Electrochemical Energy Storage
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Module - 08
Advanced materials and technologies for supercapacitors
Lecture - 39
Electrolytes for Supercapacitors: Aqueous/Organic Liquid Electrolytes/Ionic Liquid Electrolyte/Solid Electrolyte

Welcome to my course Electrochemical Energy Storage, this is module number 8 Advanced materials and technologies for Supercapacitors. This is lecture number 39 where we will be describing the Electrolytes for Supercapacitors which include Aqueous Electrolyte and Organic Electrolyte, Ionic Liquid types of Electrolyte and also Solid Electrolyte.

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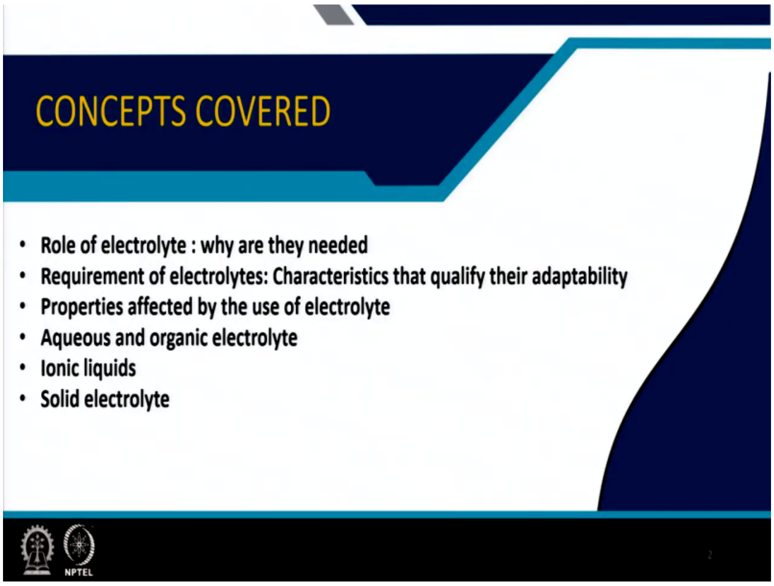

Something similar to the concept I already taught while we describe the battery type of materials. So, first we will talk about the role of electrolyte why they are needed, requirement of the electrolytes the characteristics that qualify their adaptability. So, that will be covered then what are the properties that basically affected and how they are affected by the use of the electrolyte. Then aqueous and organic electrolyte will be described followed by ionic liquids and finally, the solid electrolytes.

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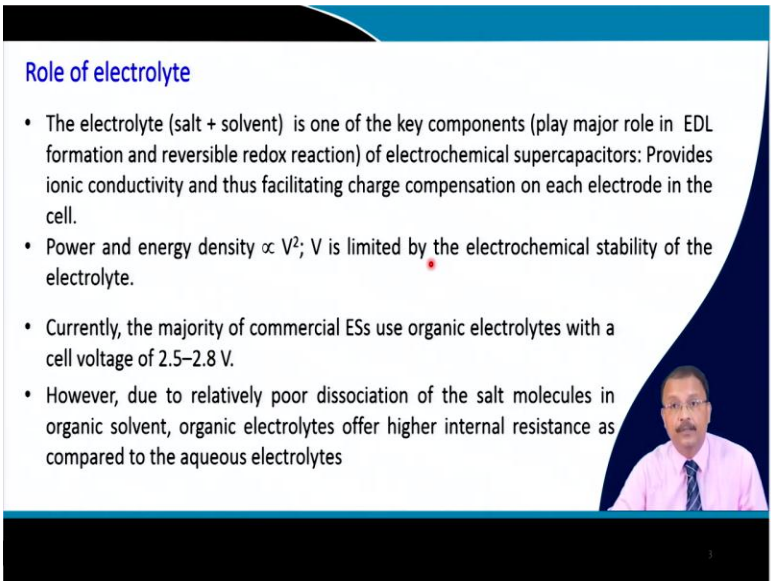

So, electrolyte as you know that is it is having a salt and solvent and it plays a major role for the formation of electric double layer and also reversible redox reaction. So, mostly we will be concentrating on this two types of ultra capacitors and similar electrolyte they are also being used in case of asymmetric supercapacitor and hybrid capacitors which I described in as a part of my last lecture in this module.

So, it provides it should have good ionic conductivity and therefore, it facilitates the charge compensation on each electrode of the electrochemical cell. Power density that is proportional both power and energy density is proportional to voltage that you know. So, the voltage is limited by the electrochemical stability of the electrolyte. So, you cannot un indefinitely increase the voltage while you operate the cell.

So, your electrolyte will decide that what is the applicable voltage range. So, if you consider the commercial electrochemical cells they all use this organic electrolyte and typical cell voltage is about 2.5 to 2.8.

And, there is a problem that dissociation of the salt molecule that is being used along with the solvent in the electrolyte in organic solvent dissociation is relatively poor as compared to the aqueous electrolyte. So, water most of this salt is ready readily dissociated dissolved. So, usually the organic electrolyte they offer relatively higher internal resistance.

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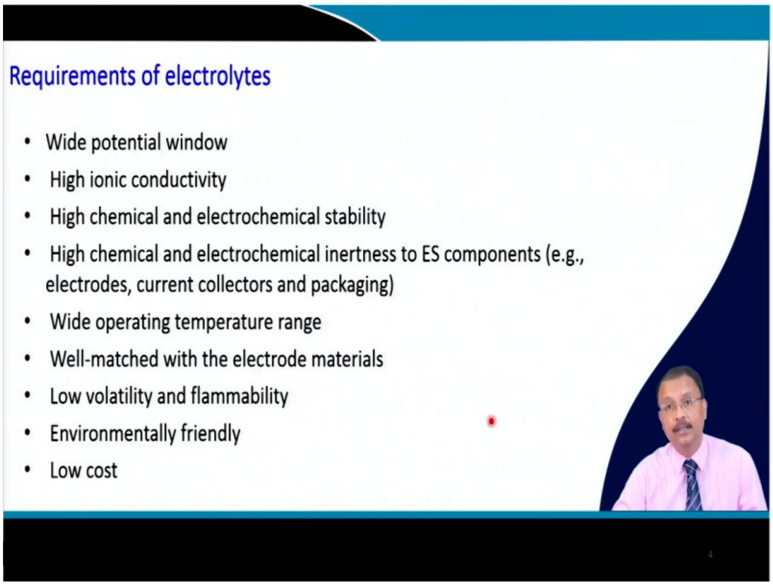

So, as you can understand that we need to have high potential window, so that we can have higher energy density and power density of the cell. Conductivity should be high. Chemical as well as electrochemical stability is required. So, electrochemical stability in aqueous electrolyte you cannot use at higher voltage because the water will get dissociated.

So, organic electrolyte is better in that sense and also they should be inert to all the supercapacitor components that you are talking about the electrode, then current collectors, then all packaging material if it leaks then it should not do harm to the user. So, they should have it should be basically inert to this components.

And, temperature is important we are using the supercapacitor at free I mean in a place where the temperature goes quite low or places like India, where in the summer time it goes as high as 46 – 47 degree Celsius. So, operating temperature they should withstand without sacrificing their properties and they should match well with the electrode materials. They should wet it well. So, that in EDLC type of material it penetrates in the poor volume.

And, flammability should be less because if it catches fire because of some abusive use, then particularly a stack of the supercapacitor they should not catch fire and of course, you will have to dispose it. So, it should be in environmental friendly the material and of course, on top of that the cost should be low.

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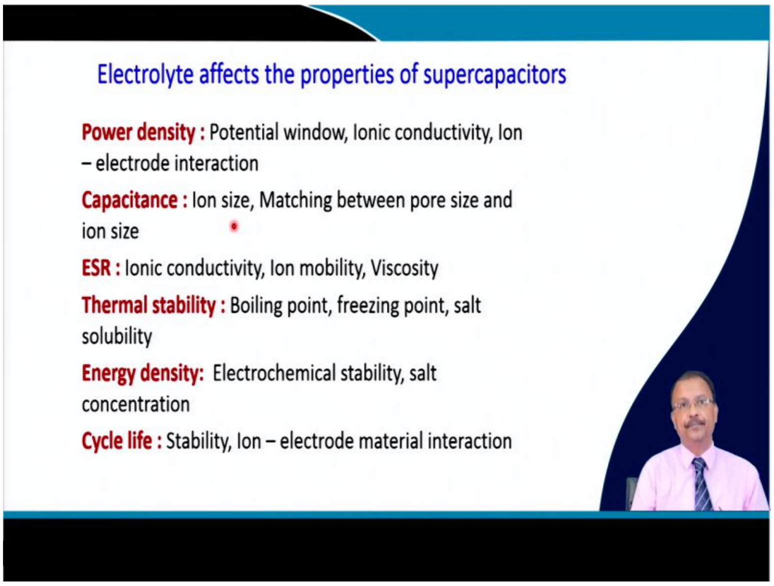

So, if you consider the power density so, from the relations that we all already described the potential window is important ionic conductivity is important and this ion and electrode interaction is important. So, these three things it is coming from the electrolyte.

Capacitance it depends on the ion size particularly in EDLC if the ion size is too big then it adhered, but penetration of the electrolyte that will be problematic and also it will be solvated. So, pore size and ion size this matching is important and this series resistance ionic conductivity, ionic mobility and not only that the viscosity is also important.

If it is too viscous then the ionic conduction will get disturbed and the conductivity and mobility I mean you know the charge mobility and the concentration that decides the conductivity. So, this ESR is an important parameters to be controlled by the electrolyte that you are using.

Thermal stability as I told that the boiling point or the freezing point or the salt solubility in a particular solvent that is decided by the temperature as well. So, the thermal stability should also be high. Energy density is also affected by the use of the electrolyte because the electrochemical stability, the voltage range that you are using your electro electrolyte should not get dissociated.

Salt concentration is also important that what is their saturation level, how much salt you can dissolve in a solvent. Cycle life is also affected by the stability and particularly this ion and electrode material interaction. So, electrolyte also plays a major role.

It is not only the electrode materials that decides the properties of the supercapacitors, but electrolyte also plays a very major role in deciding the electrochemical performance of the ultra capacitors.

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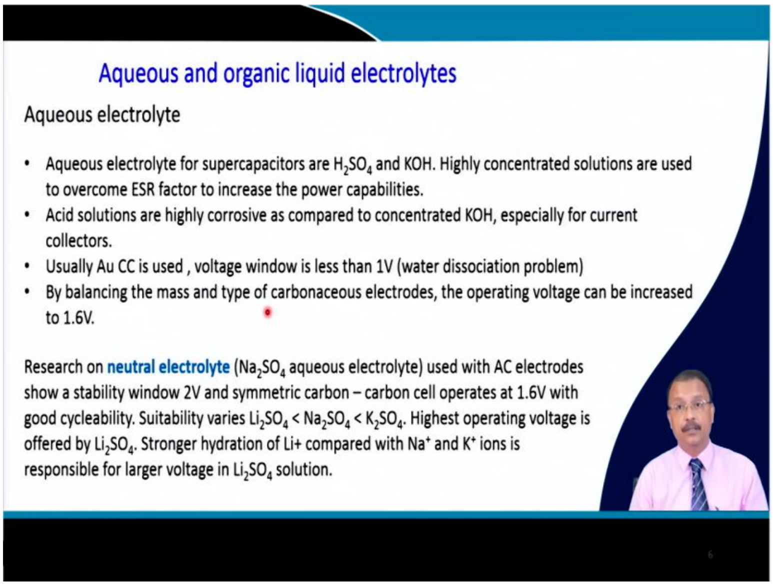

So, first we will talk about the aqueous and then organic liquid electrolytes. So, aqueous electrolyte you know that sometimes people use concentrated sulfuric acid and alkali. So, that to control this resistance factor and thereby the power capabilities of the capacitor increases.

But, as you can understand if you use a metallic component as current collector you know in the battery we already described you need a current collector, you need a composite electrode and that is the separator is dipped into the electrolyte and your positive electrode is there in the other side and everything is packaged together to form the battery something similar construction that also we do for supercapacitors.

So, this current collector particularly they are very; I mean if the electrolyte is very corrosive. So, acid is more corrosive as compared to the alkali for the current collector.

So, one should keep it in mind. So, for this acid and alkali for use sometimes the gold electrode is used as current collector.

So, aqueous electrolyte has another major problem because of the water dissociation you will have to use less than 1 volt. In certain extent you can increase it the balancing the mass and type of carbonaceous electrode, this operating voltage that can be increase to 1.6 volt in case of aqueous electrolyte.

Now, something interesting came up which is called neutral electrolyte where this sodium sulfate this aqueous electrolyte is used. So, this salt is used in water particularly activated carbon types of electrolyte, they usually exhibit much larger potential window especially for symmetric carbon – carbon cell and it operates quite good window is about 2 volt and it operation voltage window is about 1.6 volt cycleability performance also has been reported to be quite good.

Now, one can use this types of sulfate salt lithium sulfate, sodium sulfate, potassium sulfate. So, in terms of this usability so, this will give you a decent idea that what type of salt neutral electrolyte one can use. It has been experimentally verified that the operating voltage lithium sulfate there is more.

So, one can use the capacitor at relatively high voltage and this is due to the fact that hydration of the lithium ion is stronger as compared to; because as I have shown you that this once it dissociates the salt then they are solvated. And, this stronger hydration of lithium ion with respect to sodium and potassium and that is explained to be responsible for larger voltage window in lithium sulfate solution. So, these salts are also used as neutral electrolyte.

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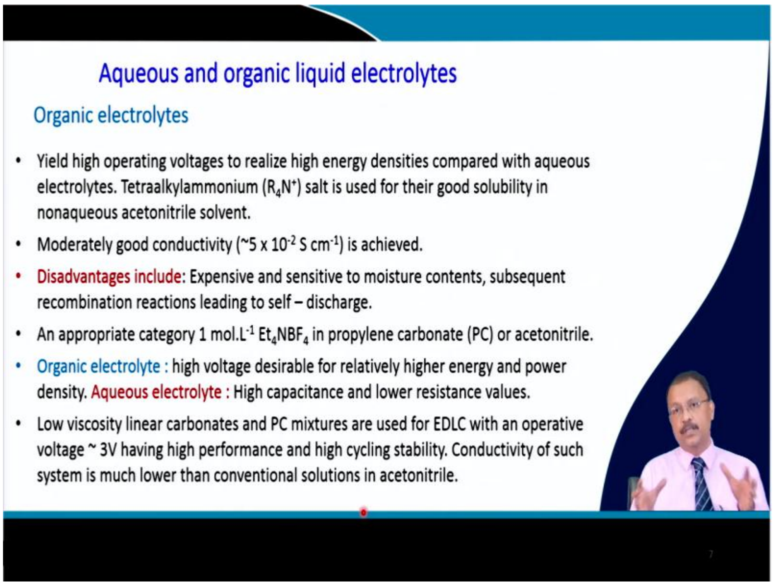

Now, in case of organic electrolyte certainly will get the operating voltage as you know that it is much higher as compared to aqueous electrolyte. So, it high energy density is achievable if you use organic electrolyte. So, this is very common tetra alkyl ammonium.

So, this is the alkyl group and ammonium group is also there. So, that type of salt that is usually they have good solubility in a organic type of acetonitrile solvent. So, that combination is used in most of the cases as you can see the conductivity is reasonably good 10 raised to minus 2 Siemens per centimeter.

But they have disadvantage because this is quite expensive and also it is moisture sensitive and sometimes the recombination reaction takes place. So, if the charges are recombined somehow. So, that will lead to the self discharge. So, usually you know that 1 mole per liter this concentration this ethyl NBF 4 that is used in propylene carbonate you know that this is a solvent or acetonitrile is also used.

So, this kind of organic electrolyte with this salt is quite commonly used for the supercapacitor. And in case of organic electrolyte as you already I have told several times that high voltage is desirable for both high power and energy density. Aqueous electrolyte is a trouble problem it can give you better capacitance because of the salt dissociation is relatively better as compared to the salt dissolve in organic electrolyte.

So, and also aqueous electrolyte offers lower resistance values, but the voltage range you cannot increase. So, plus minus advantage and disadvantage both we have for these two types of solvents. Relatively viscosity is also important as I already mentioned. So, linear carbonates and if you use it with propylene carbonate, I have already talked about this solvent in the earlier part. So, I am not going into details what is the linear one, what is the cyclic one you already know it.

So, usually they are used for EDLC and that operating voltage is about 3 volt and cycleability and performance is far better and conductivity of such system that is much lower than the conventional solutions in acetontrile.

So, there is a combination of the solvent and salt that basically govern the ionic conductivity of this electrolyte and also it is temperature dependent and viscosity is also another factor. So, all these factors actually affect the performance of the electrolyte and thereby the performance of the ultra capacitors.

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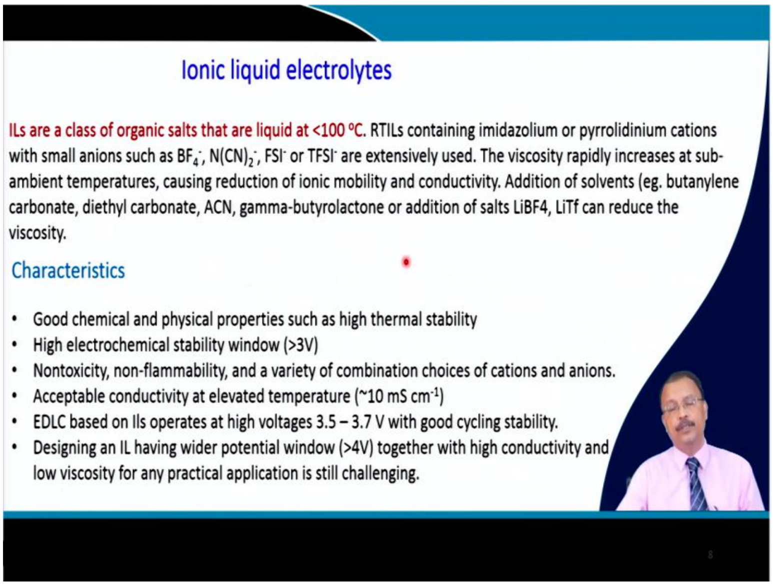

Ionic liquid already it is introduced earlier and this is you know that it is a class of organic salts that is at room temperature it is liquid or less than 100 degree Celsius liquid. So, imidazolium or pyrrolidinium cations with small anion like BF 4 or NC 2 or FSI or TFSI, they are actually used as the ionic liquid.

Now, viscosity is one problem one once you reduce the temperature the viscosity is abruptly increases and that eventually it will reduce the ionic mobility and thereby conductivity also.

So, the solvent like butanyl butanylene carbonate or diethyl carbonate ACN or gamma butyro butyrolactone this kind of additives addition to this type of salt like L i B F 4 or L i T f that reduces the viscosity. So, there are lot of things people do to reduce the viscosity to increase the ionic mobility, but ionic liquid is having a good chemical or physical properties and the thermal stability is excellent.

So, that is one thing electrochemical stability window is also equivalent or better than your organic electrolyte, they are non-toxic as I said it is non-flammable also. Conductivity is a bit poor particularly at room temperature if you go to high temperature conductivity is reasonably good, but 10 millisecond per centimeter is a reasonable number, when you use it with EDLC this ionic liquid operates at a voltage 3.5 to 3.7. So, this voltage window is quite good, stability is also quite good.

So, more than 4 volt if you can design it together with high conductivity and low viscosity particularly at lower temperature than the ambient temperature that is still challenging. So, why I am saying that because this ionic liquid if you want to use with the battery supercapacitor hybrid which I described earlier. So, battery material if you introduce then the voltage will be certainly more than 3 volt.

So, you need an electrolyte particularly if you use the 5 volt cathode, then you do need it to increase the potential window further. So, that is quite challenging because first of all their viscosity is relatively higher once you go to low temperature and the mobility also is affected by the viscosity and maintaining this higher conductivity even at room temperature that is also challenging.

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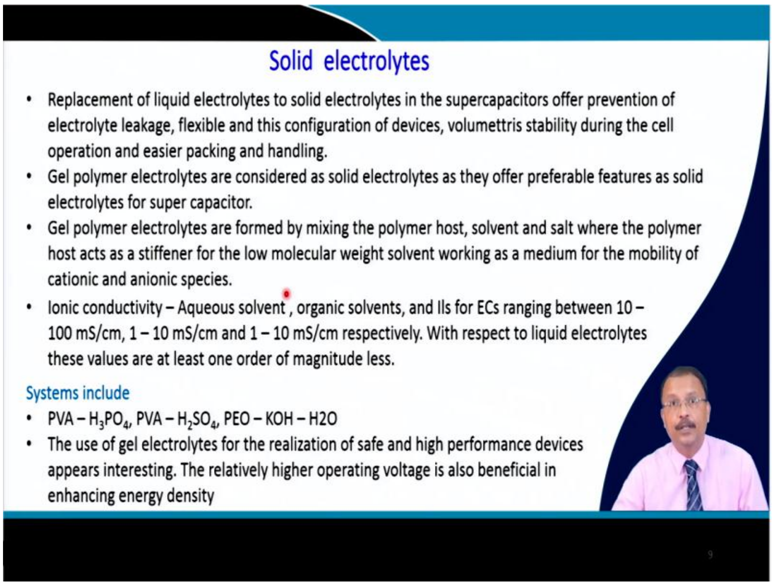

Now, people also use solid state electrolytes. So, if you completely liquid electrolyte if you eliminate it then the leakage problem will be gone and also nowadays you know the flexible power source is important. So, there with the liquid it is indeed challenging. So, people are using this gel polymer which are flexible and volume is also stable during cell operation and packaging handling is relatively there is no problem with leakage of the problem like that.

So, gel polymer is commonly used. So, that is considered as a solid electrolyte and this is formed by mixing a polymer host, then you need a solvent and salt where the polymer host will act as a stiffener for lower molecular weight solvent and working as a medium for the mobility of the cation and anion species. So, it is in true sense it is not really a solid electrolyte, but it is a gel polymer electrolyte.

So, lithium polymer battery also they use this kind of gel polymer electrolyte. So, ionic conductivity if you compare with aqueous solvent and organic solvent and ionic liquids so, the range usually from 10 to 100 millisiemens per centimeter for aqueous and for this organic solvent and this gel polymer electrolyte 1 to 10 millisiemens per centimeter is quite common.

So, if you compare it with the liquid electrolyte this values are reasonably less. So, still you need to increase the ionic conductivity. So, this is a common system PVA the polymer part with H 3 PO 4 or with H 2 SO 4 or water based alkali solution and PEO.

So, this gel electrolyte is safe and this is high performance device this seems to be inter interesting if the conductivity can further be increased operating voltage is reasonably high and that is also beneficial for increasing the energy density. So, solid electrolyte is a quite a good choice.

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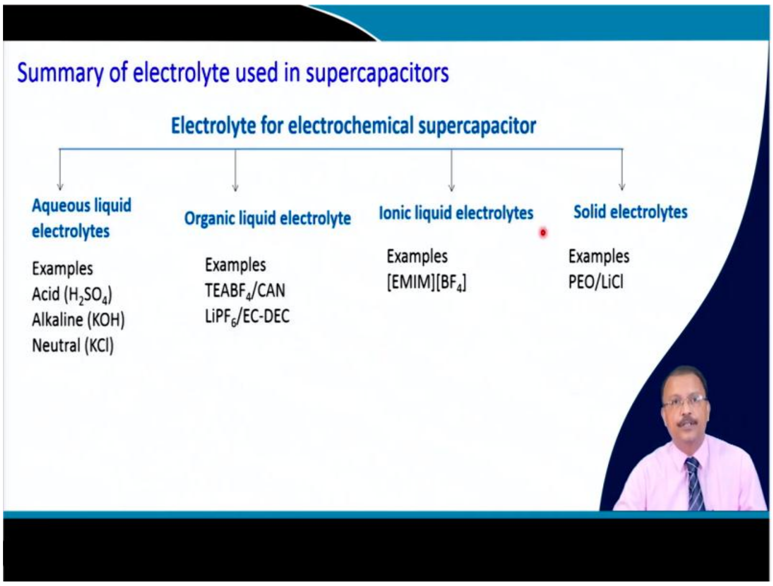

So, if I summarize it then electrolyte for this electrochemical capacity supercapacitors as you can see aqueous base, then organic liquid electrolyte base ionic liquid electrolyte base and solid electrolyte base this four are operative for the commercial supercapacitors.

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So, the same study material is used I mean to read it there and also you can have a look of this references and which this reference for example, is quite informative and this is a nicely described the battery and then fuel cell supercapacitors along with the book by Conway it is quite interesting and informative also. And, also in our book chapter which recently published you can also look at it.

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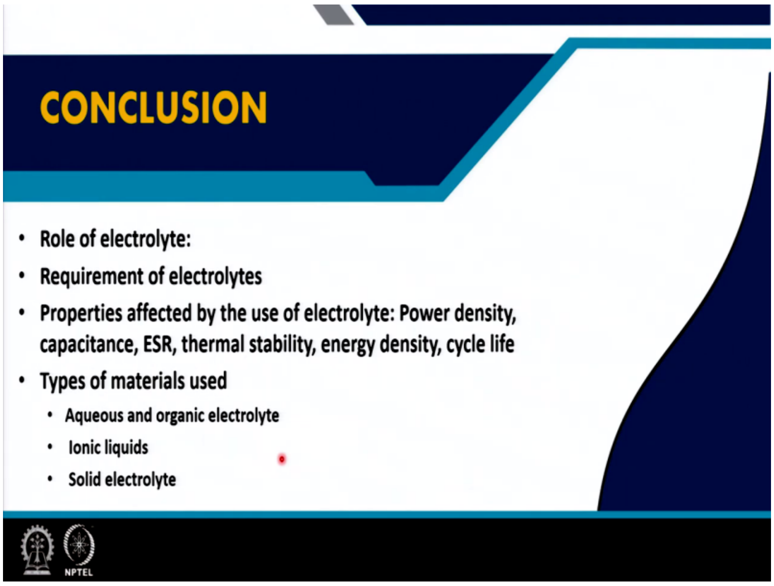

So, in this particular lecture we talked about the role of the electrolyte and what are the requirements of the electrolyte for the supercapacitors and properties that are affected by the electrolyte like power density, capacitance, then series resistance, then thermal stability, energy density, etcetera. These are basically affected by the use of the electrolyte. So, it is not all about the electrode, but the electrolyte also plays a major role in deciding the electro chemical performance of the ultra capacitors.

And, the type of material that is used their mostly it can be categorized as aqueous or organic electrolyte based on the solvent that it uses. Then ionic liquids they are also being researched commercially, I do not think that they have been used in commercial supercapacitors. And, then finally, solid electrolyte although it is a gel polymer electrolyte, but we still term is a solid electrolyte which is quite effective for designing the flexible supercapacitors in near future.

Thank you for your interest.