured NaMnPO₄ based Supercapacitors – Electrochemical Performances under Ambient and Non- Ambient Conditions*, A. Chowdhury, PhD Thesis, IIT Kharagpur, 2021.

The slide features a dark blue header with the word 'REFERENCES' in yellow. Below the header, there are four bullet points in a light blue font. On the right side of the slide, there is a small video inset showing a man in a white shirt speaking. At the bottom left, there are logos for IIT Kharagpur and NPTEL.

These are the major references which were used and in the next lecture, I will move on to pseudocapacitors and I hope by the time we end the next lecture, you will be able to combine the

information you have gathered in today's lecture with the information in the next lecture and you will get an idea how to make the hybrid paste supercapacitors. Thank you very much.