Physics of Renewable Energy Systems
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Lecture 32
Pseudocapacitors

Welcome again, let us start the last lecture of this week. In the first two lectures, I talked to you about the super capacitors the history of super capacitors how we have moved on from conventional capacitors to super capacitors. Then in the previous lecture, I had talked to you about the advent of electric double layer capacitors, what are the theoretical models which can explain the formation of double layer in these capacitors and I had also introduced the word pseudo capacitor in one of the lectures. And in today's lecture, I will spend the next 30 odd minutes in giving you the details about the pseudocapacitors.

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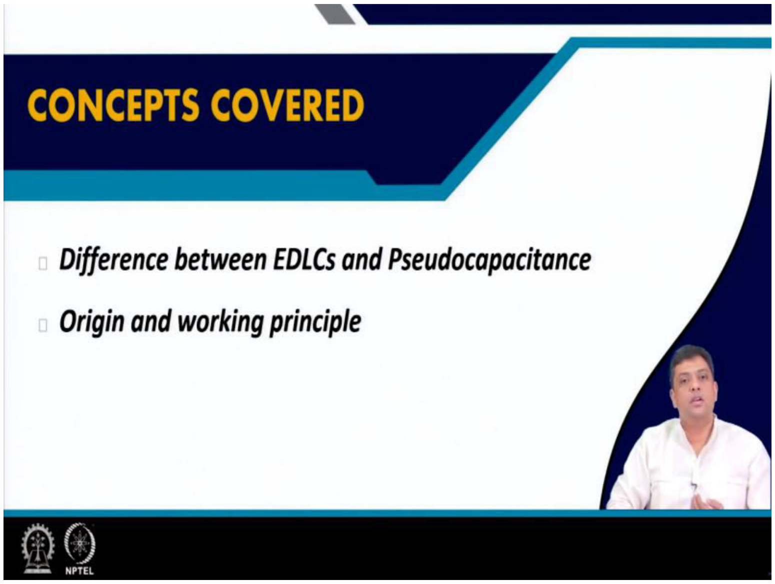

CONCEPTS COVERED

- Difference between EDLCs and Pseudocapacitance
- Origin and working principle

By the time we will finish this lecture you should be able to clearly differentiate between the EDLC’s type and pseudocapacitors you will see what is the origin of pseudocapacitors and how do we fabricate pseudocapacitors and what is the working principle which leads to the appearance of capacitance in these devices.

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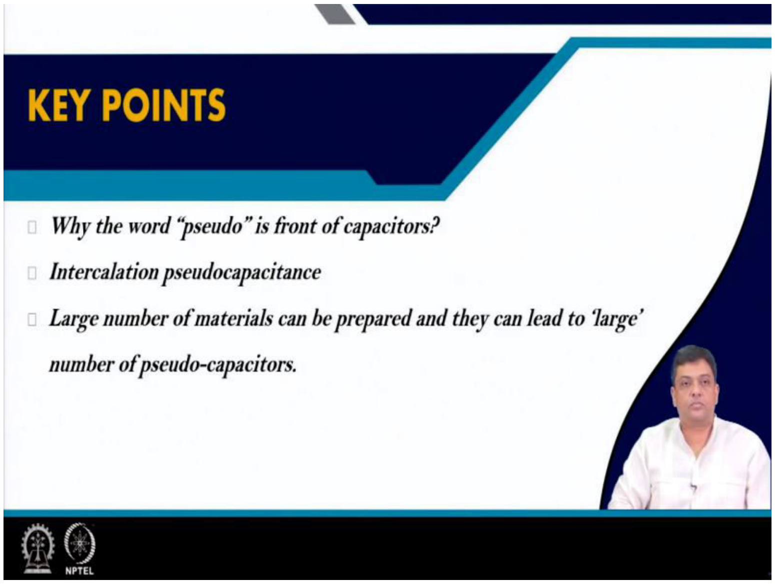

KEY POINTS

- *Why the word "pseudo" is front of capacitors?*
- *Intercalation pseudocapacitance*
- *Large number of materials can be prepared and they can lead to 'large' number of pseudo-capacitors.*

One should be very clear that if I understand a concept then I should be able to explain it to others also and the first thing which most of your friends who are interested in this topic would be asking you would be why do you call these kind of capacitors a pseudocapacitors. Are you not actually getting a capacitance but then also you are saying it is a capacitor?

Is it the reason why you are calling it pseudocapacitors because the word pseudo means that something which appears to be there even when it is not there. So, pseudocapacitance or pseudocapacitors means what you will be able to understand the reason why these kinds of capacitors are actually called pseudocapacitors.

What is the intercalation phenomena associated with these pseudocapacitors and if you look around, there are large number of materials which have actually been proposed for using these technologies or devices and a large number of new materials will come in future also which will lead to further improvement in these devices.

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- Pseudocapacitance arises because of some electrosorption process and redox reactions at the electrode-electrolyte interface.
- Pseudocapacitors complements the EDLCs.

Pseudo capacitance if I asked you what is it then pseudo capacitance is a phenomena which arises because of some electrosorption process and or a redox reaction at the electrode electrolyte interface. So, this is what pseudo capacitance is all about and pseudo capacitances are clearly different from EDLC's but they very nicely complement EDLC's.

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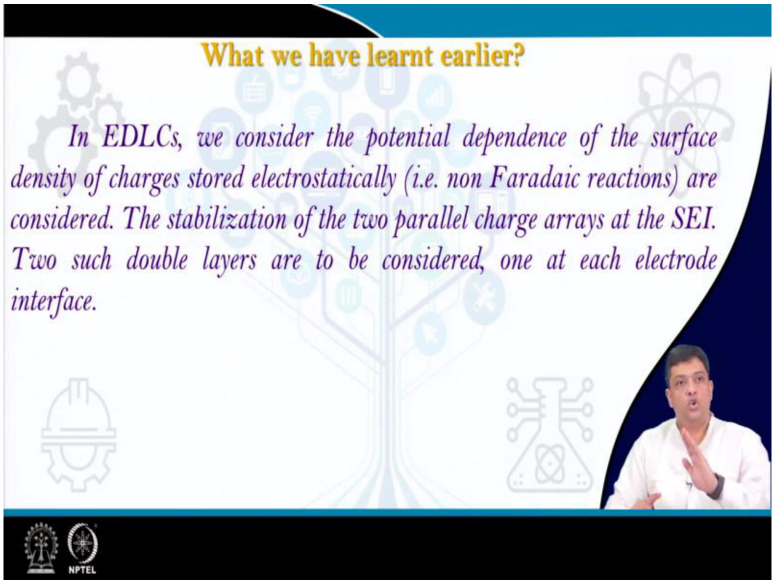

What we have learnt earlier?

In EDLCs, we consider the potential dependence of the surface density of charges stored electrostatically (i.e. non Faradaic reactions) are considered. The stabilization of the two parallel charge arrays at the SEI. Two such double layers are to be considered, one at each electrode interface.

Till now, what have we learned? We have learned about electric double layer capacitors. Where we saw that you have to consider the potential dependence of the surface density of charges which were stored electrostatically means you were not considering any faradic reaction there was no charge exchange between the species.

So, there was no faradic reaction taking place at the interface and the stabilization of the two parallel charge arrays at the electrode electrolyte interface was leading to the appearance of the capacitor light device. Why two such layers were being considered because you were constrained two double layers one at each electrodes.

So, double layer at one electrode between electrode one and the interface with the electrolyte and then there was an interface near the electrode to show you we are getting the two such double layers This is what we have understood till now.

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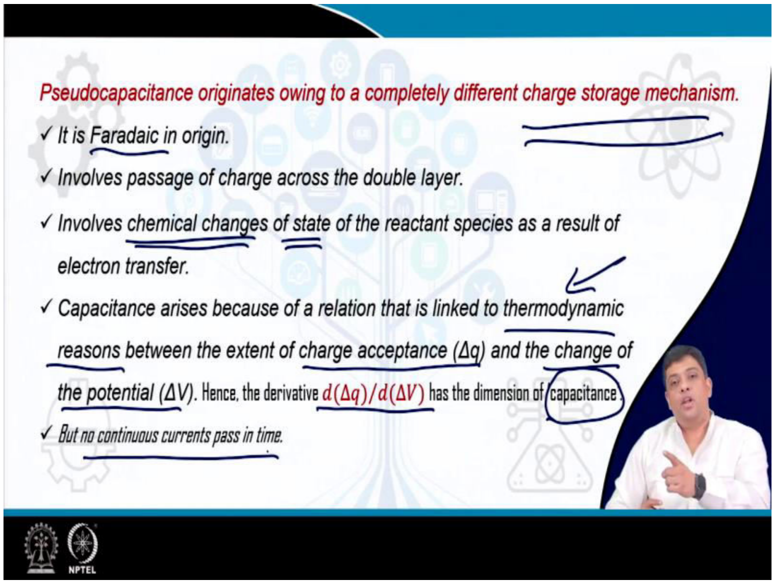

Pseudocapacitance originates owing to a completely different charge storage mechanism.

- ✓ It is Faradaic in origin.
- ✓ Involves passage of charge across the double layer.
- ✓ Involves chemical changes of state of the reactant species as a result of electron transfer.
- ✓ Capacitance arises because of a relation that is linked to thermodynamic reasons between the extent of charge acceptance (Δq) and the change of the potential (ΔV). Hence, the derivative $d(\Delta q)/d(\Delta V)$ has the dimension of capacitance.
- ✓ But no continuous currents pass in time.

If you compare pseudo capacitance, then you will find that it is very different from electric double layer capacitance in EDLC's what was happening you were considering non faradic type condition and the layer of two arrays facing each other one of the charge layer in the electrode side and the other in the electrolyte region forming.

But non faradic type reaction. In comparison in pseudocapacitance or pseudocapacitors, you will find that the charged storage mechanism is having its origin in faradic type reactions that means, it involves passage of charges across the double layer and if the charges are moving from one side of the layer to the other or vice versa that means, what you are actually considering chemical changes of state of the reactants.

Why because charges if you consider let us say electron transfer then either electron is being given or electron is being taken back then, what you are looking at you are talking about a reduction or oxidation processes and then you have the chemical changes linked to it. The capacitors actually arises because of thermodynamic reasons, what are these reasons?

See, when you are accepting the charge, let us say you are accepting the charges such that you give the charge acceptance delta q you are accepting the charge and then as you are accepting charge you are having the change in potential. And if you are monitoring it as a function of time what are you getting you are getting the derivative d delta q by d delta V.

Now, q by V is capacitance and therefore, d delta q by d delta V has the dimensions of capacitance and therefore, it appears as if you are measuring parameter which is very similar to capacitance but, it is originating due to the thermodynamic reasons and across these layer is no continuous current which passes in time. So, why we are calling it as pseudo capacitance because, it is appearing in the picture due to a phenomena which is actually occurring and then it gives us the dimension of a parameter that we had earlier called as capacitance.

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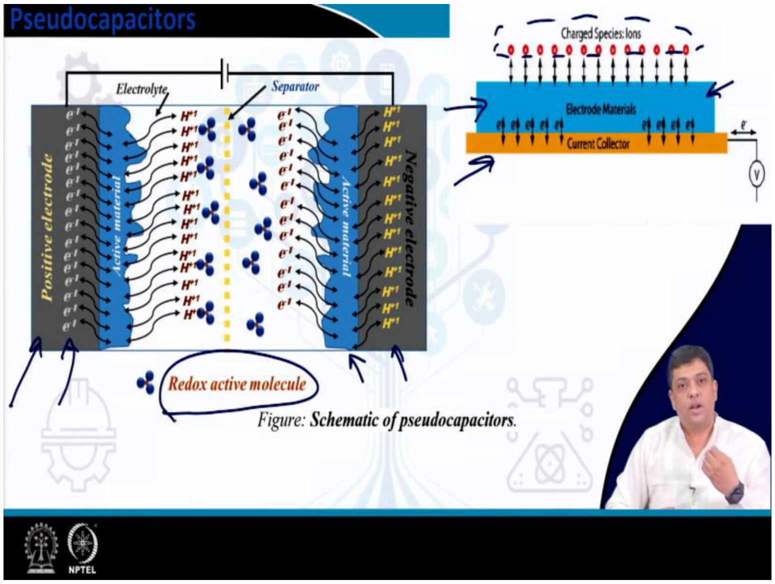

Pseudocapacitors

Figure: Schematic of pseudocapacitors.

So, you have charge exchanges being taking place at the electrodes and because of this you have the appearance of the quantity d delta q by d delta V, which has the dimension of capacitance. So, if you take the current collector on which you deposit the electrode material that is the active material where these charge transfer phenomena will take place then the material as a function of time or as a function of field or voltage you will see varying conditions of dq by dV and you will find the appearance of capacitance type parameter.

So, this is what is happening and therefore, you are talking about a material which is a redox active means, a material which can undergo reduction or a material which can go under oxidation process. So, reduction process or oxidation process can be associated with the material. So, a redox material is generally considered when you are describing pseudocapacitors.

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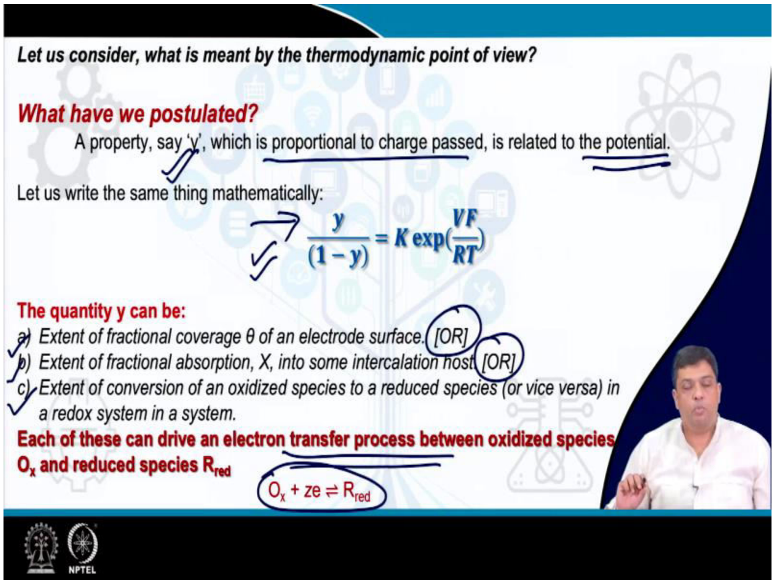

Let us consider, what is meant by the thermodynamic point of view?

What have we postulated?

A property, say 'y', which is proportional to charge passed, is related to the potential.

Let us write the same thing mathematically:

$$\frac{y}{(1-y)} = K \exp\left(\frac{VF}{RT}\right)$$

The quantity y can be:

a) *Extent of fractional coverage θ of an electrode surface. [OR]*
b) *Extent of fractional absorption, X, into some intercalation host [OR]*
c) *Extent of conversion of an oxidized species to a reduced species (or vice versa) in a redox system in a system.*

Each of these can drive an electron transfer process between oxidized species O_x and reduced species R_{red}

$$O_x + ze \rightleftharpoons R_{red}$$

So, what do we mean when we say thermodynamic point of view, let us consider a parameter y which is proportional to the charge which is passed across the double layer and it is related to the potential So, you have a property let us say y which is proportional to a charge which passes through the double layer and is related to the potential because that is driving its flow.

So, mathematically we can write y by 1 by y is equal to K exponential VF by RT this quantity y can be what it can be an extent of the fractional coverage theta of an electrodes surface. So, how much surface is getting covered by the charges or the active material or the double layer is active there or the extent of fractional adsorption X into some intercalation host.

So, if you are having layered structures or any structure which is allowing the intercalation of charges or the electron like ion which can induce the redox activities then what is the fractional adsorption of the quantity into the host lattice or we extent of conversion of an oxidized species to a reduce species or vice versa.

So, how much of the species can get oxidized or how much it can get reduced in a redox system. So, these are the parameters or conditions which can affect the variation of y and the combination of these factors can also be considered. Now, each of these points drive and electron transfer process redox reaction is taking place.

So, what are you saying you are saying that it is driving an electron transfer process between the oxidized species or the reduced species. So, you can write the oxidized species plus ze is going to reduce species or if you take the reverse then the reduced species is going to an oxidized species plus you are getting the ze charge. So, this is what we can write thermodynamically just by considering a property which is vary as a function of potential and is proportional to the charge which passes through the double layer.

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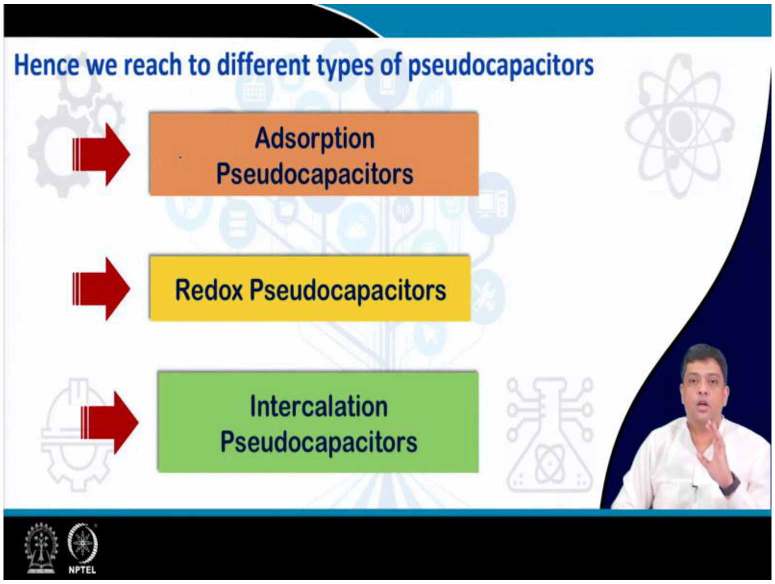

Hence we reach to different types of pseudocapacitors

- Adsorption Pseudocapacitors
- Redox Pseudocapacitors
- Intercalation Pseudocapacitors

So, what kind of phenomena can take place adsorption, the redox activity and the intercalation that are the three factors and that defines the three types of pseudocapacitors which we have, we have adsorption type pseudocapacitors, the redox types pseudocapacitors or intercalation types pseudocapacitors, you can easily explain what which of the phenomena are going to play the dominant role in these types of pseudocapacitors.

So, if I say I give you an intercalation type pseudocapacitors, what am I talking about? Probably I am talking about a pseudo capacitor where the intercalation of charge species will play the prominent role and the more charges we can store the higher is the storage capacity.

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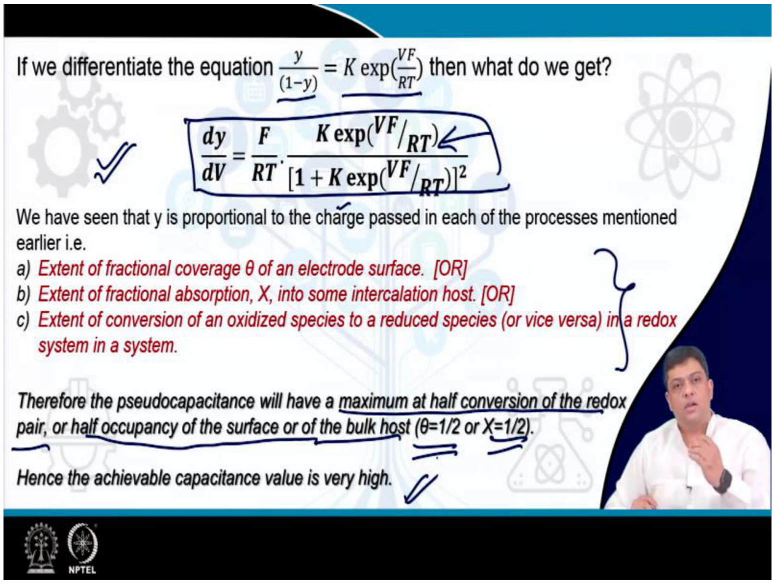

If we differentiate the equation $\frac{y}{(1-y)} = K\exp(\frac{VF}{RT})$ then what do we get?

$$\boxed{\frac{dy}{dV} = \frac{F}{RT}\cdot\frac{K\exp({}^{VF}/_{RT})}{[1+K\exp({}^{VF}/_{RT})]^2}}$$

We have seen that y is proportional to the charge passed in each of the processes mentioned earlier i.e.

a) *Extent of fractional coverage θ of an electrode surface. [OR]*
b) *Extent of fractional absorption, X, into some intercalation host. [OR]*
c) *Extent of conversion of an oxidized species to a reduced species (or vice versa) in a redox system in a system.*

Therefore the pseudocapacitance will have a maximum at half conversion of the redox pair, or half occupancy of the surface or of the bulk host (θ=1/2 or X=1/2).

Hence the achievable capacitance value is very high.

So let us go back and look into this equation once again which we consider what was the equation we had considered a parameter y, which is proportional to the charge which passes through the layer and we had also discussed that it is dependent on the potential. So, y by 1 by y is equal to K exponential VF by RT this is what we had write, take a derivative of this we have dy by dv equals to F by RT into k exponential VF by RT into 1 plus K exponential VF by RT whole square.

So, we get a derivative. We can clearly see that there are various parameters, which are going to affect the value of y one of them is clearly temperature, just remember this point at this stage in the next week lecture, when we start talking about various kind of super capacitors and parameters, thermodynamic or any external parameters that can affect the performance of energy storage devices, then this concept will become very critical.

So, we have taken a derivative and we have already seen earlier that what are the features that can affect the variation of y. To get this maximum for these derivative, we will find that maximum is obtained at the half conversion of the redox species pair or the half occupancy of the surface or of the bulk host. So, either theta can be taken as 1 by 2 or X is equal to 1 by 2. So, if you take this value as half, then you will find that you will be achieving very very high capacitance values. This is a very simple way of explaining the appearance of pseudo capacitance.

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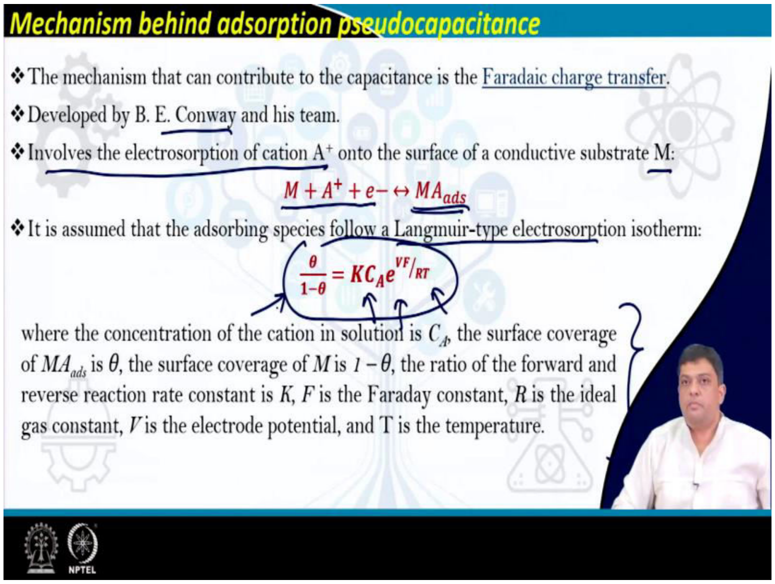

Mechanism behind adsorption pseudocapacitance

- The mechanism that can contribute to the capacitance is the Faradaic charge transfer.
- Developed by B. E. Conway and his team.
- Involves the electrosorption of cation A^+ onto the surface of a conductive substrate M:

$$M + A^+ + e- \leftrightarrow MA_{ads}$$

- It is assumed that the adsorbing species follow a Langmuir-type electrosorption isotherm:

$$\frac{\theta}{1-\theta} = KC_A e^{VF/RT}$$

where the concentration of the cation in solution is C_A, the surface coverage of MA_{ads} is θ, the surface coverage of M is $1-\theta$, the ratio of the forward and reverse reaction rate constant is K, F is the Faraday constant, R is the ideal gas constant, V is the electrode potential, and T is the temperature.

To understand it further, you can see the thermodynamic consideration more in detail, which was developed by Conway and his team there are other mechanisms which by which you can explain the pseudocapacitors that will be explained bit later, but let us consider with what was done by Conway and it is based on the thermodynamical concentrations.

So if you take the electrosorption of cation A onto a surface, so I have taken an electrode and on top of this, I have the conductive substrate M and then I am talking about the electrosorption of cations A plus then M plus A plus plus e is equal to MA adsorbed it is assumed that the adsorbed species follows a Langmuir type electrode option isotherm.

So, what is the nature of adsorption depends on the Langmuir type electrode option. This is given by theta 1 by theta is equal to KCA e raise to power VF by RT and the details about the each of the parameters are mentioned here. So again, what are the parameters which are going to affect the final capacitance. You can see it is the concentration of the cations. You can find the voltage, you will find the temperature and also the coverage. So, you will find that various factors are going to affect the performance of the final device. But the main one is for just mentioned.

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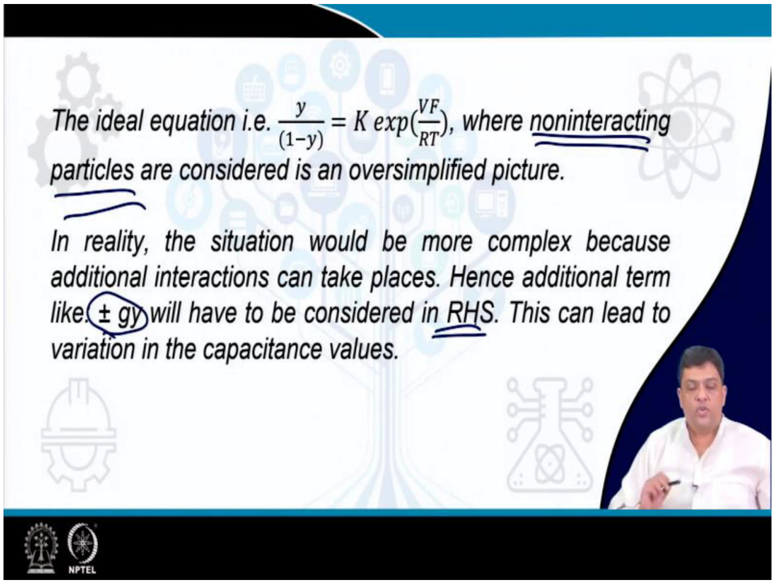

The ideal equation i.e. $\frac{y}{(1-y)} = K\,exp(\frac{VF}{RT})$*, where noninteracting particles are considered is an oversimplified picture.*

In reality, the situation would be more complex because additional interactions can take places. Hence additional term like $\pm\, gy$ *will have to be considered in RHS. This can lead to variation in the capacitance values.*

In this equation which is an ideal and an oversimplified picture, we have considered the that all the particles are non interacting particles, but in reality, the situation is more complex because additional reactions or interactions can take place and hence, an additional term like plus minus gy will have to be considered in the right hand side of this equation.

And then that equation if you take the derivative and then solve it will give you a better feel about the capacitance value that can be obtained and you will find that, because of this parameter the capacitances values can be much lower than what you were obtaining by considering non interacting particles. So, you can try this exercise.

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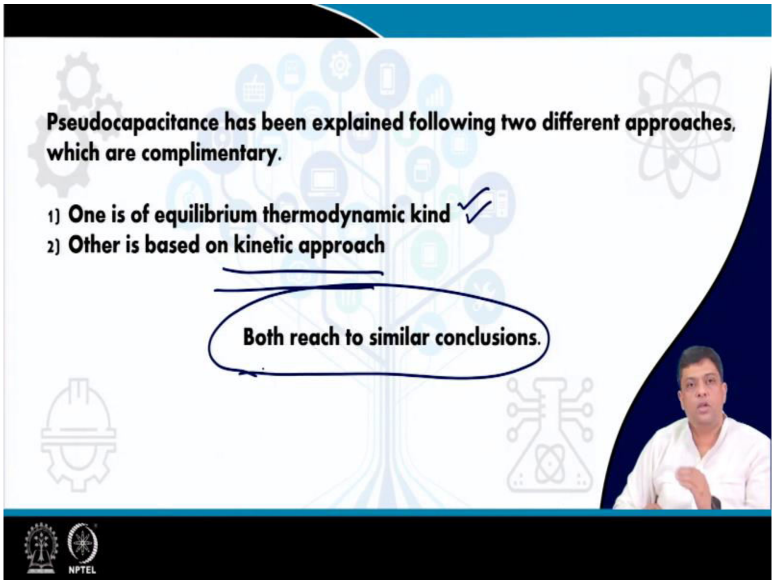

Pseudocapacitance has been explained following two different approaches, which are complimentary.

1) **One is of equilibrium thermodynamic kind**
2) **Other is based on kinetic approach**

Both reach to similar conclusions.

So, in this case what have we done, we have explained the formation of a capacitance type parameter using the equilibrium thermodynamic kind of approach and there is another set of people who have used the kinetic approach to explain the formation of this parameter and dq by db. But, both reach to similar conclusions and are able to explain the appearance of capacitance.

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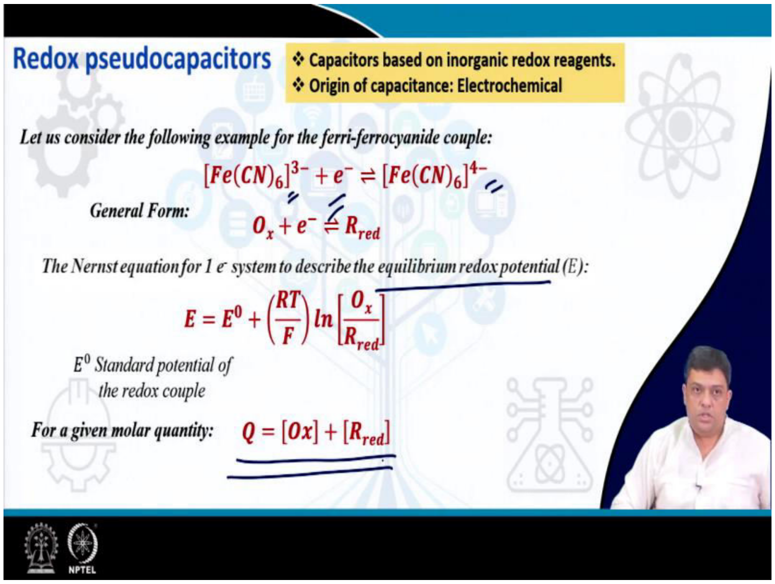

Redox pseudocapacitors

- ❖ Capacitors based on inorganic redox reagents.
- ❖ Origin of capacitance: Electrochemical

Let us consider the following example for the ferri-ferrocyanide couple:

$$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$$

General Form: $O_x + e^- \rightleftharpoons R_{red}$

The Nernst equation for 1 e^- system to describe the equilibrium redox potential (E):

$$E = E^0 + \left(\frac{RT}{F}\right) ln\left[\frac{O_x}{R_{red}}\right]$$

E^0 Standard potential of the redox couple

For a given molar quantity: $Q = [Ox] + [R_{red}]$

We have seen there are three types of pseudocapacitors, what have we seen, we have seen the adsorption type, the redox, pseudocapacitors and the intercalation. The appearance of the parameter dq by dv in the adoption type was just discussed. Let us, see what happens when we talk about redox types of capacitors. Here also the origin of capacitance is electrochemical in nature. So, let us consider the example of ferri-ferrocyanide couple.

So, you have this couple pair where either you can get an electron or you can take an electron and then you will have the transformation. So, what you are doing either you are going from an oxidize specie to a reduced specie or vice versa. So, if you have the Nernst equation, then the equilibrium redox potential can be written as E is equal to E0 RT by F ln oxidizing species by the reducing species where E0 is the standard potential of the redox couple.

Now for a given molar quantity Q Ox plus the R reduced species is considered. So, Q is equal to the oxidizing species and the reducing species.

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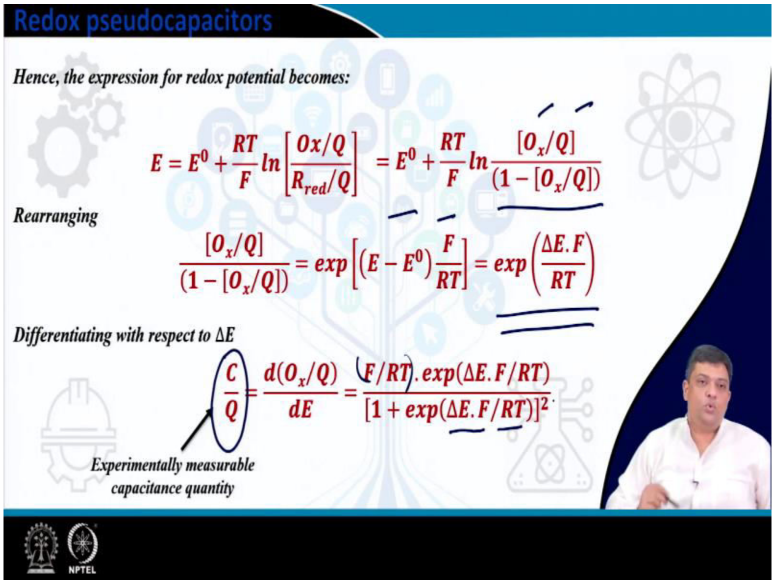

Redox pseudocapacitors

Hence, the expression for redox potential becomes:

$$E = E^0 + \frac{RT}{F} ln\left[\frac{Ox/Q}{R_{red}/Q}\right] = E^0 + \frac{RT}{F} ln \frac{[O_x/Q]}{\underline{(1-[O_x/Q])}}$$

Rearranging

$$\frac{[O_x/Q]}{(1-[O_x/Q])} = exp\left[(E-E^0)\frac{F}{RT}\right] = \underline{\underline{exp\left(\frac{\Delta E.F}{RT}\right)}}$$

Differentiating with respect to ΔE

$$\boxed{\frac{C}{Q}} = \frac{d(O_x/Q)}{dE} = \frac{(F/RT).exp(\Delta E.F/RT)}{[1+exp(\Delta E.F/RT)]^2}.$$

Experimentally measurable capacitance quantity

Hence, you can write the redox potential as E0 RT by F ln Ox by Q by 1 minus of Ox by Q you can rearrange and you can get the same relation in terms of exponential delta E dot F by RT. Now, if you differentiate with respect to delta E, you have the term C by Q which is equal to F by RT into exponential delta E dot F by RT divided by 1 plus exponential delta E dot F by RT whole square and C by Q is the measurable capacitance quantity.

So, you can actually measure this quantity and you will get the capacitance which you will obtain from the devices you are fabricating.

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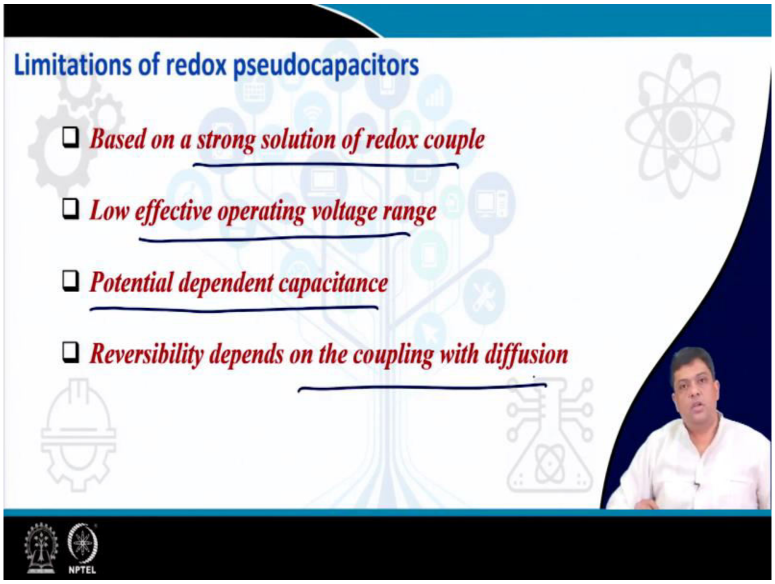

Limitations of redox pseudocapacitors

☐ *Based on a strong solution of redox couple*

☐ *Low effective operating voltage range*

☐ *Potential dependent capacitance*

☐ *Reversibility depends on the coupling with diffusion*

But the limitations of these redox based pseudocapacitors are they strongly depend on the solution of the redox couple they have low effective operating voltage range also you can change the capacitance value significantly by changing the potential and the reversibility depends on the coupling with diffusion.

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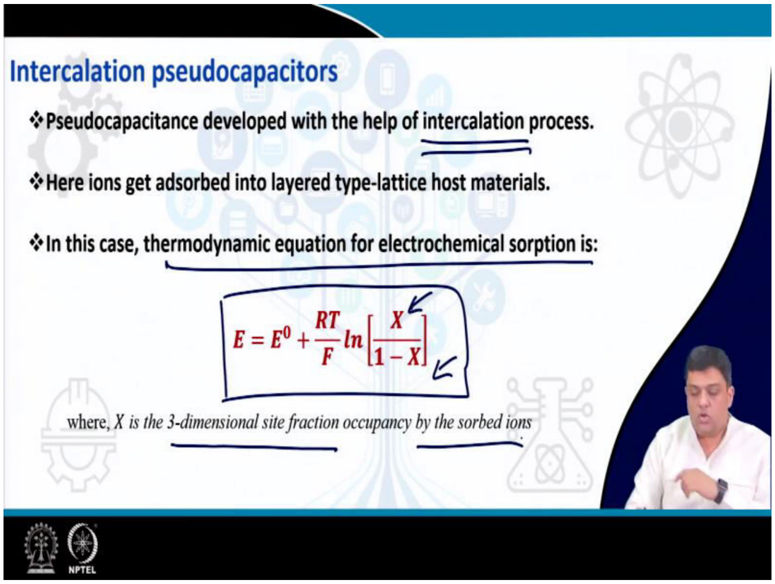

Intercalation pseudocapacitors

❖ Pseudocapacitance developed with the help of intercalation process.

❖ Here ions get adsorbed into layered type-lattice host materials.

❖ In this case, thermodynamic equation for electrochemical sorption is:

$$\boxed{E = E^0 + \frac{RT}{F} ln\left[\frac{X}{1-X}\right]}$$

where, *X is the 3-dimensional site fraction occupancy by the sorbed ions*

The third type of pseudocapacitors which we have indicated earlier were the intercalation pseudocapacitors and therefore, in this capacitors, the intercalation processes would be playing a critical role here the ions will get adsorbed into the layered type lattice of the host material and let us see how to mathematically understand the appearance of capacitance in these materials.

So, the thermodynamic equation for the electrochemical sorption is given by as we saw earlier E equal to E0 plus RT by F ln X divided by 1 minus X where X is a three dimensional site fraction of occupancy by the sorbed ions.

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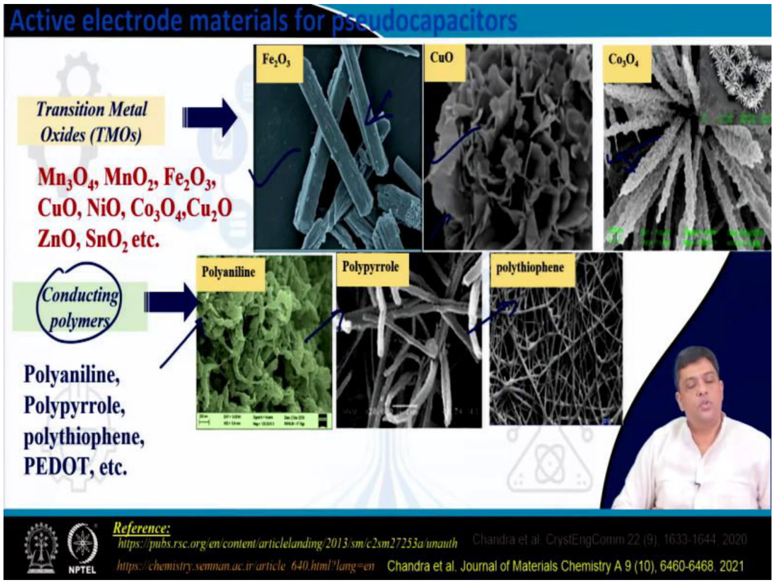

Active electrode materials for pseudocapacitors

Transition Metal Oxides (TMOs)

Mn_3O_4, MnO_2, Fe_2O_3, CuO, NiO, Co_3O_4, Cu_2O ZnO, SnO_2 etc.

Conducting polymers

Polyaniline, Polypyrrole, polythiophene, PEDOT, etc.

Reference:
https://pubs.rsc.org/en/content/articlelanding/2013/sm/c2sm27253a/unauth
https://chemistry.semnan.ac.ir/article_640.html?lang=en
Chandra et al. CrystEngComm 22 (9), 1633-1644, 2020
Chandra et al. Journal of Materials Chemistry A 9 (10), 6460-6468, 2021

So, it is clear that the electric field or the value depends strongly on the nature of the material and how the chart species are getting adsorbed on these surfaces. We have also seen that the pseudo capacitance appears in materials which can undergo the redox activity and hence, you are looking into the materials which are the transition metal based oxides.

If you look into the various materials which are mentioned on the top, you can clearly see that their nature of particles which are getting formed are very different and hence their site occupancies and their lattices would be very different and hence, the chart options would be very different and hence, the specific capacitance which you will obtain would also be different.

You can obtain similar kind of behaviours using conducting polymers and they can also be obtained in various forms with their various morphologies and hence, you get different kinds of pseudo capacitances.

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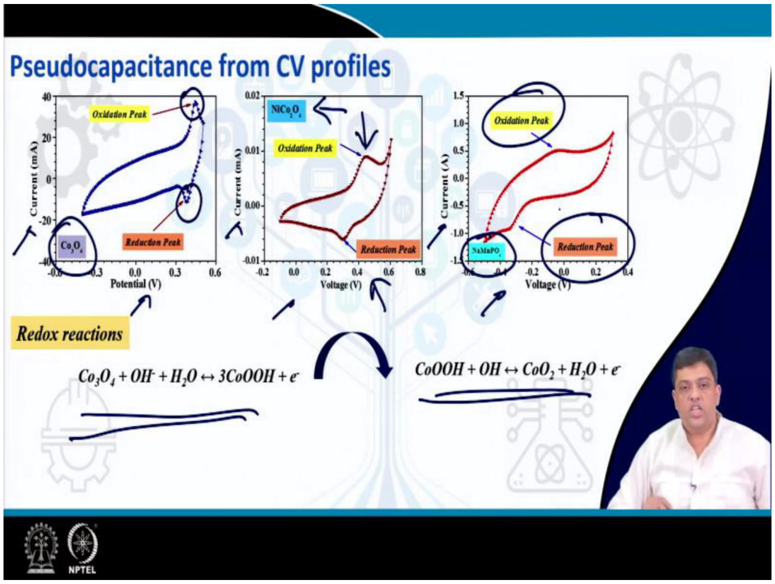

Pseudocapacitance from CV profiles

Redox reactions

$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-$

$CoOOH + OH \leftrightarrow CoO_2 + H_2O + e^-$

So, if you do the CV that is the charge current potential curves then, these are the typical kinds of curves. For example, if you see for cobalt oxide, then you get an oxidation peak and the reduction peak in the CV cycle and that indicates that the there is the redox reaction taking place as a function of charging or discharging cycle.

And if you go to even slightly modified structure so, if you take structures which were let us say nickel is doped into this lattice, then the nature of the curves once again change quite significantly and then you get different kind of behaviour. You can choose different materials and you have different oxidation and reduction things. So, different oxidation reduction peaks different redox potentials, hence, you will get different kinds of working voltage window as well as the specific capacitances.

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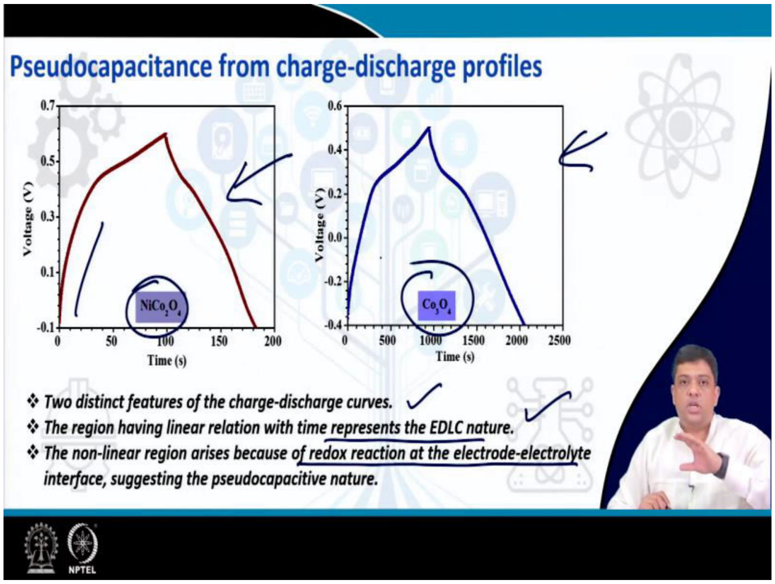

Pseudocapacitance from charge-discharge profiles

- *Two distinct features of the charge-discharge curves.*
- *The region having linear relation with time represents the EDLC nature.*
- *The non-linear region arises because of redox reaction at the electrode-electrolyte interface, suggesting the pseudocapacitive nature.*

So, if you look into the charge discharge profiles, the typical measurements you do for a capacitor like device, then there are two distinct features which you observe one is linear region. So, when you see a linear region which is attributed to the EDLC behaviour and then you have a nonlinear region, which appears because of the redox reactions at the electrode electrolyte interface.

We will spend one dedicated lecture to understand the CD profiles that will be bit later, but you can clearly see from these two curves that the natures are very different even if you slightly modify the lattice then the behaviour of the material changes quite significantly and the storage capacity will also change this is linked because of the change in the lattice and what you talk in terms of the intercalation size which are becoming available for the charge species.

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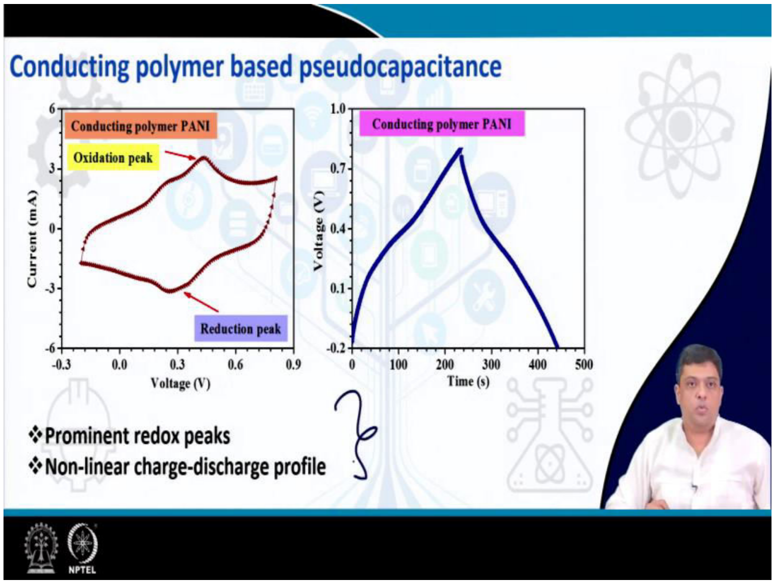

Conducting polymer based pseudocapacitance

- ❖Prominent redox peaks
- ❖Non-linear charge-discharge profile

Similar kind of behaviours can also be discussed using conducting polymer based pseudo capacitance.

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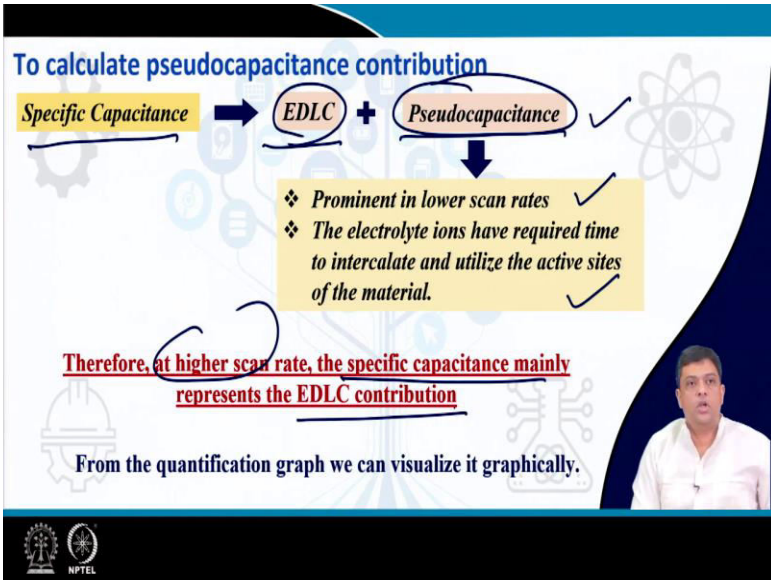

To calculate pseudocapacitance contribution

Specific Capacitance → EDLC + Pseudocapacitance

- ❖ Prominent in lower scan rates
- ❖ The electrolyte ions have required time to intercalate and utilize the active sites of the material.

Therefore, at higher scan rate, the specific capacitance mainly represents the EDLC contribution

From the quantification graph we can visualize it graphically.

So, what you saw you saw that if you are having material which is giving pseudocapacitors then it has to contribute EDLC type behaviour alright pseudo capacitance type behaviour. So, the total capacitance would be a combination of EDLC as well as pseudo capacitor. So, specific capacitance equal to EDLC plus pseudocapacitors.

Pseudo capacitance this is prominent at lower scan rates such that electrolyte ions have the required time to intercalate utilize the active sites of the materials and then induce the variation dq by dv. If you are having very fast scan rate that means you are sending in ion bringing it out sending in the ion and bringing it out then what you are doing you are actually not giving it enough time to utilize the active sites.

Therefore, prominent at lower scan rate are the pseudo capacitance at higher scan rates this specific capacitance is mainly dominated by the EDLC contribution and how do you distinguish from the data.

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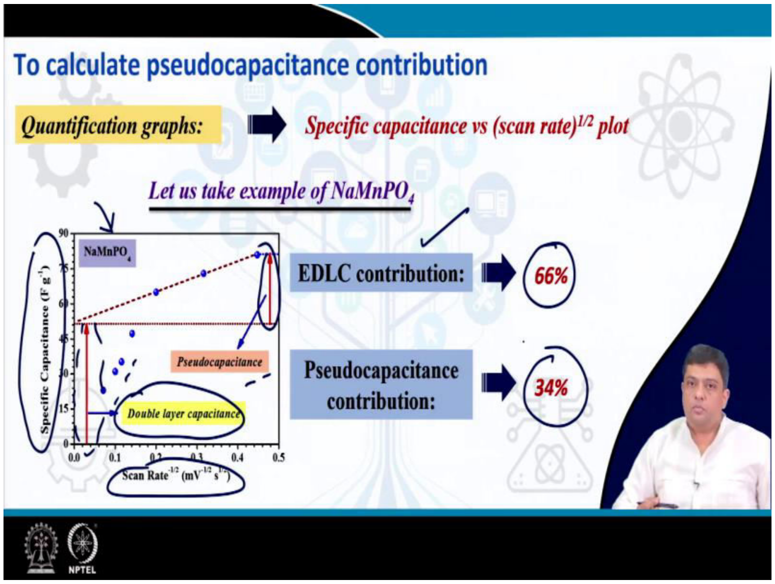

To calculate pseudocapacitance contribution

Quantification graphs: → *Specific capacitance vs (scan rate)$^{1/2}$ plot*

Let us take example of $NaMnPO_4$

EDLC contribution: → 66%

Pseudocapacitance contribution: → 34%

So, what you do you plot specific capacitance as a function of scan rate. So, you perform the measurement at different scans and as a function of scan rate, you plot the data. So, at higher scan rates what is going to contribute you will find that at higher scan rate EDLC's will contribute and at lower scan rate what is going to happen it is the double layer capacitance which is going to contribute.

So, you can have the contribution from pseudo capacitance and you have the contribution from double layer capacitance. For this data which is for sodium manganese phosphate based pseudocapacitors the typical contribution from EDLC is 66 percent and the remaining is coming from the pseudo capacitance. So, in pseudocapacitors you will always have the contribution of EDLC and pseudo capacitance parts.

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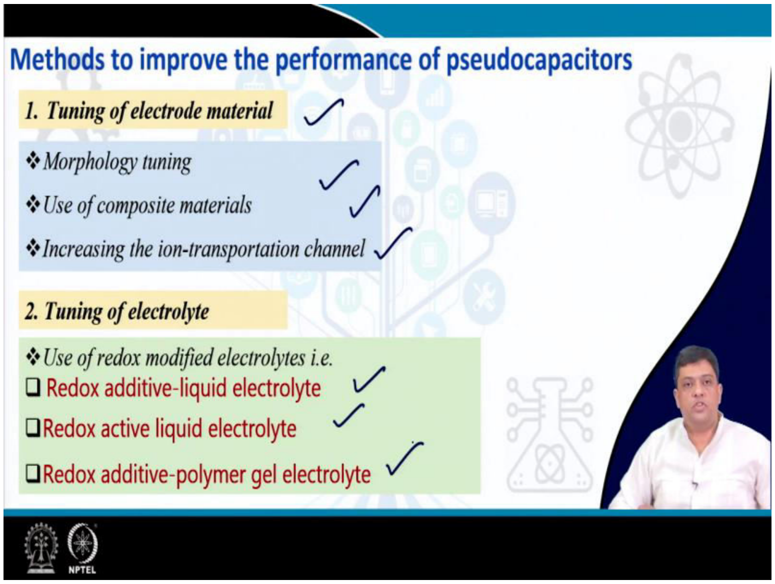

Methods to improve the performance of pseudocapacitors

1. Tuning of electrode material

- *Morphology tuning*
- *Use of composite materials*
- *Increasing the ion-transportation channel*

2. Tuning of electrolyte

- *Use of redox modified electrolytes i.e.*

☐ Redox additive-liquid electrolyte
☐ Redox active liquid electrolyte
☐ Redox additive-polymer gel electrolyte

The major methods to improve the performance as you saw it is all based on the tuning of the electrode material how do you tune change the morphology change the lattice change the structure make new materials or you can change the electrolyte, you can have redox additives which can induce more redox active ion or species.

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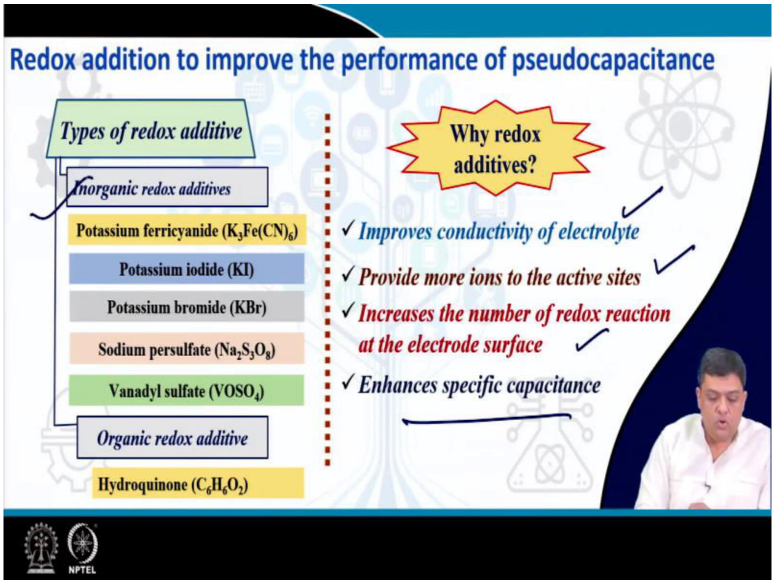

Redox addition to improve the performance of pseudocapacitance

Types of redox additive

Inorganic redox additives

Potassium ferricyanide ($K_3Fe(CN)_6$)
Potassium iodide (KI)
Potassium bromide (KBr)
Sodium persulfate ($Na_2S_3O_8$)
Vanadyl sulfate ($VOSO_4$)

Organic redox additive

Hydroquinone ($C_6H_6O_2$)

Why redox additives?

✓ *Improves conductivity of electrolyte*
✓ *Provide more ions to the active sites*
✓ *Increases the number of redox reaction at the electrode surface*
✓ *Enhances specific capacitance*

For example, what will happen if you have redox addition then it can improve the conductivity of the electrolyte provide more ions for to the active sites, increase the number of redox reactions at the electrode electrolyte interfaces and announced the specific capacitors. So, you can have inorganic redox additives or you can have organic redox additives.

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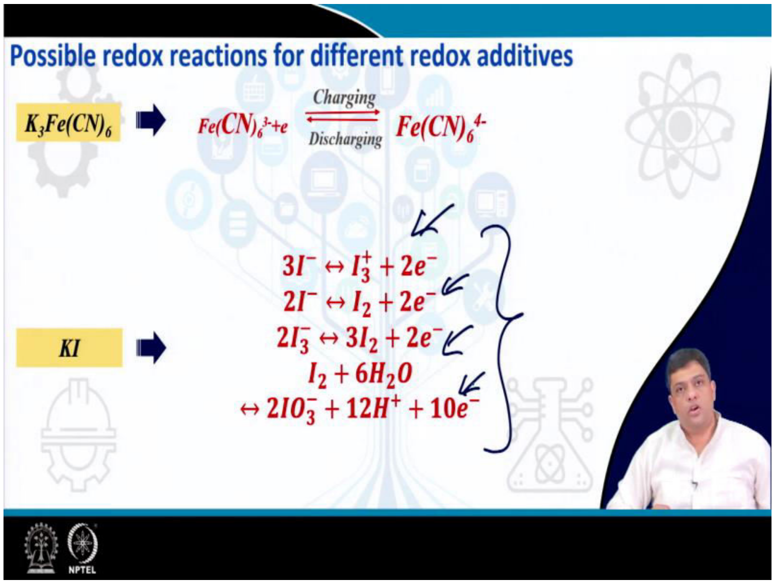

Possible redox reactions for different redox additives

$K_3Fe(CN)_6$ → $Fe(CN)_6^{3-} + e \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftarrows}} Fe(CN)_6^{4-}$

KI →

$3I^- \leftrightarrow I_3^+ + 2e^-$

$2I^- \leftrightarrow I_2 + 2e^-$

$2I_3^- \leftrightarrow 3I_2 + 2e^-$

$I_2 + 6H_2O$

$\leftrightarrow 2IO_3^- + 12H^+ + 10e^-$

For example, if you say take into put potassium iodine based redox additives, then you can clearly see that because of this electrolyte you can get various kind of poly iodides getting formed and then they are contributing to more charges in the electrolyte and that is driving your redox reactions.

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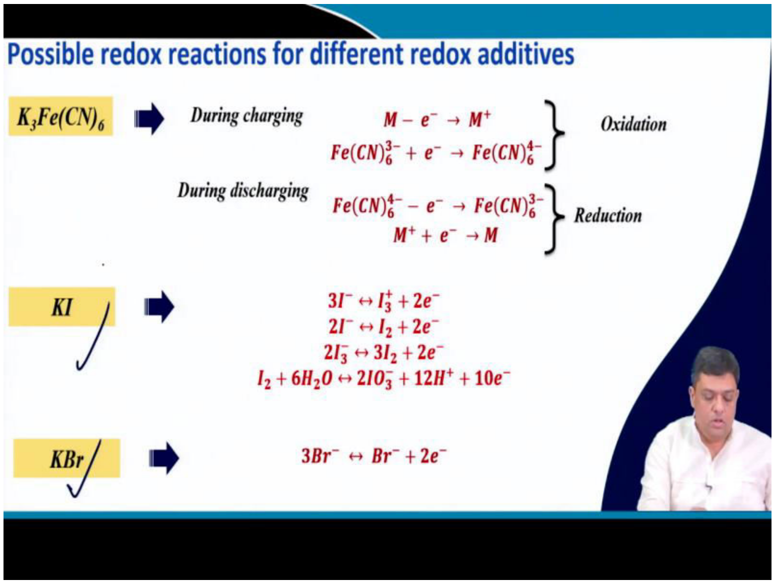


Possible redox reactions for different redox additives

$K_3Fe(CN)_6$ →

During charging

$M - e^- \rightarrow M^+$

$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$

Oxidation

During discharging

$Fe(CN)_6^{4-} - e^- \rightarrow Fe(CN)_6^{3-}$

$M^+ + e^- \rightarrow M$

Reduction

KI →

$3I^- \leftrightarrow I_3^+ + 2e^-$

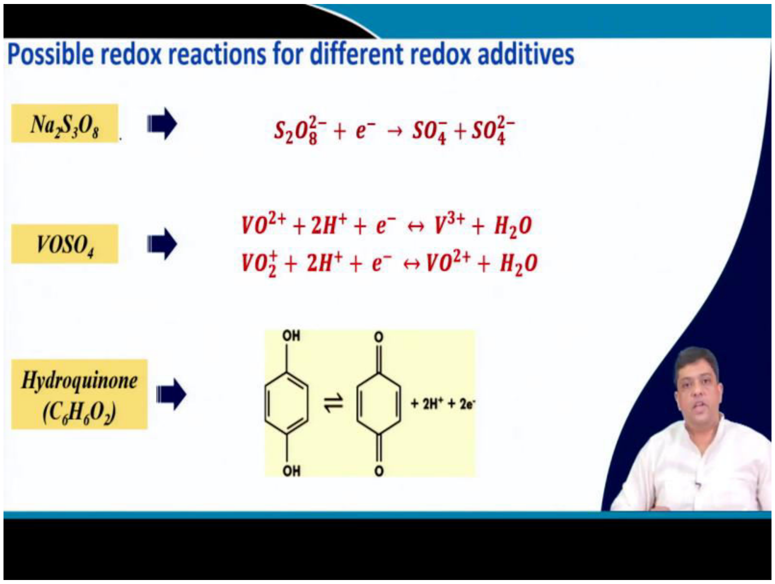
$2I^- \leftrightarrow I_2 + 2e^-$

$2I_3^- \leftrightarrow 3I_2 + 2e^-$

$I_2 + 6H_2O \leftrightarrow 2IO_3^- + 12H^+ + 10e^-$

KBr →

$3Br^- \leftrightarrow Br^- + 2e^-$



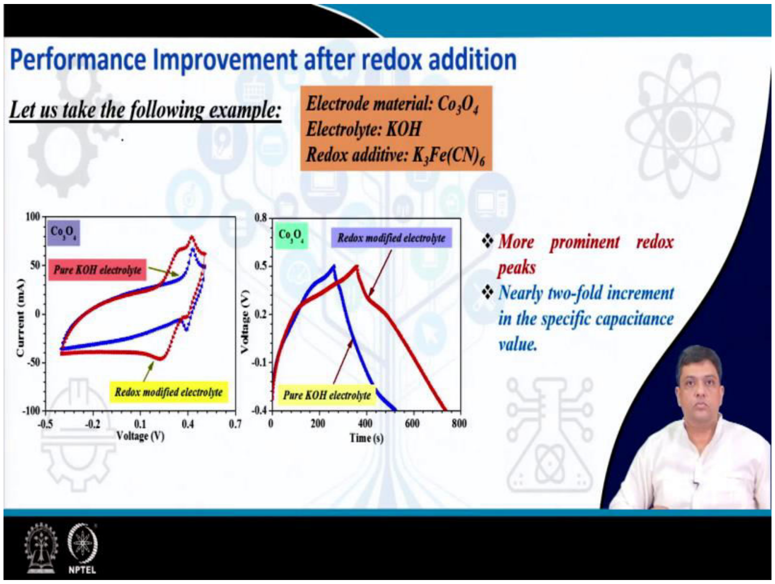
Possible redox reactions for different redox additives

$Na_2S_3O_8$ ➡ $S_2O_8^{2-} + e^- \rightarrow SO_4^- + SO_4^{2-}$

$VOSO_4$ ➡ $VO^{2+} + 2H^+ + e^- \leftrightarrow V^{3+} + H_2O$

$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$

Hydroquinone ($C_6H_6O_2$) ➡



Performance Improvement after redox addition

Let us take the following example:

Electrode material: Co_3O_4
Electrolyte: KOH
Redox additive: $K_3Fe(CN)_6$

- ❖ *More prominent redox peaks*
- ❖ *Nearly two-fold increment in the specific capacitance value.*

Similarly, you can write for various types of redox additives. So, these additives are added to the pure electrolyte, but they also need to be optimized and their concentration also needs to be optimized because if you add beyond a certain concentration, then they will lead to significant IR drops and then the device will not be performing.

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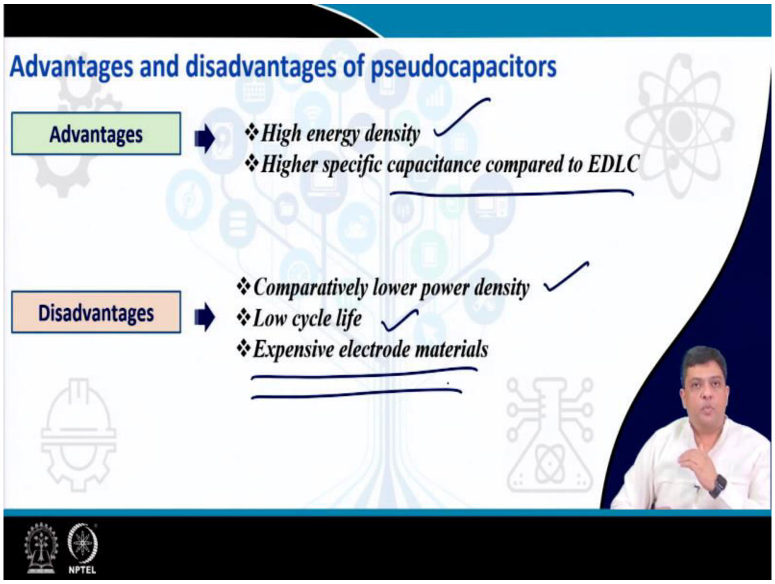

Advantages and disadvantages of pseudocapacitors

Advantages

- *High energy density*
- *Higher specific capacitance compared to EDLC*

Disadvantages

- *Comparatively lower power density*
- *Low cycle life*
- *Expensive electrode materials*

So, the major advantages of pseudocapacitors are they have very high energy densities much higher than EDLC's, but the disadvantages are they have low power densities in comparison to EDLC's they have slightly lower cycle life and many of these systems which are high performing are still using expensive electrode materials.

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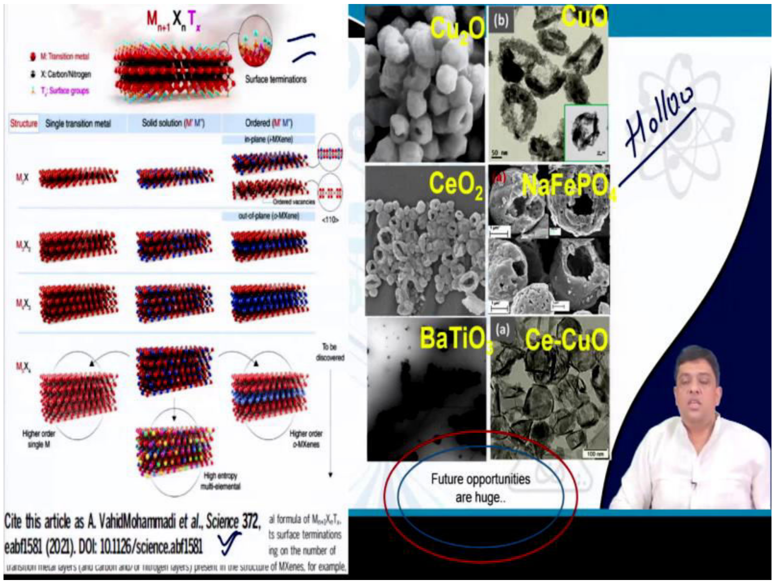
New trend in materials...



Cite this article as A. VahidMohammadi et al., Science 372, eabf1581 (2021). DOI: 10.1126/science.abf1581

Future opportunities are huge..

But, the moment I talk about expensive electrode materials that means, you can go into an regime where you can work on new materials and develop more economically viable alternatives and that is the new trend in discovering materials and they are mostly based on the use of layered structures.

This is a paper which came out very recently and so, you can see these are the emic scenes based structures, which are layered structures and you have the lattices which are giving you layer type structures and leading to very high specific capacitance. In addition, there are other types of materials which are being proposed were these are called hollow structures.

So, they are Nano structures, but they are also hollow from inside and they lead to very high surface area and you get much more enhanced active sites for performing the redox actions and the two dimensional structures and the hollow structures are the future for pseudocapacitors.

The hollow structures also have an additional advantage that if you perform a molecular dynamical studies then these structures actually simulate the pseudo 2 dimensional structures. So, they have properties which are very similar to 2 dimensional structures even when these are 3 dimensional structures.

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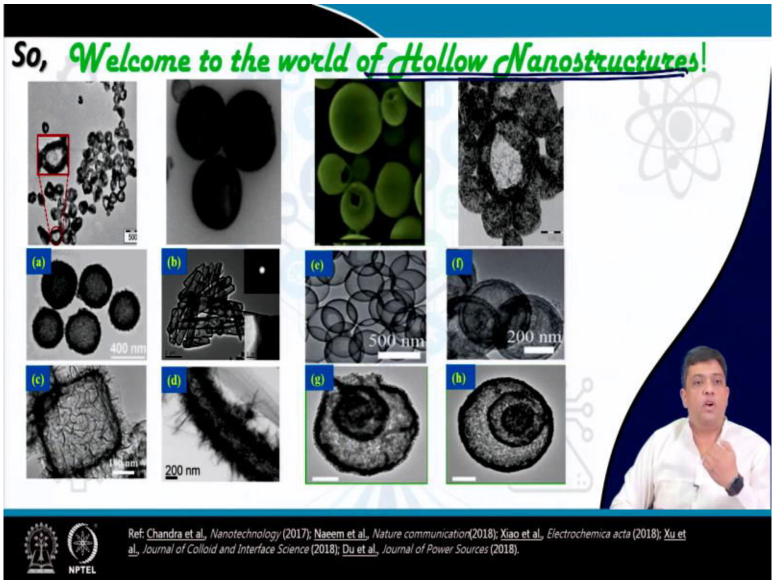

So, Welcome to the world of Hollow Nanostructures!

Ref: Chandra et al., *Nanotechnology* (2017); Naeem et al., *Nature communication*(2018); Xiao et al., *Electrochemica acta* (2018); Xu et al., *Journal of Colloid and Interface Science* (2018); Du et al., *Journal of Power Sources* (2018).

And this is what one is saying today that the hollow structures or hollow Nano structures are going to be the future for energy devices and we will spend significant amount of time in coming 2 modules where we will talk about the synthesis, the formation and the reasons why these kinds of structures are extremely useful for energy devices.

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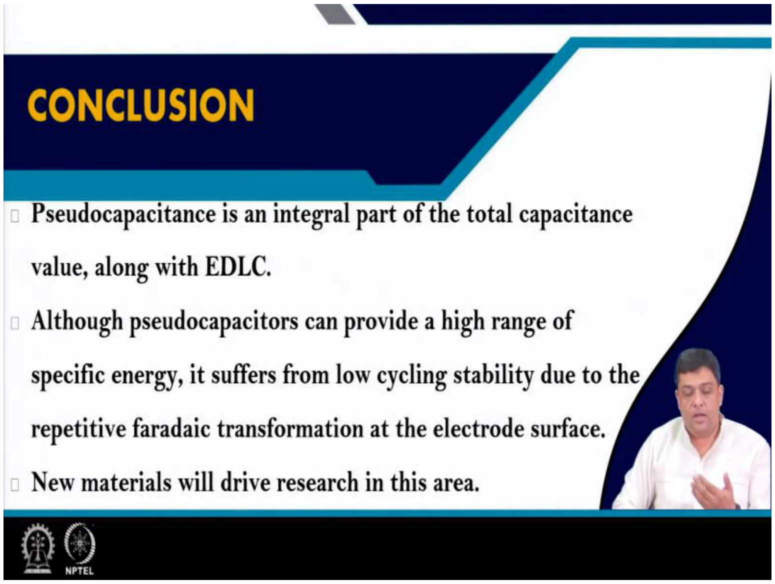

CONCLUSION

- Pseudocapacitance is an integral part of the total capacitance value, along with EDLC.
- Although pseudocapacitors can provide a high range of specific energy, it suffers from low cycling stability due to the repetitive faradaic transformation at the electrode surface.
- New materials will drive research in this area.

After hearing today's lecture, it must be clear that pseudo capacitance is an integral part of the total capacitance value along with EDLC's were in devices where are you are going to use the transition metal oxide based electrodes. Although pseudocapacitors can provide a high range of specific energies, they suffer from low cycling stability and the reason is mostly because of the degradation of the electrode surface as a function of cycling.

But to counter the limitations which are associated with the kinds of materials that are being used in today's pseudocapacitors, new materials are coming to the forefront and the ones which are becoming very important are the layered structures, 2D structures or pseudo 2D structures which are based on hollow structures.

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- Chandra et al. CrystEngComm 22 (9), 1633-1644, 2020
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These are the references which were used in today's slide and with this we will finish this week's lectures and in the next week, we will talk about the parameters which can affect the performance of a real super capacitor device, the parameters such as temperature, magnetic field, external vibrations or similar parameters which are encountered in real world applications that is what we are going to discuss in the next week. Thank you very much.