Electrochemical Energy Storage
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Module - 01
Introduction to electrochemical energy storage and conversion
Lecture - 03
Supercapacitors

Welcome to the course Electrochemical Energy Storage, and this is module number 1: Introduction to electrochemical energy storage and conversion. This is lecture number 3 where I will be introducing the concept of Supercapacitors.

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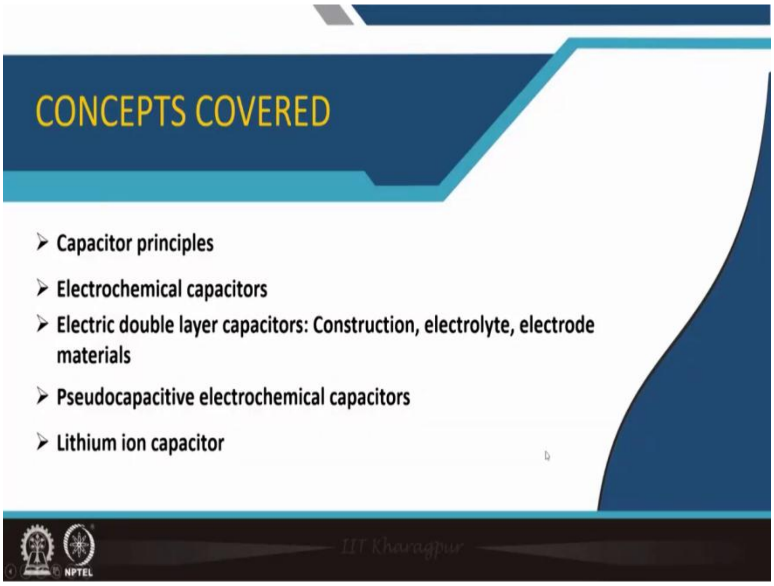

CONCEPTS COVERED

- Capacitor principles
- Electrochemical capacitors
- Electric double layer capacitors: Construction, electrolyte, electrode materials
- Pseudocapacitive electrochemical capacitors
- Lithium ion capacitor

In the last lecture we talked about various types of battery: primary battery, secondary battery, redox flow battery, and futuristic lithium air battery.

So, battery needs time for discharging its capacity while capacitor can instantaneously discharge the stored capacity. So, we will first introduce the principle of operation of capacitors. Then, we will be talking about electrochemical capacitor. We will introduce various concepts such as Electrical double layer capacitor abbreviated EDLC, their construction, and the electrolyte and electrode materials that is used. We will also introduce pseudocapacitive electrochemical capacitors. Finally, lithium ion capacitor will be introduced in this lecture.

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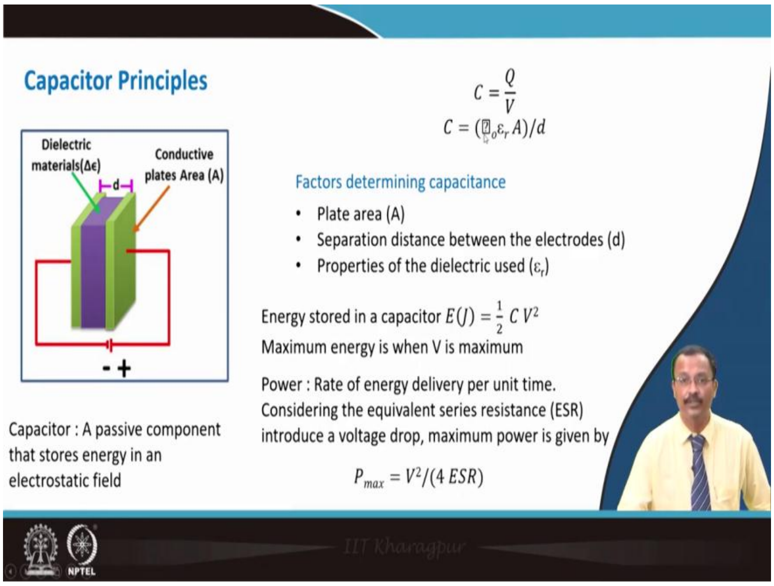

Capacitor Principles

$C = \frac{Q}{V}$

$C = (\varepsilon_0 \varepsilon_r A)/d$

Capacitor : A passive component that stores energy in an electrostatic field

Factors determining capacitance

- Plate area (A)
- Separation distance between the electrodes (d)
- Properties of the dielectric used (ε_r)

Energy stored in a capacitor $E(J) = \frac{1}{2} C V^2$

Maximum energy is when V is maximum

Power : Rate of energy delivery per unit time. Considering the equivalent series resistance (ESR) introduce a voltage drop, maximum power is given by

$P_{max} = V^2/(4\,ESR)$

So, probably the capacitor principle is well known to you. Capacitance is the ratio of stored charge by voltage. The formula for capacitance is given below:

$$C = \frac{Q}{V}$$

$$C = (\varepsilon_O \varepsilon_r A)/d$$

So, from the equation you can see that the factors that determine the capacitance is plate area and the separation. Smaller the plate separation, the capacitance will be more. Energy stored in the capacitors that usually you can estimate from this simple relation half CV square.

$$E(J) = \frac{1}{2} C\, V^2$$

Maximum energy is when the applied V is largest. Power is the rate of energy delivered per unit time. The equivalent series resistance abbreviated as ESR introduces a voltage drop from all the connecting wires etc. Maximum power is given as:

$$P_{max} = V^2/(4\ ESR)$$

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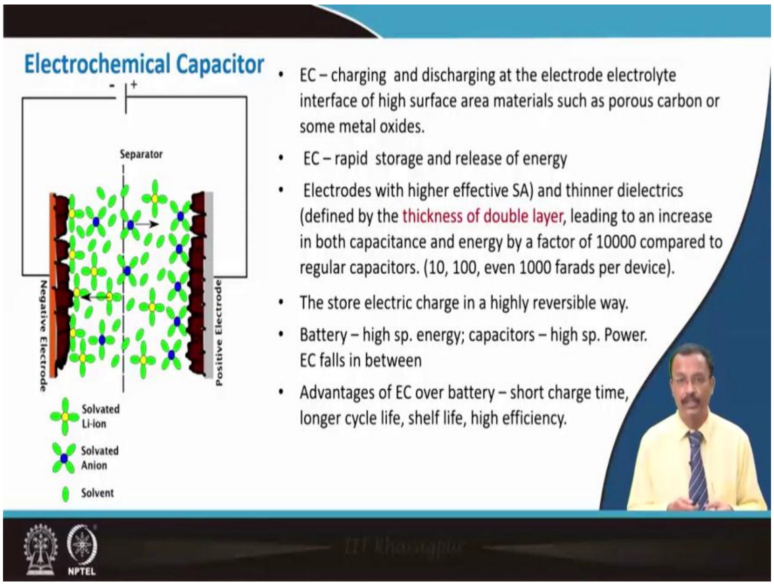

Electrochemical Capacitor

- EC – charging and discharging at the electrode electrolyte interface of high surface area materials such as porous carbon or some metal oxides.
- EC – rapid storage and release of energy
- Electrodes with higher effective SA) and thinner dielectrics (defined by the thickness of double layer, leading to an increase in both capacitance and energy by a factor of 10000 compared to regular capacitors. (10, 100, even 1000 farads per device).
- The store electric charge in a highly reversible way.
- Battery – high sp. energy; capacitors – high sp. Power. EC falls in between
- Advantages of EC over battery – short charge time, longer cycle life, shelf life, high efficiency.

During the operation of an electrochemical capacitor with a high surface area material such as porous carbon or some metal, the electrode-electrolyte interface plays a major role.

So, the electrode of the porous carbonaceous material is getting negatively charged here and you have electrolyte which is having which are solvated cation. So, they form a very firm layer across electrode-electrolyte contact region, which is then followed by the diffuse layer. So, that constitutes a very high capacitance because eventually the d value is very small here. So, it can be rapidly store charge (because it is just surface adsorption) and rapidly discharge it. So, electrodes with higher effective surface area and thinner dielectric (defined by a thickness of the double layer) leads to an increase in both capacitance and energy by a factor, maybe 10000 more, as compared to regular capacitor. So, usually the capacitance is ten, hundred or even 1000 farad per device. So, this kind of capacitor they store electric charge in highly reversible way. Batteries have high specific energy while capacitors have high specific power. Electrochemical capacitor falls in between regular capacitor and a battery.

Advantage of electrochemical capacitors over battery is that it is having very short charge time. It has long cycle time, shelf life; and of course it is having high efficiency.

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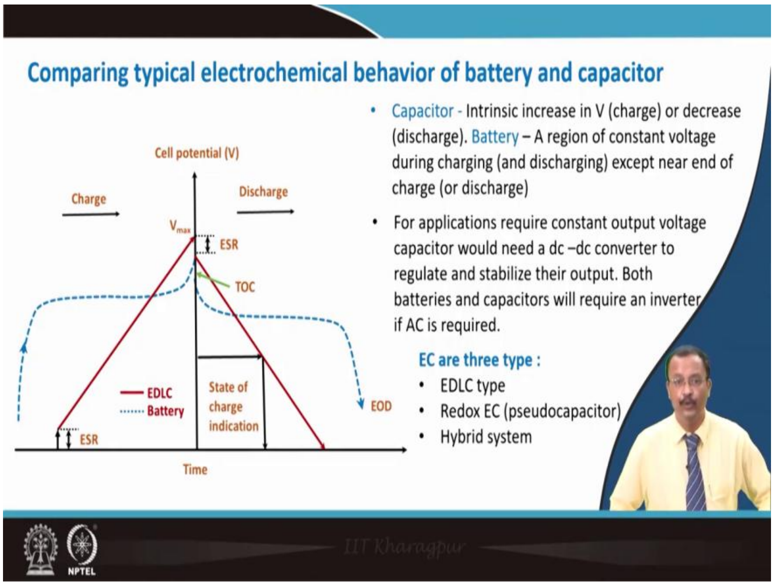

Comparing typical electrochemical behavior of battery and capacitor

- Capacitor - Intrinsic increase in V (charge) or decrease (discharge). Battery – A region of constant voltage during charging (and discharging) except near end of charge (or discharge)
- For applications require constant output voltage capacitor would need a dc –dc converter to regulate and stabilize their output. Both batteries and capacitors will require an inverter if AC is required.

EC are three type :

- EDLC type
- Redox EC (pseudocapacitor)
- Hybrid system

As shown in the slides, the voltage change during galvanostatic charge-discharge of a capacitor is linear, except near end of charge. The equivalent series resistance is also reflected here in the plot. In case of battery, you observe a plateau region, except near the two ends. The explanation for this will be provided in subsequent lectures during the course.

So, capacitor would certainly need a dc-dc converter to regulate and stabilize their output for applications which require constant output voltage. Both batteries and capacitor will require an inverter if the AC conversion is required.

So, the electrochemical capacitors are of 3 types: electric double layer type, redox electrochemical capacitors or pseudo capacitor, and hybrid system.

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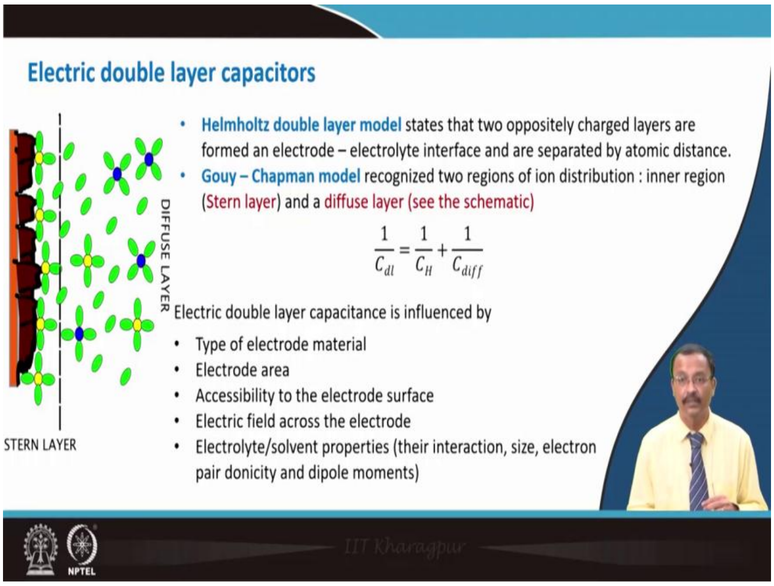

Electric double layer capacitors

- **Helmholtz double layer model** states that two oppositely charged layers are formed an electrode – electrolyte interface and are separated by atomic distance.
- **Gouy – Chapman model** recognized two regions of ion distribution : inner region (Stern layer) and a diffuse layer (see the schematic)

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}}$$

Electric double layer capacitance is influenced by

- Type of electrode material
- Electrode area
- Accessibility to the electrode surface
- Electric field across the electrode
- Electrolyte/solvent properties (their interaction, size, electron pair donicity and dipole moments)

Helmholtz double layer model states that 2 oppositely charged layers are formed at the electrode-electrolyte interface, and are separated by atomic distance. So, once this is negatively charged, the solvated cation will come in close proximity and form a very strong layer called as the stern layer. This distance is of atomic order.

This model was then further modified by Gouy-Chapman. So they recognize 2 regions of ion distribution; one is this inner region which is termed as stern layer and a diffuse layer. Diffuse layer means then not all cations are in close proximity. Some anions are also there so the charge distribution seems diffused. The double layer capacitances are all connected in series, and the net contribution is given as:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}}$$

So, the electric double layer capacitance is influenced by type of the electrode material, how much is the electrolyte penetrated inside the pores, how much surface area is available, how much counter ion the surface can adsorb etc. So that means, the electrode area is also playing a major role, and not only the material. Accessibility of the electrode surface, electric field across the electrode, and electrolyte solvent properties also play an important role. The interaction size, electron pair donicity, and also the dipole moment determine the double layer capacitance.

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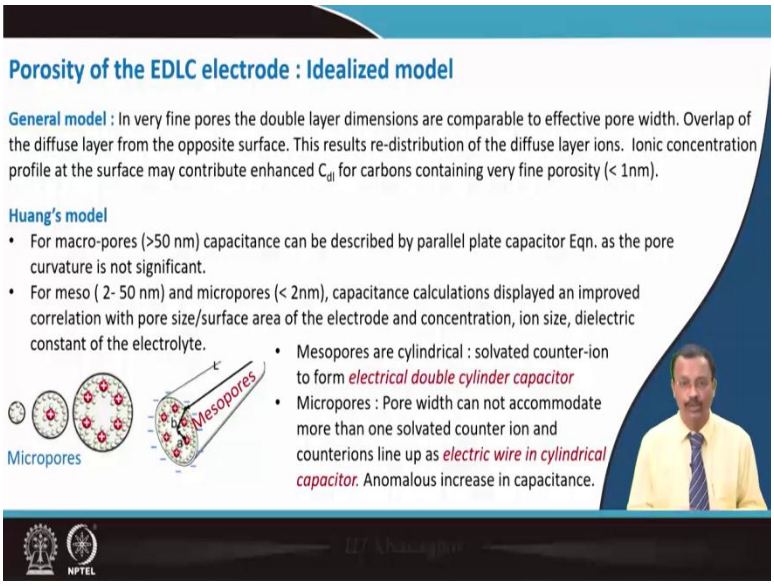

Porosity of the EDLC electrode : Idealized model

General model : In very fine pores the double layer dimensions are comparable to effective pore width. Overlap of the diffuse layer from the opposite surface. This results re-distribution of the diffuse layer ions. Ionic concentration profile at the surface may contribute enhanced C_{dl} for carbons containing very fine porosity (< 1nm).

Huang's model

- For macro-pores (>50 nm) capacitance can be described by parallel plate capacitor Eqn. as the pore curvature is not significant.
- For meso (2- 50 nm) and micropores (< 2nm), capacitance calculations displayed an improved correlation with pore size/surface area of the electrode and concentration, ion size, dielectric constant of the electrolyte.
- Mesopores are cylindrical : solvated counter-ion to form *electrical double cylinder capacitor*
- Micropores : Pore width can not accommodate more than one solvated counter ion and counterions line up as *electric wire in cylindrical capacitor.* Anomalous increase in capacitance.

There are various idealized model for the porosity in EDLC’s. The general model is that very fine pores of comparable size to the double layer overlap with the diffuse layer from the opposite surface, creating an effective pore width. This results in the redistribution of charges in the diffuse layer. An ionic concentration profile at the surface may contribute to the double layer capacitance, which is mostly for carbonaceous material containing very fine porosity of less than 1 nanometer.

Huang developed a model based on the influence of the pore size on the capacitance value. For macro pores more than 50 nanometer in diameter, capacitance can be described almost like a parallel plate capacitor. So, we can consider it as a parallel plate capacitor since the curvature is not very significant (the pore size is relatively large). But for mesopores (which are in the range from 2 to 50 nanometer) and also micro pores (which are less than 2 nanometer), capacitance calculations display some kind of correlation with the pore size, surface area of the electrode, the concentration of electrolyte, ion size, and dielectric constant of the electrolyte.

For example, the mesopores are cylindrical in size. The solvated ions form an electric double layer inside these cylindrical pores to ultimately form an electrical double cylinder capacitor. In case of micropores, pore width cannot accommodate more than 1 solvated ion since they are smaller in diameter. The counter ions basically line up and act like an electric wire in cylindrical capacitor. Due to this, there is an anomalous increase in capacitance. So, the capacitance value is dependent on the pore size according to the Huangs model.

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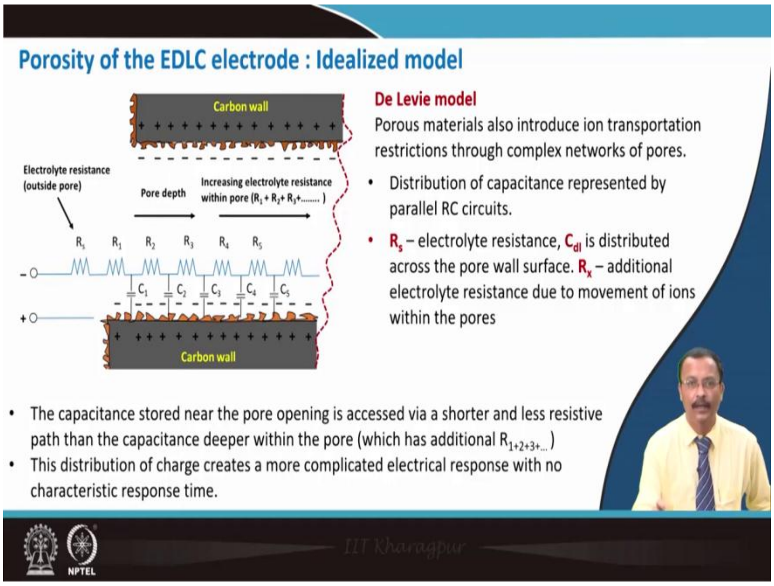

Porosity of the EDLC electrode : Idealized model

De Levie model

Porous materials also introduce ion transportation restrictions through complex networks of pores.

- Distribution of capacitance represented by parallel RC circuits.
- **R_s** – electrolyte resistance, **C_{dl}** is distributed across the pore wall surface. **R_x** – additional electrolyte resistance due to movement of ions within the pores

- The capacitance stored near the pore opening is accessed via a shorter and less resistive path than the capacitance deeper within the pore (which has additional $R_{1+2+3+\dots}$)
- This distribution of charge creates a more complicated electrical response with no characteristic response time.

De Levie came up with a model; wherein he says that porous material also introduce ion transport restriction, because the solvated ion cannot penetrate if the pore size is too small. So, there is a distribution of capacitance which is actually modeled by several RC circuit (parallel RC circuit as you can see here).

So, here R_s value is the electrolyte resistance and C_{DL} is your double layer capacitance distributed across the pore wall surface. The resistor here is R_X: additional electrolyte resistance due to the movement of the ions within the pore. So, progressively it will have more resistance as you it goes inside the pore.

The capacitance stored near the pore opening is accessed by a shorter and less resistive path which is clear from this diagram. But once it moves deeper in the pore depth, then it has additional component R1 plus R2 plus R3. So, the distribution of charge creates a more complicated electrical response with eventually no characteristic response time. So, RC time constant differ dramatically as you move on.

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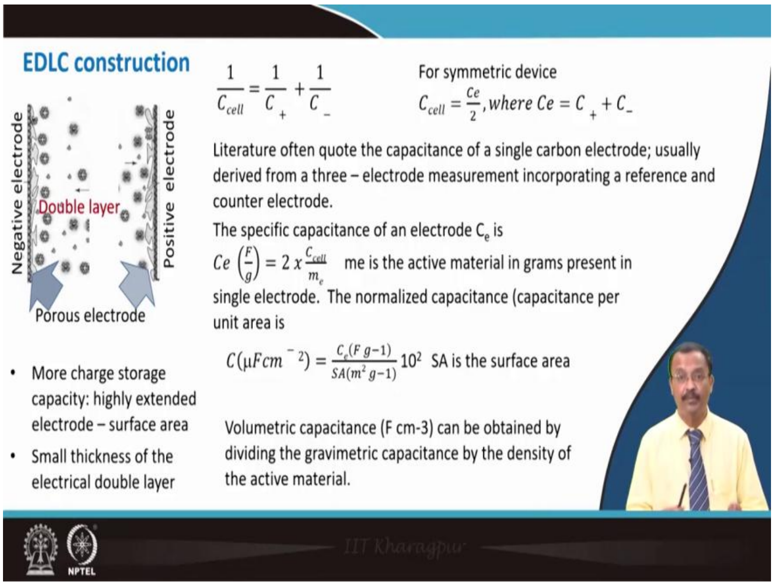

EDLC construction

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

For symmetric device

$C_{cell} = \frac{Ce}{2}, where\ Ce = C_{+} + C_{-}$

Literature often quote the capacitance of a single carbon electrode; usually derived from a three – electrode measurement incorporating a reference and counter electrode.

The specific capacitance of an electrode C_e is

$Ce\left(\frac{F}{g}\right) = 2\,x\,\frac{C_{cell}}{m_e}$ me is the active material in grams present in single electrode. The normalized capacitance (capacitance per unit area is

$C(\mu F cm^{-2}) = \frac{C_e(F\,g-1)}{SA(m^2\,g-1)} 10^2$ SA is the surface area

- More charge storage capacity: highly extended electrode – surface area
- Small thickness of the electrical double layer

Volumetric capacitance (F cm-3) can be obtained by dividing the gravimetric capacitance by the density of the active material.

In case of this EDLC construction, you have a negative electrode and a positive electrode which are porous and connected in series.

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

Now, if it is symmetric device (both this electrode are similar type), then this is C_e by 2, where C_e is nothing but C_{plus} plus C_{minus}.

$$C_{cell} = \frac{Ce}{2},\ where\ Ce = C_{+} + C_{-}$$

So, in literature you will find they often quote for the capacitance for a single carbon electrode, derived from a 3 electrode measurement incorporating a reference and a counter electrode.

So, the specific capacitance can be calculated as 2 times C of cell by m_e, where m_e is the active material in grams that is present in a single electrode.

$$Ce\left(\frac{F}{g}\right) = 2\,x\,\frac{C_{cell}}{m_e}$$

The normalized capacitance implies the capacitance per unit area that you can determine by this simple equation

$$C\left(\mu\text{Fcm}^{-2}\right) = \frac{C_e(\text{F g-1})}{\text{SA}(\text{m}^2\text{ g-1})}10^2$$

And the volumetric capacitance can be obtained by dividing the gravimetric capacitance by density of the active material. The capacitance also depends on the types of the pore whether they are torturous or they are connected. This will determine whether the electrolyte can go inside this pore and form the double layer. Small thickness of the electric double layer will give you more capacitance in this EDLC.

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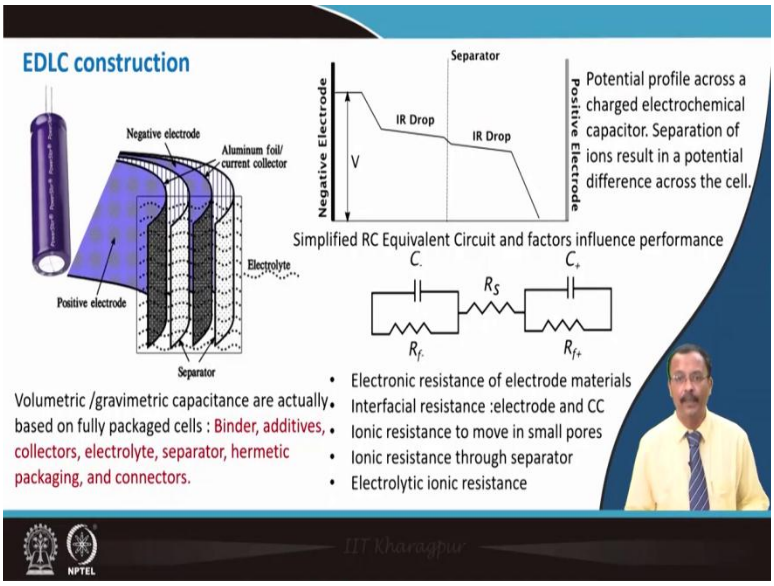

EDLC construction

Potential profile across a charged electrochemical capacitor. Separation of ions result in a potential difference across the cell.

Simplified RC Equivalent Circuit and factors influence performance

Volumetric /gravimetric capacitance are actually based on fully packaged cells : Binder, additives, collectors, electrolyte, separator, hermetic packaging, and connectors.

- Electronic resistance of electrode materials
- Interfacial resistance :electrode and CC
- Ionic resistance to move in small pores
- Ionic resistance through separator
- Electrolytic ionic resistance

Several negative and positive electrodes are wrapped to increase the area. The area is further increased when they are packed to form this kind of commercial EDLC. If you consider the potential profile across a charged electrochemical capacitor, separation of ions result in a potential difference across the negative and positive terminal and voltage profile is shown here. A simplified RC circuit can be developed with positive and negative capacitance and it is in between this internal resistance. So, the capacitance value can be modeled like this.

The electronic resistance of electrode material, interfacial resistance, electrode and current collector constitutes this resistive path. Ionic resistance to move in small parts also contributes through the separator and electrolytic ionic resistance.

The Estimated or Calculated volumetric or gravimetric capacity should be based on the fully packaged cell, not only 1 or 2 electrodes. In a fully packaged cell, binder, additives, collectors, electrolytes, separator and hermetic packaging connectors are present. So, all components should be included as either weight or volume to have a reasonable value. In the research papers, people only consider the active material and its corresponding weight, giving you a large value. But if you consider all this construction material weight, which are dead weight, then the value is significantly lowered.

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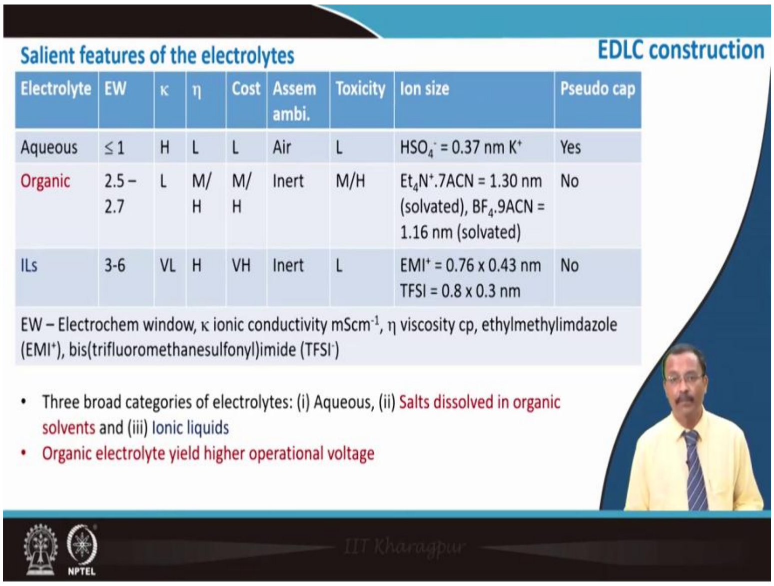

Salient features of the electrolytes

EDLC construction

Electrolyte	EW	κ	η	Cost	Assem ambi.	Toxicity	Ion size	Pseudo cap
Aqueous	≤ 1	H	L	L	Air	L	HSO_4^- = 0.37 nm K^+	Yes
Organic	2.5 – 2.7	L	M/H	M/H	Inert	M/H	Et_4N^+.7ACN = 1.30 nm (solvated), BF_4.9ACN = 1.16 nm (solvated)	No
ILs	3-6	VL	H	VH	Inert	L	EMI^+ = 0.76 x 0.43 nm TFSI = 0.8 x 0.3 nm	No

EW – Electrochem window, κ ionic conductivity $mScm^{-1}$, η viscosity cp, ethylmethylimdazole (EMI^+), bis(trifluoromethanesulfonyl)imide ($TFSI^-$)

- Three broad categories of electrolytes: (i) Aqueous, (ii) Salts dissolved in organic solvents and (iii) Ionic liquids
- Organic electrolyte yield higher operational voltage

For the electrolyte, three different types of electrolytes are used. It could be aqueous electrolyte. And depending on what kind of counter ions are there, we know that what the typical dimension is. They are pretty small as compared to organic, or as compared to ionic liquid. And here EW stands for the electro chemical window and kappa is the ionic conductivity (given in millisiemens per centimeter), eta is the viscosity (in centipoise).

So, there are 3 broad categories, and you we can compare their window. Aqueous voltage window is relatively less because of the problem of H_2O dissociation. But their ionic conductivity is quite high. Viscosity is also quite low, cost is low, and you can assemble this kind of super capacitor in open ambient.

So, aqueous is a bit attractive, but it has low potential window. But if you go to ionic liquid, you obtain ionic conductivity etcetera in this range. The viscosity is also high, but it yields high operational voltage.

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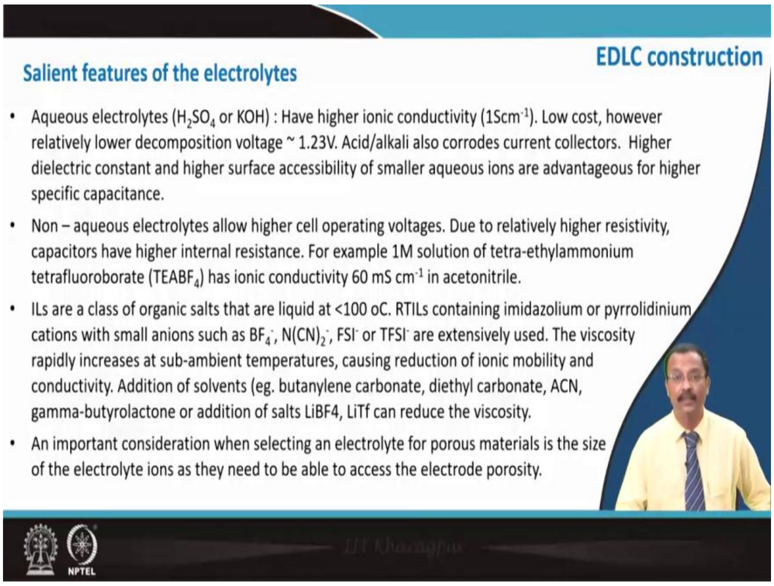

EDLC construction

Salient features of the electrolytes

- Aqueous electrolytes (H_2SO_4 or KOH) : Have higher ionic conductivity ($1 Scm^{-1}$). Low cost, however relatively lower decomposition voltage ~ 1.23V. Acid/alkali also corrodes current collectors. Higher dielectric constant and higher surface accessibility of smaller aqueous ions are advantageous for higher specific capacitance.
- Non – aqueous electrolytes allow higher cell operating voltages. Due to relatively higher resistivity, capacitors have higher internal resistance. For example 1M solution of tetra-ethylammonium tetrafluoroborate ($TEABF_4$) has ionic conductivity 60 mS cm^{-1} in acetonitrile.
- ILs are a class of organic salts that are liquid at <100 oC. RTILs containing imidazolium or pyrrolidinium cations with small anions such as BF_4^-, $N(CN)_2^-$, FSI^- or $TFSI^-$ are extensively used. The viscosity rapidly increases at sub-ambient temperatures, causing reduction of ionic mobility and conductivity. Addition of solvents (eg. butanylene carbonate, diethyl carbonate, ACN, gamma-butyrolactone or addition of salts LiBF4, LiTf can reduce the viscosity.
- An important consideration when selecting an electrolyte for porous materials is the size of the electrolyte ions as they need to be able to access the electrode porosity.

The salient features of the electrolytes are highlighted here in the slides. Examples for non-aqueous electrolytes are 1 molar tetra ethylammonium tetrafluoroborate in acetonitrile ACN, which has an ionic conductivity of 60 millisiemens per centimeter. Ionic liquid is a class of organic salt which are liquid at less than 100 degree Celsius; and it contains imidazolium or pyrrolidinium cations with small anions such as BF_4^-. Viscosity rapidly increases once you go to sub-ambient temperature. This causes in the reduction of ionic mobility, and also the conductivity. Additional solvents are sometimes introduced in the ionic liquid to reduce its viscosity and maintain its ionic conductivity, particularly at 0^oC.

So, an important consideration when selecting an electrolyte for porous material is the size of the electrolyte ion, and whether they will be able to access the electrode porosity.

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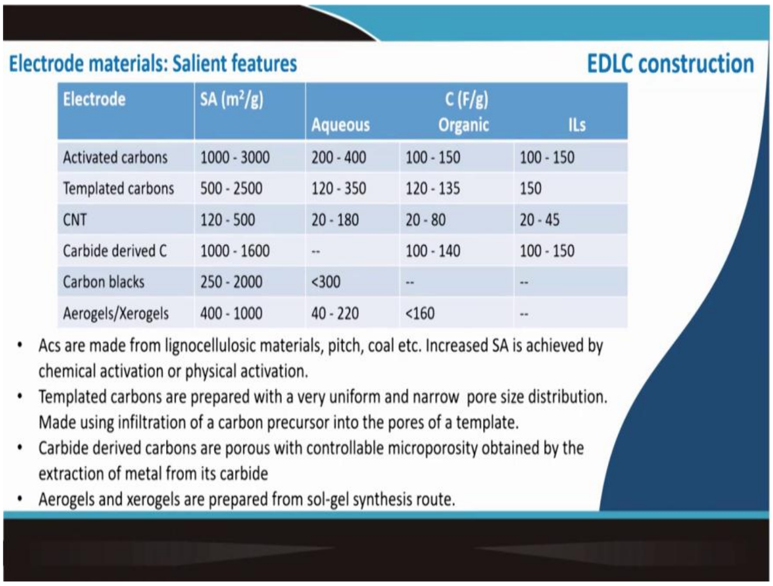

Electrode materials: Salient features

EDLC construction

Electrode	SA (m^2/g)	C (F/g)		
		Aqueous	Organic	ILs
Activated carbons	1000 - 3000	200 - 400	100 - 150	100 - 150
Templated carbons	500 - 2500	120 - 350	120 - 135	150
CNT	120 - 500	20 - 180	20 - 80	20 - 45
Carbide derived C	1000 - 1600	--	100 - 140	100 - 150
Carbon blacks	250 - 2000	<300	--	--
Aerogels/Xerogels	400 - 1000	40 - 220	<160	--

- Acs are made from lignocellulosic materials, pitch, coal etc. Increased SA is achieved by chemical activation or physical activation.
- Templated carbons are prepared with a very uniform and narrow pore size distribution. Made using infiltration of a carbon precursor into the pores of a template.
- Carbide derived carbons are porous with controllable microporosity obtained by the extraction of metal from its carbide
- Aerogels and xerogels are prepared from sol-gel synthesis route.

Electrode materials such as activated carbon are generally used. Templated carbon is also used for which the typical surface area values are provided here. Capacitance values are also tabulated to give a better view.

Activated carbons are usually made from economic lignocellulose material pitch coal. Increased surface area is achieved by either chemical activation and or physical activation, which I will talk in details in later part of this course. Templated carbon has a very uniform and narrow pore size distribution. Usually zeolite etc. is used, where carbon precursors are forced into the pores of the template.

The carbide derived carbons are porous with controllable micro porosity obtained by extraction of metal from it is carbide. Aerogel and xerogel are prepared from sol gel synthesis route.

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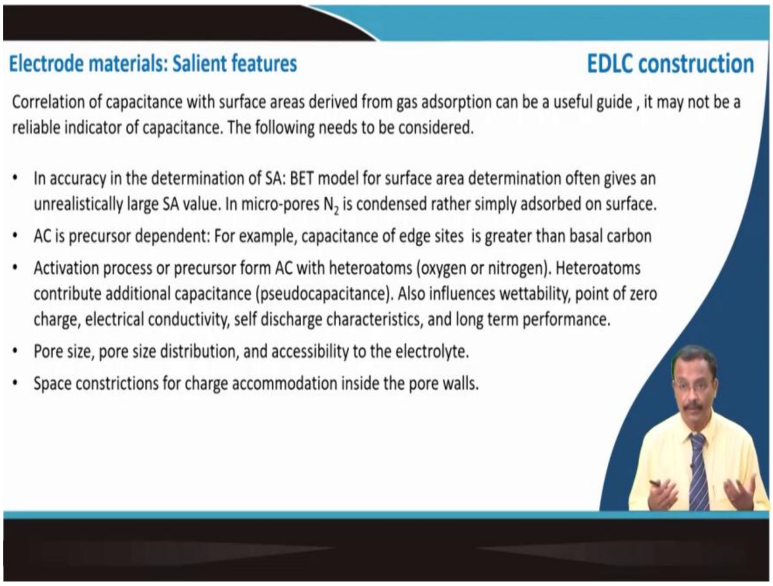

Electrode materials: Salient features

EDLC construction

Correlation of capacitance with surface areas derived from gas adsorption can be a useful guide , it may not be a reliable indicator of capacitance. The following needs to be considered.

- In accuracy in the determination of SA: BET model for surface area determination often gives an unrealistically large SA value. In micro-pores N_2 is condensed rather simply adsorbed on surface.
- AC is precursor dependent: For example, capacitance of edge sites is greater than basal carbon
- Activation process or precursor form AC with heteroatoms (oxygen or nitrogen). Heteroatoms contribute additional capacitance (pseudocapacitance). Also influences wettability, point of zero charge, electrical conductivity, self discharge characteristics, and long term performance.
- Pore size, pore size distribution, and accessibility to the electrolyte.
- Space constrictions for charge accommodation inside the pore walls.

So, capacitance with surface area derived from gas adsorption is usually a useful guide, but it is not a reliable indicator. Its accuracy is determined by the BET method and sometimes nitrogen is not actually adsorbed, but it is condensed inside the pore which gives erroneous results.

For Activated carbon prepared from different types of precursor, the edge site of the capacitance is more or as compared to the basal carbon. So, that will also influence the capacity value of this EDLC. Activation process of this activated carbon and the associated heteroatoms like oxygen and nitrogen sometimes exhibit a pseudocapacitive behavior. So, they increase the capacitance and self discharge characteristics including long term performance. Pore size and pore size distribution along with accessibility to the electrolyte is also important. Space constriction of charge accommodation inside the pore wall also influences the capacitative value.

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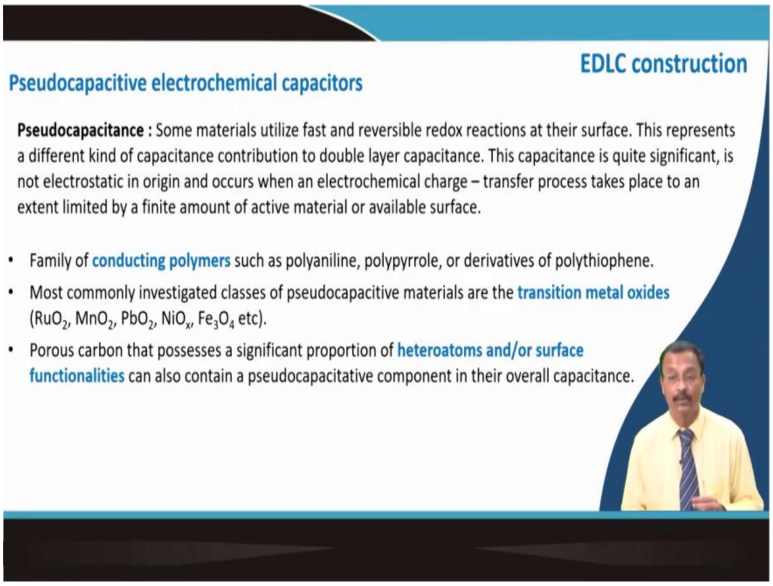

EDLC construction

Pseudocapacitive electrochemical capacitors

Pseudocapacitance : Some materials utilize fast and reversible redox reactions at their surface. This represents a different kind of capacitance contribution to double layer capacitance. This capacitance is quite significant, is not electrostatic in origin and occurs when an electrochemical charge – transfer process takes place to an extent limited by a finite amount of active material or available surface.

- Family of conducting polymers such as polyaniline, polypyrrole, or derivatives of polythiophene.
- Most commonly investigated classes of pseudocapacitive materials are the transition metal oxides (RuO_2, MnO_2, PbO_2, NiO_x, Fe_3O_4 etc).
- Porous carbon that possesses a significant proportion of heteroatoms and/or surface functionalities can also contain a pseudocapacitative component in their overall capacitance.

Now, pseudocapacitance; there are some materials which utilize fast and reversible redox reaction and not only adsorption. So, mostly three types of pseudocapacitors are identified; one is the conducting polymer polyanion, polyaniline, polypyrrole or the derivative of polythiophene. Most commonly investigated class of pseudocapacitor material is transition metal like ruthenium oxide etcetera. Porous carbon that possesses a significant amount of hetero atoms at the surface also increases the pseudo capacitative component.

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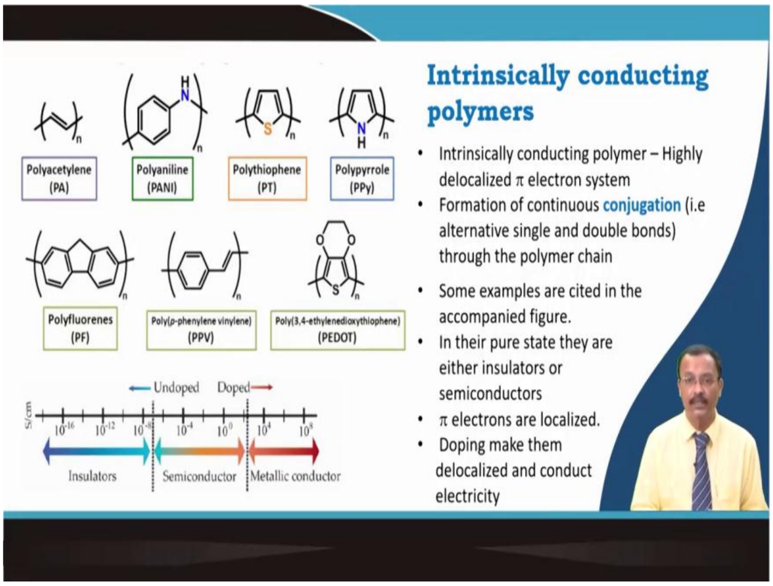

Intrinsically conducting polymers

- Intrinsically conducting polymer – Highly delocalized π electron system
- Formation of continuous conjugation (i.e alternative single and double bonds) through the polymer chain
- Some examples are cited in the accompanied figure.
- In their pure state they are either insulators or semiconductors
- π electrons are localized.
- Doping make them delocalized and conduct electricity

So, intrinsically conducting polymers have highly delocalized pi electron system and they form a continuous conjugation that is alternative single and double bonds in all this polymers. So, some of these polymers examples are cited, so here pi electrons are localized; only when you dope them do they become delocalized and conduct electricity.

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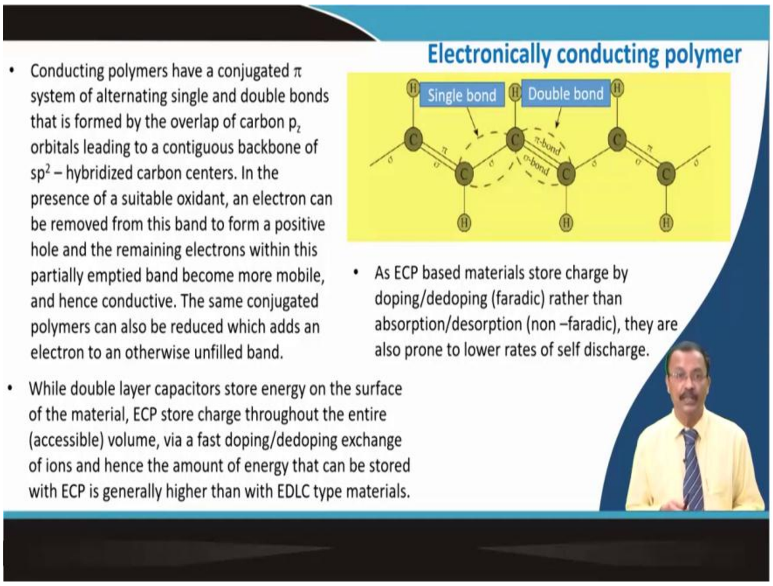

Electronically conducting polymer

- Conducting polymers have a conjugated π system of alternating single and double bonds that is formed by the overlap of carbon p_z orbitals leading to a contiguous backbone of sp^2 – hybridized carbon centers. In the presence of a suitable oxidant, an electron can be removed from this band to form a positive hole and the remaining electrons within this partially emptied band become more mobile, and hence conductive. The same conjugated polymers can also be reduced which adds an electron to an otherwise unfilled band.
- As ECP based materials store charge by doping/dedoping (faradic) rather than absorption/desorption (non –faradic), they are also prone to lower rates of self discharge.
- While double layer capacitors store energy on the surface of the material, ECP store charge throughout the entire (accessible) volume, via a fast doping/dedoping exchange of ions and hence the amount of energy that can be stored with ECP is generally higher than with EDLC type materials.

So, conducting polymers have a conjugate pi system of alternate single and double bonds that is formed by overlap of a carbon p_z orbital leading to a continuous backbone of sp^2 hybridized carbon center.

In the presence of a suitable oxidant an electron can be moved from the band to form a positive hole and remaining electron within the partially emptied band become more mobile; and hence it becomes conductive. The same conjugated polymers can also be reduced which adds electron to the other wised unfilled band.

While double layer capacitor store energy on the surface of the material, ECP store charges throughout the entire accessible volume via fast doping and dedoping. Hence, the amount of energy that can be stored with this electronically conducting polymer are usually higher than EDLC.

ECP store charge by doping and dedoping which is basically faradic rather than absorption and desorption. They are also prone to lower rates of self discharge.

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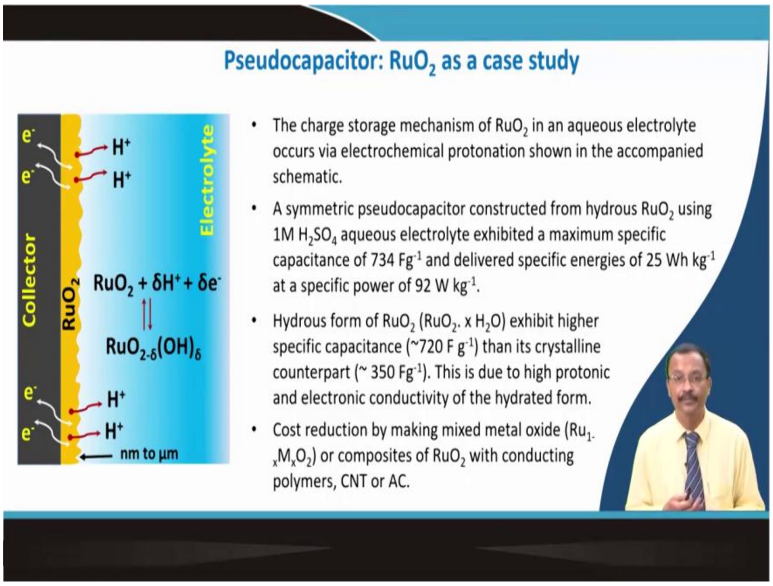

$$RuO_2 + \delta H^+ + \delta e^- \rightleftharpoons RuO_{2-\delta}(OH)_\delta$$

Pseudocapacitor: RuO_2 as a case study

- The charge storage mechanism of RuO_2 in an aqueous electrolyte occurs via electrochemical protonation shown in the accompanied schematic.
- A symmetric pseudocapacitor constructed from hydrous RuO_2 using 1M H_2SO_4 aqueous electrolyte exhibited a maximum specific capacitance of 734 Fg^{-1} and delivered specific energies of 25 Wh kg^{-1} at a specific power of 92 W kg^{-1}.
- Hydrous form of RuO_2 (RuO_2. x H_2O) exhibit higher specific capacitance (~720 F g^{-1}) than its crystalline counterpart (~ 350 Fg^{-1}). This is due to high protonic and electronic conductivity of the hydrated form.
- Cost reduction by making mixed metal oxide ($Ru_{1-x}M_xO_2$) or composites of RuO_2 with conducting polymers, CNT or AC.

So, ruthenium oxide was one of the first pseudocapacitor materials which were studied. The charge storage mechanism, as you can see here, the reaction that takes place at the surface is not simple absorption. But the valence state is also changing. Usually 1 molar of H_2SO_4 aqueous electrolyte is used and that gives a maximum specific capacitance about 734 farad per gram which is quite a high value. Hydrous form of ruthenium oxide exhibit higher specific capacitance and that is due to high protonic and electronic conductivity in the hydrous form.

And one can reduce the cost of this ruthenium oxide by making a metal oxide dopant. Several metal oxide is doped in RuO_2, or one can make composite with conducting polymer just I mentioned, or with CNT and activated carbon to make this kind of pseudocapacitors.

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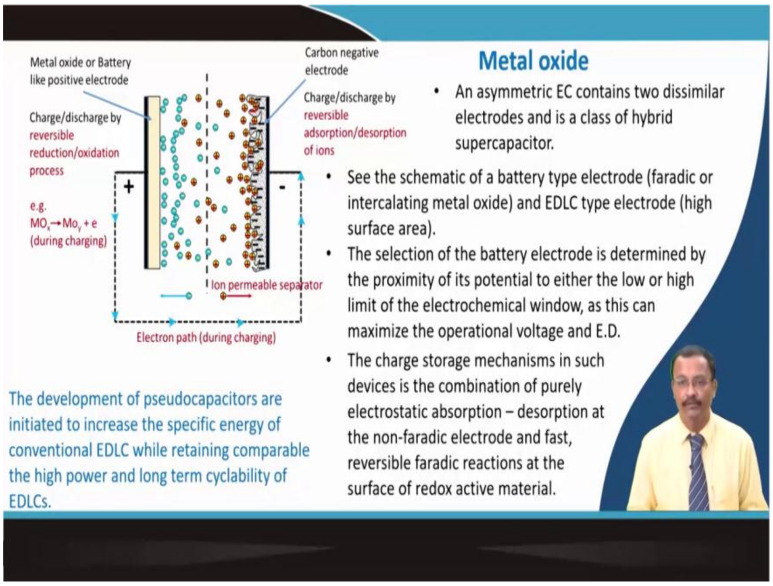

Metal oxide

Metal oxide or Battery like positive electrode

Charge/discharge by reversible reduction/oxidation process

e.g. $MO_x \rightarrow Mo_y + e$ (during charging)

Carbon negative electrode

Charge/discharge by reversible adsorption/desorption of ions

Ion permeable separator

Electron path (during charging)

- An asymmetric EC contains two dissimilar electrodes and is a class of hybrid supercapacitor.
- See the schematic of a battery type electrode (faradic or intercalating metal oxide) and EDLC type electrode (high surface area).
- The selection of the battery electrode is determined by the proximity of its potential to either the low or high limit of the electrochemical window, as this can maximize the operational voltage and E.D.
- The charge storage mechanisms in such devices is the combination of purely electrostatic absorption – desorption at the non-faradic electrode and fast, reversible faradic reactions at the surface of redox active material.

The development of pseudocapacitors are initiated to increase the specific energy of conventional EDLC while retaining comparable the high power and long term cyclability of EDLCs.

Now, so far we talked about symmetric capacitor where the electrodes are of same type. As shown here in this schematic for asymmetric electro chemical capacitor, it consists of two dissimilar electrodes, and this is called hybrid super capacitor. So, here one type is EDLC type absorption type of electrode another one is a pseudo capacitor type.

So, the selection of this battery type electrode that is determined of course within the proximity of its potential, because these two potential should match such that they should not be very different potential regime and depending on that one will act as negative and positive electrode.

The charge storage mechanism for such device is a combination of purely electrostatic absorption desorption at the non faradic electrode and fast reversible faradic reaction at the surface of the redox material. So, the diffusion is limited here and this charged cation or anion they do not go far into the electrode.

So, developments of this pseudocapacitor are initiated to increase the specific energy of the conventional EDLC material while retaining the comparable high power capacity and cycleability of the EDLC.

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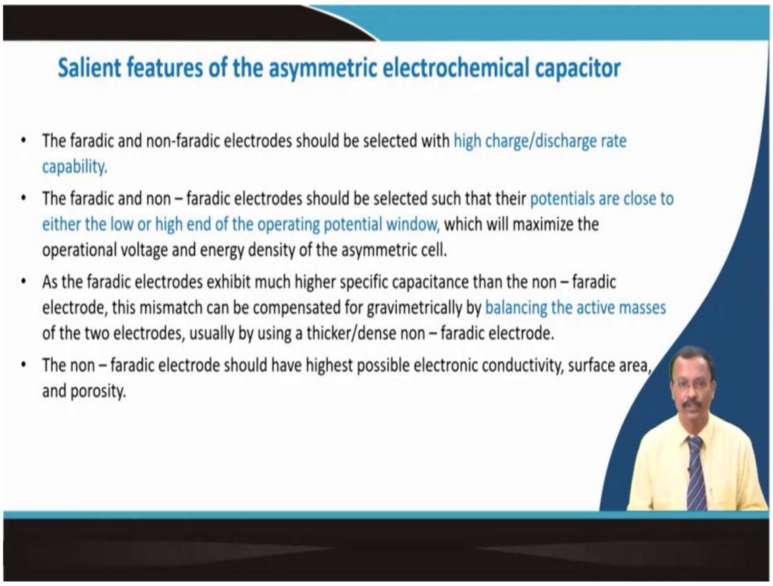

Salient features of the asymmetric electrochemical capacitor

- The faradic and non-faradic electrodes should be selected with high charge/discharge rate capability.
- The faradic and non – faradic electrodes should be selected such that their potentials are close to either the low or high end of the operating potential window, which will maximize the operational voltage and energy density of the asymmetric cell.
- As the faradic electrodes exhibit much higher specific capacitance than the non – faradic electrode, this mismatch can be compensated for gravimetrically by balancing the active masses of the two electrodes, usually by using a thicker/dense non – faradic electrode.
- The non – faradic electrode should have highest possible electronic conductivity, surface area, and porosity.

So, the salient feature as I mentioned faradic and non faradic electrode should be selected with high charge discharge rate capability. Faradic and non faradic electrodes should be selected such that their potential is close to either low or high end of the operating potential window that you are talking about.

As the faradic electrodes exhibit much higher specific capacitance than the non faradic electrode, their charge must be balance through proper gravimetry (the balancing of the active mass). The one having larger capacity should be thinner to maintain the total charge.

And the non faradic electrode should have highest possible electronic conductivity, surface area and porosity.

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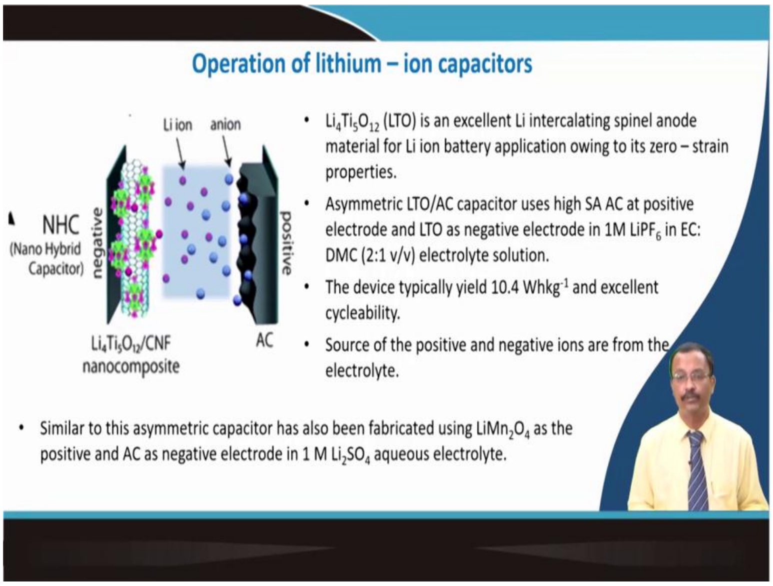

Operation of lithium – ion capacitors

- $Li_4Ti_5O_{12}$ (LTO) is an excellent Li intercalating spinel anode material for Li ion battery application owing to its zero – strain properties.
- Asymmetric LTO/AC capacitor uses high SA AC at positive electrode and LTO as negative electrode in 1M $LiPF_6$ in EC: DMC (2:1 v/v) electrolyte solution.
- The device typically yield 10.4 $Whkg^{-1}$ and excellent cycleability.
- Source of the positive and negative ions are from the electrolyte.

- Similar to this asymmetric capacitor has also been fabricated using $LiMn_2O_4$ as the positive and AC as negative electrode in 1 M Li_2SO_4 aqueous electrolyte.

So, as an example on the operation of one of such kind of lithium ion capacitor, one can have lithium titanium oxide (which is an excellent lithium intercalating spinel anode material) to form an asymmetric LTO AC capacitor using high surface area activated carbon. And the electrolyte is 1 molar $LiPF_6$ in EC. This device in a packaged state typically yields 10.4 watt hour per kg with an excellent cycleability. Source of positive and negative ions are from the electrolyte.

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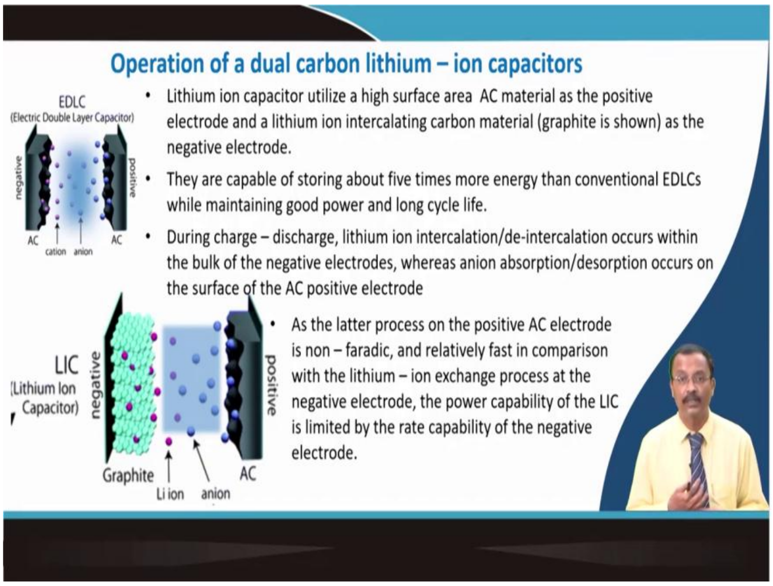

Operation of a dual carbon lithium – ion capacitors

- Lithium ion capacitor utilize a high surface area AC material as the positive electrode and a lithium ion intercalating carbon material (graphite is shown) as the negative electrode.
- They are capable of storing about five times more energy than conventional EDLCs while maintaining good power and long cycle life.
- During charge – discharge, lithium ion intercalation/de-intercalation occurs within the bulk of the negative electrodes, whereas anion absorption/desorption occurs on the surface of the AC positive electrode
- As the latter process on the positive AC electrode is non – faradic, and relatively fast in comparison with the lithium – ion exchange process at the negative electrode, the power capability of the LIC is limited by the rate capability of the negative electrode.

Another example is lithium ion capacitor that uses a high surface area as the positive electrode and lithium ion intercalating carbon material as the negative electrode. So, this is asymmetric carbon-carbon type, and here again an asymmetric type is used during charge discharge wherein lithium ion intercalation occur within the bulk of the negative electrode. The anions absorb and desorb occurs at the surface of the positive electrode same for the last case. The latter process on the positive AC electrode is non-faradaic and relatively fast in comparison with the lithium base electrode here which is graphite. One is EDLC type and another one is intercalated type. And again, the ions are coming from the electrolyte itself for the formation of this kind of lithium ion capacitors.

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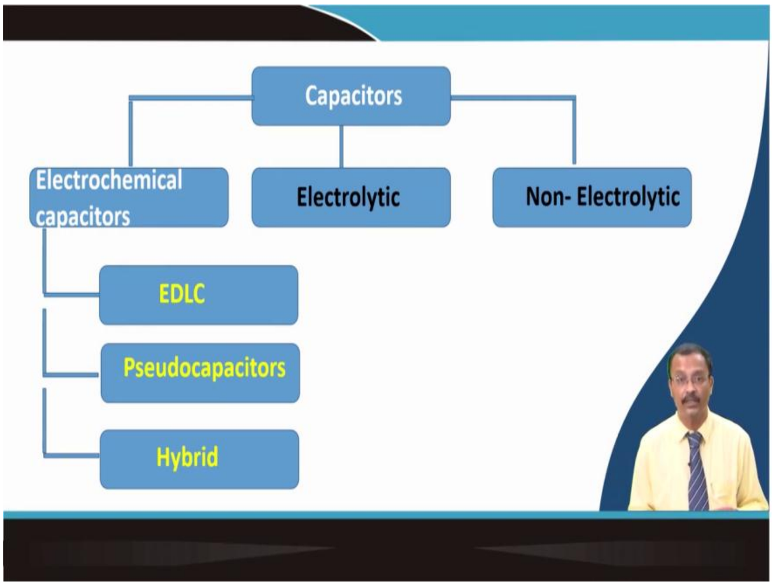
Capacitors

Electrochemical capacitors

Electrolytic

Non- Electrolytic

EDLC

Pseudocapacitors

Hybrid

So, if I compile all types of capacitors you can see capacitor can be divided into three broad category; electrochemical capacitor, electrolytic capacitor and non electrolytic capacitor. Now, electrochemical capacitor could be of EDLC type or pseudocapacitor type; and finally we have talked about the hybrid type capacitors.

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REFERENCES

- **Supercapcitors: Materials, Systems, and Applications, 1st Edition Edited by Francois Beguin and Elzbieta Frackowiak,** Chapter 2 : General Properties of Electrochemical Capacitors, page 69 – 101, Wiley – VCH Verlag GmbH &Co KGaA 2013 (Study materials)
- **A. Yu, V. Chabot, J. Zhang** Electrochemical supercapacitors for energy storage and delivery: Fundamentals and applications, CRC Press (Taylor and Francis group) (2013)

So, the study material for this is shown in red and apart from that the book electrochemical super capacitor by Chabot and Zhang is a good source for a study material.

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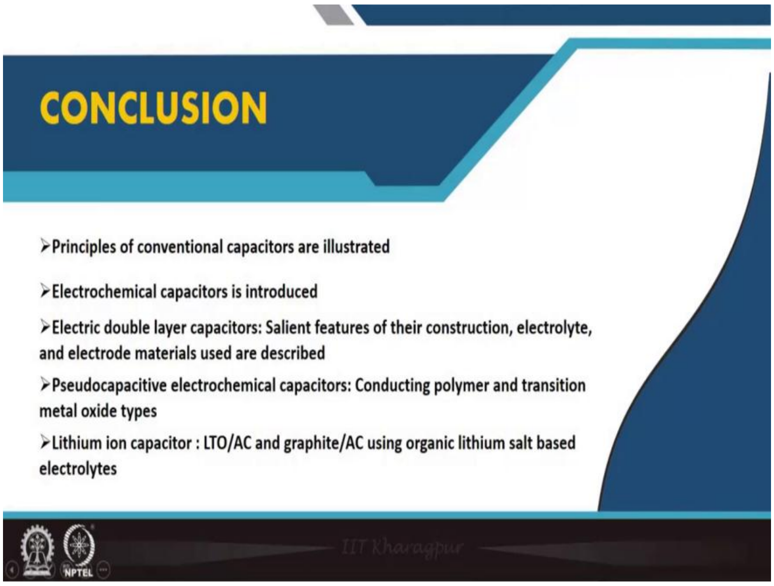

CONCLUSION

- Principles of conventional capacitors are illustrated
- Electrochemical capacitors is introduced
- Electric double layer capacitors: Salient features of their construction, electrolyte, and electrode materials used are described
- Pseudocapacitive electrochemical capacitors: Conducting polymer and transition metal oxide types
- Lithium ion capacitor : LTO/AC and graphite/AC using organic lithium salt based electrolytes

So, I can conclude that in this particular lecture, we have talked about various types of electrochemical capacitor; first EDLC was introduced, second we have talked about pseudocapacitors (mostly polymer based pseudo capacitor) and transition oxide base super capacitor pseudocapacitor. Finally the hybrid pseudocapacitor was introduced.

Thank you for your attention.