Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture - 18
Supercapacitors

Hello my friends, in this particular lecture, we are going to discuss about the Supercapacitors. So, as I told in the introduction chapter that supercapacitor is nothing but it is a one kind of energy storage systems. So, how we have come into that concept of the supercapacitor

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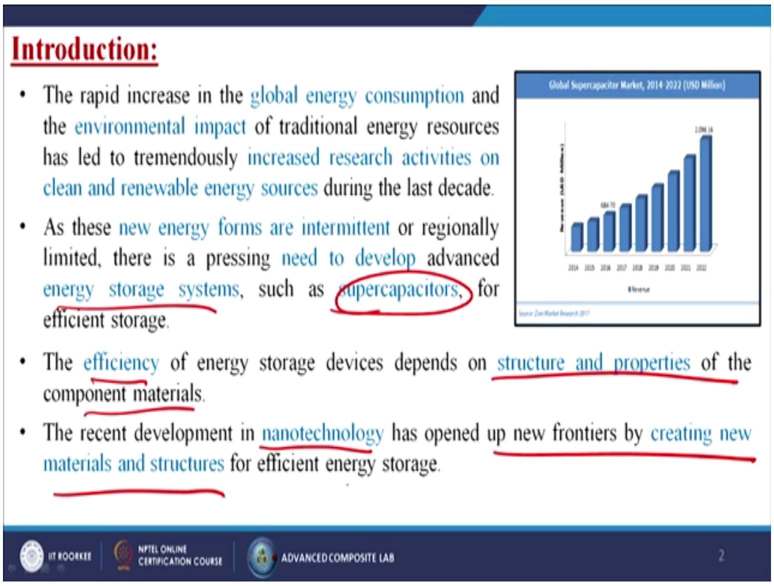

So, basically the rapid increase in the global energy consumption and the environmental impact of traditional energy sources has led to tremendously increased research activities and clean and renewable energy sources during the last decades. Yes, because till now we are working on the batteries, but the batteries is problem is that sometimes during the chemical reactions, it can generate some kind of toxic gases, it can corrode, the cathode and anode and also it does not have that longer life. Maybe if we use the solid materials for the batteries sometimes, it is may be one time use sometimes, we can recharge the battery, but that is also having some limitations.

So, basically we are talking about the super capacitors, so we can store the electrical energy in to it, and it should be renewable energy sources because it will not generate any kind of toxic gases, it is not harmful to the human mankind. So, basically these new energy systems or maybe the energy forms are intermittent or regionally limited there is a pressing need to develop advanced energy storage systems such as super capacitors, for efficient storage system. The efficiency of energy storage device depends on structure and properties of the component materials.

The recent development is nanotechnology has opened up new frontiers by creating new materials and structures for different energy storage. Now, we can see that in the global market scenario how the super capacitors is demands is going to be higher and higher. You can see in the year 2014 we are there in this particular case, but in now we are standing over here. And expected in 2022 will reach up to this level that is 2096.16 USD million from this particular technology.

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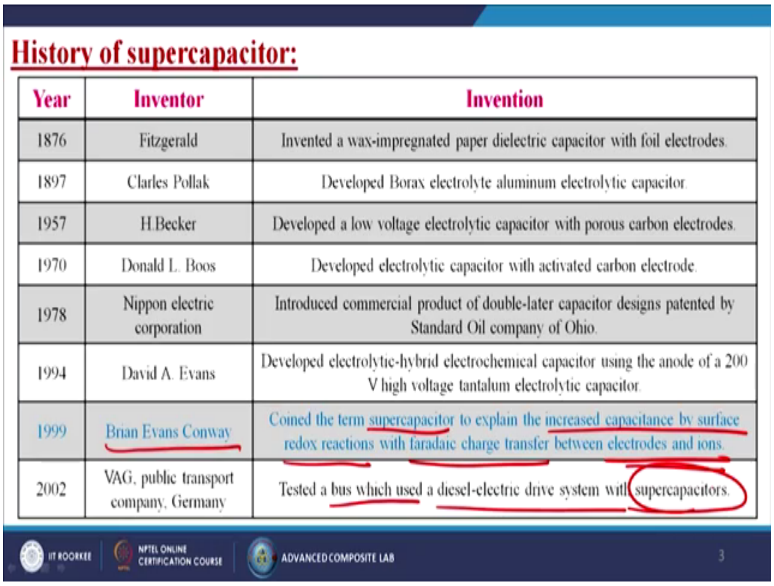
History of supercapacitor:

Year	Inventor	Invention
1876	Fitzgerald	Invented a wax-impregnated paper dielectric capacitor with foil electrodes.
1897	Clarles Pollak	Developed Borax electrolyte aluminum electrolytic capacitor.
1957	H.Becker	Developed a low voltage electrolytic capacitor with porous carbon electrodes.
1970	Donald L. Boos	Developed electrolytic capacitor with activated carbon electrode.
1978	Nippon electric corporation	Introduced commercial product of double-later capacitor designs patented by Standard Oil company of Ohio.
1994	David A. Evans	Developed electrolytic-hybrid electrochemical capacitor using the anode of a 200 V high voltage tantalum electrolytic capacitor.
1999	Brian Evans Conway	Coined the term supercapacitor to explain the increased capacitance by surface redox reactions with faradaic charge transfer between electrodes and ions.
2002	VAG, public transport company, Germany	Tested a bus which used a diesel-electric drive system with supercapacitors.

Now, if we come to the discussions that how the super capacitor has come into the picture. So, you can see in the year of 1876 by Fitzgerald, he has invented a wax impregnated paper dielectric capacitor with foil electrodes. Then a scientist has done so many modifications, and new mechanisms they have invented, new materials they have used.

Then in the year of 1999 by Brian Evans Conway, he coined the term super capacitor to explain the increased capacitance by surface redox reactions with faradic charge transfer between electrodes and the ions. Now, in the year of 2002 VAG public transport company, Germany, they have tested a bus which used a diesel electric drive system with super capacitors; that means, from that year 2002 it has come into the market or may be for commercial use.

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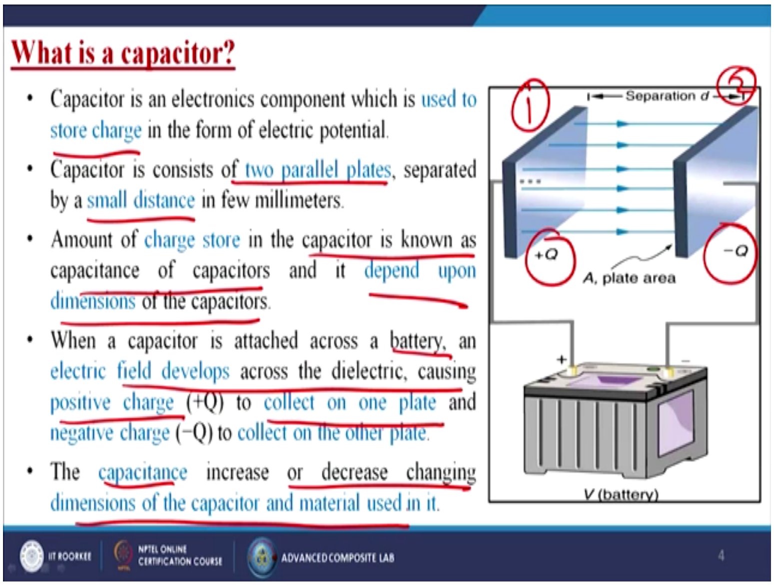

Now, before going to discuss about the super capacitors, just let us know what is capacitors. Capacitor is an electronic component which is used to store charge in the form of electric potential. Capacitor is consists of two parallel plates separated by a small distance in few millimeters. Amount of charge store in the capacitor is known as capacitance of capacitors and is depend upon dimensions of the capacitors itself.

So, simple we are having two plates over there 1 and 2, when a capacitor is attached across a battery and electric field develops across the dielectric causing positive charges to collect on one plate, and negative charges collects on to the another. The capacitance increase or decrease changing dimensions of the capacitor and the material used in it. It totally depends upon the dimensions shape and size of these particular materials and the material properties.

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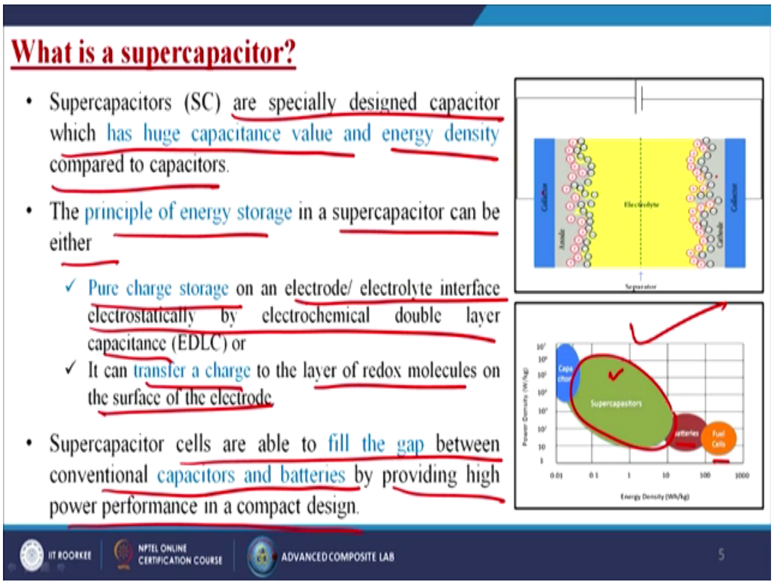

Now, let us know what is super capacitor. So, basically the super capacitors are specially designed capacitors which has huge capacitance value and energy density compared to capacitors. The principle of energy storage in a super capacitor can be either pure charge storage on an electrode or may be the electrolyte interface electrostatically by Electrochemical Double Layer Capacitance or in the short we are calling it as a EDLC, or it can transfer it charge to the layer of redox molecules on the surface of the electrode itself.

So, in this particular case, you can see we are having two collectors, basically it is known as the current collector. We are having that anode material and we are having that cathode material; and in between that we are having that electrolyte. And this anode and cathode is separated by one materials or maybe the membrane that is known as the separator.

Super capacitor cells are able to fill the gap between conventional capacitors and batteries by providing high power performance in the compact design, which you can get the information from this particular image. So, now, if we talk about the energy capacitor, the super capacitor plays and bridge role in between the capacitors and the batteries.

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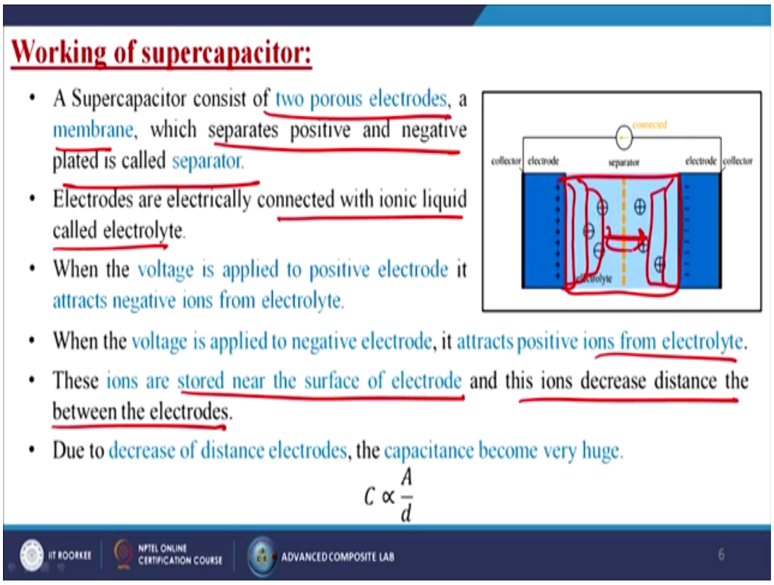

Now, working of the super capacitor, a super capacitor consists of two porous electrodes a membrane, which separates positive and negative plated is called the separator. Electrodes are electrically connected with ionic liquid called the electrolyte. So, this area is totally filled by this electrolyte, so this area basically. When the voltage is applied to positive electrode, it attracts negative ions from the electrolyte, so negative ions are coming over here.

When the voltage is applied to negative electrode, it attracts the positive ions from electrolyte. These ions are stored near the surface of electrode and these ions decrease the distance of between the electrodes, because it is making one layer, then another layer, then another layer same thing is these sides also, so automatically it is reducing the distance in between the anode and cathode. Due to decrease of distance of electrodes, the capacitance become very huge that is C directly proportional to capital A by small d.

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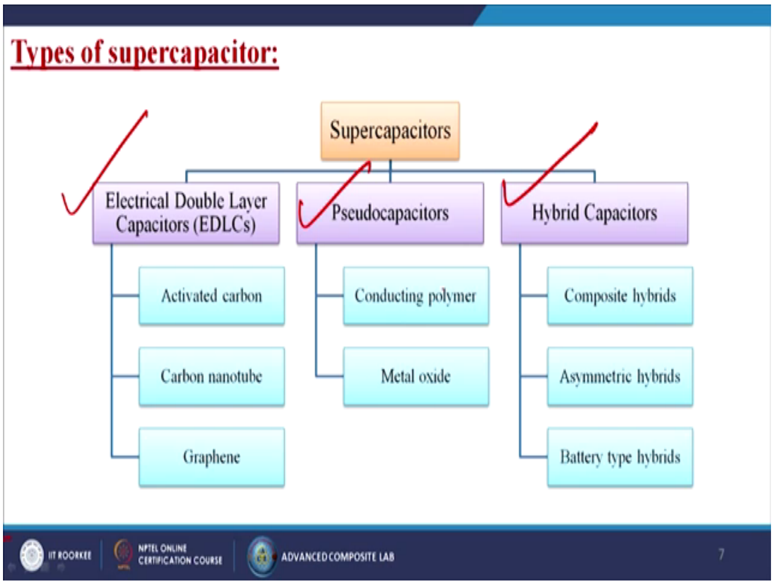

Now, types of super capacitor. So, basically these three are the principles by which the super capacitor works. One is called the Electrical Double Layer Capacitors, it is known as the EDLCs. Then second one is called the pseudo capacitors and third one is called the hybrid capacitors. If we talk about the EDLCs, basically we are using the activated carbon, carbon nanotube, grapheme, these kind of materials. If we talk about the pseudo capacitors, basically we are using the conducting polymer or maybe the metal oxide materials. And when you are talking about the hybrid capacitors we are using the composite hybrids, asymmetric hybrids and the battery type hybrids.

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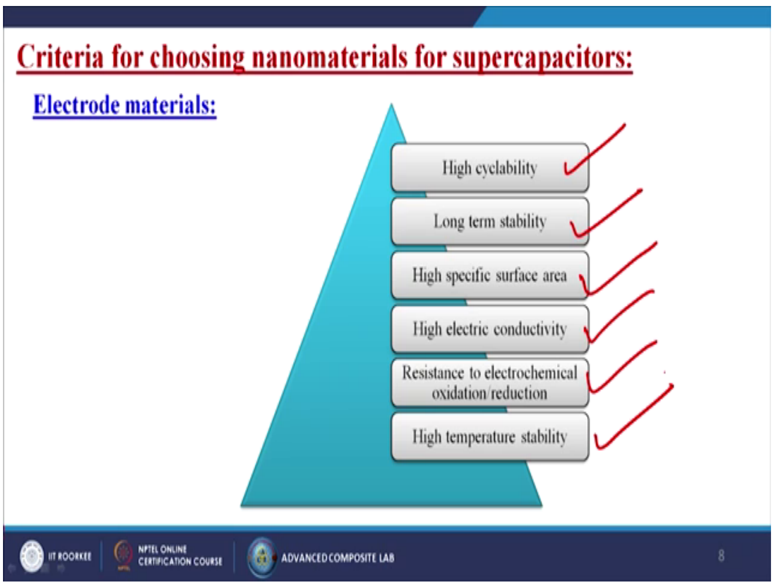

Now, what are the criteria? Not maybe the what are the parameter for choosing the nano materials for super capacitor. If we talk about the electrometer electrode materials point of view we need the high cyclability, long term stability, high specific surface area, high electric conductivity, resistance to electric electrochemical oxidation or maybe the reduction and the high temperature stability.

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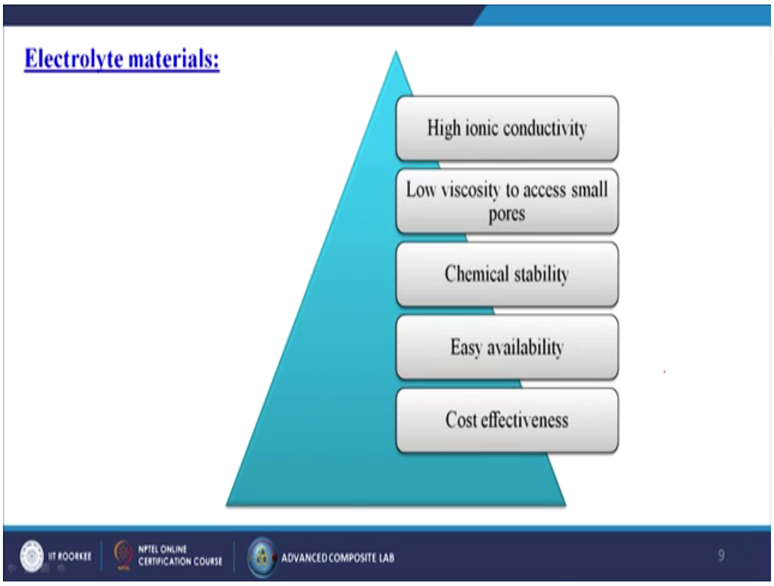

And if we talk about the electrolyte materials, we should have high ionic conductivity, low viscosity to access small pores, chemical stability, easy availability and the cost effectiveness.

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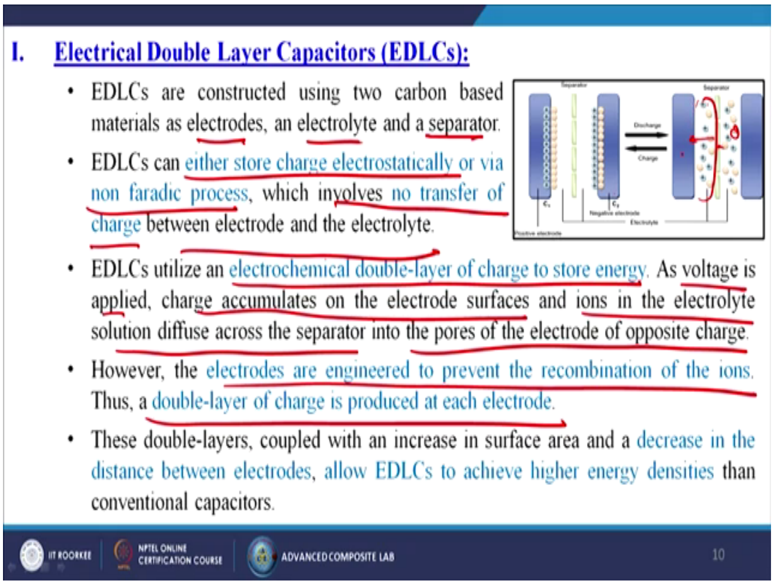

Now, let us discuss on Electrical Double Layer Capacitors or it may be the in short it is called the EDLC. EDLC are constructed using two carbon based materials as electrodes, an electrolyte and the separator. So, simple both are carbon based, so that is why it is c 1 and c 2. One will be the positive one, another will be the negative one; in between that we are using the separator and we are using the electrolyte.

EDLC can either store charge electrostatically or via non faradic process, which involves no transfer of charge between electrode and the electrolyte. EDLCs utilizes an electrochemical double layer of charge of store energy. As voltage is applied, charge accumulates on the electrode surface and ions in the electrolyte solution diffuses across the separator into the pores of the electrode of opposite charges.

So, what will happen? Separator, but it is the pores. So, both the sides the electrolytes are there. So, if it is positive, what will happen, whatever the negative ion are present from this side, it will come over here. Also through this pore these negative ions from the other side also it will come on to these sides also. However, the electrodes are engineered to prevent the recombination of the ions. Thus, a double-layer of charge is produced as each electrode.

So, first the electric ion over come over here, and then from this side also another negative ion will come over here, so they will form the double layer on that particular sides. These double layers coupled with an increase in surface area and decrease in the distance between the electrodes allow EDLC to achieve higher energy densities than the conventional capacitors.

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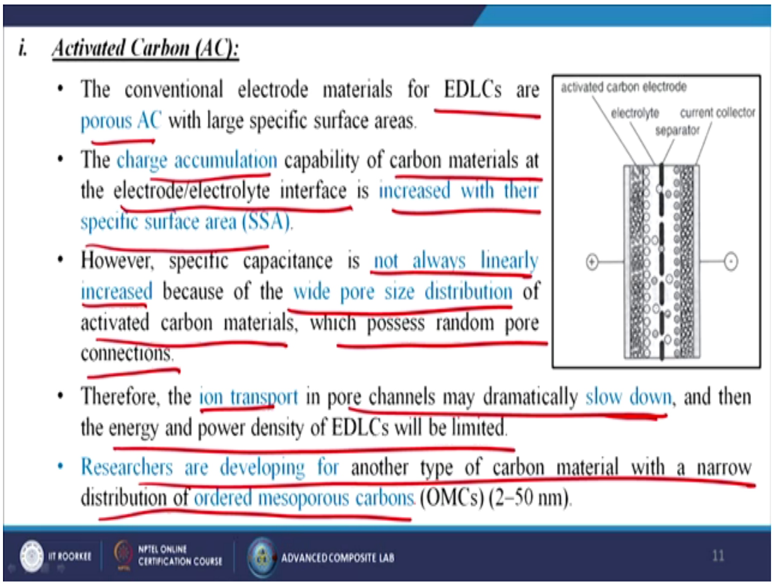

What kind of materials basically, we can use? Maximum cases we are using the activated carbon. The conventional electrode materials for EDLCs are porous activated carbon with large specific areas. The charge accumulation capability of carbon materials at the electrode electrolyte interface is increased with the specific surface area.

However, the specific capacitance is not always linearly increased because of the white pore size distribution of activated carbon materials, which possess random pore connections. Therefore, the ion transport in pore channels may dramatically slow down and then the energy and power density of EDLCs will be limited. Researchers are developing for another type of carbon material with a narrow distribution of ordered mesoporous carbon size is 2 to 50 nanometer.

So, in this particular case, what we are using, you see we are using the activated carbon from the both the sides these allowed the current connector, we are using the electrolyte and we are using the porous membrane over there. So, one side will be become positive, one side became will became negative. And first the negative will come from these sides and then through this porous membrane, also another negative will come over here and they will form the double layer over there. So, that is why it is called the EDLC technology.

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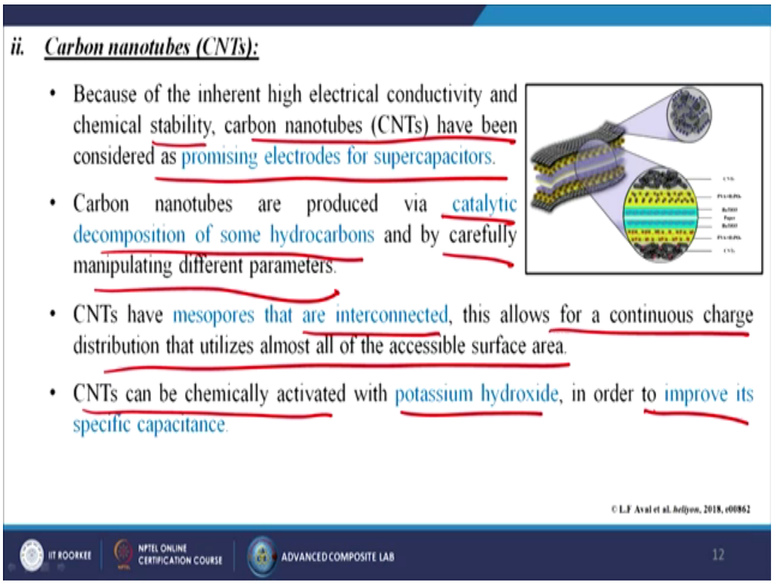

Next, carbon nanotubes because of the inherent high electrical conductivity and chemical stability, carbon nanotubes have been considered as promising electrodes for the super capacitors. Carbon nanotubes are produced via catalytic decomposition of some hydrocarbons and by carefully manipulating different parameters. CNTs have mesoporous that are interconnected, this allows for a continuous charge distribution that utilizes almost all of the accessible surface area. CNTs can be chemically activated with potassium hydroxide in order to improve its specific capacitance.

Now, you can see that how people are making or maybe scientist and making the sandwich structure. So, they are using the carbon nanotubes both the sides as a carbon electrode materials and in between that they are using the PBA H 3 PO 4 BaTiO3, then paper as a separator and then in the opposite sides. So, in this particular case, the CNT both the sides is acting as a electrode material.

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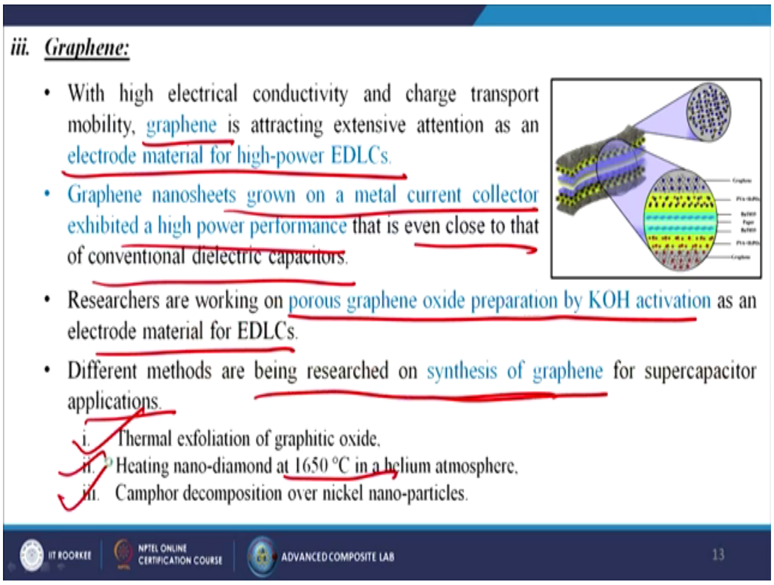

Next, we are using the grapheme, so basically with high electrical conductivity and charge transport mobility, graphene is attracting extensive attention and as an electrode material for high power EDLC. Graphene nanosheets grown on a metal current collector exhibited a high power performance that is even close to that of conventional electric capacitors.

Researchers are working on porous graphene oxides by potassium hydroxide activation as an electron material for EDLC. Different methods are being researched on synthesis of graphene for super capacitor applications like thermal exfoliation of the graphitic oxides they are making the reduced graphene oxides generally we are calling it. Heating nano-diamond at 1650 degree centigrade in a helium atmosphere in a inert gas atmosphere. And the third one is that Camphor decomposition over nickel nano-particles.

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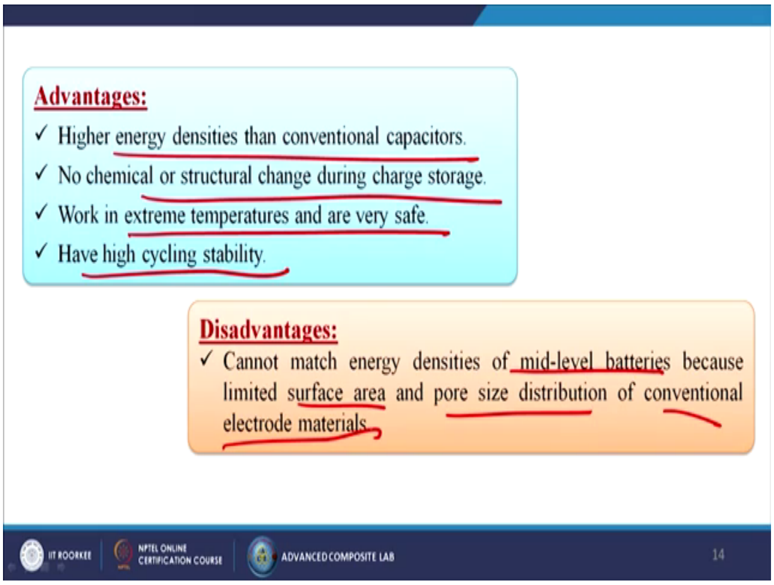

What are the advantages? High energy densities than conventional capacitors, no chemical or structural change during charge storage, work in extreme temperatures and are very safe, have high cycling stability. Of course, there are certain disadvantages cannot match energy densities of mid level batteries because limited surface area and pore size distribution of conventional electrode materials.

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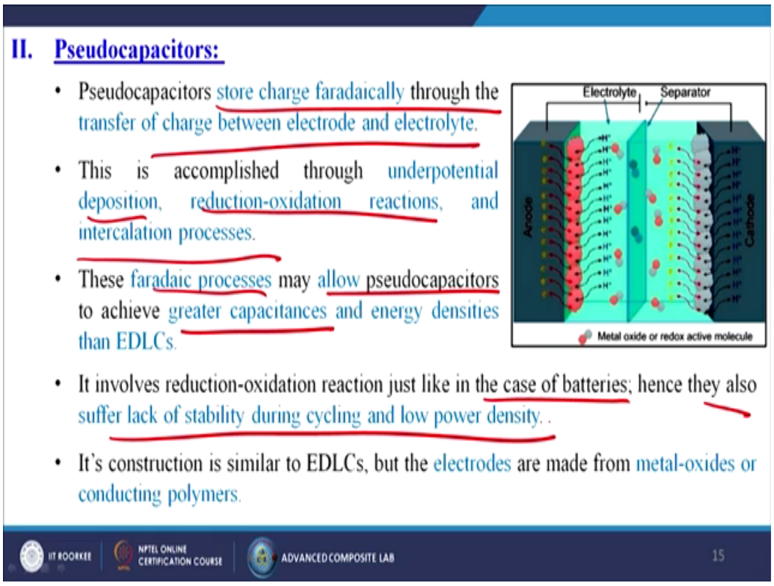

Now, let us discuss about the pseudocapacitors. Pseudocapacitor stores charged faradaically through the transfer of charge between the electrode and the electrolyte. This is accomplished through under potential deposition reduction oxidation reactions, and intercalation process. This faradaic process may allow pseudocapacitors to achieve greater capacitance and energy densities than the EDLCs.

It involves reduction oxidation reaction just like in the case of batteries; hence they also suffer lack of stability during the cycling and low power density. It is constructed in similar to it will EDLCs, but the electrodes are made from metal oxides or maybe the conducting polymers. So, it is not that much of porous like EDLC.

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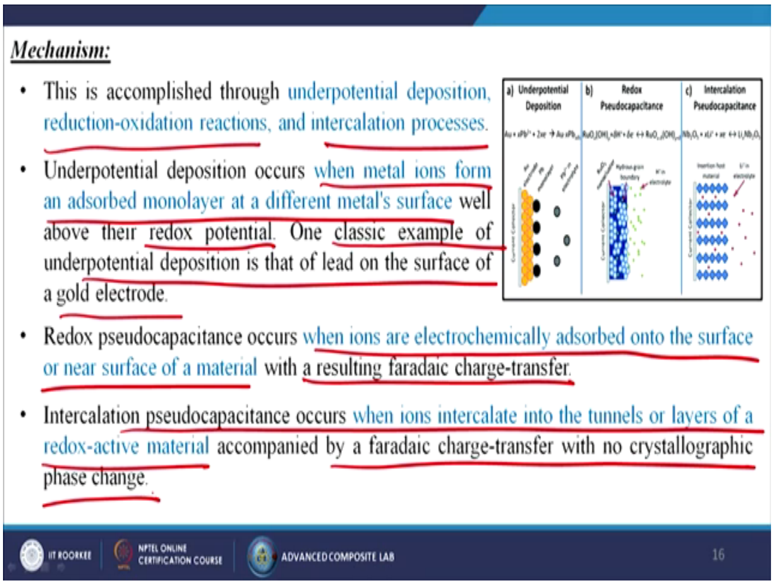

What is the mechanism basically? This is accomplished through under potential depositions, reduction oxidation reactions and the intercalation process. Underpotential deposition occurs when metal ions form and absorbed monolayer at different metal surfaces well above their redox potential. One classic example of underpotential deposition is that of lead on that surface of a gold electrode. Redox pseudocapacitance occurs, when ions are electro chemically adsorbed onto the surface or near surface of a material.

That means the material will simply stay onto the surface of that electrode itself with a resulting faradaic charge transfer. Intercalation pseudocapacitance occur, when ions intercalate into the tunnels or layers of a redox active material accompanied by a faradaic charge transfer with no crystallographic phase change. So, in this particular case under potential deposition is taking place. We are having that current collectors on that, we are having that gold electrode then lead monolayer and then lead 2 plus ion in the electrolyte it is coming towards it.

So, these reaction is taking place, then redox pseudo capacitance. So, how it is current collector we are having the ruthenium dioxide nanocluster, and then hydras grain boundary it is taking place, and h plus ion from the electrolyte it is coming and it is going captured inside it. And for the intercalation pseudocapacitance this reaction is taking place. Simple, the material is acting as a composites over there. So, insertion whole materials, so it is a one kind of doping of the material in this particular case.

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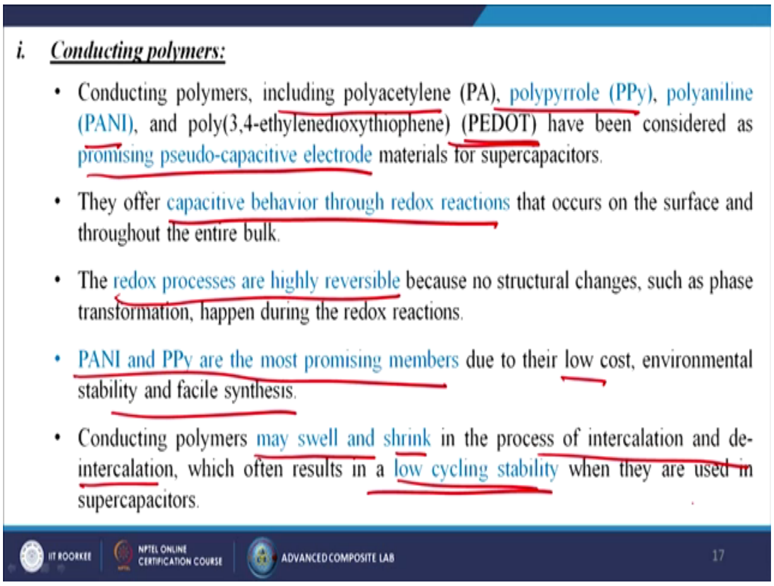

Now, what kind of materials basically we are using, so conducting polymers. Conducting polymers including polyacetylene, polypyrrole, polyaniline and the poly 3, 4 ethylenedioxythiophene, in short basically we are calling it as a PEDOT materials have been considered as promising pseudocapacitive electrode material for super capacitors.

They offer capacitive behavior through redox reactions that occurs on the surface and throughout the entire bulk. The redox processes are highly reversible because no structural changes such as phase transformation happen during the redox reactions. PANI and PPy are the most promising members due to their low cost, environmental stability and facile synthesis. Conducting polymers may swell and shrink in the process of intercalations and de-intercalations, which often results in a low cycling stability when they are used in super capacitors.

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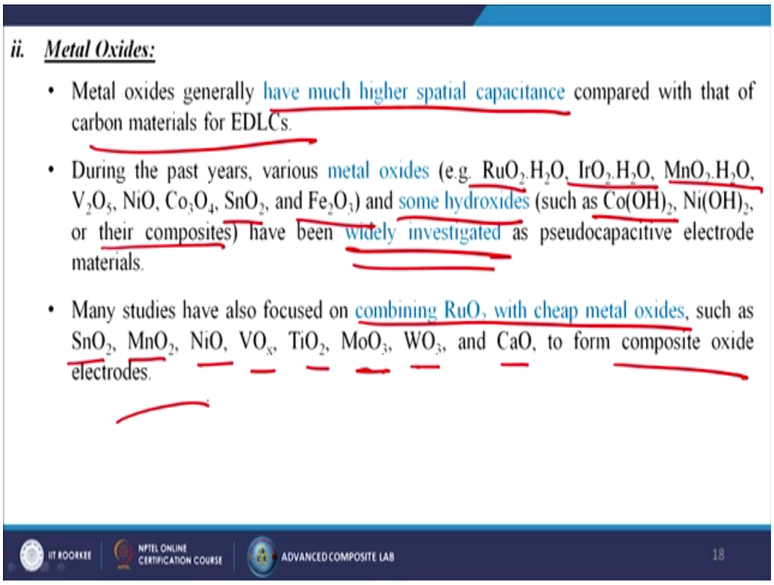

Metal oxides also we are using; metal oxides generally have much higher spatial capacitance compared with that of carbon materials for EDLCs. During the past years various metal oxides like ruthenium oxide H 2 O, IrO 2 H 2 O, MnO 2 H 2 O, V 2 O 5, NiO, Co 3 O 4, SnO 2, oxides Fe 2 O 3, ferrous oxide, some hydroxides such as cobalt hydroxide, nickel hydroxide or their composites have been widely investigated as pseudocapacitive electrode materials. Many studied have also focused on combining the ruthenium oxide with cheap metal oxides such as SnO 2, Mn O 2, NiO 2, VO x, TiO 2, MoO 3, WO 3 and CaO 2 to form composite oxide electrodes.

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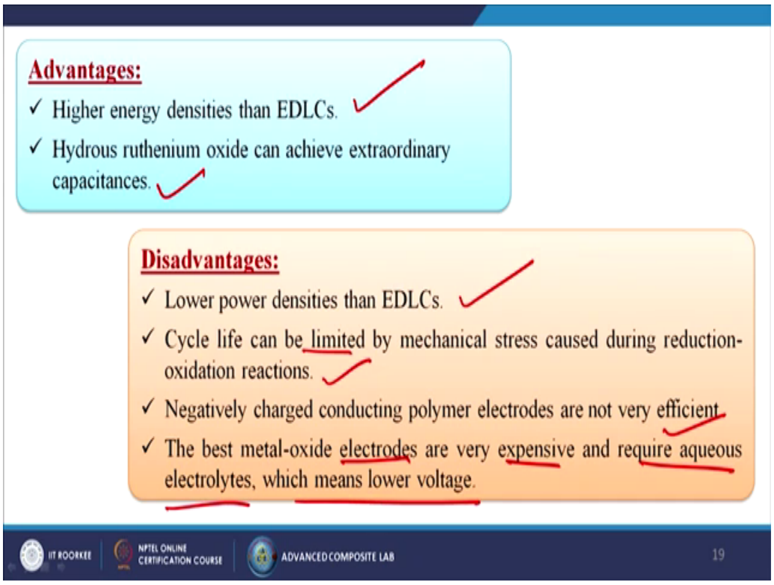

Now, what are the advantages higher energy densities than EDLCs. Hydroxide ruthenium oxides can achieve extraordinarily capacitance, but still people are working on it just to increase more and more. Disadvantages it is having lower power densities than EDLC. Cycle life can be limited by mechanical stress caused during reduction oxidation reaction. Negatively charged conducting polymer electrodes are not very efficient. The best metal oxide electrodes are very expensive and require aqueous electrolytes which means the lower voltage.

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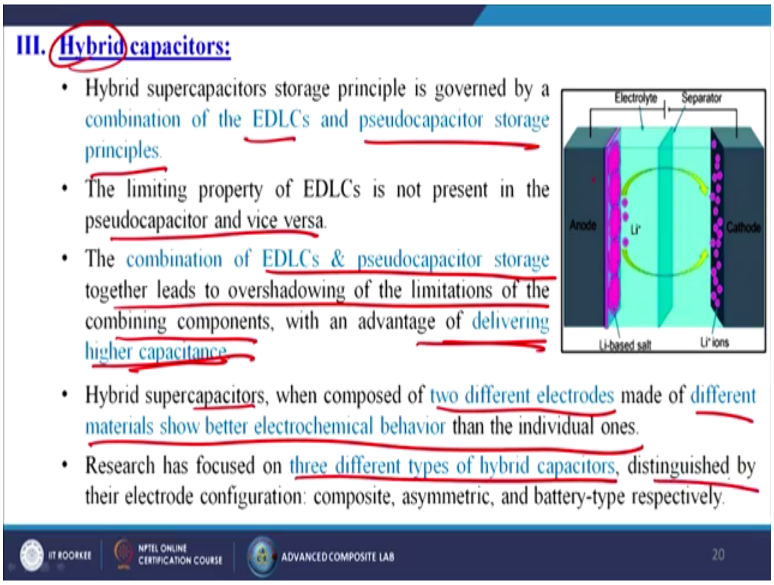

Now, come to the last one that is called the hybrid capacitors. So, hybrid super capacitors storage principle is governed by a combination of EDLCs and the pseudocapacitor storage principle. The limiting property of EDLCs is not present in the pseudocapacitor and the vice versa. So, actually why we have done it? There are certain advantages for the EDLC, and there are certain disadvantages too. Same thing for the pseudo capacitance also some advantages and some disadvantages. Now, what to a scientists are doing they are adding both the mechanisms just to reduce all the disadvantages from there.

The combination of EDLC and pseudocapacitor storage together leads to overshadowing of the limitations of the combining components, with an advantage of delivering higher capacitance. So, that is the motto that is why it is called the hybrid. Hybrid super capacitors, when composed of two different electrodes made of different materials show better electrochemical behavior than the individual, ones. If you remember that in the EDLC case our anode and cathode materials was the same. So, in this particular case what we are doing, we are using that technology, but anode and cathode materials are different. Researchers focused on three different types of hybrid capacitors distinguished by their electrode configurations like composite, asymmetric, and battery type respectively.

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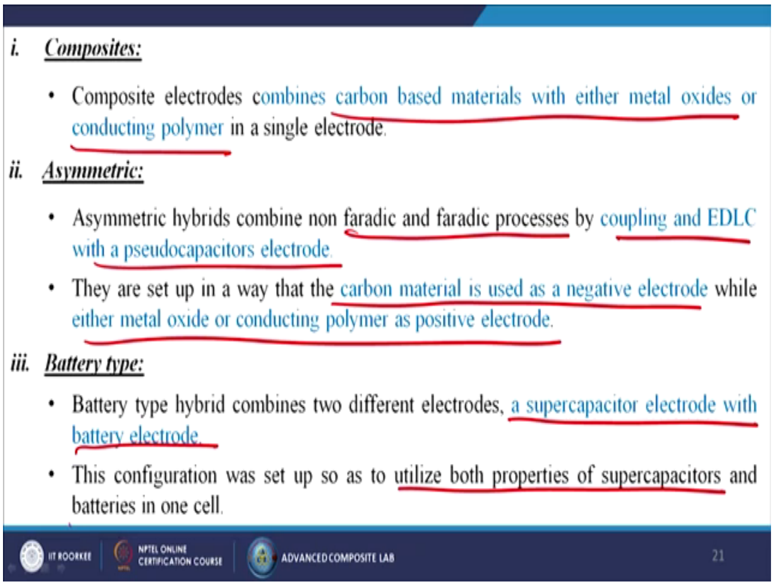

So, what is composites? Composite electrodes combines carbon based materials with either metal oxides or conducting polymer in a single electrode. Asymmetric; asymmetric hybrid combined non faradic and faradic process by coupling and EDLC with a pseudocapacitors electrode. They are set up in a way that the carbon material is used as a negative electrode while either metal oxide or conducting polymer as positive electrode. Battery type; battery type hybrid combines two different electrodes a super capacitor electrode with battery electrode. This configuration was set up, so as to utilize both properties of super capacitors and batteries in one cell.

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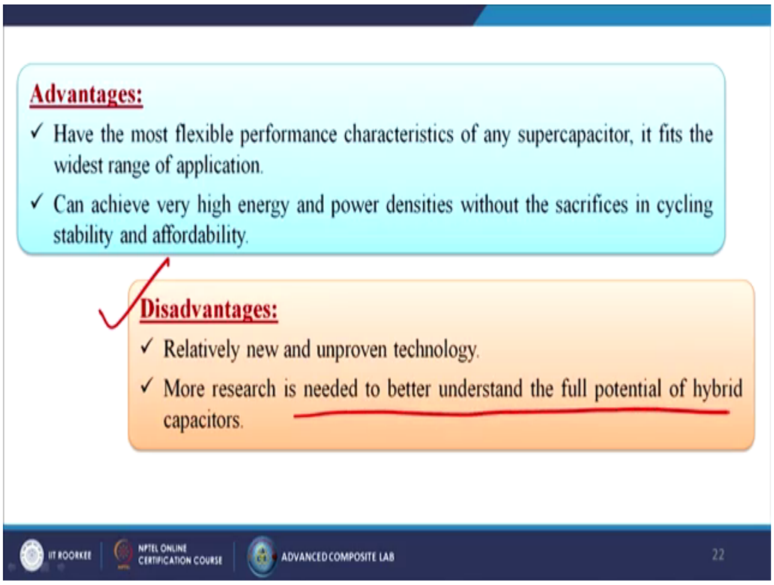

Advantages have the most flexible performance characteristics of any super capacitor, it fits the widest range of applications. Can achieve very high energy and power densities without the sacrifices in cycling stability and affordability. Of course, there are certain disadvantages, relatively new and unproven technology because it is a mixing up of those technologies EDLC and the pseudo capacitance. More research is needed to better understand the full potential of hybrid capacitors.

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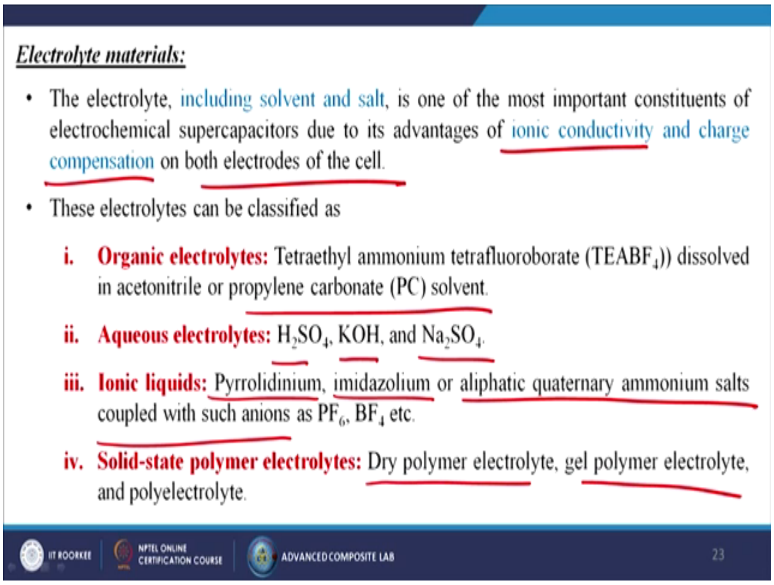

Now, what kind of electrolyte materials basically, we are using? The electrolyte including solvent and salt, is one of the most important constituents of electrochemical super capacitors due to its advantages of ionic conductivity and charge compensation on both electrodes of the cell. So, basically it is a combinations of your electrode as well as the electrolyte material. These electrolytes can be classified as organic electrolytes like tetraethyl ammonium tetrafluorocarbonate TEABF 4 dissolved in acetonitrile or propylene carbonate solvent.

Aqueous electrolyte like sulfuric acid, potassium hydroxide, and the sodium sulfate. Ionic liquids like pyrrolidinium, imidazolium or maybe aliphatic quaternary ammonium salts coupled with such anions as PF 6, BF 4 etcetera. Solid-state polymer electrolytes, dry polymer electrolyte, gel polymer electrolyte, and the polyelectrolyte.

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What are the applications? Basically, nowadays applications are plenty. We have given some important applications like supercapacitor electric bus, to power the note 9 stylus, HD car camcorder, to light LEDs, for IoT, solar super capacitors for wearable sensors.

Now, we have come to the last slide of this particular lecture. So, in summary, we can say that efficient of energy storage devices depends on structure and properties of the component materials and that is also based on two things, one is the electrode, another one is the electrolyte. Super capacitor cells are able to fill the gap between the conventional capacitors and batteries by providing high power performance in a compact design. In super capacitors, due to decrease of distance electrodes, the capacitance become very huge. Many researchers across the globe are working on different metals to improve the performance of super capacitors. Conducting polymers result in a low cycling stability when they are used in super capacitors.

Thank you.