Electrochemical Energy Storage
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Module - 08
Advanced materials and technologies for supercapacitors
Lecture - 37
Pseudocapacitor

Welcome to my course Electrochemical Energy Storage. And this is module number-8 where I am teaching Advanced materials and technologies for supercapacitors. And this is lecture number 37. In continuation to lecture number 36, this is the second type of the ultracapacitors which we defined as Pseudocapacitor.

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CONCEPTS COVERED

- Nature and origin of pseudocapacitors
- Cyclic voltammetry measurements
- Electrode materials
  - Redox-active metal oxides and /or nitrides
  - Electronically conducting polymers
  - Composite materials

So, first I will talk about the nature and origin of this pseudocapacitors. And then again through cyclic voltammetry if you once you do the cyclic voltammetry it is possible for you to delineate the surface charge storage part from the diffusion controlled redox base storage part which is prominent for pseudocapacitive material.

And then we will talk about the electrode materials for the pseudocapacitors which include the redox active metal oxide or metal nitrides. Then electronically conducting polymers which will also be considered, and the composite material we will be talking about.

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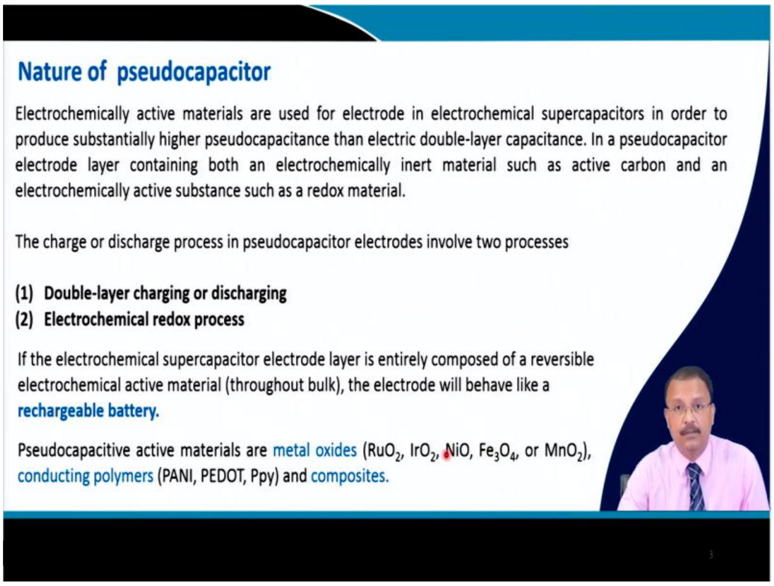

Nature of pseudocapacitor

Electrochemically active materials are used for electrode in electrochemical supercapacitors in order to produce substantially higher pseudocapacitance than electric double-layer capacitance. In a pseudocapacitor electrode layer containing both an electrochemically inert material such as active carbon and an electrochemically active substance such as a redox material.

The charge or discharge process in pseudocapacitor electrodes involve two processes

1. **Double-layer charging or discharging**
2. **Electrochemical redox process**

If the electrochemical supercapacitor electrode layer is entirely composed of a reversible electrochemical active material (throughout bulk), the electrode will behave like a **rechargeable battery.**

Pseudocapacitive active materials are metal oxides (RuO_2, IrO_2, NiO, Fe_3O_4, or MnO_2), conducting polymers (PANI, PEDOT, Ppy) and composites.

So, this electrochemically active materials they are used for electrochemical supercapacitors that you have seen that there is a possibility to have higher capacitance value as compared to the electric double layer capacitor. And this electrode layer which is electrochemically active. So, this layer that may contain electrochemically non-active inert material. And this is particularly required when you do not have sufficient electronic conductivity of your electroactive materials.

So, then ideally many of the super capacitors they contain a EDLC type material as well as a pseudocapacitor type material So, according to that, you have two types of process; which are operative in pseudo capacitor. The first one when you have a carbonaceous material which is basically being introduced to increase the electronic conductivity.

So, there that is double layer charging and discharging that is operative. And for the electrochemically active material where the transition metal oxide it could be where the redox reaction is involved, so that these two mechanisms are simultaneously operative in this type of pseudocapacitors.

So, as I said if the supercapacitors electrode layer that is composed of a reversible electrochemical active material throughout it is bulk, then it will behave as a rechargeable battery that I have cited several examples that the whole material whole material the redox reaction is operative. So, say lithium is inserting into the material, and their transition metal cation their charge is changed, so it is a slow process. And then we define the that is a battery.

So, pseudocapacitor this charge transfer takes place, but it is only at a very thin layer at the surface of the material not throughout the bulk. So, in many instances you use a very thin layer which is also which is electrochemically active. So, typical examples are different transition metal cations involved this oxides and conducting polymers. And I will explain the composite material as well.

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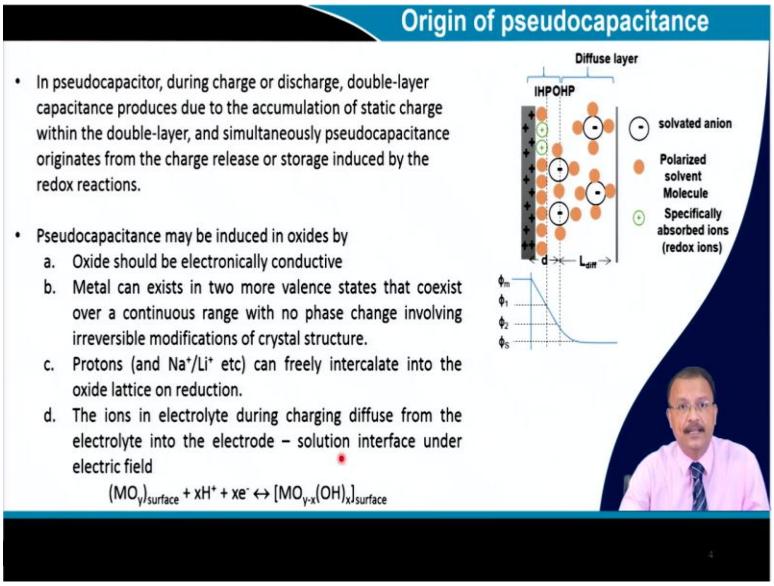

Origin of pseudocapacitance

- In pseudocapacitor, during charge or discharge, double-layer capacitance produces due to the accumulation of static charge within the double-layer, and simultaneously pseudocapacitance originates from the charge release or storage induced by the redox reactions.
- Pseudocapacitance may be induced in oxides by
  a. Oxide should be electronically conductive
  b. Metal can exists in two more valence states that coexist over a continuous range with no phase change involving irreversible modifications of crystal structure.
  c. Protons (and Na^+/Li^+ etc) can freely intercalate into the oxide lattice on reduction.
  d. The ions in electrolyte during charging diffuse from the electrolyte into the electrode – solution interface under electric field

$$(MO_y)_{surface} + xH^+ + xe^- \leftrightarrow [MO_{y-x}(OH)_x]_{surface}$$

So, the charge storage process that is quite interesting. So, during charge and discharge this double layer capacitors, they produce due to the accumulation of the static charge within the double layer. And simultaneously pseudocapacitance that is originating from the charge release or charge storage by the redox reaction. So, both are operating simultaneously. So, with the potential is somewhat similar which I actually explained for EDLC type of material.

And there are certain criteria that must be satisfied, so that this pseudocapacitance originates. The first one is if you are using an oxide material, they should be electronically conducting ok. So, same thing in battery also you need to have a conducting additive added with the active material along with the binder also so to make the battery. So, similar to that, in case of oxide, most of the oxides certain oxides they are electronically conducting like ruthenium oxide there you do not need that.

And the electroactive material whatever you using, they should have two or more valence state that coexist. And ideally we will expect that there is no phase change involved when this redox reaction will take place. When the transition metal cation will change its valance state, then the phase will remain same as it has while it started the reaction. And typically sodium and lithium ions, they also can intercalate into the oxide lattice similar to that of sodium and lithium ion batteries.

And this ions in the electrolyte while it charge, they diffuse from the electrolyte into the electrode solution interface under some kind of electric field. So, when it have this kind of reaction remember in the third lecture of module number 1, we talked about we showed that in case of R u O 2 how it works in a details.

So, there is a proton involved in this particular case particularly when we are using aqueous electrolyte. And this is diffusing into the surface. And as a result the valance state of the M changes, but not throughout the bulk of the material that is also quite limited to the surface.

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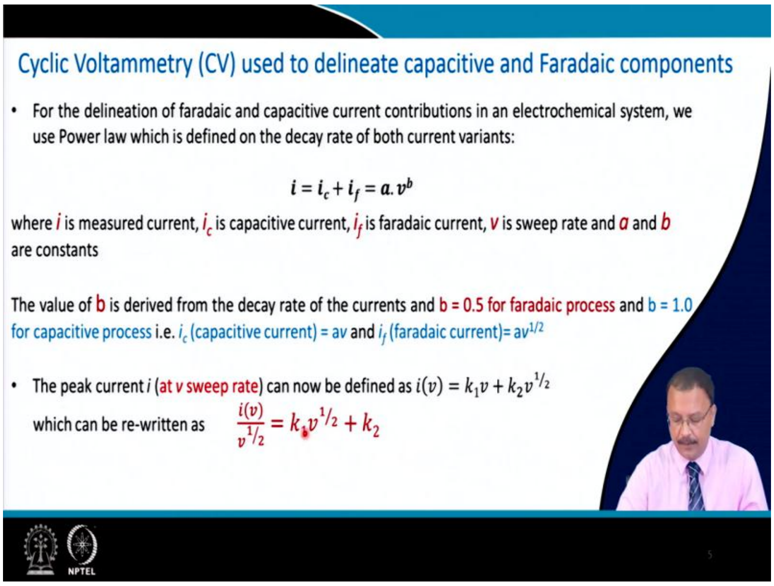

Cyclic Voltammetry (CV) used to delineate capacitive and Faradaic components

- For the delineation of faradaic and capacitive current contributions in an electrochemical system, we use Power law which is defined on the decay rate of both current variants:

$$i = i_c + i_f = a.v^b$$

where i is measured current, i_c is capacitive current, i_f is faradaic current, v is sweep rate and a and b are constants

The value of b is derived from the decay rate of the currents and b = 0.5 for faradaic process and b = 1.0 for capacitive process i.e. i_c (capacitive current) = av and i_f (faradaic current)= $av^{1/2}$

- The peak current i (at v sweep rate) can now be defined as $i(v) = k_1 v + k_2 v^{1/2}$ which can be re-written as $\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2$

Now, cyclic voltammetry that is a use we one can use to delineate this capacitive current contribution in an electrochemical system, and a power law is involved. In fact, this particular process also I described in one of my earlier lectures when I think I was talking the cyclic voltammetry what purpose they can use. So, this specific purpose it is quite useful.

So, current has two components, one is this capacitive component, and another one is a Faradaic component where the redox is involved. So, this current they have this kind of power relationship. So, here the capacitive component is i c and Faradaic current component is i f. And this um I should say it is a nu or v. So, it is nu. Nu is the sweep rate, the voltage sweep rate what you apply while you measure the c v.

$$i = i_c + i_f = a\nu^b$$

And a and b, they are constants. So, the, this b value is quite significant. And this is basically derived from the decay current when you discharge the capacitor. So, typically when this is 0.5, then it is a battery like process faradaic process. And when it is 1, it is a linear type of process from the normal charge discharge you can actually see that its signature and also cyclic voltammetry you are able to see it.

So, that part when v is equal to when 1, then it is a capacitive process. So, so this capacitive current is a into nu. And this Faradaic current I can call a into nu to the power half. So, as you can understand that although it is not very, very prominent in case of the pseudocapacitive material, there is a peak current involved when this oxidation and reduction takes place.

So, this peak current you can define as i as a function of v, so that is one part k 1 into nu plus k 2 another constant into nu to the power half; one for the Faradaic process, another for the capacitive process. So, it is just I have rewritten it like this from the earlier equation.

$$i(\mathrm{v}) = k_1\mathrm{v} + k_2\mathrm{v}^{0.5}$$

$$\frac{i(\mathrm{v})}{\nu^{0.5}} = k_1\mathrm{v}^{0.5} + k_2$$

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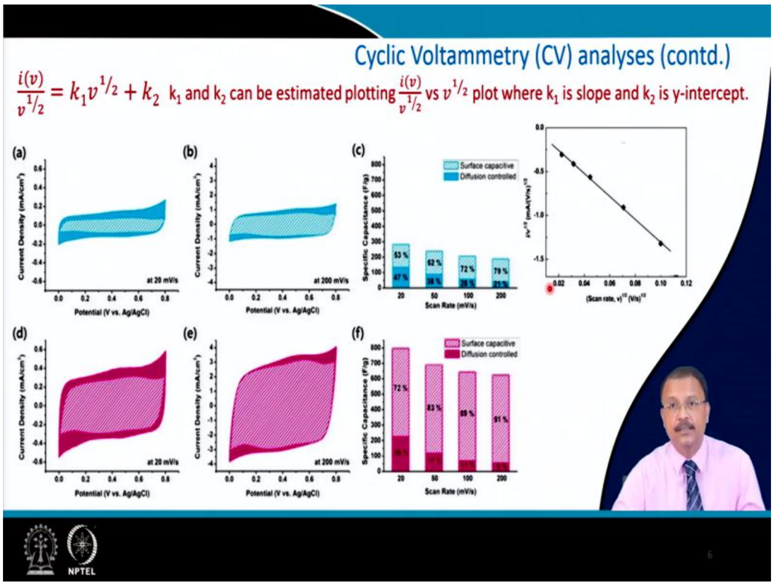

Cyclic Voltammetry (CV) analyses (contd.)

$\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2$ k_1 and k_2 can be estimated plotting $\frac{i(v)}{v^{1/2}}$ vs $v^{1/2}$ plot where k_1 is slope and k_2 is y-intercept.

And then this k 1 and k 2 that you can estimate, if you plot this i as a function of v, sorry sometimes I talk about v, sometimes it is nu, but you follow that this is nu which denotes the voltage sweep rate. So, i v by i nu by nu to the power half, so that gives this relation.

So, this you can estimate, if you plot this versus nu to the power half. So, it is shown there. So, this is this has been plotted with the scan rate. And the from the slope and intercept, from the slope and intercept, you can estimate the value of k 1 and k 2.

So, once you do that, then from a typical pseudo capacitive material as you can see that it is almost like EDLC part at lower scan rate and progressively sorry at the higher scan rate. It progressively once you change the scan rate, then it is more and more capacitive.

At lower scan rate, there is a probability for you to get a small hump the oxidative peak because of the oxidation of the electrochemically active material. But it is not that prominent as we have seen for the battery because this part this is not throughout the bulk of the material. But still you can estimate that, and you will find that if you plot this as a function of the scan rate that at lower scan rate, this rate part is diffusion control.

So, this diffusion control is indeed very small throughout all scan rate, but it is actually relatively large for lower scan rate, so that it gets some time for the diffusion to take place. But once you increase the scan rate to 200 millivolt per second, then you will see that it is almost controlled by the capacitive effect the EDLC effect, so that is some kind of technique that usually adapted to delineate the EDLC type behaviour and pseudocapacitive behaviour.

It works well with the battery type of material where mostly we will find it is other way around the faradic process they contribute more as compared to the charge storage through EDLC type of behaviour, but this is one thing which is quite interesting.

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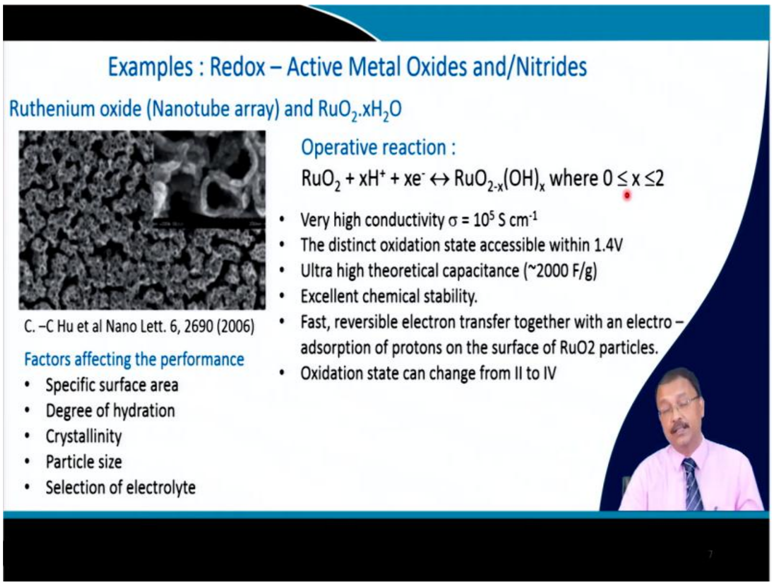

Examples : Redox – Active Metal Oxides and/Nitrides

Ruthenium oxide (Nanotube array) and $RuO_2.xH_2O$

C. –C Hu et al Nano Lett. 6, 2690 (2006)

Factors affecting the performance

- Specific surface area
- Degree of hydration
- Crystallinity
- Particle size
- Selection of electrolyte

Operative reaction :

$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x$ where $0 \leq x \leq 2$

- Very high conductivity $\sigma = 10^5$ S cm^{-1}
- The distinct oxidation state accessible within 1.4V
- Ultra high theoretical capacitance (~2000 F/g)
- Excellent chemical stability.
- Fast, reversible electron transfer together with an electro – adsorption of protons on the surface of RuO2 particles.
- Oxidation state can change from II to IV

So, redox active material, they can be classified as I have said into three types. The first one is the metal oxide or metal nitride. So, this RuO_2 is one of them, both ruthenium oxide and hydrated ruthenium oxide. And as you can see that this protonation, so this schematic already I showed you earlier.

And the value of this proton that can go in that is from 2 to 0, so that depending on that that basically control when x equal to 0, then it is basically ruthenium, it is basically ruthenium oxide. And it could be 2 as well when it is ruthenium hydroxide.

So, the valance of ruthenium it changes across two valance state. And it has certain criteria. And the first criteria is the specific surface area, certainly the smaller size is better And the degree of hydration is also important. The crystallinity of the material is important. The particle size is important because that is directly related to the specific surface area. And also the selection of the electrolyte is important.

So, this micrograph showed that this is a nanotube array of ruthenium oxide So, the advantage of RuO_2 is that that it is having a very high conductivity most like a metal like conductivity 10 rise to 5 Siemens per centimetre. And the oxidation state is accessible, and the voltage window is about 1.4 volt.

And you can calculate the capacity theoretical capacity is about 200 farad per gram. And it is chemically stable; it will not get attacked with the electrolyte which is in contact with it. And oxidization state can change as I said from 2 to 4 which you have seen depends on the value of x. So, it is considered one of the good material, but that is very expensive RuO_2 is a very expensive material.

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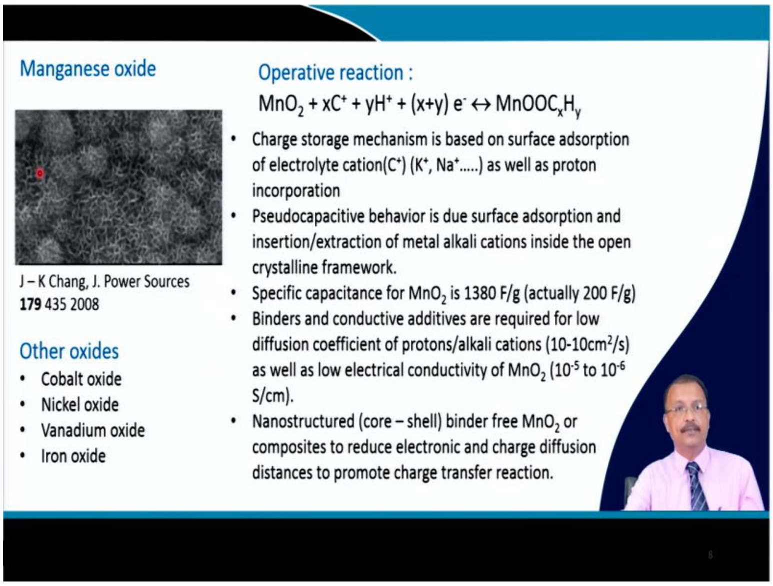

Manganese oxide

J – K Chang, J. Power Sources **179** 435 2008

Other oxides
- Cobalt oxide
- Nickel oxide
- Vanadium oxide
- Iron oxide

Operative reaction :

$MnO_2 + xC^+ + yH^+ + (x+y)\ e^- \leftrightarrow MnOOC_xH_y$

- Charge storage mechanism is based on surface adsorption of electrolyte cation(C^+) (K^+, Na^+.....) as well as proton incorporation
- Pseudocapacitive behavior is due surface adsorption and insertion/extraction of metal alkali cations inside the open crystalline framework.
- Specific capacitance for MnO_2 is 1380 F/g (actually 200 F/g)
- Binders and conductive additives are required for low diffusion coefficient of protons/alkali cations (10-10cm^2/s) as well as low electrical conductivity of MnO_2 (10^{-5} to 10^{-6} S/cm).
- Nanostructured (core – shell) binder free MnO_2 or composites to reduce electronic and charge diffusion distances to promote charge transfer reaction.

So, manganese oxide that is relatively better. So, this is structured manganese oxide, but it has one problem that this does not have sufficient electronic conductivity. So, the charge storage mechanism is something similar to the ruthenium oxide.

But here the depending on the salt, you are using in the electrolyte potassium sodium that also intercalate along with this proton in corporation in case of this aqueous type of electrolyte. And the pseudocapacity behavior that is both the surface adsorption and also insertion and extraction of the metal alkali ions.

Specific capacity is quite interesting about 1380 farad per gram, but that is theoretical, theoretical capacity, you can able to calculate it. But actually the achievable thing is about 200 farad per gram that is due to the fact that active material content is reduced because this is not conducting. And you need to use binder, conductive agent that is required because of the slow diffusion of both proton and alkali cations.

So, the diffusion constant as you can see it is around 10 centimetre square per sorry 10 to the power minus 10 centimetre square per second, this will be subscript, superscript 10 raised to minus 10. And electrical conductivity is low 10 raised to minus 5 to 10 raised to minus 6 Siemens per centimetre.

So, sometimes you have this kind of nano structure particularly the core shell kind of binder free MnO_2 or you can make composite with some conducting agent, so that reduce this electronic and charge diffusion distances once you do this nano structuring. And eventually that will promote the charge transfer reaction.

So, as such you will have to do some kind of modification in the structure, so that you get a better capacitive properties. So, like manganese oxide there are several other oxide that people have tried; cobalt oxide is one of them, nickel oxide, vanadium oxide, iron oxide.

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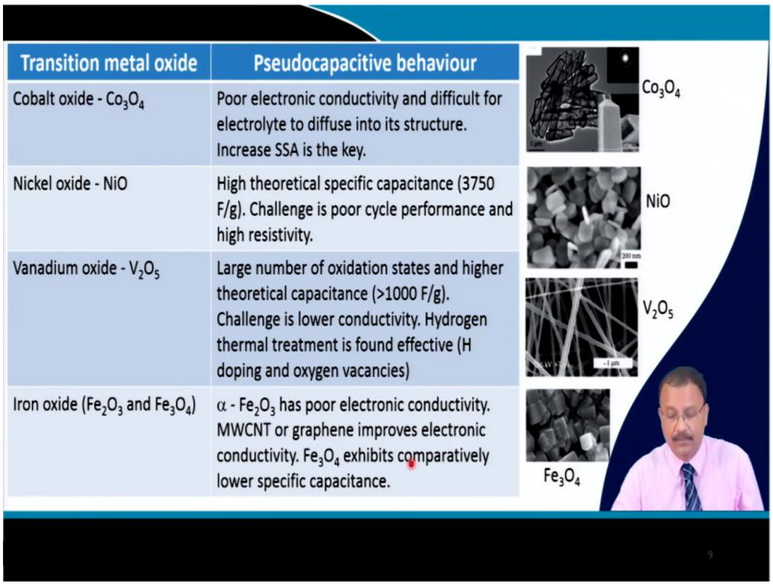

Transition metal oxide	Pseudocapacitive behaviour
Cobalt oxide - Co_3O_4	Poor electronic conductivity and difficult for electrolyte to diffuse into its structure. Increase SSA is the key.
Nickel oxide - NiO	High theoretical specific capacitance (3750 F/g). Challenge is poor cycle performance and high resistivity.
Vanadium oxide - V_2O_5	Large number of oxidation states and higher theoretical capacitance (>1000 F/g). Challenge is lower conductivity. Hydrogen thermal treatment is found effective (H doping and oxygen vacancies)
Iron oxide (Fe_2O_3 and Fe_3O_4)	α - Fe_2O_3 has poor electronic conductivity. MWCNT or graphene improves electronic conductivity. Fe_3O_4 exhibits comparatively lower specific capacitance.

So, I just got tabulated. And you can see the most of them they are having some kind of structured material growth because mainly for the poor electronic conductivity. This is apparent from cobalt oxide. And it is difficult for the electrolyte to diffuse into the structure. So, you will have to increase the specific surface area.

And one way to do that, either you can do the structured growth of the oxides or you can reduce the particle size, but you will have to get rid of the agglomeration because of the finer particle size due to Van der Waals force and high specific surface energy they will also get agglomerated. So, structured growth of this kind of oxide that is quite, quite effective.

Nickel oxide is another material usually they have very high specific capacitance. And but in this case, the cyclability is an issue because mostly for his high resistive values, I mean high resistivity. Vanadium oxide it is effective because large number of oxidation state, you can see that it can change up to plus five valence state. Its theoretical capacity is quite good about more than 1000 farad per gram. Again conductivity is a problem.

So, sometimes we will do the hydrogen thermal treatment. So, if you treat it with hydrogen, then what happens, that hydrogen dope the lattice. And also due to the reductant ambient, it creates oxygen vacancies. So, they promote electronic conductivity because of this defect generation.

Iron oxide, they have usually poor electronic conductivity. So, it is basically multi wall carbon nanotube or graphene electrical conductive that is used to improve the electronic conductivity and due to this fact usually they exhibit lower specific capacitance, so that is the problem for this oxide material.

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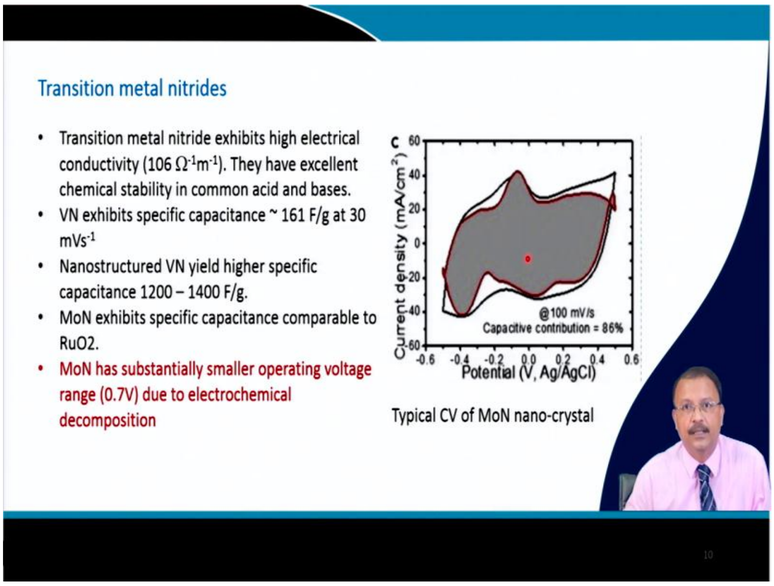

Transition metal nitrides

- Transition metal nitride exhibits high electrical conductivity (106 $\Omega^{-1}m^{-1}$). They have excellent chemical stability in common acid and bases.
- VN exhibits specific capacitance ~ 161 F/g at 30 mVs^{-1}
- Nanostructured VN yield higher specific capacitance 1200 – 1400 F/g.
- MoN exhibits specific capacitance comparable to RuO2.
- MoN has substantially smaller operating voltage range (0.7V) due to electrochemical decomposition

Typical CV of MoN nano-crystal

Transition metal nitride they are having a good electrical conductivity in the order of 10 raise to 6 ohms per meter. And they have also good chemical stability in most of the aqueous electrolyte which is which uses acid or base. Vanadium nitride is one such material which exhibit a specific capacitance not that good, but 160 farad per gram this is at a particular scan rate. And then again you do nano structuring of this vanadium nitride. And you will improve its specific capacitance; it ranges from 1200 to 1400 farad per gram.

Molybdenum nitride that is another material which is almost comparable to RuO_2, but it is having a problem because this as you can see that the operating voltage range is pretty small. And this um is due to the fact that this material they basically decompose if you increase the potential range. So, it is not very effective. And this is the example of estimating the capacitance by measurement of the area which I showed earlier how to do that from a cyclic voltammetry curve.

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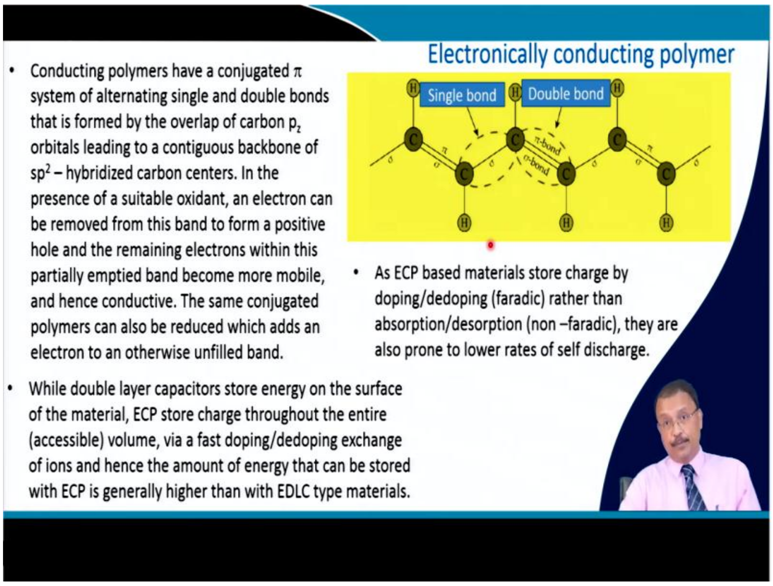

Electronically conducting polymer

- 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.

Now, conducting polymer, they are also used. And this conducting polymer you know that they have a conjugated pi bond, it is a alternate single bond and double bonds. And that basically is due to the overlap of the carbon orbitals. So, that leads to a contiguous back bone of sp 2 kind of hybridization of the carbon center.

So, in the absence of if you have a oxidant the presence of an oxidant, so electron can be removed from a positive from this band, so that it creates a positive hole, and the remaining electron in this partially emptied band they are more mobile. So, they turns to be conductive.

And this also I have earlier described this slide in one of my earlier lectures in detail. So, the double layer capacitor usually they store charge on the surface of the material. This electronically conducting polymer, they store the charge throughout the entire volume which is accessible. And this is due to a fast doping as well as undoping due to the exchange of the ions. And the energy that can be stored is far higher as compared to the EDLC type material.

So, this is a faradic process. This doping and dedoping, and it is not really the absorption and desorption, so that is not non-faradic. And the problem is that they are having a self discharge characteristics. So, if you just leave this capacitor, so they will discharge automatically, so that is one of the problems of this.

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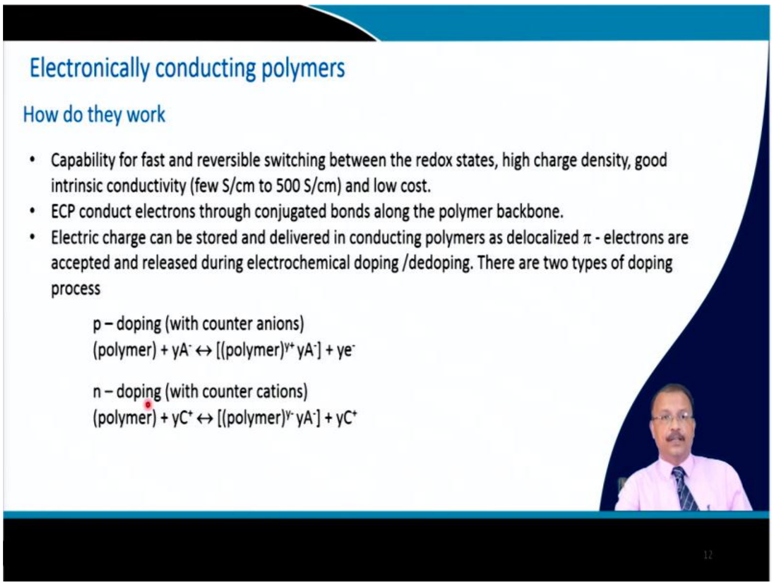

Electronically conducting polymers

How do they work

- Capability for fast and reversible switching between the redox states, high charge density, good intrinsic conductivity (few S/cm to 500 S/cm) and low cost.
- ECP conduct electrons through conjugated bonds along the polymer backbone.
- Electric charge can be stored and delivered in conducting polymers as delocalized π - electrons are accepted and released during electrochemical doping /dedoping. There are two types of doping process

p – doping (with counter anions)

$(\text{polymer}) + yA^- \leftrightarrow [(\text{polymer})^{y+} yA^-] + ye^-$

n – doping (with counter cations)

$(\text{polymer}) + yC^+ \leftrightarrow [(\text{polymer})^{y-} yA^-] + yC^+$

So, they are capable for fast reversible switching between the redox state. And they have high charge density and intrinsic conductivity is also acceptable. So, as I have mentioned that they conduct the electrons both through the conjugated bond along with the backbone of the polymer. And the charge that is stored can be delivered in the conducting polymers that is due to the delocalized pi electrons that are basically accepted and released during this electrochemical dedoping and doping which I was mentioning.

So, there are p-type of doping that is possible with counter iron So, the polymer they form this kind of structure for a p-doping material. And for n-doping which is having a counter cations, so that also gives a this relation when the n-doping is operative.

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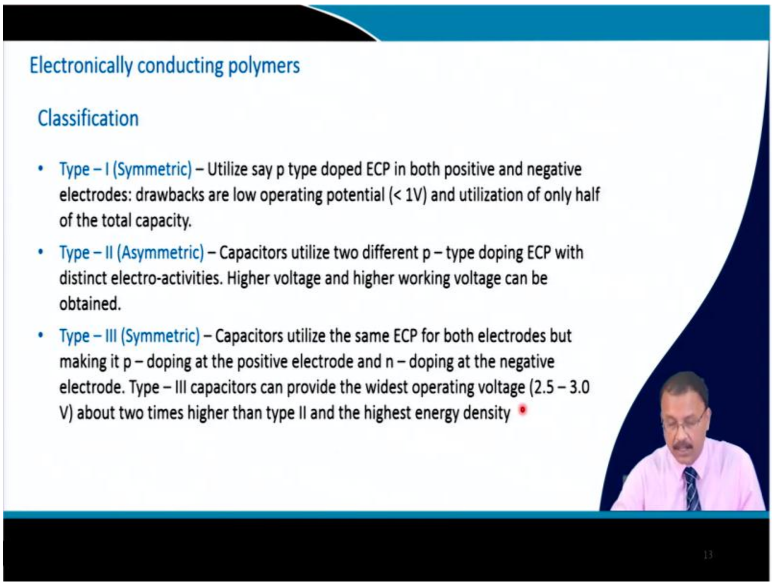

Electronically conducting polymers

Classification

- Type – I (Symmetric) – Utilize say p type doped ECP in both positive and negative electrodes: drawbacks are low operating potential (< 1V) and utilization of only half of the total capacity.
- Type – II (Asymmetric) – Capacitors utilize two different p – type doping ECP with distinct electro-activities. Higher voltage and higher working voltage can be obtained.
- Type – III (Symmetric) – Capacitors utilize the same ECP for both electrodes but making it p – doping at the positive electrode and n – doping at the negative electrode. Type – III capacitors can provide the widest operating voltage (2.5 – 3.0 V) about two times higher than type II and the highest energy density

Now, this electronically conducting polymer you can classify into three type of structure. The first type is called a symmetric say it uses a p-type dope ECP That is both in positive and negative electrodes. And operating potential is not that high. And it uses basically half of the total capacity because it is symmetric in nature.

You can use asymmetric type. So, you can use two different types of p-type or n-type ECP. So, they have distinct electro activities, electrochemical activities. And you can attain the high voltage higher voltage can be achieved. Type- III also is a symmetric type. So, they use same type of ECP for both electrodes, but making it p-doping at the positive electrode and n-doping at the negative electrodes.

So, type- III capacitors they are interesting they can give you a wide potential range from 2.5 to 3 volt around, and that is sufficiently higher than type- II. So, once the voltage is high you know that capacitance half CV square, so the energy density also is higher.

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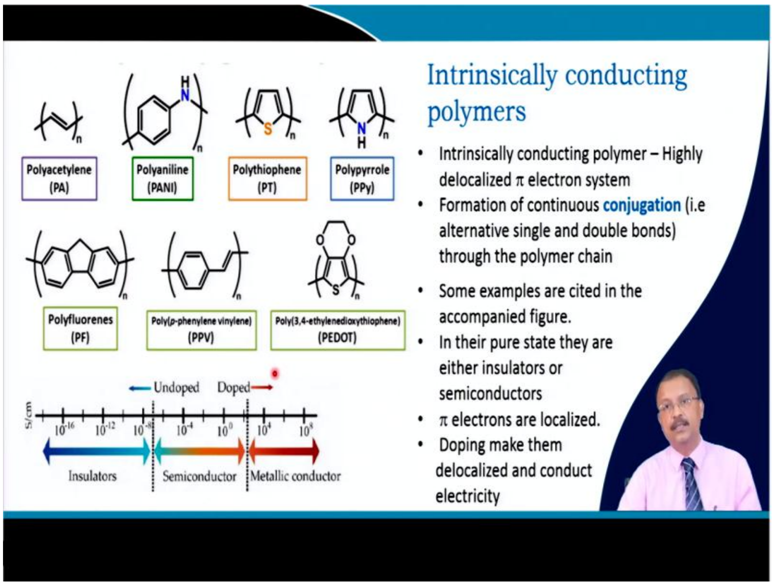

Intrinsically conducting polymers

- 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, these are some examples of intrinsically conducting polymers. This I already talked about in my earlier lectures So, this is basically due to highly delocalized pi electron system. And it forms a continuous conjugation alternate single and double bond in the polymer chain. So, there are some popular conducting polymers.

And in the doped state, you see that they can be a metallic conductor. And depending on the doping, it can be treated as semiconductor. But if you do not dope, it then it is insulating in nature. So, this pi electrons they are basically localized. And once you dope it, then they are delocalized and then they conduct electricity.

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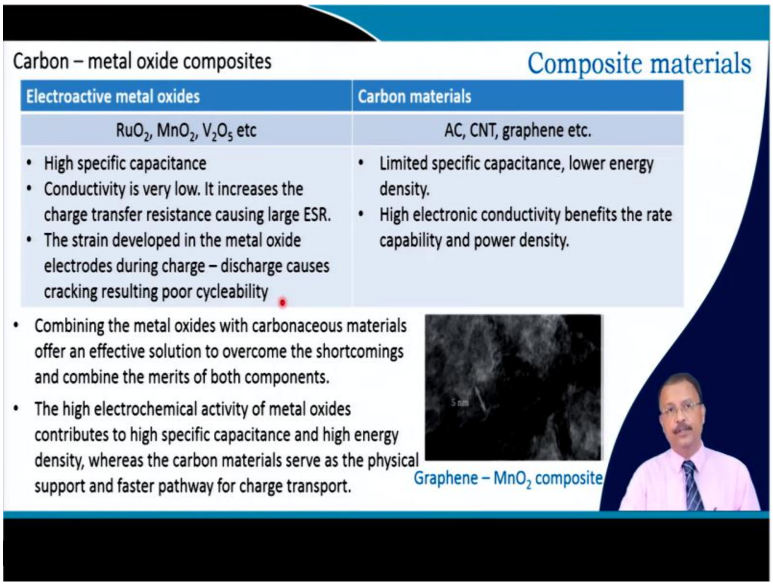

Carbon – metal oxide composites

Composite materials

Electroactive metal oxides	Carbon materials
RuO_2, MnO_2, V_2O_5 etc	AC, CNT, graphene etc.
• High specific capacitance • Conductivity is very low. It increases the charge transfer resistance causing large ESR. • The strain developed in the metal oxide electrodes during charge – discharge causes cracking resulting poor cycleability	• Limited specific capacitance, lower energy density. • High electronic conductivity benefits the rate capability and power density.

- Combining the metal oxides with carbonaceous materials offer an effective solution to overcome the shortcomings and combine the merits of both components.
- The high electrochemical activity of metal oxides contributes to high specific capacitance and high energy density, whereas the carbon materials serve as the physical support and faster pathway for charge transport.

Graphene – MnO_2 composite

So, the third category is composite materials. So, you know that this electroactive metal oxide if you take like RuO_2, MnO_2, and V_2O_5 which is pseudo capacitive. And carbonaceous material the which is activated carbon, or carbon nanotube, or graphene.

Then in this case you can see that they have high specific capacitance then the except RuO_2, the conductivity is very low. So, once the conductivity is very low, then suddenly the charge transfer resistance from the surface to the some part of the bulk that will cause a high value of the series resistance.

And also the there is another problem that strain is developed while you do a repeated charge and discharge cycles. So, once the strain is involved, when the charge charging and discharging is involved in this pseudo capacitative material, then basically the cyclability a deteriorates the characteristic cyclability deteriorates.

On the other hand, if you go for this EDLC type of material, they have specific capacitance which is low, but they have high electronic conductivity. So, it is quite useful to combine these two. So, metal oxide is combined with carbonaceous material so that is an of a effective solution.

Sometimes you know that not only they increase the conductivity. But carbonaceous material like graphene or carbon nanotube if you use, then this problem is solved also because the cracking due to this repeated charge discharge that stress is buffered by this carbonaceous material. So, this is a view graph of graphene M n O 2 type of composite. So, that is sometimes it is quite effective.

So, the electrochemical activity what is there in the pseudocapacitor that actually offers a reasonably good high capacitance, and therefore, high energy densities because their voltage range is also higher, so that energy density q into v that also increases.

And carbon material they act as a physical support, and also the conducting path. And the stress buffering agent I mean you can also use it as a buffering the stress which is operative during charge discharge. So, this compositor quite useful.

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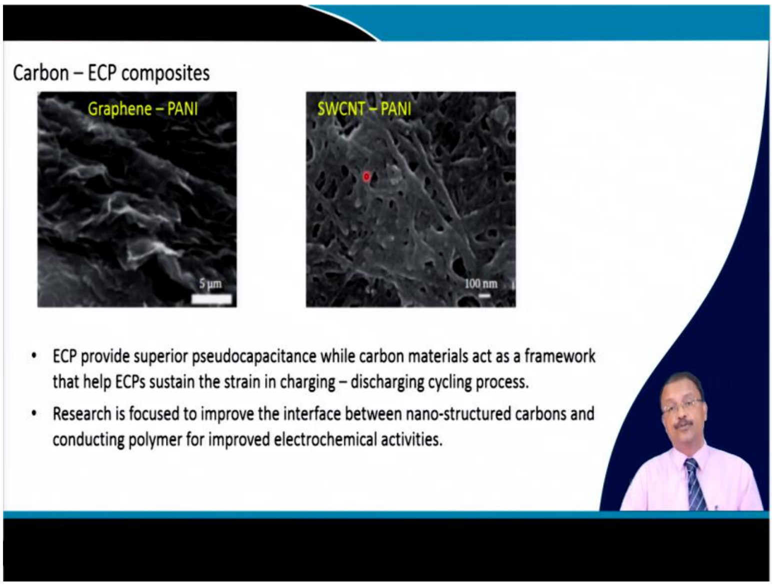
Carbon – ECP composites

- ECP provide superior pseudocapacitance while carbon materials act as a framework that help ECPs sustain the strain in charging – discharging cycling process.
- Research is focused to improve the interface between nano-structured carbons and conducting polymer for improved electrochemical activities.

You can make carbon and electronically conducting polymers also So, this ECP they provides actually superior pseudocapacitance. And the carbon material they acts as a framework. So, this is one example with graphene and PANI; another one is single wall carbon nanotube with PANI.

So, the control of the interface remains a problem because they are two dissimilar materials. So, research that is basically focus to improve this interface between this nanostructured carbonaceous material and the electronically conducting polymers and that actually is required to improve the electrochemical characteristics.

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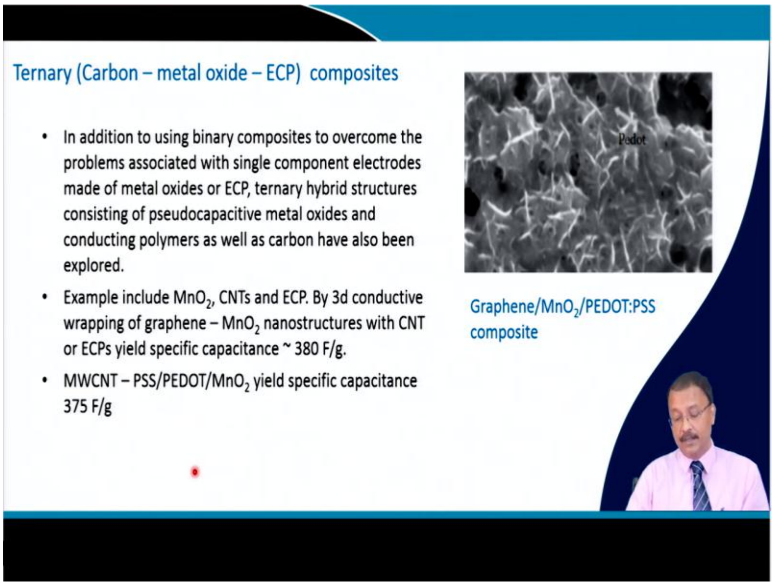

Ternary (Carbon – metal oxide – ECP) composites

- In addition to using binary composites to overcome the problems associated with single component electrodes made of metal oxides or ECP, ternary hybrid structures consisting of pseudocapacitive metal oxides and conducting polymers as well as carbon have also been explored.
- Example include MnO_2, CNTs and ECP. By 3d conductive wrapping of graphene – MnO_2 nanostructures with CNT or ECPs yield specific capacitance ~ 380 F/g.
- MWCNT – PSS/PEDOT/MnO_2 yield specific capacitance 375 F/g

Graphene/MnO_2/PEDOT:PSS composite

Then you can have the third category, a ternary kind of system which uses carbon, and then metal oxide and electronically conducting polymer composites So, this is one example. Graphene is a carbonaceous material; M n O 2 is a pseudo capacitive, and PEDOT PSS that is the polymer part. So, this is a hybrid structure and also sometimes manganese dioxide CNT and ECP is used.

So, as I said that sometimes this wrapping is important with the carbonaceous material, you wrap the oxide part. And the specific capacitance is quite effective around 380 farad per gram. And if you go for this structure M n O 2 with multiple carbon nanotube and this conducting polymer, this is also reasonably high about 375 farad per gram.

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- **A. Yu, V. Chabot, and J. Jhang.** "Electrochemical Supercapacitor for Energy Storage and Delivery: Fundamentals and Applications" Taylor & Francis group, 2013.
- **B. E. Conway** ""Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications" Springer Science+Business Media, New York, 1999.
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So, this part of the lecture that the study material is again the book Electrochemical Energy. And apart from that the other books on Supercapacitor that is also quite effective which already I told in the last lecture.

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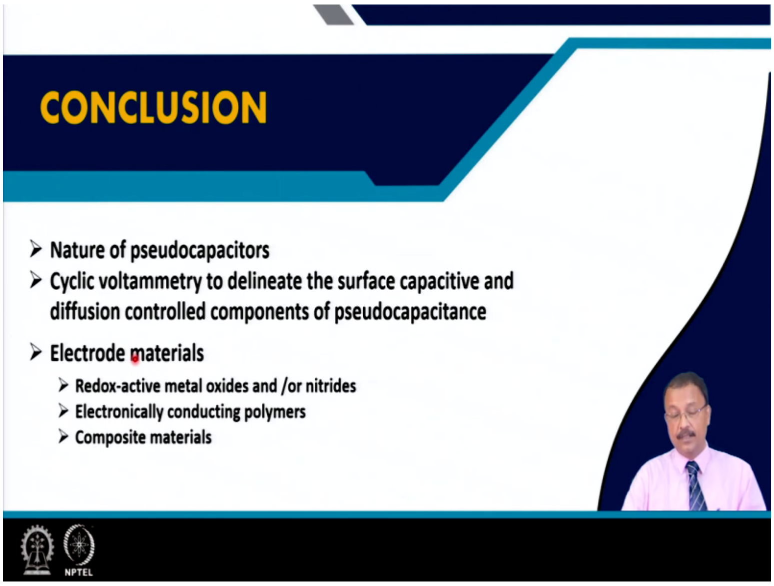

CONCLUSION

- Nature of pseudocapacitors
- Cyclic voltammetry to delineate the surface capacitive and diffusion controlled components of pseudocapacitance
- Electrode materials
  - Redox-active metal oxides and /or nitrides
  - Electronically conducting polymers
  - Composite materials

So, in this particular lecture, we talked about the nature of the supercapacitor, pseudocapacitors, and how the cyclic voltammetry is used to delineate the surface capacitive and diffusion controlled component of the pseudocapacitance. Although it is it may not be that much effective, you do not get a prominent peak during oxidation and reduction, but you can estimate it anyway, but it is not as easy once you do for a battery material. And electrode material are distinctly three different types. The first one is redox-active metal oxide or metal nitride.

And then we talked about the electronically conducting polymers that is used, but the doping is required in order to make it conducting. And um composite material which is binary type, and ternary type also we have described in this particular lecture.

Thank you for your attention.