Electrochemical Energy Storage
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Module - 08
Advanced materials and technologies for supercapacitors
Lecture - 36
Classification of Supercapacitors: EDLC and Pseudocapacitative Type

Welcome to my course Electrochemical Energy Storage and this is module number 8 Advanced materials and technologies for supercapacitors and this is lecture number 36 where I will be describing the classification of the super capacitors; which is of electric double layer capacitor type and pseudocapacitative type. So, in this particular lecture I will concentrate mostly on EDLC type that is electric double layer type supercapacitors.

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CONCEPTS COVERED

- Classification of supercapacitors
- Electrode materials
  - Activated carbon
  - Carbon nanotube
  - Other carbonaceous materials
- Pseudocapacitive materials

So, the first is the classification of super capacitors then we will talk about the electrode materials for EDLC Electric Double Layer Capacitor which mostly includes activated carbon and also carbon nanotube and other carbonicious materials so that will be introduced in this lecture. And then finally, we will describe the pseudocapacitative materials basic principle and in the subsequent lecture we will talk more about pseudocapacitive materials.

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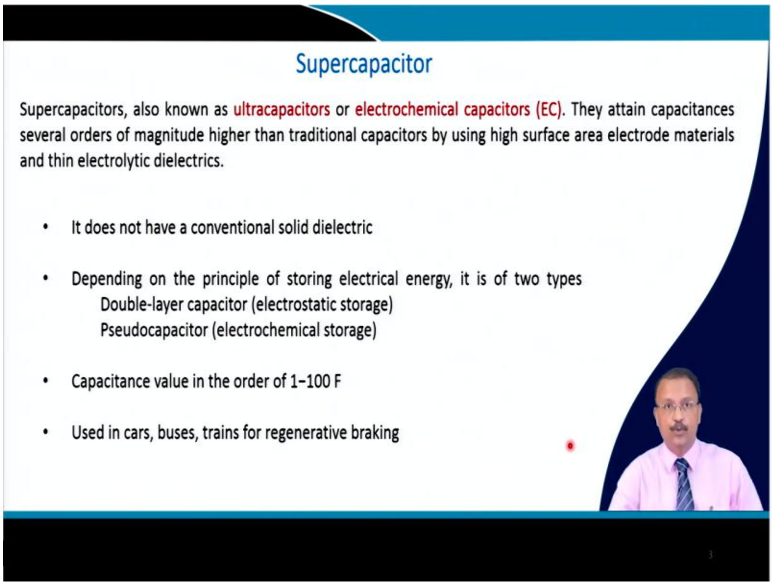

Supercapacitor

Supercapacitors, also known as ultracapacitors or electrochemical capacitors (EC). They attain capacitances several orders of magnitude higher than traditional capacitors by using high surface area electrode materials and thin electrolytic dielectrics.

- It does not have a conventional solid dielectric
- Depending on the principle of storing electrical energy, it is of two types
  - Double-layer capacitor (electrostatic storage)
  - Pseudocapacitor (electrochemical storage)
- Capacitance value in the order of 1–100 F
- Used in cars, buses, trains for regenerative braking

So, the super capacitors they are also termed there are two terminology that is used for supercapacitors one is ultracapacitors and sometimes they are called electrochemical capacitors as well. So, as compared to the traditional capacitor that you would might be knowing 2 metal plate and a dielectric there inside.

So, the capacitance of the traditional capacitor whatever is that as compared to that this supercapacitors or ultracapacitors they have several orders of magnitude higher capacitance. And that is basically due to the fact that in case of this supercapacitors high surface area is used initially I introduced the supercapacitor in a gist form in my first module lecture and lecture number 3 we talked about supercapacitors.

So, there you have gotten the idea that what I mean by high surface area electrode materials and also thin electrolytic dielectrics. So, it is the charge separation at the surface of the electrode. So, the value of d is very small and value of the a that is very large so they constitutes what we call this ultracapacitor.

So, if you want to make a difference between this traditional capacitors and supercapacitors in the latter form they do not have a solid dielectric which usually we have seen in case of normal traditional capacitors. And there are two different types of charge storage mechanism.

So, based on this charge principle of charge storage we will differentiate between double layer capacitor which store the charge electrostatically. And there is a second variety which is a bit difficult to understand you will see that why I am saying that that is known as pseudocapacitors and in many instances they are somewhat similar to the battery type material so I will differentiate that.

So, the capacitance value this is very high in the order of 1 to 100 farad you can get and mostly they are used in car or bus or trains where during braking when they are in motion and then you apply a break that energy is used to charge this capacitor And if you differentiate between battery and capacitor you might be knowing that in case of battery it requires some time because diffusion is involved. Some time to charge the battery supercapacitor charge charging is instantaneous.

So, this regenerative braking that is used basically to charge this capacitor and they are used when lot of current is required during its operation. For example, when the train or bus is accelerating then you need lot of current so capacitive part gives that current and when you break it then it recharges back the capacitor.

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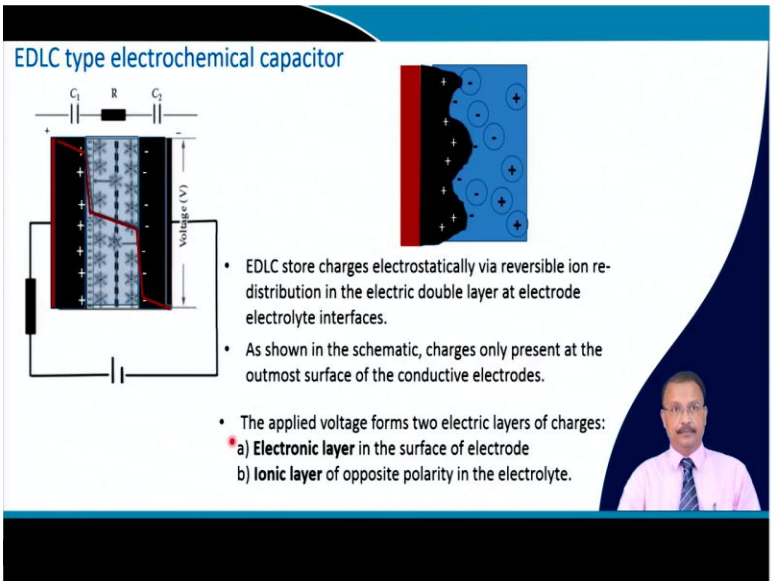

EDLC type electrochemical capacitor

- EDLC store charges electrostatically via reversible ion re-distribution in the electric double layer at electrode electrolyte interfaces.
- As shown in the schematic, charges only present at the outmost surface of the conductive electrodes.
- The applied voltage forms two electric layers of charges:
  a) **Electronic layer** in the surface of electrode
  b) **Ionic layer** of opposite polarity in the electrolyte.

So, if you see a normal electric double layer type electrochemical capacitors or super capacitors they basically store the charge electrostatically. So, here are the example there are 2 electrodes and you know that during charging you will have to charge it. So, there is a surface charge in the electrode surface only the surface phenomena is involved and then you have electrolyte and electrolyte has counter charges.

And they basically adhered to this charge capacitor one is positive another one is negative so counter ions are different. And they are only present in the outermost surface of the conductive electrode. So, if you look at the electrode you have a current collector and then you have a electric double layer capacitor.

So, this is charged only at its surface and you have counter ions if it is positively charged you have counter ions which are basically solvated and then you see that they are attached to the surface and they constitute a double layer capacitor. So, you can find there is a electronic layer in the surface of the electrode and there are ionic layers which is having opposite polarity then this surface charges and that this opposite polarity ionic layer they reside at the surface.

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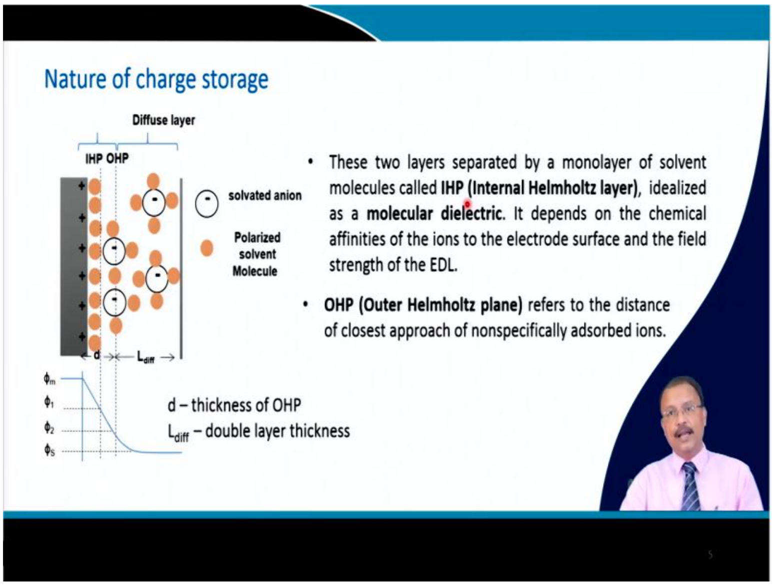

Nature of charge storage

- These two layers separated by a monolayer of solvent molecules called **IHP (Internal Helmholtz layer)**, idealized as a **molecular dielectric**. It depends on the chemical affinities of the ions to the electrode surface and the field strength of the EDL.
- **OHP (Outer Helmholtz plane)** refers to the distance of closest approach of nonspecifically adsorbed ions.

d – thickness of OHP
L_{diff} – double layer thickness

So, if you look at it and there are different models for how this supercapacitor actually store charge and this is the latest one so it evolves over time. So, initially it was just the adherence of charge, but later people have described that there are two distinct layer that is formed.

And the first one is internal Helmholtz layer and this is just like a molecular dielectric and mostly it is now understood that the solvated counter ion. You know that this is solvated so it is also polarized and this is adhered to the surface of the electrode and that forms this internal Helmholtz layer.

And then of course, it depends on the chemical affinities of the ions to the electrode surface. And of course, the field strength that also decides this adhesion and then you have an outer Helmholtz plane and that refers to the distance I mean the distance is from the surface till the outer Helmholtz layer and after that you can have a complete diffuse layer.

So, I have shown only the negative solvated anions negatively charged, but there are progressively positive charge as well. So, if you see the potential so the charge is maximum here and then inner surface layer it is basically they get neutralized. So, the potential drop is there and you can define this two different potential phi 1 and phi 2.

So, phi 1 and phi 2 that basically decides the thickness of the so called outer Helmholtz plane that layer and then the potential is almost constant in and this layer we define as a double layer. So, this L diff that is defined as the double layer thickness.

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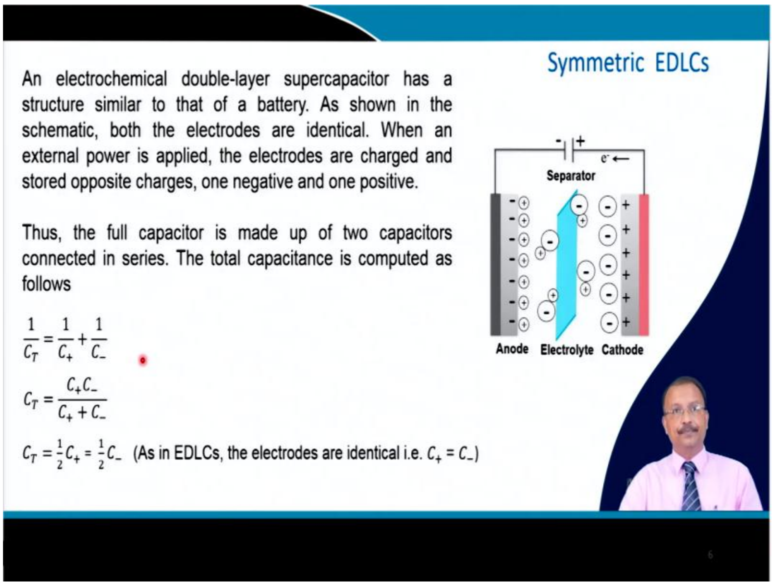

Symmetric EDLCs

An electrochemical double-layer supercapacitor has a structure similar to that of a battery. As shown in the schematic, both the electrodes are identical. When an external power is applied, the electrodes are charged and stored opposite charges, one negative and one positive.

Thus, the full capacitor is made up of two capacitors connected in series. The total capacitance is computed as follows

$$\frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-}$$

$$C_T = \frac{C_+ C_-}{C_+ + C_-}$$

$C_T = \frac{1}{2}C_+ = \frac{1}{2}C_-$ (As in EDLCs, the electrodes are identical i.e. $C_+ = C_-$)

Now, if you consider an electrochemical double layer supercapacitor. So, they usually have a structure that is similar to the battery in battery also you have similar types of structure 2 electrodes that is separated by a separator and you need an electrolyte and the ions and count counter ions they are there inside the electrolyte. So, in that way it is quite similar to the battery, but the performance wise it is different.

So, here as you can see that when I try to charge this kind of EDLC Electric Double Layer Capacitor then ions and counter ions depending on which one is your positive electrode that is cathode and which one is your negative electrode. So, accordingly you have this formation of this double layer and this is eventually two capacitors which are connected in series.

So, you know that when you connect it in series then the total capacitance you can write using this formula. And the total capacitance you can evaluate from this particular formula and if two same type of materials are used then this C plus and C minus they are similar. So, the total capacitor is basically decided by either positive or negative capacitance. So, you are losing the capacitance if you have symmetric kind of capacitor EDLC type.

$$\frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-}$$

$$C_T = \frac{C_+ C_-}{C_+ + C_-}$$

$$C_T = \frac{C_+}{2} = \frac{C_-}{2} \quad for\ symmetrical\ electrodes$$

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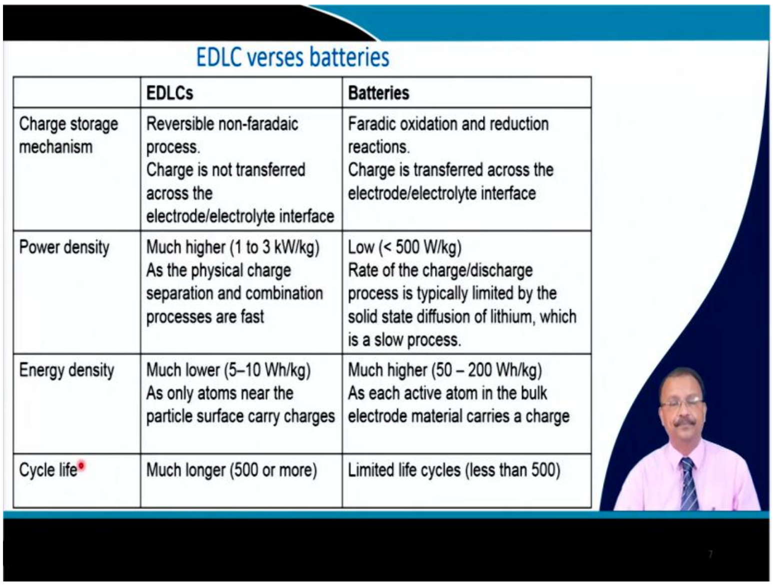

EDLC verses batteries

	EDLCs	Batteries
Charge storage mechanism	Reversible non-faradaic process. Charge is not transferred across the electrode/electrolyte interface	Faradic oxidation and reduction reactions. Charge is transferred across the electrode/electrolyte interface
Power density	Much higher (1 to 3 kW/kg) As the physical charge separation and combination processes are fast	Low (< 500 W/kg) Rate of the charge/discharge process is typically limited by the solid state diffusion of lithium, which is a slow process.
Energy density	Much lower (5–10 Wh/kg) As only atoms near the particle surface carry charges	Much higher (50 – 200 Wh/kg) As each active atom in the bulk electrode material carries a charge
Cycle life	Much longer (500 or more)	Limited life cycles (less than 500)

So, if you want to differentiate the walking principle of an EDLC and the batteries it is quite straight forward. First let us consider the charge storage mechanism and in this case this is non faradaic process because there is no charge transfer there is no change in the materials redox potential. So, valence state does not change unlike the battery material and therefore, the charge is not transferred across the electrode and electrolyte interface.

And in case of battery you need finite time so that the charge is diffused inside the electrode material. So, there is one distinction that one can make if I compare the double layer capacitor with the batteries. Now, if you consider the power density it is certainly much higher because it is just the adherence of the charge and detachment of the charge so this is a very fast process.

So, the power density is quite high in case of EDLCs typically 1 to 3 kilowatt per kilogram is a common power density. But in battery it is significantly low because it is limited by the diffusion inside the electrode material particularly we have seen in case of lithium ion battery or sodium ion battery it needs a finite time to get diffuse inside or outside inside or from the electrode materials so it is basically a slow process.

But energy density is quite large because of the fact that it is only at the surface that carries the charge. So, the energy density in battery is much higher typically 50 to 200 watt hour per kg, but in case of the EDLC type of ultracapacitor the energy density is very low as compared to this one.

But since it is a very fast process so the cyclability if you consider it is quite long 500 or more so easily you can go up to thousand cycles without the any loss of the capacity. But in case of battery you have seen that this is a major problem that progressively you lose capacity with charge discharge cycling. So, these are the common distinction between the ultracapacitor which is EDLC type and the normal battery which we have already described part of this course.

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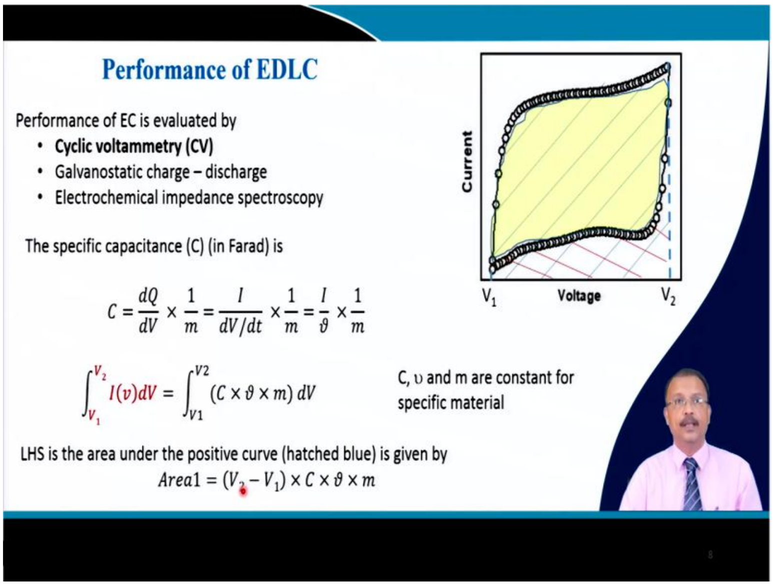

Performance of EDLC

Performance of EC is evaluated by

- **Cyclic voltammetry (CV)**
- Galvanostatic charge – discharge
- Electrochemical impedance spectroscopy

The specific capacitance (C) (in Farad) is

$$C = \frac{dQ}{dV} \times \frac{1}{m} = \frac{I}{dV/dt} \times \frac{1}{m} = \frac{I}{\vartheta} \times \frac{1}{m}$$

$$\int_{V_1}^{V_2} I(v)dV = \int_{V1}^{V2} (C \times \vartheta \times m)\, dV$$

C, υ and m are constant for specific material

LHS is the area under the positive curve (hatched blue) is given by

$$Area1 = (V_2 - V_1) \times C \times \vartheta \times m$$

So, the performance of EDLC that is basically evaluated by the cyclic voltammetry already I have introduced the characterization tools. And also charge discharge characteristics galvanostatic charge discharge applying a constant current you can do the galvanostatic charge discharge measurement. And also electrochemical impedance spectroscopy that also give you lot of idea about the performance of this electric double layer capacitor.

$$C = \frac{dQ}{dV} * \frac{1}{m} = \frac{I}{\frac{dV}{dt}} * \frac{1}{m} = \frac{I}{vm}$$

$$\int_{V_1}^{V_2} I(v)dV = \int_{V_1}^{V_2} Cvm\, dV$$

$$Area\ 1 = (V_2 - V_1)Cvm$$

So, you know Q the charge store is c into v so I can write this equation for specific capacitance. So, that is d Q by d V divided by m, m is the material active material weight. So, this is done and then we do little bit of jugglery because d Q by dt is I so I can always write that I divided by d V dt and 1 by m stays here. So, that means, this is nothing but d V dt is nothing, but the scan rate of this CV.

So, I can write this relation 1 by nu that is the scan rate for doing the cv and the mass involved is there. So, now, if I want to have an idea about the total current that I get out of this process. So, I can write this relation that I which is a function of v of course, it changes with v. So, that is a function of v d V into the range of 2 known potentials. So, if I integrate from V 1 to V 2 so that is the 2 terminal voltage of this cyclic voltammetric curve then I get this relation so C nu and m that is d V and this is from V 1 to V 2.

So, this left hand side is nothing, but the area under the curve so I is nothing, but current and this is the voltage. So, you know that that gives you the area under the curve the total area. So, this is the hatched blue area you can see this hatched blue line and it goes up to here. So, there is the total area that you are getting.

So, this area I am termed, I am terming as area number 1. So, if you integrate this then you will get V 2 minus V 1 and this will come out because the capacitance of a material the new value and m that I consider constant.

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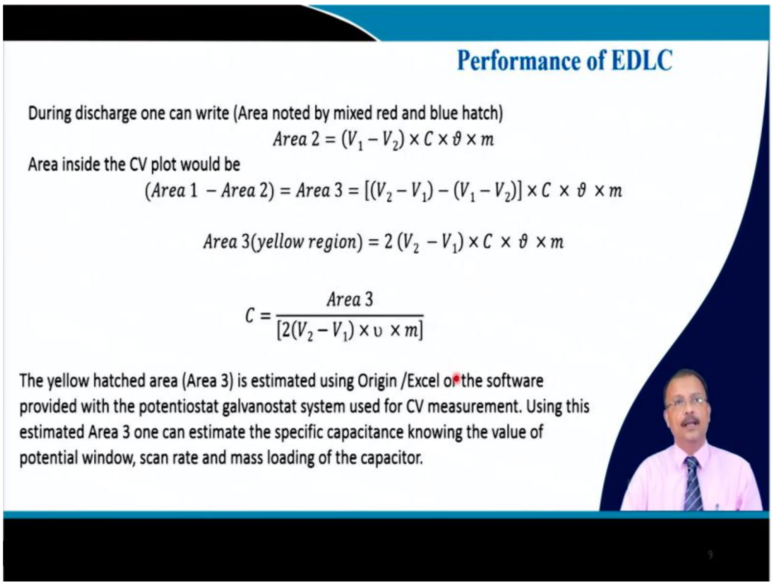

Performance of EDLC

During discharge one can write (Area noted by mixed red and blue hatch)

$$Area\ 2 = (V_1 - V_2) \times C \times \vartheta \times m$$

Area inside the CV plot would be

$$(Area\ 1\ - Area\ 2) = Area\ 3 = [(V_2 - V_1) - (V_1 - V_2)] \times C \times \vartheta \times m$$

$$Area\ 3(yellow\ region) = 2\,(V_2 - V_1) \times C \times \vartheta \times m$$

$$C = \frac{Area\ 3}{[2(V_2 - V_1) \times \upsilon \times m]}$$

The yellow hatched area (Area 3) is estimated using Origin /Excel or the software provided with the potentiostat galvanostat system used for CV measurement. Using this estimated Area 3 one can estimate the specific capacitance knowing the value of potential window, scan rate and mass loading of the capacitor.

$$Area\ 2 = (V_1 - V_2)Cvm$$

$$Area\ 3\ (Yellow\ region) = 2(V_2 - V_1)Cvm$$

$$C = \frac{Area3}{2(V_2 - V_1)vm}$$

Now, if you go for the discharge so this is the charge operation from here up to here. So, I got the total area which is the hatch this portion the blue portion the total blue portion. And now I will do the discharge from here down to this voltage. So, from V 2 to V 1 I am discharging it. So, that area I can also estimate which is the hatched area say red line and this blue line.

So, that also I can estimate and using the same terminology this I will get V 1 minus V 2 and the C capacitance the scan rate millivolt per millivolt per second and the mass of the electrode material. So, eventually I am interested to know the area under this curve. So, I will have to subtract this whole area which is area 1 and then this part this hatched part. So, if I subtract this I will get the area inside the CV loop. So, this also you can done you can do, that area 1 minus area 2 and that will give you area 3.

So, you just put back the value whatever i have gotten for area 1 area 2 and this yellow region you get this relation twice this V 2 minus V 1 and this term will also there. So, eventually we get the area divided by 2 into the terminal voltage that is the potential window voltage window that I am using into your scan rate and the active material.

So, usually we use either the software which is associated with this galvanostatic, galvanostat potentiostat system which we usually use to measure the cyclic voltammetry. That software is used or the current and voltage data that you can plot in software like origin or excel. And then you can estimate this area from the curve that you have gotten and then once you get that then you basically you know what is the value of V 2 and V 1.

And what is the scan weight that you have used to measure the CV and you can actually estimate the specific capacitance. So, the specific capacitance if you have a CV plot for a EDLC from a potentiostat galvanostat system. So, this is the procedure that is used to estimate it in farad per gram what is the specific capacitance of this capacitor.

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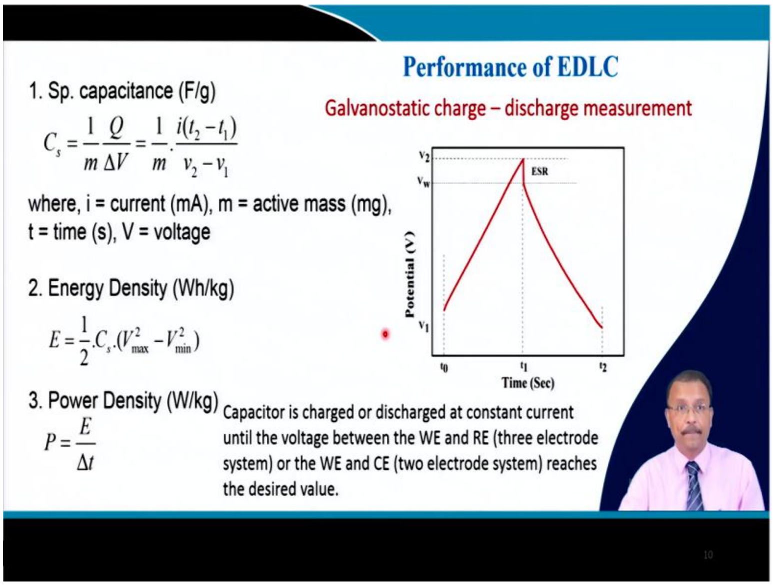

Performance of EDLC

Galvanostatic charge – discharge measurement

1. Sp. capacitance (F/g)

$$C_s = \frac{1}{m}\frac{Q}{\Delta V} = \frac{1}{m}.\frac{i(t_2 - t_1)}{v_2 - v_1}$$

where, i = current (mA), m = active mass (mg), t = time (s), V = voltage

2. Energy Density (Wh/kg)

$$E = \frac{1}{2}.C_s.(V_{max}^2 - V_{min}^2)$$

3. Power Density (W/kg)

$$P = \frac{E}{\Delta t}$$

Capacitor is charged or discharged at constant current until the voltage between the WE and RE (three electrode system) or the WE and CE (two electrode system) reaches the desired value.

You can also use the charge discharge measurement and this is this will certainly be a straight line. Because it is the adherence of the charge and coming out of the charge from the surface so it is a straight line. And this drop usually comes from the (Refer Time: 20:06) resistance of the capacitor that already I have defined.

So, you start from your open circuit potential and then go up to the maximum of the voltage window and then there is a drop due to the value of internal resistance. And then you discharge it up till a voltage of this v one. So, called V 1 is here so V 1 you discharge it.

So, this time basically you are measuring. So, the capacitance you can calculate this is quite straight forward the value of Q by del V into m. So, it is coming just simple like Q equal to CV, this relation and m is the active material weight. So, get basically the specific capacitance which is measured by farad per gram. And 1 by m comes out and this Q is again the relation is i the current is d Q by dt. So, the total charge is i into the difference in time.

$$C = \frac{Q}{\Delta V} * \frac{1}{m} = \frac{i(t_2 - t_1)}{m(V_2 - V_1)}$$

So, if I call it for the discharge then the difference in time is t 2 minus t 1 and the voltage is from v 2 minus v 1. So, this relation from this relation it is very straightforward to measure the specific capacitance. Once you have the specific capacitance then you can go ahead and estimate the energy density the dimension is watt hour per kg.

So, you know that this energy is half capacitance C V square. So, this voltage window is V square max and V square min. So, within that range you can put this voltage value so you can get the energy density. And power density as already I have discussed in one of my earlier lectures that is the energy density divided by the time that it takes so that will give you the power.

$$E = \frac{1}{2}C(V_{max}^2 - V_{min}^2)$$

So, power density also you can estimate. So, actually the capacitor is charged or discharged at constant current until the voltage between, if it is a 3 electrode system until the voltage between the walking electrode and the reference electrode in a 3 electrode system. Or the if you have a 2 electrode system where the counter electrode and the reference electrode is shorted so that is a 2 electrode system. So, that reaches the desired value.

$$P = \frac{E}{\Delta t}$$

So, this voltage selection is based on you know the linear swift voltammetry which I introduce, so based on that you know what is the potential range that you will have to use for this kind of measurement. So, those are the characteristics that you want to measure in case of electric double layer capacitor.

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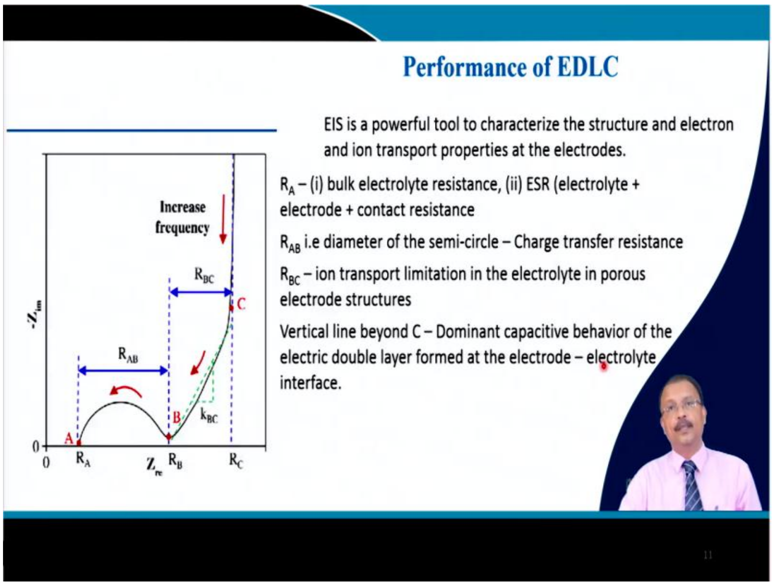

Performance of EDLC

EIS is a powerful tool to characterize the structure and electron and ion transport properties at the electrodes.

R_A – (i) bulk electrolyte resistance, (ii) ESR (electrolyte + electrode + contact resistance

R_{AB} i.e diameter of the semi-circle – Charge transfer resistance

R_{BC} – ion transport limitation in the electrolyte in porous electrode structures

Vertical line beyond C – Dominant capacitive behavior of the electric double layer formed at the electrode – electrolyte interface.

The performance of the double layer capacitor that also can be estimated by a electrochemical impedance spectroscopy. And, then I already described that how you can plot from the imaginary part of the impedance, and the real part of the impedance how you can plot the so called nyquist plot. So, this is the typical nyquist plot that you will be getting. So, as you can see that the value this R A that basically denotes the electrolyte resistance.

So, that is the value of ESR so that estimate the not only the electrolyte, but the contact resistance electrode electrolyte and the contact resistance. So, that gives you this resistive value R A. Then R AB is the diameter although sometimes it is suppressed, but eventually this is the diameter of this semicircle and that usually gives you the charge transfer resistance. Already, I have described that where from what is the physical significance of that.

So, this diameter is the charge transfer resistance and then you see that there is a line in this BC. So, this kind of line that this red arrow this shows that the change in the frequency while you do the measurement. So, progressively the frequency changes from here because here you will not find the frequency I am plotting only 2 impedance value.

So, the frequency changes from lower frequency and up to the higher frequency. So, at medium frequency range this resistance R BC, this line that actually denotes the ion transport limitation in the electrolyte as well as in the porous electrode structure. So, porous electrode structure is not very significant in case of EDLC because hardly the electrolyte goes in, sorry that that suddenly goes in inside the porous electrode, but there is no change in the valence state of the active material.

So, that will also be there this polar porous electrode structure it will offer some kind of resistance and the transport of the ions through the electrolyte. So, that will contribute this BC. And this vertical line there is very characteristics of the EDLC metal material so that is a dominant capacitative behavior of the double layer formation at the electrode electrolyte interface.

So, that is an indication there is a very fast process and this basically this vertical line basically tells you that the formation of the EDLC. So, you can get this value to get the idea about the mechanistic point of view what the idea how it the EDLC type of material works.

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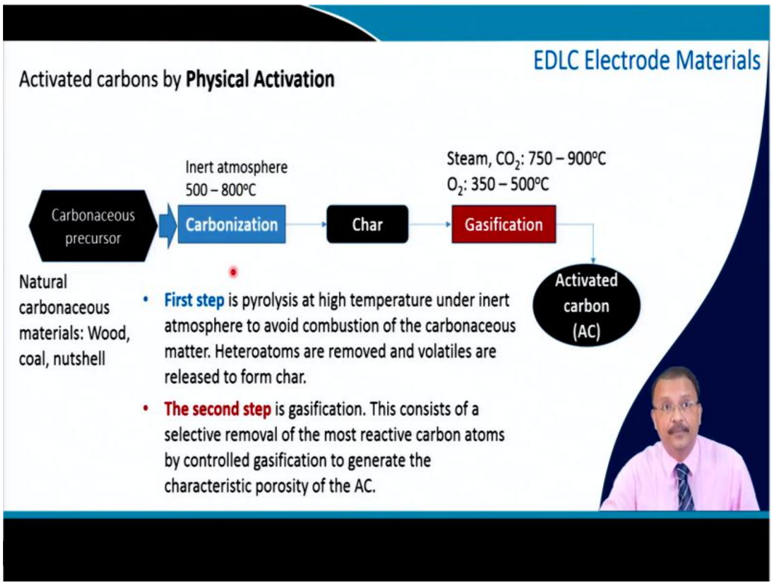

EDLC Electrode Materials

Activated carbons by **Physical Activation**

Natural carbonaceous materials: Wood, coal, nutshell

- **First step** is pyrolysis at high temperature under inert atmosphere to avoid combustion of the carbonaceous matter. Heteroatoms are removed and volatiles are released to form char.
- **The second step** is gasification. This consists of a selective removal of the most reactive carbon atoms by controlled gasification to generate the characteristic porosity of the AC.

So, the first EDLC material which is basically used for various purpose is activated carbon, and activated carbon you can make by either physical activation. So, you take any carbonaceous precursor that could be natural carbonaceous material like wood, coal or nutshell that you use, then the first step is to pyrolyse this in an inert ambient. So, why you use inert ambient? Because you avoid the combustion of this carbonaceous material so oxygen is not there. So, it will not undertake any combustion.

And all the hetero atoms that basically they are removed and also the volatile matter and they are removed and it forms basically a char. So, this char is formed and then there is a second step so in second step you do gasification. So, what you do that, selective removal of most reactive carbon atoms and you are using either steam carbon dioxide.

So, if you use that then the temperature that is required for this gasification is around at higher range 750 to 900, if you use oxygen to remove this most reactive carbon atoms and it is a controlled reaction. So, they are removed and they that actually gives the characteristic porosity.

You need a porous material so that the electrolyte can be going inside the electrode material to have a porous structure with high specific surface area and that gives you lot of capacitance and as well as specific capacity. So, you need a porous material so this porosity is generated and you get this activated carbon.

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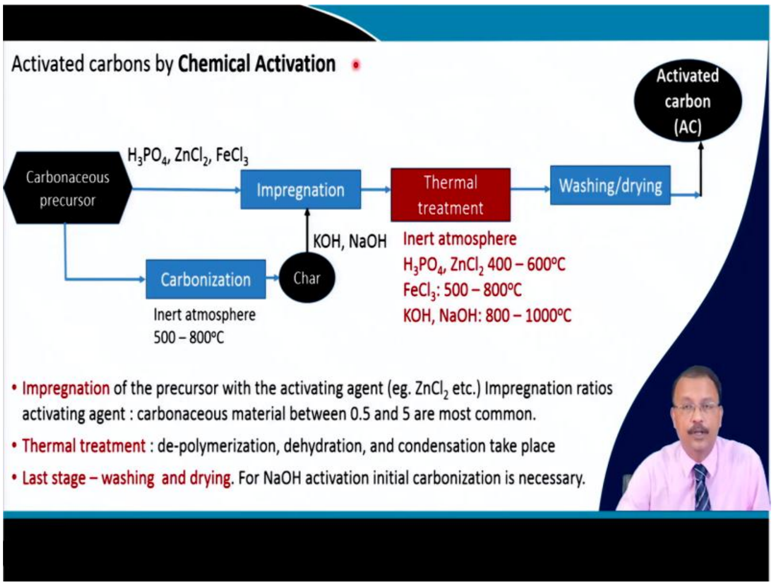

Activated carbons by **Chemical Activation**

- Impregnation of the precursor with the activating agent (eg. $ZnCl_2$ etc.) Impregnation ratios activating agent : carbonaceous material between 0.5 and 5 are most common.
- Thermal treatment : de-polymerization, dehydration, and condensation take place
- Last stage – washing and drying. For NaOH activation initial carbonization is necessary.

The second method that is used we call this is a chemical activation. So, here also you take this carbonaceous precursor and then you go for a impregnation step. So, you treat it with phosphoric acid or zinc chloride so they are called as activating agent and this impregnation ratio that is this activating agent and the carbonaceous material. So, you can change that. So, that controls the not only the porosity, but the type of the porosity. So, usually it is kept between, 0.5 to 5.

And then after the impregnation you go for the thermal treatment again at different temperatures depending on what type of this activating agents you are using, if you are using this H 3 PO 4 or zinc chloride then 400 to 600 degree Celsius and progressively it goes high if you are using iron chloride. And sometimes you would use alkali material like potassium hydroxide or sodium hydroxide then it is quite high temperature you need.

And after the thermal treatment this is washed, particularly when you are using sodium hydroxide for activation then you need to wash the material that you have gotten and that also lead you to the activated carbon. So, in case of this process sometimes, if want to do the activation with potassium hydroxide sodium hydroxide then it is found that this carbonization is necessary.

So, this carbonaceous precursor that first you do a heat treatment at inert ambient typically 500 to 800 degree Celsius to form the char, similar to the case that I have already described. And then you do the impregnation with potassium hydroxide or sodium hydroxide then you do the thermal treatment at relatively high temperature and wash this KOH and N a OH and you get this porous activated carbon.

They are commercially available different varieties are available from various vendors. And depending on the source that you are getting that will control your specific capacity of the ultracapacitors.

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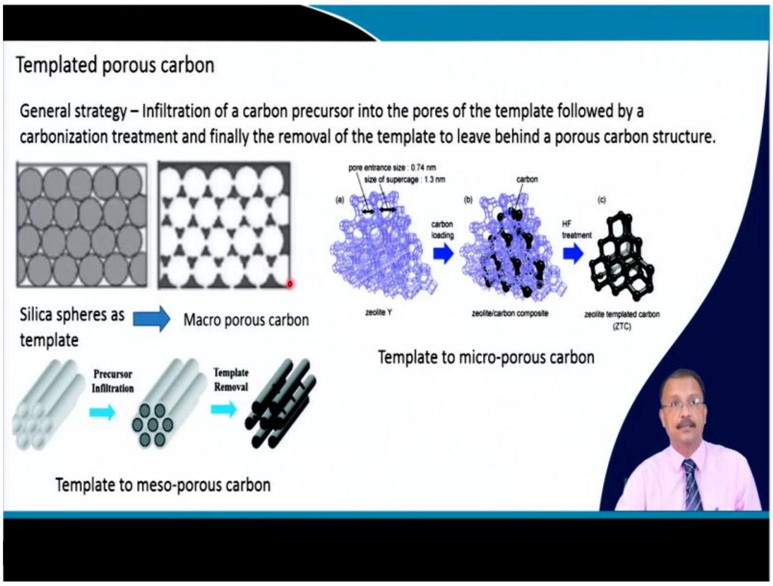

Templated porous carbon

General strategy – Infiltration of a carbon precursor into the pores of the template followed by a carbonization treatment and finally the removal of the template to leave behind a porous carbon structure.

Silica spheres as template → Macro porous carbon

Template to meso-porous carbon

Template to micro-porous carbon

Apart from that, that thing is very common, but you can use a templated porous carbon you can see that this is the template. So, you impregnate it with carbon precursor so and then you get rid of this template. So, this pores are very well defined and depending on the template that you are using you get a bigger pore.

So, silica sphere that is sometimes used which can easily be get rid of hydrofluoric acid treatment and you get a very neat porous structure and this is basically macro pores of carbon. So, you can go for micro porous material which is zeolite is one of them, and then it you load it with carbon and then you get rid of this zeolite which is aluminum silicate composition get rid of that.

And you get with silica get gets off with this HF treatment and you get a nice network porous structure for Zeolite Templated Carbon abbreviated as ZTC So, you get this is your active material for EDLC. You can also use this there are different types of pore diameter. So, macro pore are quite large, then micro porous is very small and meso porous is in between 2 to 50; 2 to 50 nanometer and this is around 2 nanometers and macro pores are in the order of microns.

So, here you take again a template material and then you go for precursor which is carbonaceous precursor infiltration. And then you remove this template and you get this kind of porous structure. So, in activated carbon the control of the pores that is difficult and some pore could be tortuous. So, tortuous pore electrolyte diffusion will be hindered, but this kind of templated structure you have a defined pore structure. So, suddenly that will give you much better values as far as the specific capacity is concerned.

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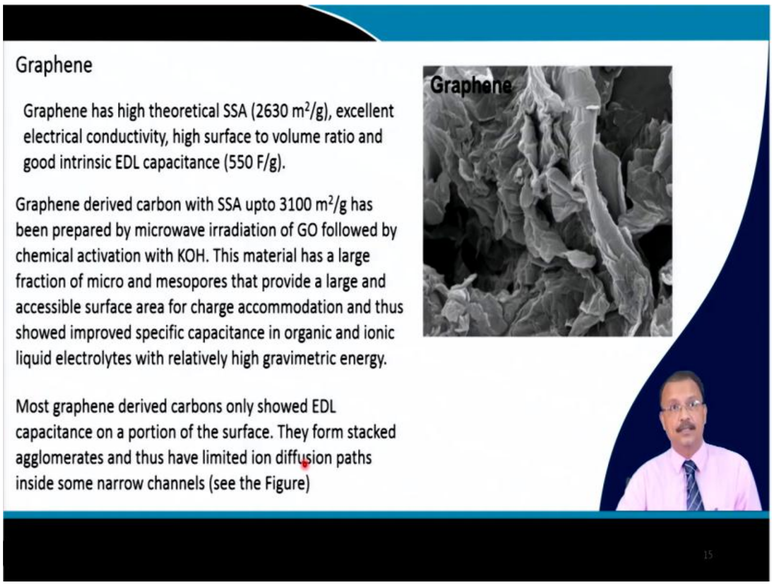

Graphene

Graphene has high theoretical SSA (2630 m^2/g), excellent electrical conductivity, high surface to volume ratio and good intrinsic EDL capacitance (550 F/g).

Graphene derived carbon with SSA upto 3100 m^2/g has been prepared by microwave irradiation of GO followed by chemical activation with KOH. This material has a large fraction of micro and mesopores that provide a large and accessible surface area for charge accommodation and thus showed improved specific capacitance in organic and ionic liquid electrolytes with relatively high gravimetric energy.

Most graphene derived carbons only showed EDL capacitance on a portion of the surface. They form stacked agglomerates and thus have limited ion diffusion paths inside some narrow channels (see the Figure)

Graphene is one material which has been proved they have very high specific surface area and also they have good electrical conductivity and good capacitance. So, typically in graphene people have reported this capacitance is 550 farad per gram. So, graphene derived carbon which is having a specific surface area higher than this so it is about 3100 meter square per gram.

So, people have used this microwave irridation of graphene oxide and then they are activated by alkali potassium hydroxide. And this type of material people have reported that they have a combination of micro and mesopore and they provide a large accessible surface area for charge of accommodation. And improved specific capacitance you will get both in organic as well as ionic liquid electrolyte, this electrolyte I will be covering in later part of the of this module lectures.

And most of these graphene derived carbons they usually exhibited this electric double layer capacitance on 1 portion of the surface. So, as you know that the graphene is a stacked structure so they have limited ion diffusion path. So, if the channels are quite narrow then electrolyte cannot be driven in that easily because this track distance is pretty small so that is one disadvantage that people have reported.

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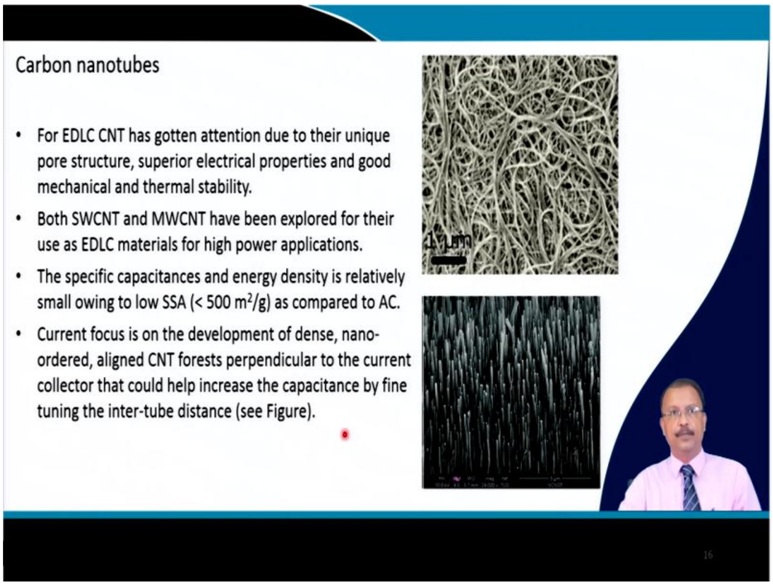

Carbon nanotubes

- For EDLC CNT has gotten attention due to their unique pore structure, superior electrical properties and good mechanical and thermal stability.
- Both SWCNT and MWCNT have been explored for their use as EDLC materials for high power applications.
- The specific capacitances and energy density is relatively small owing to low SSA (< 500 m^2/g) as compared to AC.
- Current focus is on the development of dense, nano-ordered, aligned CNT forests perpendicular to the current collector that could help increase the capacitance by fine tuning the inter-tube distance (see Figure).

Carbon nanotube is another one so, they have gotten quite good attention and you can have either spaghetti type of structure noodle like structure. So, this carbon nanotube they are good because their electrical property is conductivity is quite good and they have good mechanical as well as thermal stability.

So, one can use both single or multi layer carbon nanotube and typical surface area is relatively small as compared to your activated carbon, but due to this good electrical properties and mechanical and thermal stability, so that is quite advantageous to use carbon nanotube.

So, basically people now are trying to develop this structured nanotube. So, this is a nano ordered Carbon Nanotube they call its CNT forest and that use the current collectors. Similar, to the current collectors also you can use this nano structured carbonicious material I will describe about it in the last lecture of this module.

And you can do the fine tuning by changing this growth. So, if you can change this distance depending on your solvated ions you can make them inserted into this porous structure, so that is advantages.

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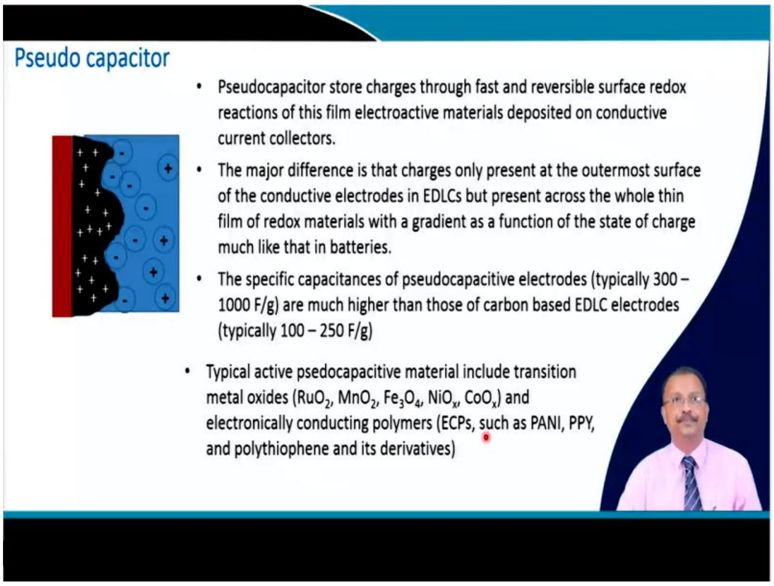

Pseudo capacitor

- Pseudocapacitor store charges through fast and reversible surface redox reactions of this film electroactive materials deposited on conductive current collectors.
- The major difference is that charges only present at the outermost surface of the conductive electrodes in EDLCs but present across the whole thin film of redox materials with a gradient as a function of the state of charge much like that in batteries.
- The specific capacitances of pseudocapacitive electrodes (typically 300 – 1000 F/g) are much higher than those of carbon based EDLC electrodes (typically 100 – 250 F/g)
- Typical active psedocapacitive material include transition metal oxides (RuO_2, MnO_2, Fe_3O_4, NiO_x, CoO_x) and electronically conducting polymers (ECPs, such as PANI, PPY, and polythiophene and its derivatives)

Now, pseudo capacitor I will be having a whole lecture on pseudo capacitor, but let me just introduce it. Unlike the surface part you see that it is a thin enough I mean still it is a surface, but it is not like a battery, but there is a change of the redox this electro active material that is used along with your EDLC type of material. So that certain pseudo capacitor, which is not electronically conducting you need to use a carbonaceous material to make a composite.

So, there the idea is the first and reversible surface redox reaction takes place it is not the absorption of the counter ions on the charge surface, but there is a redox reaction is involved. So, that is the major difference that the charge only present at the outermost surface of the conductive electrodes in EDLC. But it is present across the whole thin film region.

So, if you have a thicker material then do not expect that whole of it the redox reaction will take place then it will be a battery, but at the surface of a thin film as well as most part of the bulk you get this kind of intrusion and that results this change in the redox in the active material.

So, once it is something like this then suddenly much higher pseudo capacitance specific capacitance of pseudo capacitor is much higher about 300 to 1000 farad per gram and once you compare it with the EDLC it is only 100 to 250 farad per gram so that is why you are getting this advantage.

So, there are various types of pseudo capacitive material that I will be explaining and it is important for you to identify that what part is so called diffusion control and what part is actually adherence of the surface charge. So, that there are techniques to do that in fact, I covered this in earlier part of the lecture, but as a recapitulation again I will show you that in the next lecture.

So, metal oxide is used R u O 2 is already conducting so you do not need to add any conductive additives in R u O 2, but oxide like manganese oxide or other transition metal oxide they are used so this is one type of material. Electronically conducting polymer I already talked about it. So, ECP, they are also the candidates particularly PANI and PPY and polythiophene and also its derivatives, they use they are used as the pseudo capacitive material.

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So, the study material is the book Electrochemical Energy Advanced Material and this is your study material and along with that there are excellent books by Conway and by Jhang. So, you can have a look they are entirely on the supercapacitors super capacitive material so with these books are there.

And this book this overview you can download from the internet, and these are the good materials to have a in depth idea.

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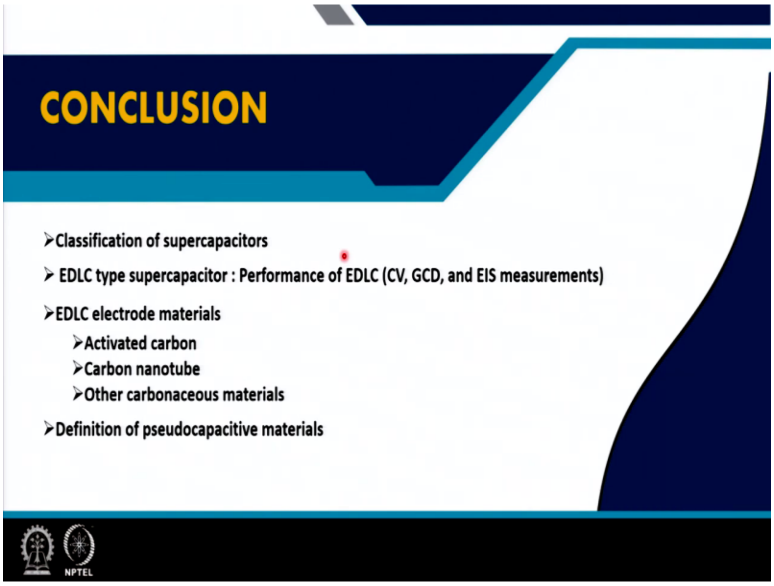

CONCLUSION

- Classification of supercapacitors
- EDLC type supercapacitor : Performance of EDLC (CV, GCD, and EIS measurements)
- EDLC electrode materials
  - Activated carbon
  - Carbon nanotube
  - Other carbonaceous materials
- Definition of pseudocapacitive materials

So, in this particular lecture we talked about the classification of the supercapacitor we made it only EDLC type and the pseudo capacitor type, but we can also expand this kind of classification. And mostly we concentrated the discussion on EDLC type supercapacitor and how the performance of EDLC you can estimate from cyclic voltammetry then, galvanostatic charge discharge or electrochemical impedance spectroscopy measurement what information you get then I provided some idea.

Then we talked about certain EDLC material mostly how activated carbons are made carbon nanotube in different form, in a structured form or in a noodles type form which can also be used as a current collector itself. You can use this material and other carbonicious material like templated growth controlling the porous structure that we introduced. And then we just define what are pseudo capacitative material and we will continue it is in the next lecture.

Thank you for your attention.