Physics of Renewable Energy Systems
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Lecture 28
Electrolytes and Seperators for Li-Batteries

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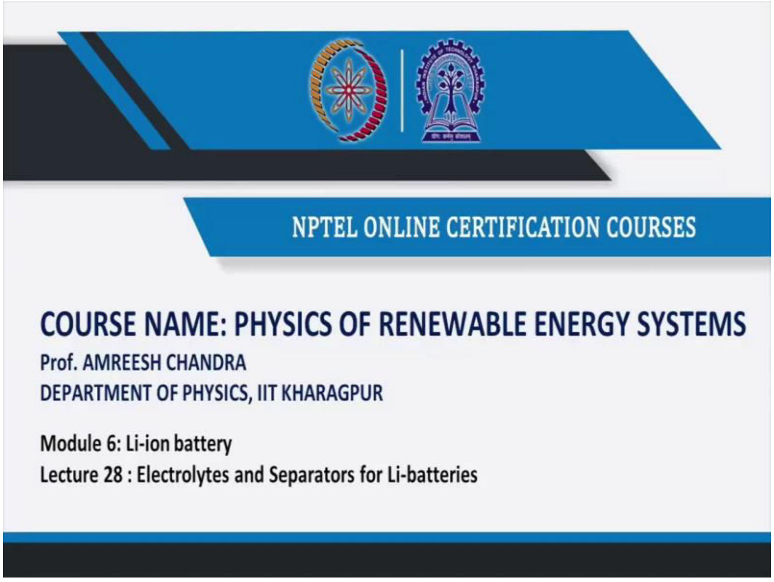

Welcomes again! Let us start this final lecture of this week and also the lecture which will discuss about the remaining components, which are used to fabricate the lithium-ion batteries. In the previous two lectures I talked to you about the cathode materials, the anode materials, what is the importance of various parameters that are used to characterize or explain those materials, how do you obtain those materials and we are also giving you a hint about the different characterization techniques or electrochemical measurements which are performed before these materials become important.

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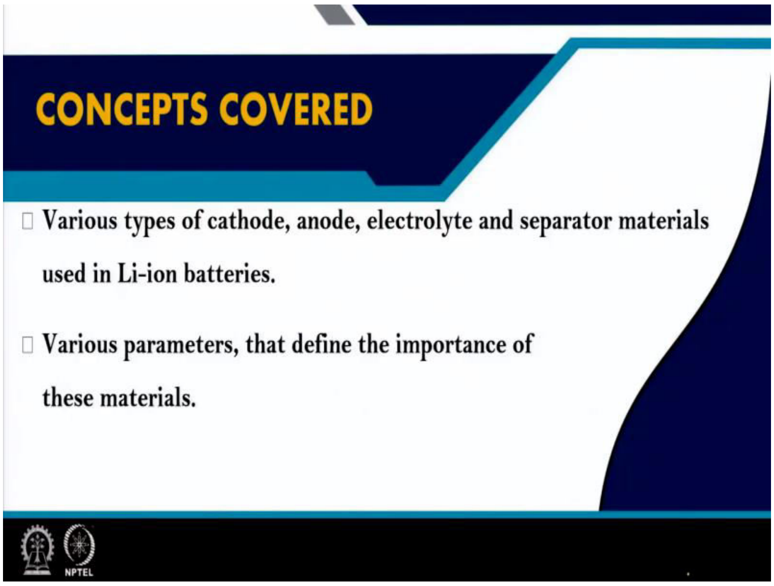

And in today's lecture we will be discussing about the electrolyte and separator materials, which are actually going to decide the performance of lithium-ion batteries along with cathode and anode, and again just like the previous two slides there are different parameters that are used to define the importance of these materials.

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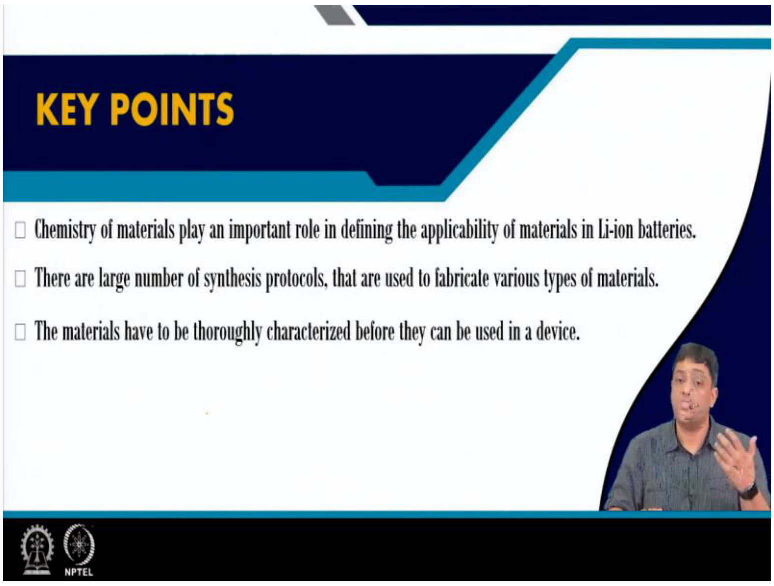

I am keeping those key points very similar to what I had in the previous two lectures, because when I talk to you about the materials aspect the key points which you will take back are similar. What are those? You must have control over the chemistry of materials, you will have large number of synthesis protocols which can be used to obtain materials, but you should choose the optimal synthesis protocol, which will give you the desired material.

And once you have obtained a material you just cannot use it directly in a device. It must be thoroughly characterized so as to understand its physical properties, its chemical properties or even its electrochemical performance then only it will become useful for any device.

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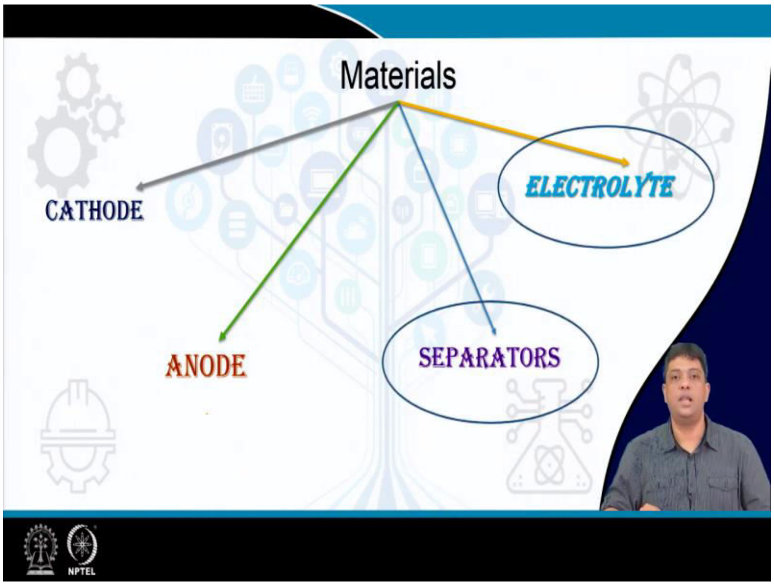

So, we have finished our discussions on cathode and anode materials in the previous two lectures and in today's lecture let us focus on separators and electrolytes.

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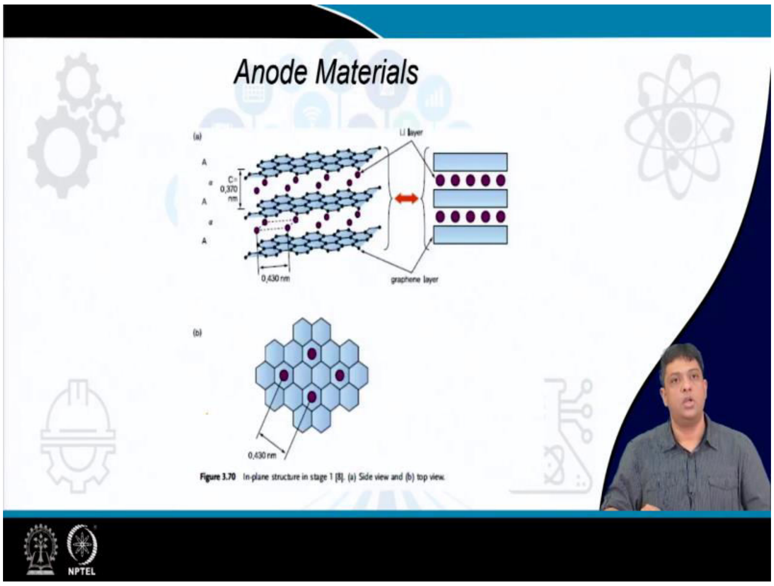

We have discussed cathode and anode both.

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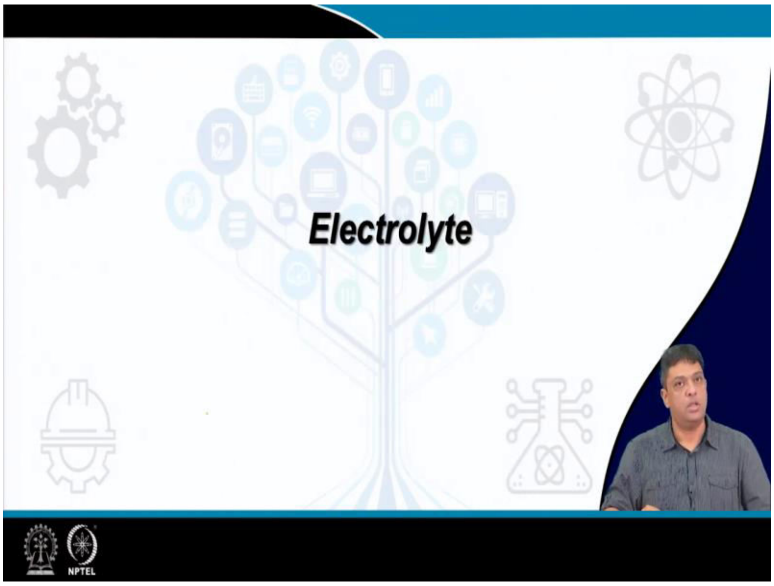

Let us start with our discussion on electrolyte.

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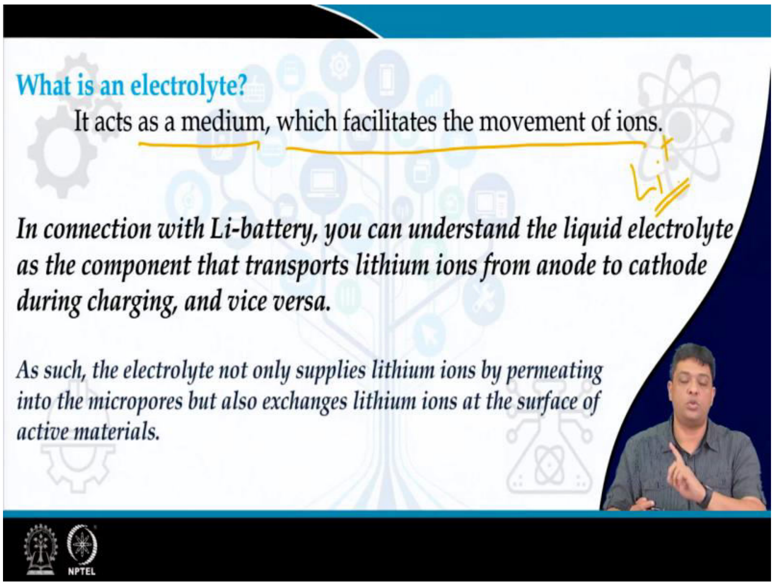

What is an electrolyte? As I mentioned in the discussions right from the first lecture of this week, what are you doing? You are having a cathode and an anode, you have a separator in the middle which separates the cathode and the anode. While ensuring the flow of ion across it but does not allow the electrons to flow across it. Hence, the electrons have to move through the outer circuit.

But the flow of lithium-ion from the cathode to the anode side is done using an electrolyte which is acting as the medium to transfer the lithium from cathode to anode during charging, and during discharging the reverse happens. What happens during reverse? Lithium goes from anode to cathode and electron goes to the external load.

What are the anode materials which we have used and discussed do you remember? Yes, the carbon based materials. What are the cathode materials we have discussed? The lithium cobalt oxide or lithium manganese oxides or lithium manganese nickel oxides or we have also indicated the lithium-ion phosphates.

So, various types of layered structures, spinel structures or polyanionic structures. Hence, for our discussion on lithium-ion batteries we would be describing an electrolyte as a medium which facilitates the movement of ions. What types of ions are we talking about various types of ions? No, we are talking about the lithium-ion so movement of lithium-ion from one electrode to the electrode.

As such the electrolyte not only supplies lithium-ions by permeating into the micro pores, but also exchanges lithium-ions at the surface of the active material. As we saw when we were finishing our discussion on the anode that you have pores in the nanostructures.

The lithium will enter these vacant sites and gets stored that will improve the storage capacity and increase the overall capacity of the device and also you will have adsorption of the lithium-ion on the surface of the anode material. And that is what is done by the transfer of lithium-ion from cathode to anode using electrolyte as a medium.

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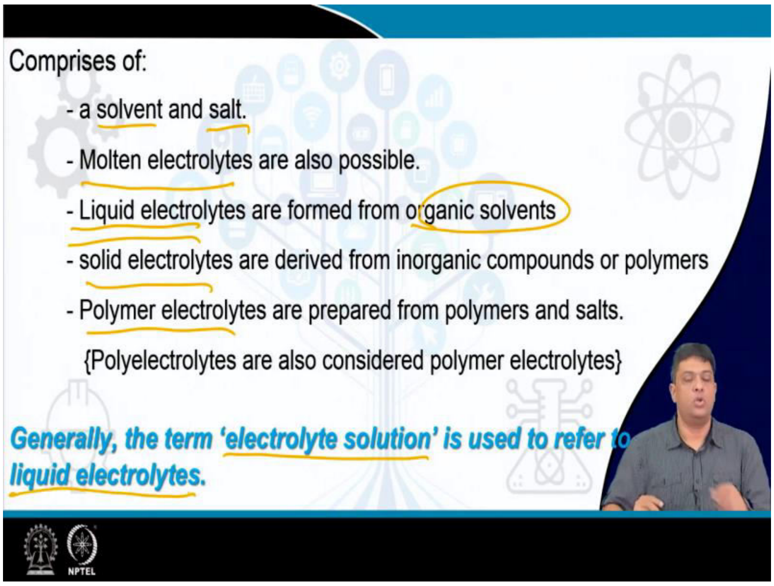

Hence, an electrolyte comprises of a solvent and a salt. Sometimes use of molten electrolytes are also possible. You have liquid electrolytes which are formed using organic solvents. In addition there are are various electrolytes such as solid electrolytes or polymer electrolytes which have come to the forefront over the last few decades, but when I mention the term electrolyte solution we will be mostly using it with reference to liquid electrolytes.

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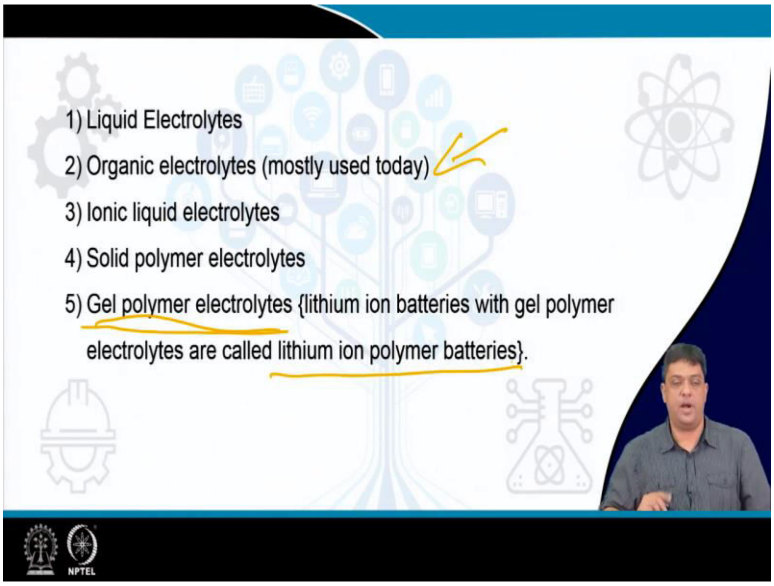

So, there are various types of electrolytes which are used and as of today in a commercial battery, which is available for normal use and application, most of the batteries have organic electrolytes. Each of them have their own advantages and disadvantages, some may be thermally stable or more stable than the other, but their ionic conductivity values may be much lower. Some may give you a higher voltage window to operate without getting dissociated, but others may actually give you more stability and low toxicity and that is where the process of optimization comes into picture.

Process which will decide what is the voltage window you can operate? What is the kind of lithium transfer number you can have? So cation transfer number which I will mention bit later. So these are various terms which are used to understand the importance and the important parameters associated with different types of electrolytes. For example, if you are using gel polymer electrolytes then these kinds of batteries are called as lithium-ion polymer batteries.

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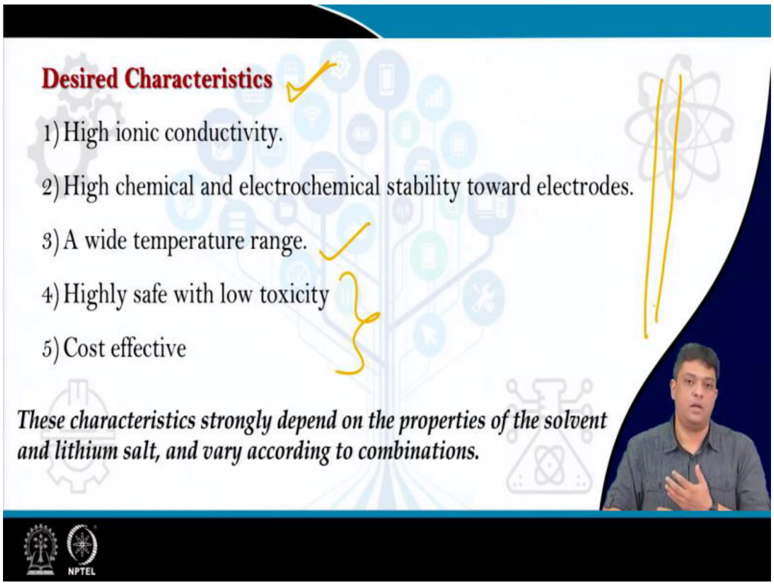

If I write the same things which I, what I said just now then the desired characteristics from the electrolytes would be high ionic conductivity. Ionic conductivity, which type of ion more, so it should have high lithium-ion conductivity. Now they should be chemically and electrochemically stable towards electrodes, what do we mean, should the electrolytes interact with the electrode surfaces and undergo chemical or electrochemical reactions.

If that happens will you have the electrolyte in the form you want it? You wanted it just as a medium which is transferring the lithium-ion if it itself start taking part in chemical reactions then everything falls apart. Hence, you should have electrolytes which have their own electrochemical stability and chemical stability which is very high in terms of reaction towards electrodes.

They should be able to operate over a wide temperature range. For example, suppose you take your mobile phone to Kashmir in winters where the temperatures may be minus 15 degrees or so or you take it to a desert region in Rajasthan during summers where the temperatures may be around 50 degrees or slightly higher. What would you like?

You would like that the phone is working in both the condition. Hence, you should have the battery which is working in both this condition and in the wide temperature range. Therefore, similar to cathode anode material requirement your electrolyte should also have a wide temperature range, should be highly safe and have low toxicity, along with that it should be cost effective.

And all these properties which are mentioned in this slide strongly depend on the properties of the solvent and the lithium salt which is used and they can vary according to combinations. What type of solvent you use, which type of lithium salt, so various solvent solute combinations are investigated and you can obtain different characteristics.

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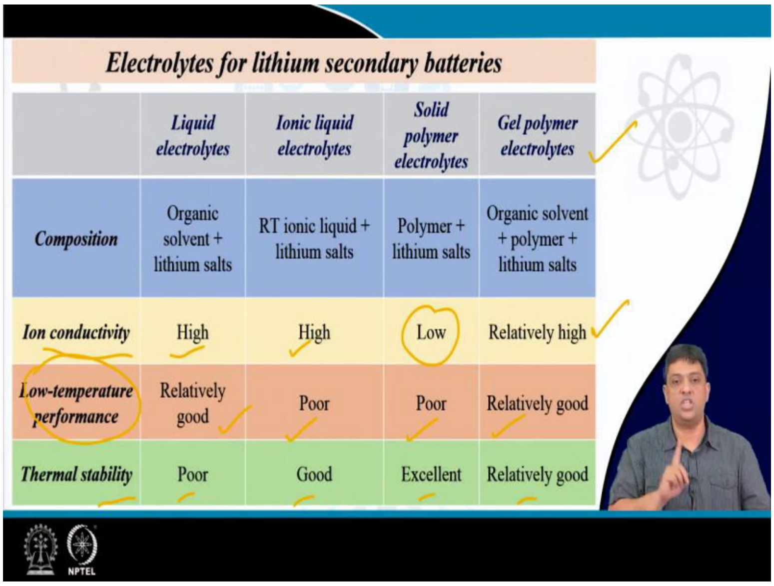

For example, you will see that if you take liquid electrolytes, their ionic conductivities are high similar to the ionic liquid based electrolytes, compared to the solid polymer electrolytes, but in comparison to these two you will find that gel polymer electrolytes also have relatively high ionic conductivity.

If you see low temperature performance, low temperature because mostly if you take aqueous base materials then what is happening you may end up getting a condition with the electrolyte itself freezes and if the electrolyte freezes your battery will not be performing. So you have to characterize them in terms of low temperature performance and then you can have different values and similar to temperature or thermal stability.

So, depending upon the range of application depending upon your end user specifications you will choose the right electrolyte that has to go in the device that is lithium-ion battery and an electrolyte which is going to combine with anode and cathode to give you the desired energy or power density.

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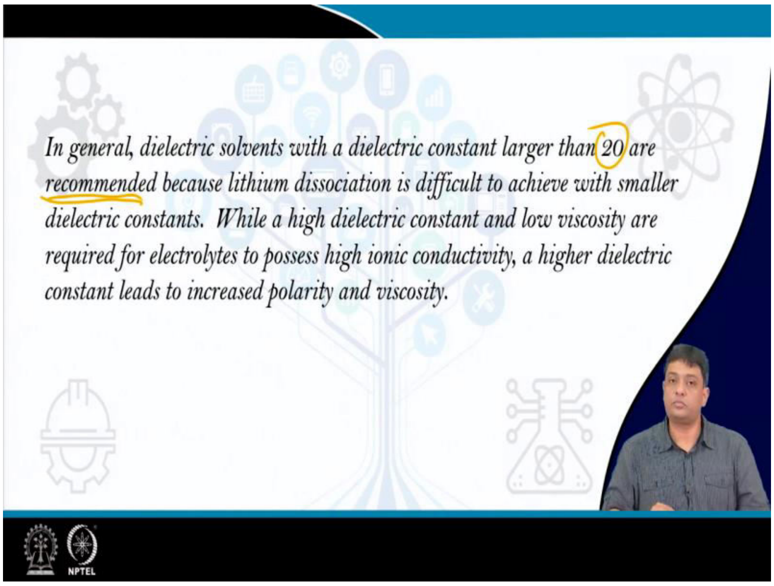

It has been seen that the dielectric solvents with dielectric constant more than twenty, mostly give you the desired performance. Why, because lithium dissociation is difficult to achieve with smaller dielectric constants. So lithium dissociation that means if you have higher dielectric constant then you are actually driving the electric field out and then if that is happening that allows the dissociation of ions, if that that is not happening then you do not have the dissociation is not possible.

So, you can even find electrolytes where you have dispersed ferroelectric ceramics to obtain the improved dielectric constant of the electrolyte dispersoid combination and then that leads to higher ionic conductivity and that improves the performance of the battery itself.

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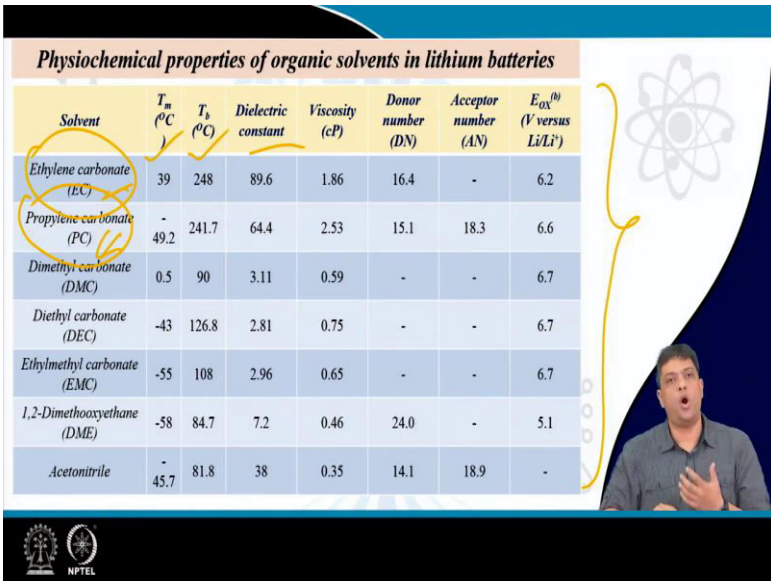

Solvent	T_m (^0C)	T_b (^0C)	Dielectric constant	Viscosity (cP)	Donor number (DN)	Acceptor number (AN)	$E_{OX}^{(b)}$ (V versus Li/Li^+)
Ethylene carbonate (EC)	39	248	89.6	1.86	16.4	-	6.2
Propylene carbonate (PC)	-49.2	241.7	64.4	2.53	15.1	18.3	6.6
Dimethyl carbonate (DMC)	0.5	90	3.11	0.59	-	-	6.7
Diethyl carbonate (DEC)	-43	126.8	2.81	0.75	-	-	6.7
Ethylmethyl carbonate (EMC)	-55	108	2.96	0.65	-	-	6.7
1,2-Dimethooxyethane (DME)	-58	84.7	7.2	0.46	24.0	-	5.1
Acetonitrile	-45.7	81.8	38	0.35	14.1	18.9	-

As I said you can see that if you look into various electrolytes or solvent salt combinations which are used then you have different solvents which can work in different range they have varying dielectric constant and other parameters are also mentioned. So depending upon your end user specification you will choose the solvent which is going to be used in lithium-ion batteries.

And mostly EC PC that is Ethylene Carbonate or Propylene Carbonate based organic solvents are used and sometimes the combination of EC and PC are used to obtain the desired parameters.

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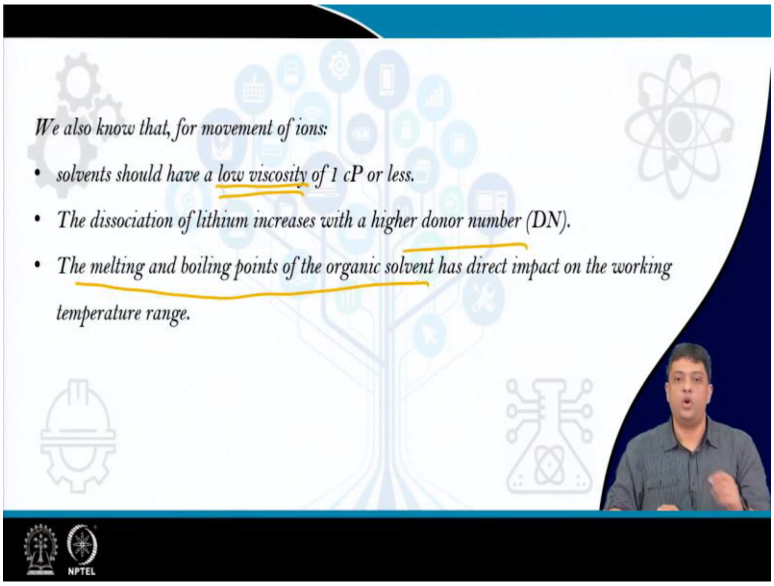

Now, we also by now understand very clearly that for the movement of ions what should happen? That you should have flow of the liquid or ions should be able to flow and if that is happening then what am I saying that these solvents must have low viscosity.

The dissociation of lithium-ion should be such that you obtain the desired donor number and if you change the temperature then you are going to impact the operation of the electrolytes directly. So the melting points in the organic of this organic solvent or the boiling point of the organic solvent also become quite critical when you are going to choose the electrolyte.

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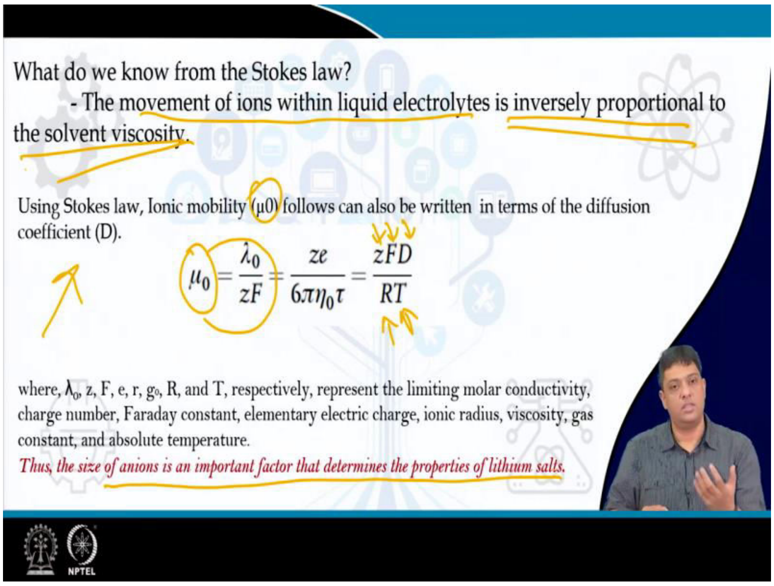

From Stoke's law, we know that the movement of ions within the liquid electrolyte is inversely proportional to the viscosity and using Stoke's law we can write the ionic mobility in terms of diffusion coefficient and you can obtain mu 0 is equal to z F into D by RT. Where you have z F R T as the molar conductivity, the charge number, F is the Faraday constant, then you have your R as the gas constant and T as the absolute temperature.

You can also write the whole equation in terms of the molar conductivity then that is written as mu 0 is equal to lambda 0 by z F where z is your charge number as I said earlier and F is the Faraday's constant. So using the Stoke's law you can correlate the movement of ions with the viscosity of the solvent or viscosity can then be expressed in terms of diffusion coefficients and you will get a relationship between ionic mobility and diffusion coefficient.

Diffusion of what it is the size of the ions or the size of the anions is an important factor that determines the properties of the lithium salts why because you are talking about the diffusion process bigger is the size less is the diffusion and so by changing the size of the anion you will have varying diffusion coefficient.

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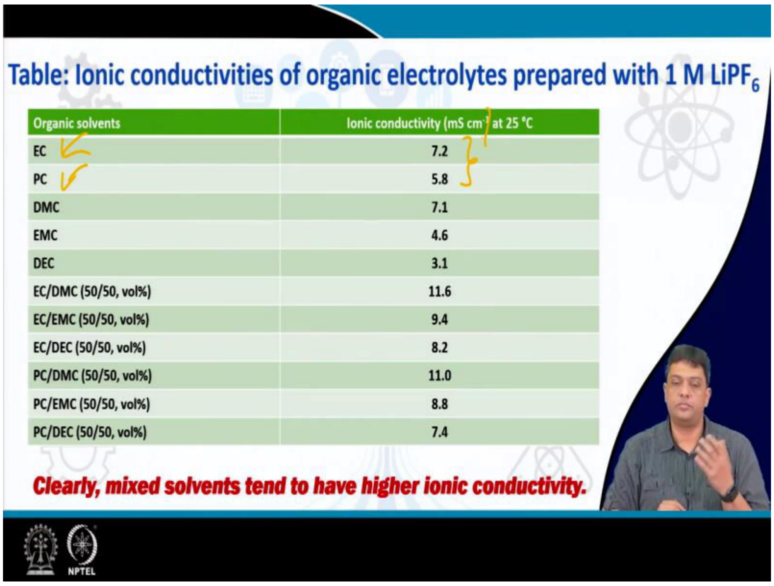

And you can see that EC PC have reasonably high ionic conductivity at 25 degrees that is EC has a ionic conductivity of lets say 7.2 millisiemens per centimeter, PC also has reasonably high, but sometimes combination of EC PC is used in combination with 1 molar lithium hexa phosphate, so then you can get the desired performance.

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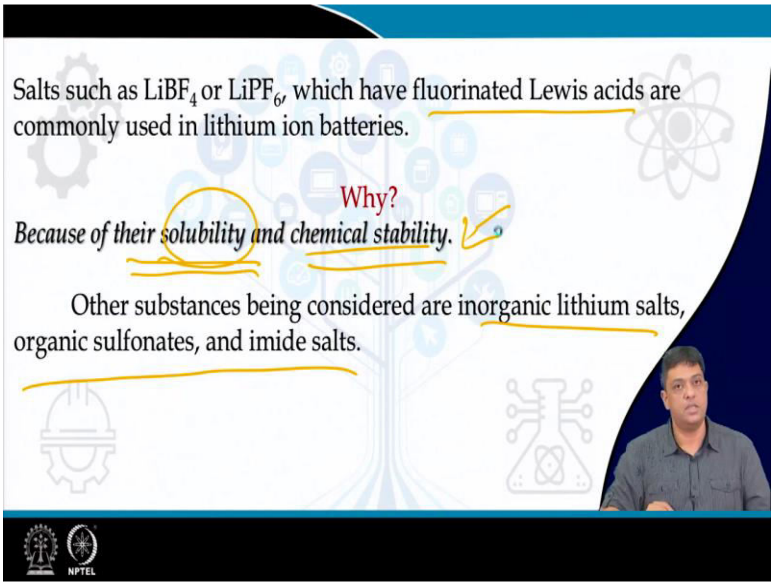

So, as I said you can use salt like $LiBF_4$ or $LiBF_6$ which are the fluorinated Lewis acids, but why will you use it? The main reason which is driving their massive using these batteries is their solubility and chemical stability, but nowadays different people are also proposing the use of inorganic lithium salts or organic sulfonates or imide based salts but most important you should ensure that their solubility is high and they are chemically stable.

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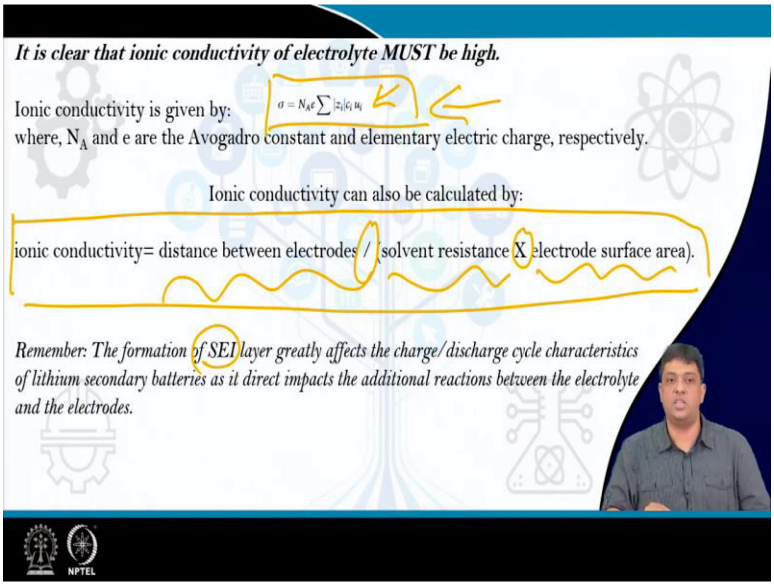

So, it is clear that the ionic conductivity must be high and ionic conductivity is given as sigma that is equal to NA into e, the summation of the zi into ci into mu i. Now you have seen that you are talking about the Avogadros number, the total charge which is available and also the mobility, so ionic conductivity is obtained using the relation mentioned.

Ionic conductivity can also be measured by the relation that it is equal to distance between the electrodes divided by the solvent resistance multiplied by electrode surface area. So distance between the electrodes divided by solvent resistance into electrode surface area, but please remember that where electrolyte is interacting with the electrode surface you have the formation of solid electrolyte interface.

And the formation of the SEI layer greatly affects the charge discharge cycle characteristics and they can impact the characteristics because if they are allowing any additional reactions between the electrolyte and the electrode then the overall performance degrades and hence it is absolutely essential that the electrolytes are chemically stable such that they do not drive any additional reactions at the SEI layer.

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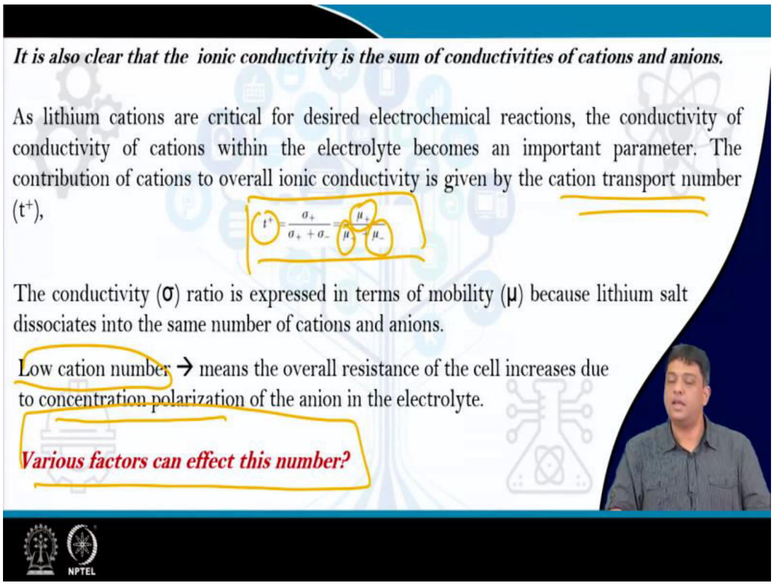

Now, the contribution of the cations to the overall ionic conductivity is given by the cation transport number given by t plus, which can be written in terms of the mobility or conductivity. And this is given as transference number t plus is equal to mu plus divided by mu plus plus mu minus.

So, you see what happens during the charging or the discharging process and then you see what the cation transport number is. Low cation number means that the overall resistance of the cell increase during the process of charging or discharging but the resistance increase is linked to the concentration polarization of the anion in the electrolyte.

So, can you list the other factors which will affect the performance or ionic conductivity of the electrolyte? I am giving you a hint; we have discussed all these points till now what about temperature? What about viscosity? What about the concentration? What is the dielectric constant role? All these aspects are going to also impact the cation transport number.

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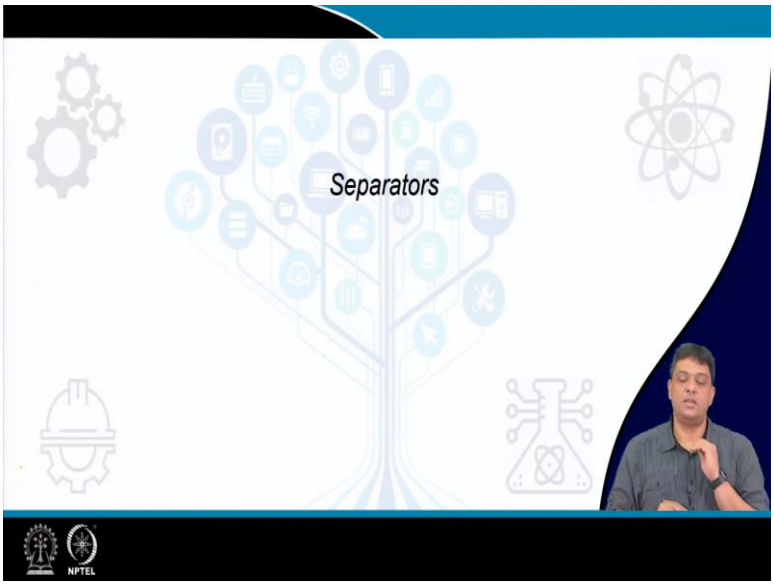

Once I have optimized the electrolyte, what is the fourth component? The fourth component is the separator.

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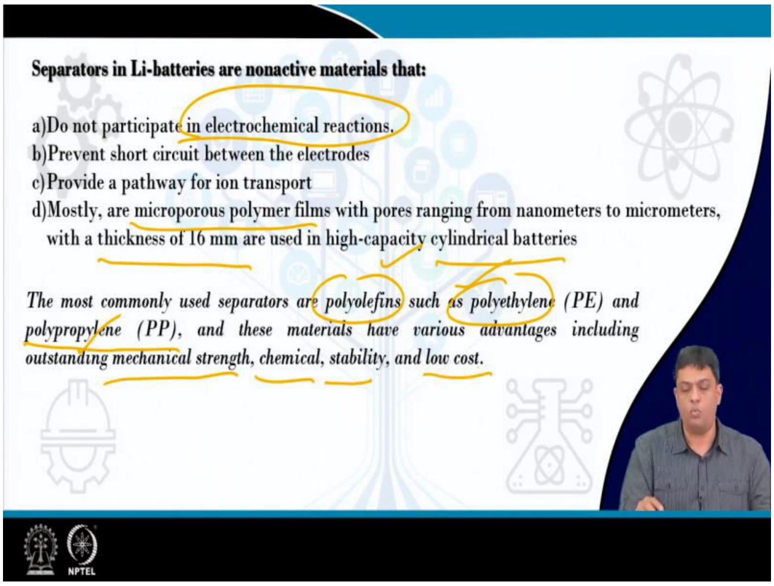

So, let us talk about separators. These are clearly the ones which are not going to take part in the electrochemical reactions, they will avoid the short circuiting, but they will provide free pathways for ion transport but will not allow electron transport. Hence, you will find that micro porous polymer films are used to act as separators and the typical thickness which are used in cylindrical batteries of these micro porous polymer films are 16 millimeters or more.

So, that is a typical thickness, so as they also ensure the mechanical integrity of the whole system. The most commonly used separators are polyolefins or polyethylene based separators, and after these two types of separators were used people have also been using polypropylene based separators. And all these materials they have the advantages such as mechanical strength, chemical strength, stability both in terms of mechanical and chemical stability, while they are also quite cost effective.

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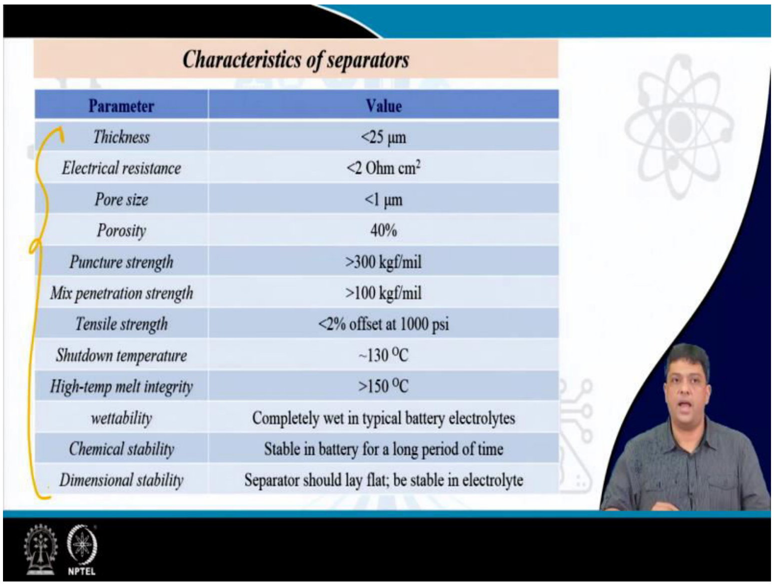

These are the characteristics of separators which are used while you choose the properties. So their requirements are very simple and straight forward. I need systems which are mechanically stable, which are chemically stable; they have high ionic transport capability. So they just do not restrict the flow of ions from one side to the other hence you choose various parameters and you will get the desired separator.

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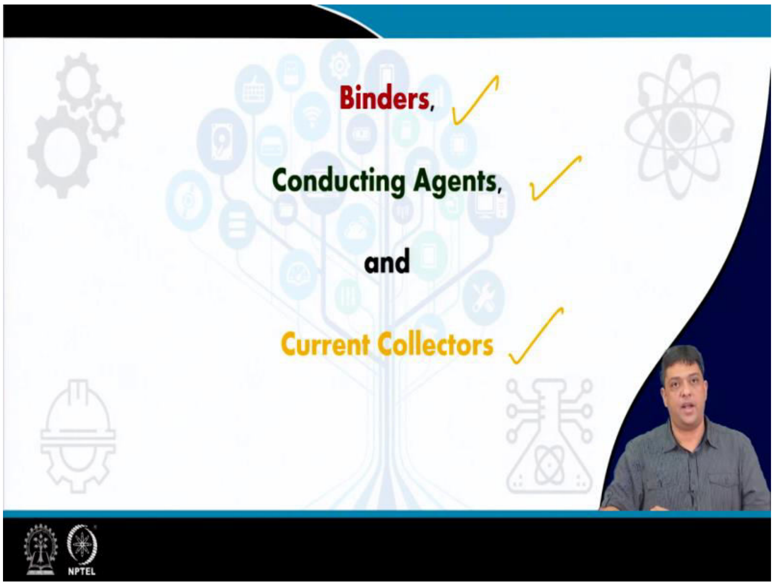

And finally, you will see that there are three more components which play important role in defining the usefulness of lithium-ion batteries. These are binders the conducting agents and the current collectors.

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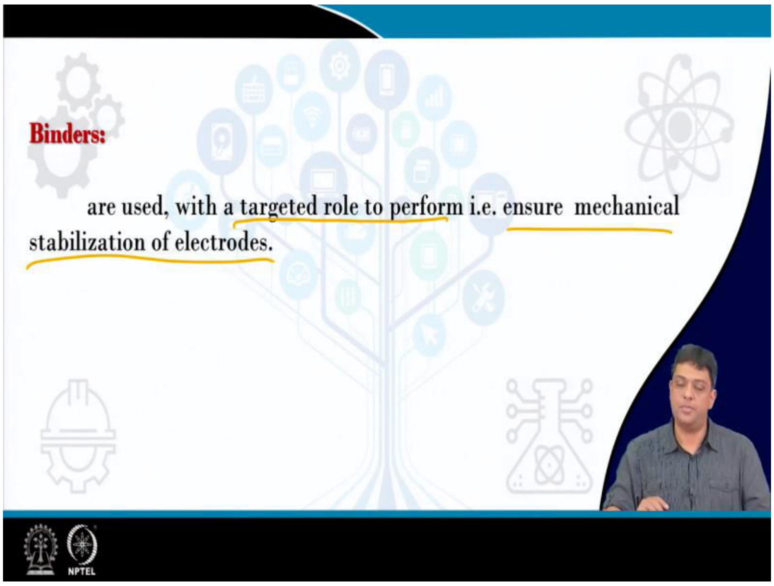

Binders, what are binders? So for example, if I have to take cathode materials which are in the form of powders and now convert them as electrode films. How will I bring these materials together in the form of a film? They are brought together and arranged in a form of a film using binder which has a targeted role to perform that is it ensures the mechanical stabilization of the electrodes.

This is what the binders are going to do, in fact after we have discussed about super capacitors we will also show you each and every step that will include the formation of electrode films where use of binders, current collectors and the conducting agents will become absolutely clear.

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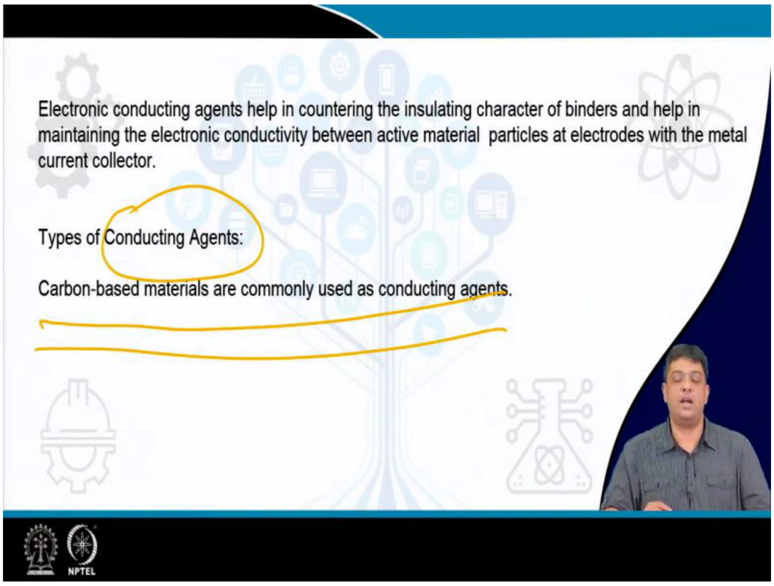

The next thing which is used are the conducting agents, and when you are using binders what are binders doing? Mostly they are polymer based binders, so they are adding insulating character to your cathode material and that is reducing the electronic conductivity. If electronic connectivity is being reduced then your overall performance will become weak because the electrons will not be able to flow out of the circuit when you are charging the battery out of the circuit means through the cathode.

And if the battery is being discharged you need electron to come out of the anode and then enter the cathode, but then I have these polymeric films which are reducing the overall electronic conductivity. So to counter the insulating character that is introduced by binders I have to add some conducting agents and these agents then ensure the similar nature of or order of electronic conductivity in the electrode films.

And carbon based materials are the most used conducting agents. So when we were talking about development of carbon structures from waste or other bio waste, I had said that you can make industries which will be making these materials that have large scale applications. So the carbon based materials which you are using as anode will also be working as conducting agents so another application.

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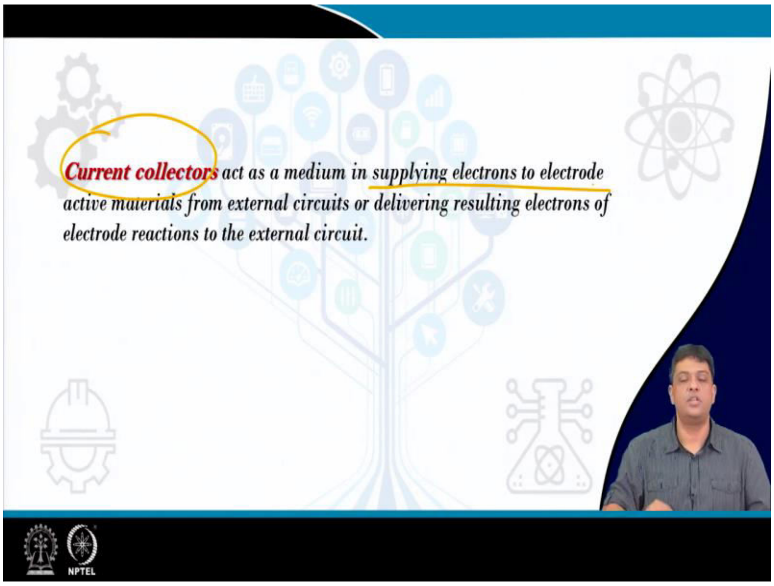

And finally the current collectors. The current collectors as the name suggest they are the ones which are supplying electrons to the electrode, which are made up of active materials and supplying from where? Supplying from the external circuits. So when you are charging electron moves out of the cathode then through the external circuit back into the anode so you extract the electron through the current collectors so the conductors then they enter the anode through the current collectors and vice versa in the discharge cycle and that is the role played by the current collectors and they should have high electronic conductivities.

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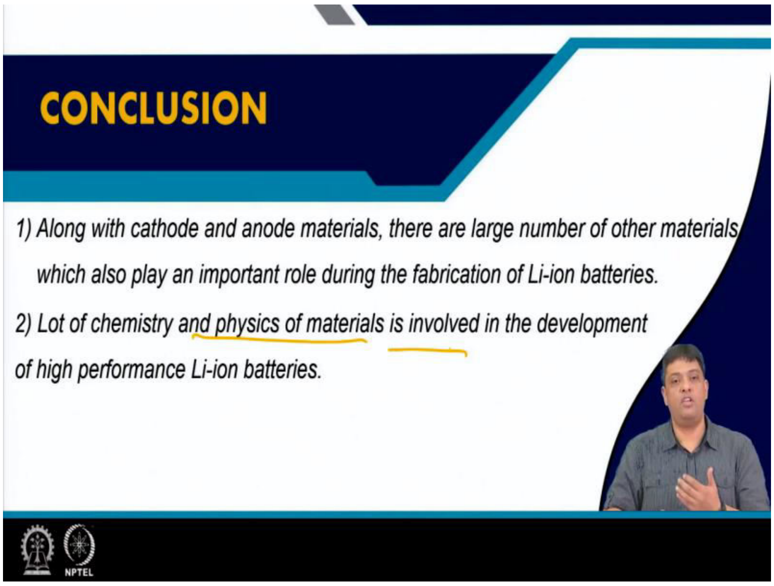

Hence, I hope it is clear after the discussion of today's lecture that along with cathode and anode materials, there are large numbers of other materials which also play a critical role during the fabrication of lithium-ion batteries. Lot of chemistry and physics of materials is involved in the development of high performance lithium-ion batteries, and if you ignore any one of these steps then you will never be able to obtain high performance batteries.

So, battery technology requires expertise from people working in the field of chemistry, physics, material science, chemical engineering, electronics, mechanical engineering and many more, and that is why it is such an interdisciplinary field, and lot of people are interested to work on these lithium-ion battery technologies which are still in the development phase and lot of improvement will be obtained in future. Even when you have you believe that lithium and batteries have reached their saturation no, in times to come you will find lot more improvement in the battery technology.

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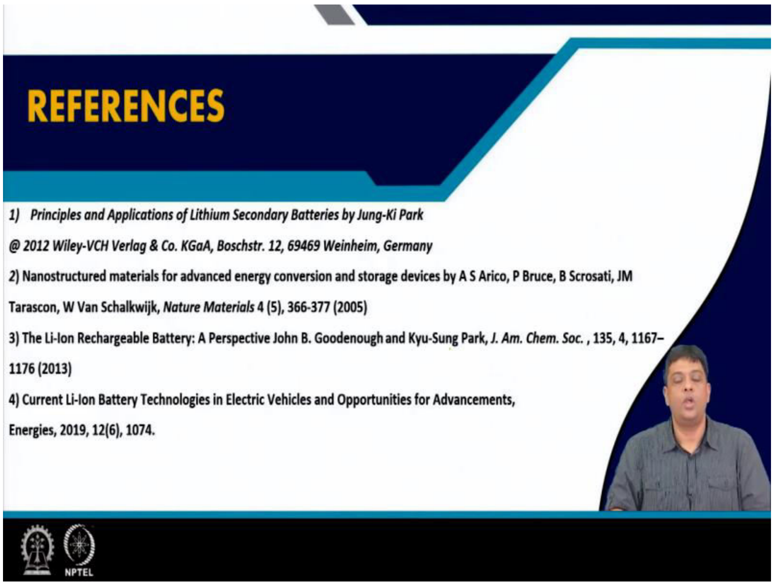

These are the references which were used, and I hope that with this final lecture on the materials used to fabricate lithium-ion batteries you have understood about the technology and the various aspects which have to be addressed, if you want to obtain lithium-ion batteries or any other batteries.

And India is moving to non lithium based batteries more so, towards sodium ion batteries just to ensure that the raw material is available to us and then we can become self-reliant in battery technology, but even if I talk about these sodium ion batteries the concepts remain the same.

In that technology you are talking about sodium ion based cathodes, carbon based anodes and electrolyte which will facilitate the transfer of sodium ion and a separator which will be ensuring smooth transfer of sodium from one side to its other side. Hence, you will be seeing lot more being talked about sodium ion batteries if you are in India. Thank you very much and enjoy!