Electrochemical Energy Storage

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Module - 08
Advanced materials and technologies for supercapacitors
Lecture - 38
Asymmetric Supercapacitor and BATCAP: Battery Supercapacitor Hybrid Electrochemical Storage

Welcome to my course Electrochemical Energy Storage and this is module number 8 where I am talking about Advanced materials and technologies for supercapacitors. This is lecture number 38, where I will describe the Asymmetric supercapacitors and battery capacitor hybrid for the electrochemical storage.

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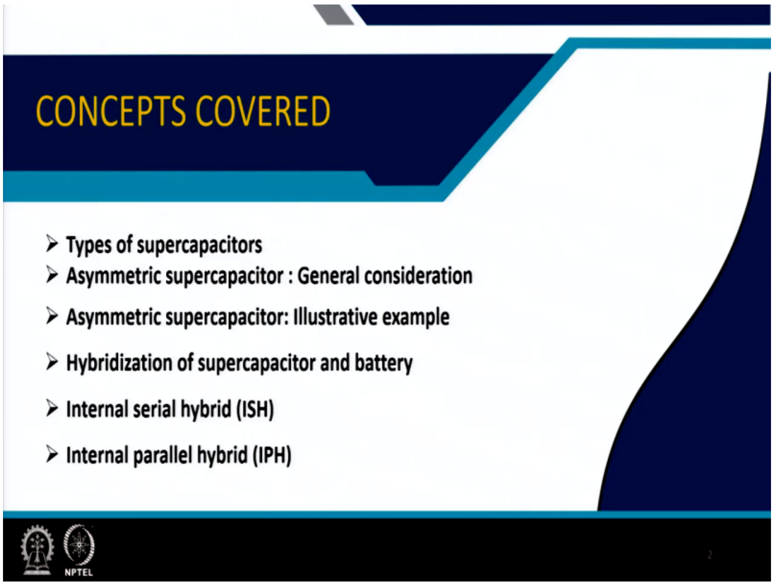

Now types of supercapacitor we will relook it, initially we talked about the supercapacitor can be divided in two part and we will elaborate it and then we talk about asymmetric supercapacitor what are their general consideration. Then an illustrative example we will put on the asymmetric supercapacitor one example, then we will go for hybridization of supercapacitor and the battery this is a very new topic and mostly it is confined to the research papers.

So, in textbook they are not being included to the best of my knowledge. So, I will just introduce this topic, it is more like a research topic. So, lot of things are coming in recent time. So, I will introduce this concepts and typically two different types of hybrid we will talk about one first one is internal series hybrid and internal parallel hybrid.

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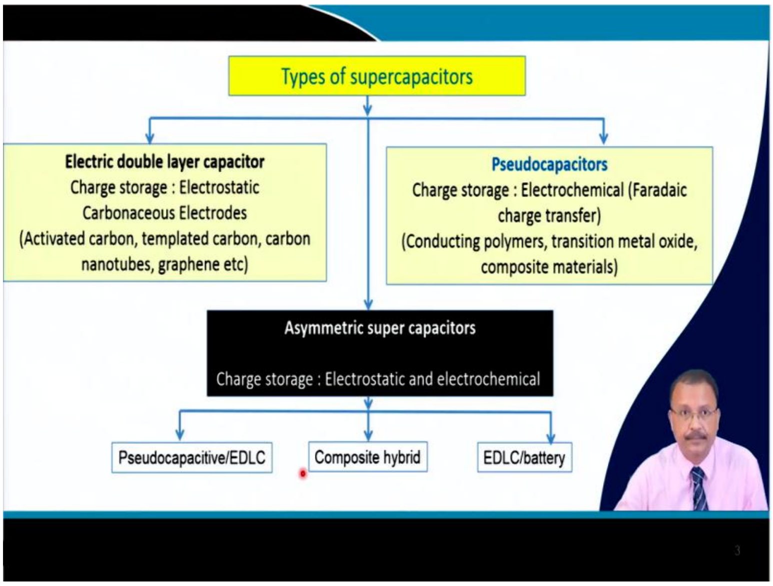

So, if you consider this types of supercapacitor which we are talking about, you have the first category which is electric double layer capacitor. So, the charge storage for this kind of capacitor is electrostatic in nature. Usually carbonaceous electrodes are used examples are activated carbon or templated carbon we talked about graphene.

In case of pseudocapacitor the charge storage is electrochemical that is the faradaic type of charge transfer takes place conducting polymer is used or transition metal oxide or their composite. Now in case of asymmetric supercapacitor the charge storage is both electrostatic and electrochemical. So, you have three categories for asymmetric supercapacitor the first one is pseudocapacitive and EDLC you can make asymmetry.

One electrode is EDLC type, another one is pseudocapacitive type. The second one I will talk about the composite hybrid and the third one is e C EDLC type and battery type. This composite hybrid is a very new concept and EDLC and battery type lot of research paper is coming in recent time.

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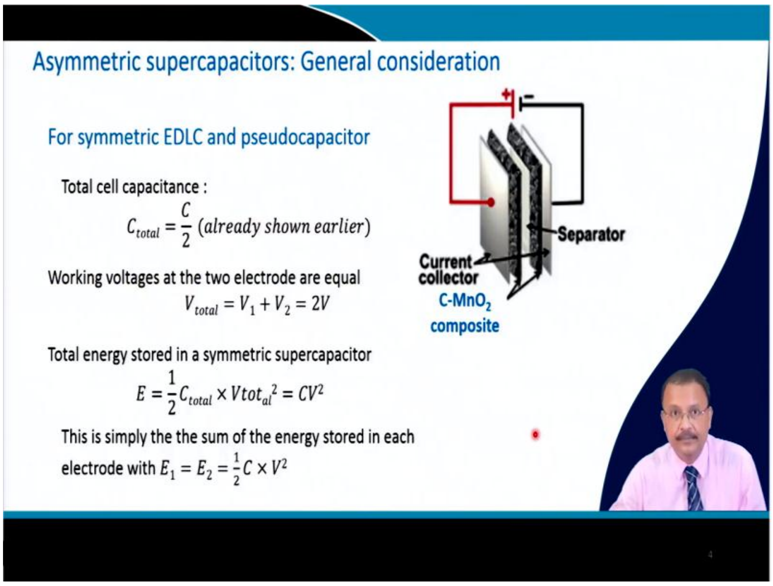

So, in case of this asymmetric supercapacitor in order to understand it is better, you need to understand the symmetric EDLC and pseudocapacitor. So, you can see that if two same type of material is used. So, this is the current collector, this is your say pseudocapacitive material which is basically a carbon MnO 2 composite.

Then you have a separator which you know by this time because you know the construction of the battery, then there is another current collector and another electrode material which is also the same material like the negative one. So, thus this is the positive electrode, this one is a negative electrode.

So, the total capacitance already we showed earlier it is C by 2. Now, if you want to estimate the working voltage. So, this working voltage is V 1 plus V 2. So, V 1 and V 2 they are same. So, that is 2V. So, the total energy stored is half C into V total whole square. So, it is only CV square if you put these values.

So, this is simply the sum of the energy stored in each electrode. So, E 1 energy stored in first electrode, energy stored in second electrode they are same and this is given by half CV square. So, that is for a symmetric type EDLC or symmetric type of pseudocapacitor.

$$C_T = \frac{C}{2}$$

$$V_T = V_1 + V_2 = 2V$$

$$E = \frac{1}{2} C_T {V_T}^2 = CV^2$$

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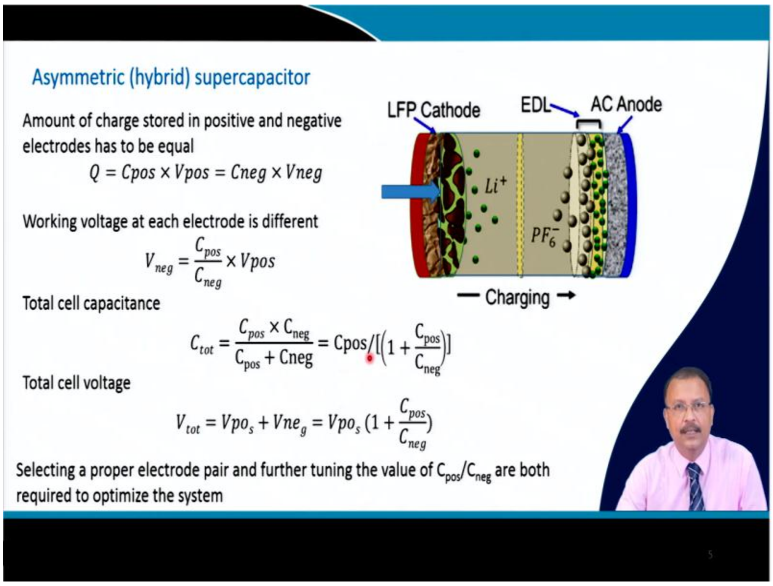

Now, consider that you have a hybrid supercapacitor. So, for example, I have shown it here that you can take a lithium iron phosphate cathode which is typical battery material and you can have an AC activated carbon which is in anode and the electrolyte could be Li PF 6 salt that is dissolved in ECDMC just like your battery. So, one type is EDLC type another one is battery type which is just to make you understand the concept.

So, here I can use a supercapacitor inside of this. So, here this whole bulk of the system is not basically the redox reaction is operative, the redox reaction is operative only at the surface of the material. So, the schematic is slightly changed because I have replaced this one not with LFP the battery material, but a pseudocapacitor. So, the basic concept is the amount of charge that is stored in the positive and negative electrode that must be equal.

So, if Q is the total charge, C is the capacitance in the positive electrode which basically we talked about cathode and the respective voltage that is equated with C negative and V negative. So, the working voltage say at the negative electrode. So, that is given by C positive by C negative into this V positive.

Total cell capacitance what will be there? 1 by C positive plus 1 by C negative. So, you can write this as C positive into C negative by C positive plus C negative this will be subscript. So, that gives you C positive by 1 plus C positive by C negative. So, this is just from this relation.

If you just divide it by C negative, then you will get this relation. So, the total cell voltage will be voltage positive plus voltage negative. Please remember this positive and negative sometimes it is a little bit disturbed I do not know why it happened, but this pos means positive, which will be subscript and neg means negative which will be subscript tot means total.

So, this please take into consideration. So, if I want to play with this total voltage, then basically this one is important either positive electrode voltage range and also the ratio of this capacitance that is important. So, I need to optimize the ratio positive by negative in case of a asymmetric pseudocapacitor and EDLC type hybrid supercapacitor.

In order to increase the voltage, I will have to play I need to know what are the voltage range for the positive electrode, what are the voltage operative range for the negative electrode and then I will have to tune the ratio of their respective capacitance and then I can increase the total voltage part.

$$Q = C_{pos}V_{pos} = C_{neg}V_{neg}$$

$$V_{neg} = \frac{C_{pos}V_{pos}}{C_{neg}}$$

$$Total\ Cell\ Capacitance\ C_T = \frac{C_{pos}C_{neg}}{C_{neg} + C_{pos}} = \frac{C_{pos}}{1 + \frac{C_{pos}}{C_{neg}}}$$

$$Total\ Voltage\ V_T = V_{pos} + V_{neg} = V_{pos} * (1 + \frac{C_{pos}}{C_{neg}})$$

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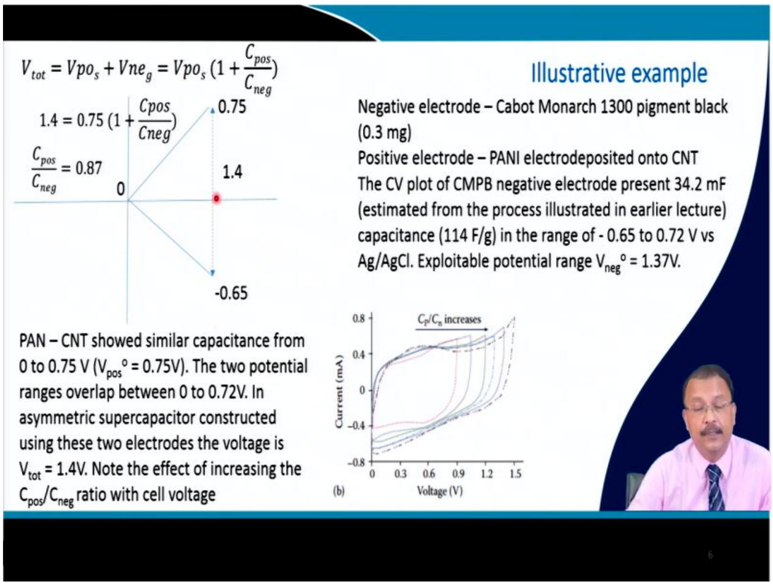

So, this is one example, say we are taking the example of this PAN CNT which is a pseudocapacitive material and in case of a negative electrode I have taken a so, called Cabot Monarch 1300 pigment black. So, this is basically a EDLC type of carbonaceous material. So, I can build a asymmetric capacitor where this PAN CNT that will be my positive electrode and the this Cabot Monarch 1300 pigment that is abbreviated as CPMB that will be my negative electrode.

So, if you consider this PAN CNT and then with a reference, the reference is taken in the aqueous state silver silver chloride reference you can take. Then the total working range of the voltage that is experimentally determined to be 0 to 0.75.

So, this 0 to 0.75 this is for the positive part. So, this is a linear part I have shown that voltage is goes from 0 to 0.75 and the other one the negative part as you know that if something is getting charged one of the electrode the other electrode is getting discharged.

So, the other electrode this Cabot this pigment, this range is 0.65 to 72. So, minus 0.65 to 0.72 that is the range for the material which is the negative material that is the carbonaceous material. So, the range that is operative here you can see that if you want to exploit the negative potential range this is around 1.37 volt right.

So, if you take the value of this the mode of this and it goes till here. So, it is 1.37 volt. So, this two potential range 0 to 7.75 and minus 0.65 to 0.72 this two range overlaps in the range from 0 to 0.72 roughly.

So, that overlaps there. So, one can construct a supercapacitor because taking the effect of the two voltage regime. So, the total voltage that you will get here you can see from here. So, from 0 to roughly 0.75 I have taken and it is negative also from discharge from 0 to minus 0.65.

So, this total voltage range is 1.4 volt maximum that we will be able to get out of this supercapacitor. Now I have already deduced this V total as V positive plus V negative and then finally, V positive getting this relation to 1 plus C positive by C negative. So, this ratio I have gotten. So, here my total voltage that is possible for me to get is 1.4 volt and this V positive here is from 0 to 75 0.75.

So, I just put this value and I get this ratio C positive by C negative that is about 0.87 so, that I am getting. So, now, if you will have to make this ratio if you can maintain this ratio, then basically you can get this whole voltage range. So, this is the full cell whatever you have constructed if you have this two ratio you change C p by C n ratio positive by negative capacitance ratio if it increases here.

So, the maximum one where you get about 1.4 volt that you can estimate that what is the ratio of the capacitance is required for you to attain this maximum voltage range. So, this is a aqueous supercapacitor. So, one-volt basically this electrolyte is stable but 1.4 is also ok if you can manipulate the electrolyte I will explain it in my next lecture. So, this is the way you can construct an asymmetric supercapacitor.

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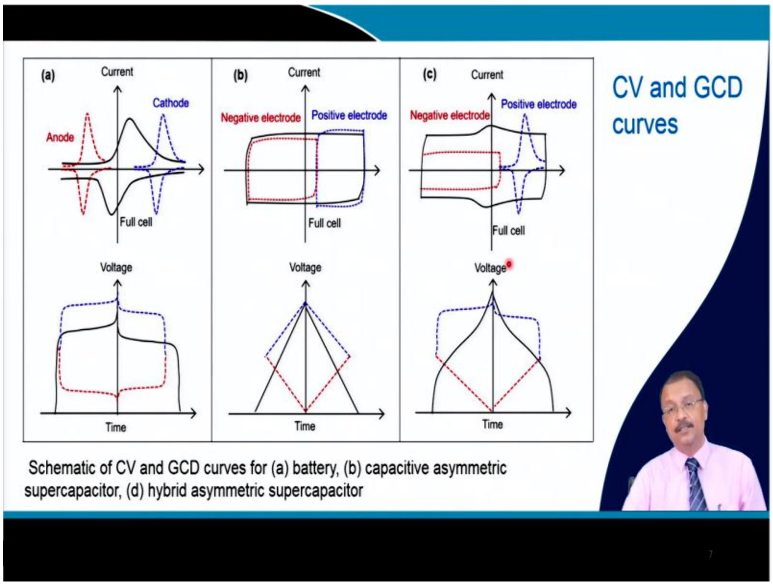

Now if you look at the cyclic voltammetry curve and the battery curve you have seen it in your earlier lectures. So, this is your cathode part and this is your anode part and then eventually from this voltage range you get a full cell characteristics for the CV characteristics and these are the respective half cells.

In case of battery also similar kind of thing you can achieve you can work on the voltage range for the half cell if the positive electrode is getting charged the negative electrode is getting discharged.

So, you can see that what kind of voltage that you will be getting out of the full cell. Now in case of a capacitive element which is asymmetric. So, this is the b part, this is a capacitive capacitive asymmetric supercapacitor. Here also you can get the CV plot and you can get the charge discharge plot and from the half cell characterizing the half cell you can easily get the full cell working potential.

Same thing you can do for hybrid asymmetric capacitor as well, which is of our interest. So, the negative electrode here is as you can see it could be pseudocapacitive and positive electrode could be a battery or it could be a negative electrode can be a EDLC type of material and positive electrode could be pseudocapacitive the example that I have shown.

So, it is important for you to characterize the half cell characteristics for each individual component and then depending on the voltage range that you are estimating you will have to construct the battery and you can estimate that what type of voltage range you will run the full cell.

And for that purpose for asymmetric purpose we will have to tune the capacitive ratio so, that you can maximize the voltage. And once you maximize the voltage the power density and energy density to some extent will get increased.

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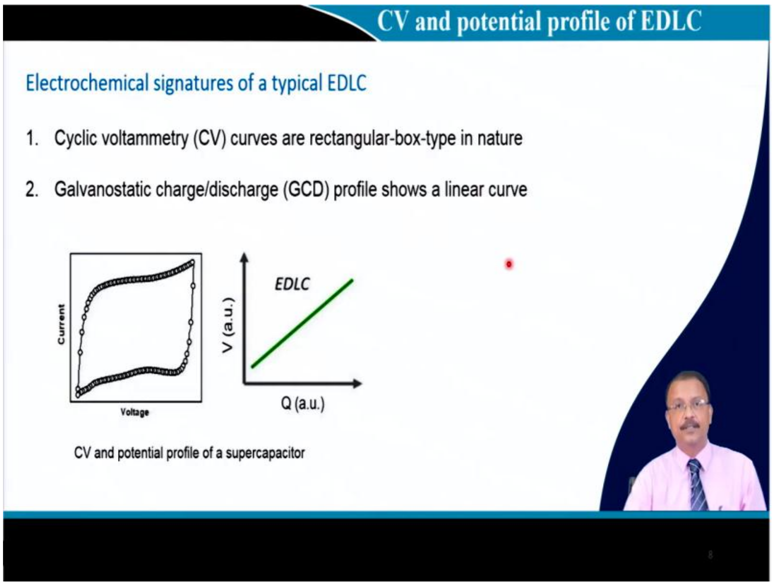

So, if you have the EDLC type by this time, you are convinced that you will get almost a square rectangular type of CV plot and a linear type of charge discharge plot.

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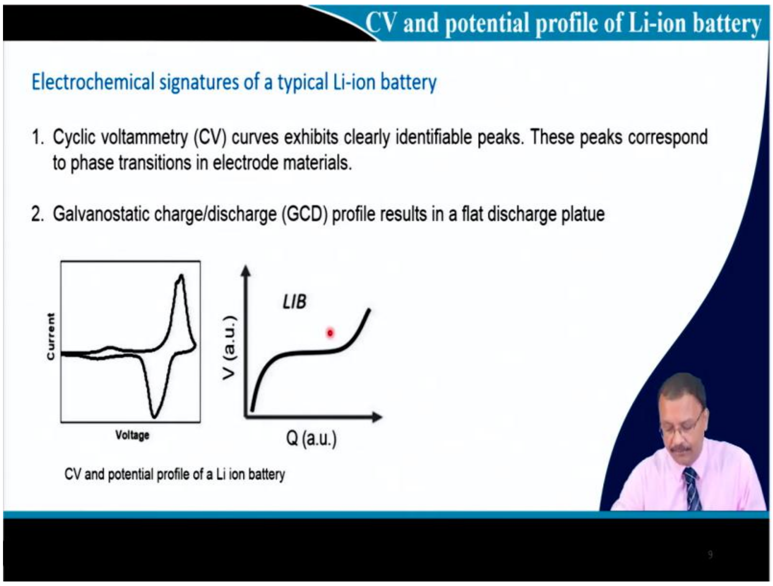

Now if you go for the cyclic voltammetry of a typical lithium ion battery, then you get a CV plot where distinct oxidative and reduction peak that is identifiable and depending on the type of the material you can get a plateau, you can have different types of shape I think that earlier lectures we have talked about it in details.

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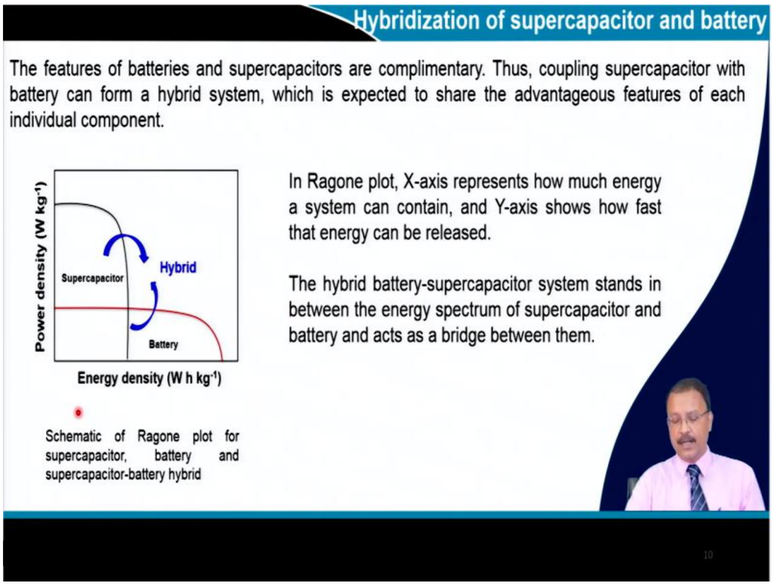

So, this kind of pattern that you will be getting. Now the third part is to make the hybridization. So, in case of supercapacitor and battery if you individually plot what we call a Ragone plot, here energy density is plotted against the power density. So, as you can see in case of supercapacitor, the energy density is relatively low, but the power density is quite high and the reverse is true for the battery.

In the case of the battery the energy density is high, but the power density is low. So, if you make a hybrid out of this two. So, you will be in between and this sometimes it will be quite advantageous. If you are using a battery material it can give you energy density large energy density.

So, you can drive your car for longer distance but if you accelerate more then you need current if you drain lot of current then the capacity goes down. So, then your power density is less. Supercapacitor is just the reverse it has a good power density particularly if you are using EDLC type and it has very poor energy density. So, make a hybrid. So, you get the advantage of both battery and supercapacitor. So, that is the idea.

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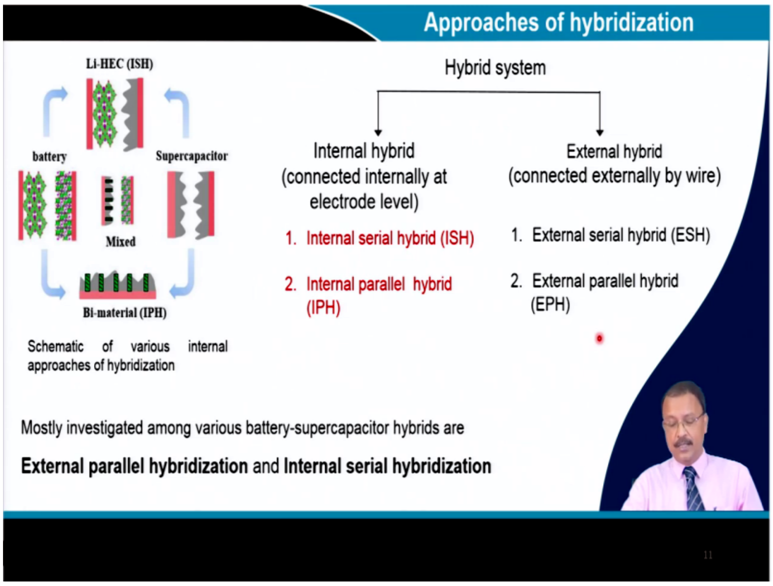

So, there are various types of thing that you can do. So, this hybrid electrochemical hybrid electrochemical capacitor which we call if the lithium ion is diffusing ion. So, in one part as you can see I have put supercapacitive material and the other electrode is a battery type of material.

So, these are individual battery type of material individual supercapacitor type of material and we call this is a symmetric capacitor and this one is also once it is a battery it could it may have different types of material always it will have.

So, this is the battery type and this is the supercapacitor type. So, one of the electrode this is a supercapacitive type another electrode is a battery type then now you can mix this two. So, depending on that this hybrid system we call its a internal hybrid. So, that is connected internally at the electrode level. So, each individual electrode we are considering. So, that could be of two type one is internal serial hybrid which we estimate I mean abbreviated ISH. So, this is one example of ISH.

So, internal serial hybrid means one of the capacitor could be an EDLC type and another one is a battery type or you can have a internal parallel hybrid. So, in case of internal parallel hybrid which sometimes we call bi material, there you can see that both this material are in the same phase.

So, in the same phase you have a supercapacitive material and also the battery material in one electrode. So, this we call a bi material electrode. So, that is each individual one. So, two electrode you can make different types of hybrid one you can take a EDLC type, another one you can take a battery type, EDLC type pseudocapacitor type.

Now in parallel hybrid you mix this supercapacitor with the battery. So, each single electrode you have supercapacitor plus battery in the same electrode. Other electrode could be a pseudocapacitor or a EDLC or a mixed type of material. So, you can imagine there are lot of combinations available and many exotic properties you can expect.

And this is clearly different from what exactly nowadays people are doing when they run electric vehicles. So, their external serial hybrid or external parallel hybrid is physically they are considering a capacitor stack and the battery stack and then they are connected it. So, this is external serial hybrid. So, this type of thing are being investigated quite rigorously.

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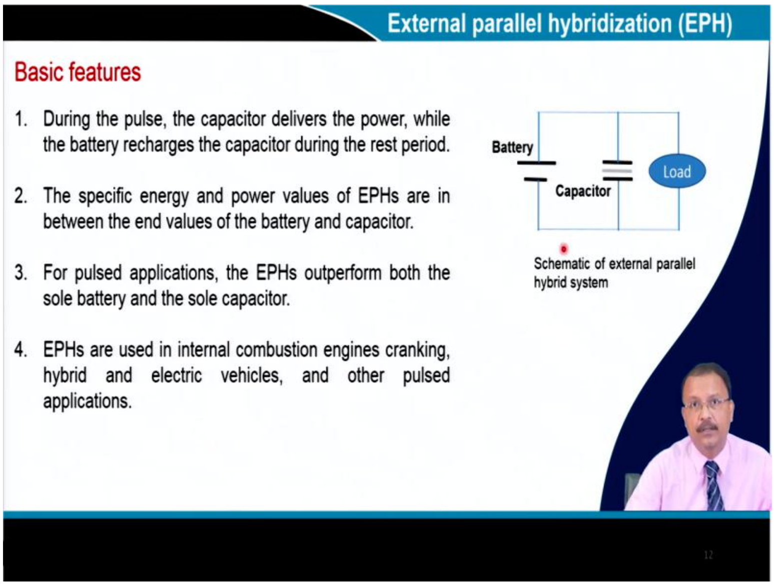

And the basic feature if you go for external parallel hybrid is you know the a battery and a capacitor is connected with the load like this. So, when there is a pulse then the capacitor drives the power and the battery recharges the capacitor when battery is kept idle. So, the specific energy and power values of external parallel hybrids the they are in between the end values of the respective battery and capacitor.

Again for the pulse application where you need lot of current, then this external parallel hybrids they outperform both the sole battery and sole capacitor. So, there are clearly synergistic effect and this are being used for the internal combustion engine cranking hybrid and electric vehicles and other pulsed applications. So, this is a well-known technology, but what we are talking about that is something different.

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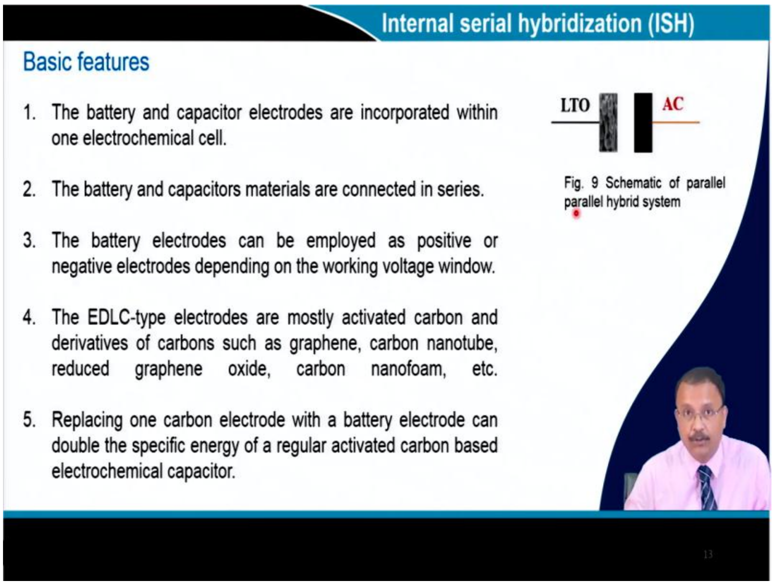

So, one example you can see that this is a battery, LTO is a battery material and AC activated carbon is a supercapacitive material. So, this battery and capacitor they are incorporated in one electrochemical cell. So, that we call internal serial hybridization I already explained it. Now they are connected in series. So, this one and this one they are connected in series. So, this battery or material that can employ both as positive or negative.

So, it will depend that what is the voltage range. So, LTO you know the voltage range is relatively lower and AC they can go to high voltage range as well. So, if you take this combination then AC is your positive electrode and LTO is your negative electrode.

So, this activated carbon they are mostly used other carbonaceous material can also be used that already I have talked about and replacing one carbon electrode with a battery electrode can double the specific energy of a regular activated carbon based electrochemical capacitor. So, it has high energy density. So, that is the same thing what I already explained. So, these are really advantageous.

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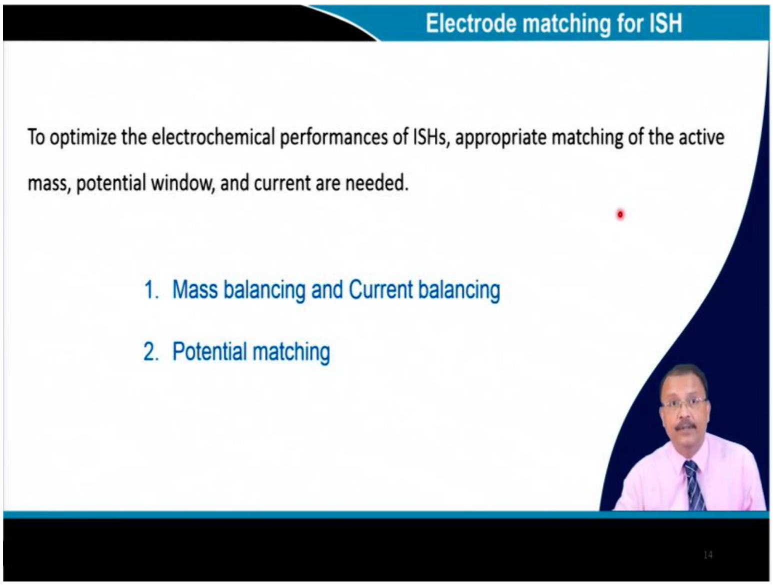

Now in order to make this kind of; this kind of device to work two things are important. First is we what you call is mass balancing you will have to balance the active mass of the material that you are using in both the electrode, you will have to balance the current. So, the first one is a mass balancing and current balancing and second one is the potential matching.

So, from my earlier description you have seen that how the potential is matched in case of this supercapacitor this earlier lecture when I talked about, you have seen it that how the total voltage you can control by controlling the individual capacitance. So, now, I will apply it for the battery as well.

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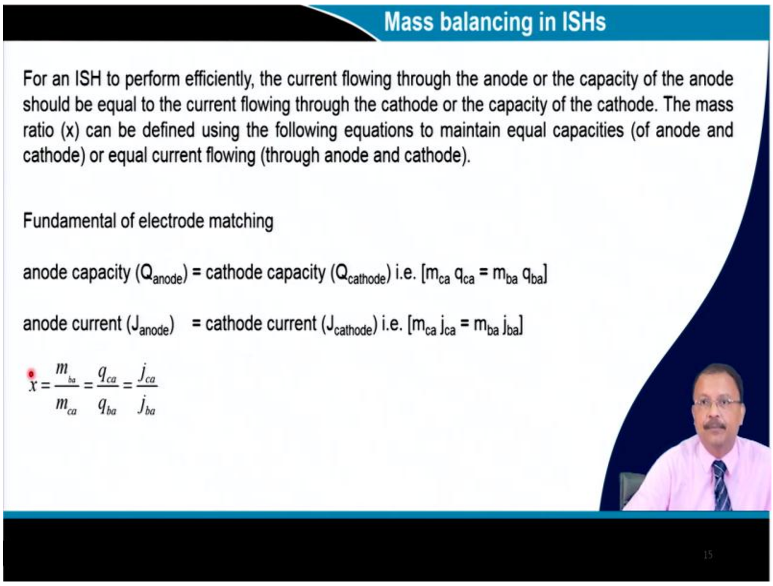

So, this serial hybrid if it want to perform it, then the current that flows through the anode and the capacity of the anode that should be equal to the current that is flowing through the cathode or the capacity of the cathode. So, the mass ratio I define this mass ratio by using the following relation of anode and cathode and also the current relation which is quite straight forward.

You see the anode capacity is will be equal to the cathode capacity. So, if you have a specific capacity q ca for cathode, then the mass that you are using. So, that will give you the total charge. So, usually this is at say milliampere hour per gram and the active material you are using that is in gram.

So, if you multiply this two then you will get the total charge and this total charge will be equal to the battery mass and the corresponding specific capacity of the battery material. So, this should be equal for anode and cathode similarly for anode current should be equal to cathode current and this is the current density of cathode and this is the current density of the anode material.

So, I define the value of x this is this mass ratio of the battery, at one end is a battery usually that acts as a cathode and another is the capacitor which acts as the anode material or I should say the positive electrode for the battery and negative electrode for the capacitor. Usually, the battery is having higher voltage limit. So, if I do that, then from this relation I can define basically this parameter x.

$$Q_{anode} = Q_{cathode} \rightarrow m_{anode}q_{anode} = m_{cathode}q_{cathode}$$

$$J_{anode} = J_{cathode} \rightarrow m_{anode}j_{anode} = m_{cathode}j_{cathode}$$

$$x = \frac{m_{cathode}}{m_{anode}} = \frac{q_{cathode}}{q_{anode}} = \frac{j_{cathode}}{j_{anode}}$$

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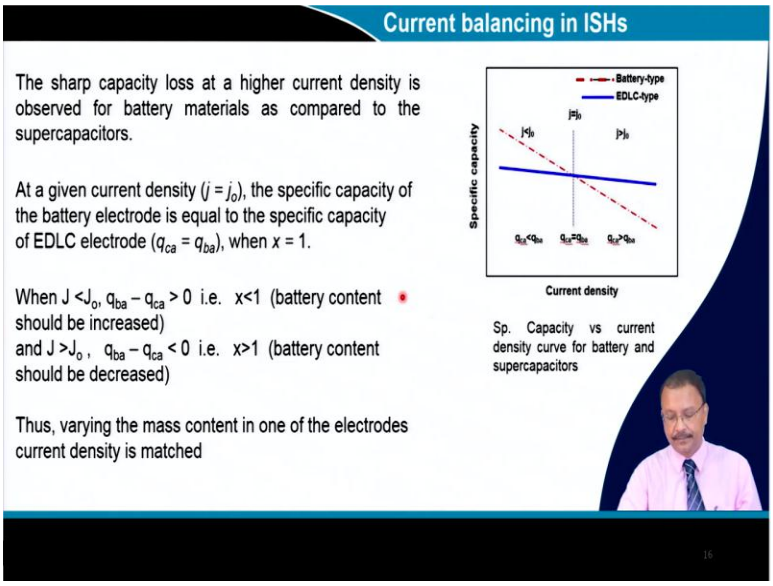

Now, if you see that the usually from your common perception in case of a battery, when you charge or discharge it at the very high current then its capacity drops down. So, the sharp capacity loss at higher current density usually that is observed in case of a battery material as compared to the supercapacitor material. Capacitor material you can drain lot of current.

So, if you have a given current density the specific capacity of the battery and electrode they are equal to the specific capacity of the EDLC type the negative electrode that is when x equal to 1 from the earlier equation.

So, when the value of the current is less than the value of this z 0 then clearly the capacity of the battery is more than the capacity of the anode material. So, the negative electrode; that means, the value of x is less than 1 and the battery component therefore, that should be increased.

But when the current is more than this critical current J 0 where the charge is actually equal, then you have the opposite relation. So, your battery is more than capacity is more than the anode then actually the battery component should be reduced. So, the varying this mass content in one electrode with respect to the other you can match the current density.

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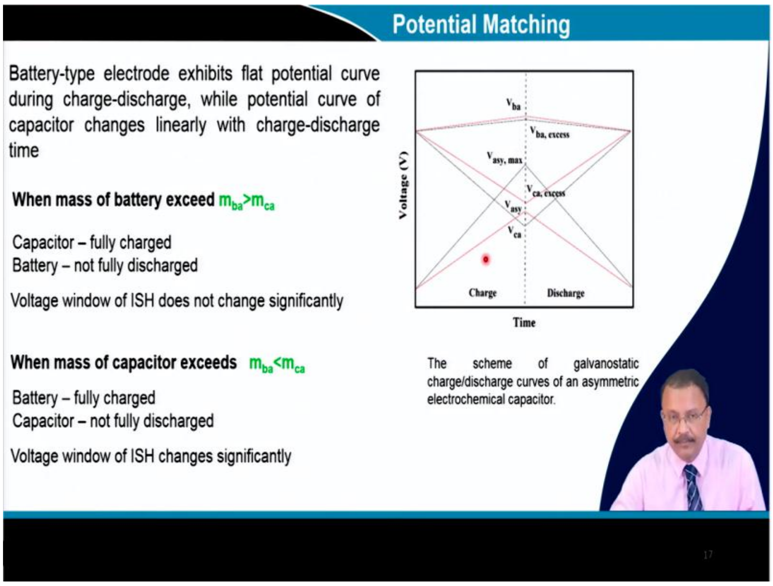

Now, you have several types of situation possible, the first one as you know that the battery type electrode they exhibit a flat potential curve during charge discharge and capacitor it changes. So, it is slightly more complicated therefore, I do not I have not used that one, but I have considered a the schematic simple schematic of a galvanostatic charge discharge curve for an asymmetric electrochemical capacitor. So, this is more or less it is a straight line.

So, you can now understand from this figure that I have shown the half-cell similar to the earlier example cited half-cell for the battery, half-cell for the capacitor and then the full cell. So, during charge what is happening to the positive material and what is happening to the negative material.

So, half cell of these two and then you combined this. So, the voltage limit you can see. So, what is important now that when mass of the battery is exceeded then what will happen? Battery has enough mass. So, the capacitor is fully charged, but battery is not fully discharged.

So, if something is getting charged the other component is getting discharged. So, the voltage window of internal serial hybrid does not change significantly, but when the mass of the capacitor exceeds then battery is fully charged, but capacitor is not fully charged. So, again the voltage window of internal serial hybrid that changes significantly. So, that is shown in this schematic value.

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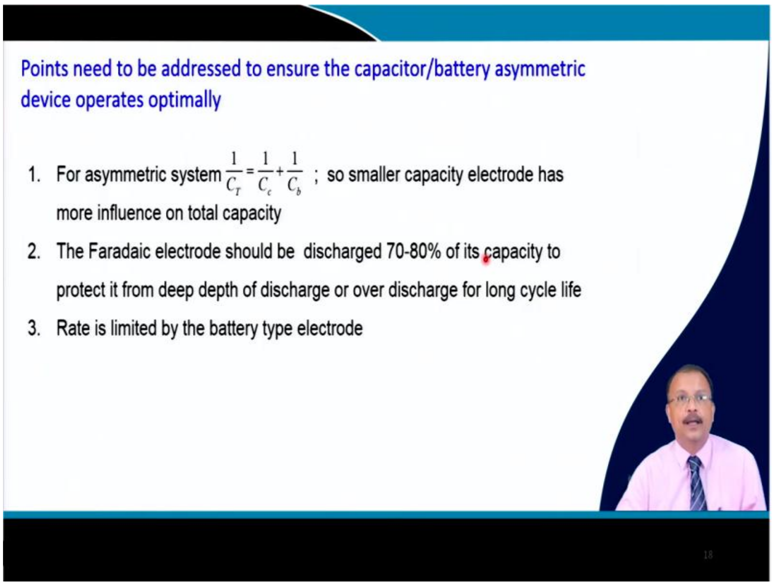

Now, the point that one should address is for an asymmetric system this equation is valid one for capacitor and this one is for the battery. Then a small capacity electrode which one is having the small capacity that basically will control the total capacity. So, that is quite obvious in case of two capacitor if you have one say 1 millifarad another one is 1 farad then 1 millifarad will control the farad one. In fact, the total capacitance will be less than the lower capacity.

Now the faradic electrode should be discharged to 70 to 80 percent of its capacity to protect it from the depth of discharge or over discharge for a long cycle life. And rate of this kind of asymmetric system the rate performance that is entirely controlled by the battery because the diffusion is involved that your capacity your capacitive material they are always ready to work for larger current, but you will be limited by the battery type of material. So, this things you will have to keep in mind.

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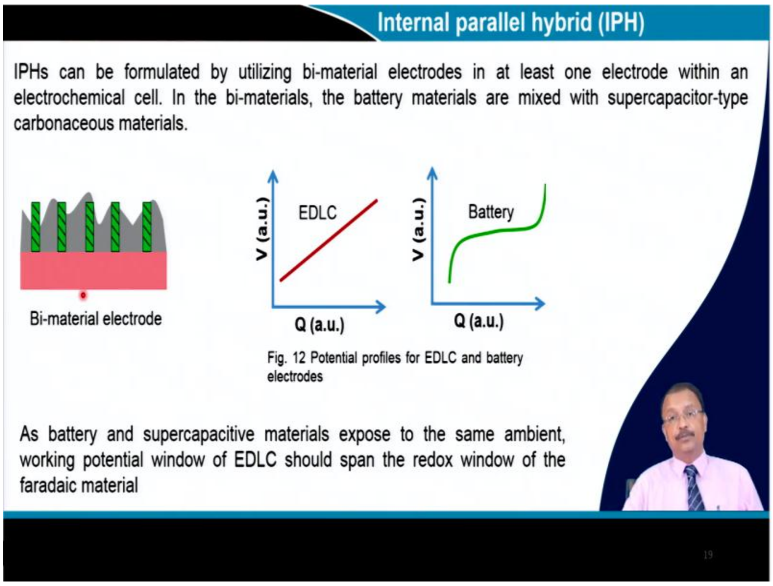

Similarly, now one can talk about not internal serial hybrid where you have a battery and you have a supercapacitor and make an asymmetric type of hybrid capacitor, but here in this case it is still more complicated where in one material this battery type sorry on one electrode this battery and supercapacitor both are in the same electrode.

Now one of the electrode is something like this, other electrode could be something similar or you could use other types of material you can use a EDLC, you can use another battery, you can use a pseudocapacitor. So, you can imagine the kind of variety that you can achieve.

So, understanding of the system is not very easy always not very easy, but this bi materials they are considered quite interesting from the research point of view we have also started working on that. That is a good review book chapter that recently we have written with one of my PhD students I have given it in a reference and I guess you will be able to download that thing.

If not then get back to me I will send you the book chapter the soft version. So, that illustration is quite within the short period I am not very comfortable to make a detailed description of this, but is quite interesting this internal parallel hybrid. So, the battery and supercapacitor they are exposed in the same ambient same environment. Working potential window of EDLC should span the redox window of the faradic material.

So, those kind of thing you should keep in mind that this voltage window is important, it is also important to have a proper mass balancing, proper current balancing. So, many parameters are involved to work on the asymmetric type of capacitor I mean it is not really a supercapacitor, but I thought this is also one of the varieties that I should introduce part of this lecture.

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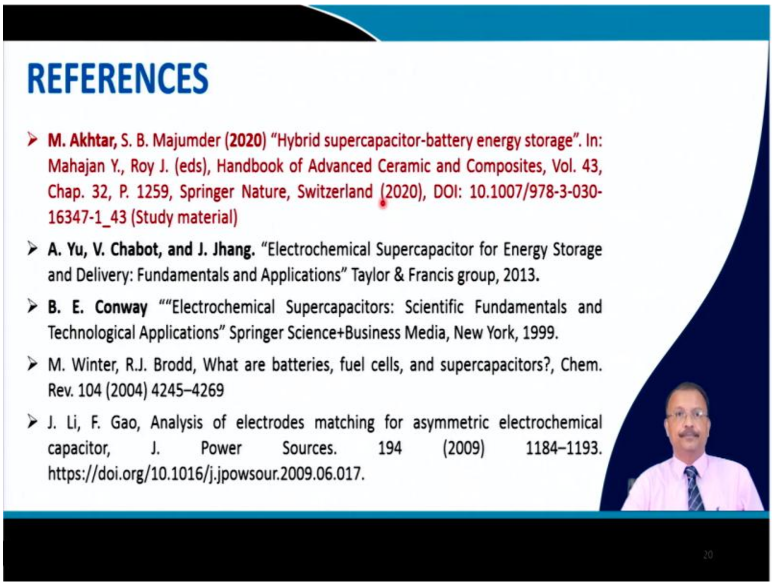

So, the reference for this type of particularly this lecture is the hybrid supercapacitor battery energy storage which is available in this particular book by Springer Nature and this is your study material and I guess that you will be able to download it from this link and apart from that there are except this two standard textbook you have this material this is also available for you to have more in depth idea about this asymmetric hybrid supercapacitor.

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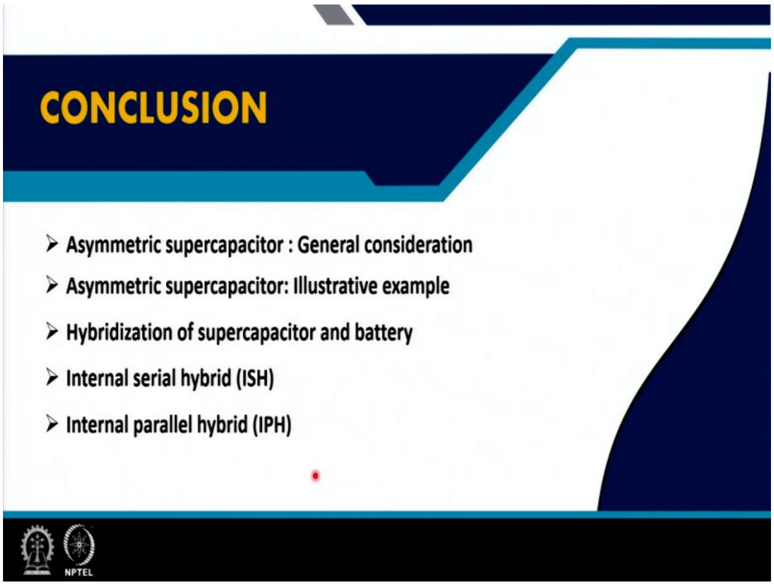

So, we have introduced asymmetric supercapacitor, what are their general consideration, then one illustrative example how to match the voltage by changing the respective capacitance, then what I meant by hybridization of supercapacitor and the battery it is in the strict sense it is not supercapacitor, but it is an interesting hybrid. So, that therefore, I have included is in the part of the lecture.

Then we talked about internal serial hybrid where you have two different types of electrode, one is your battery type, another one EDLC type and then internal parallel hybrid where in the same electrode you are using both supercapacitor and battery type so.

Thank you for your interest.