Electrochemical Energy Storage

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Module - 04
Basic components in Li – ion batteries: Electrodes, Electrolytes, and collectors
Lecture - 18
Electrolyte: Liquid Electrolyte, Polymer Electrolyte

Welcome to my course Electrochemical Energy Storage and this is module number 4 where we are discussing Basic components of Lithium-ion batteries including Electrodes, Electrolytes and Collectors. And, this is lecture number 18 where we will talk about the Electrolyte, mostly Liquid Electrolyte and Polymer Electrolyte that will be introduced.

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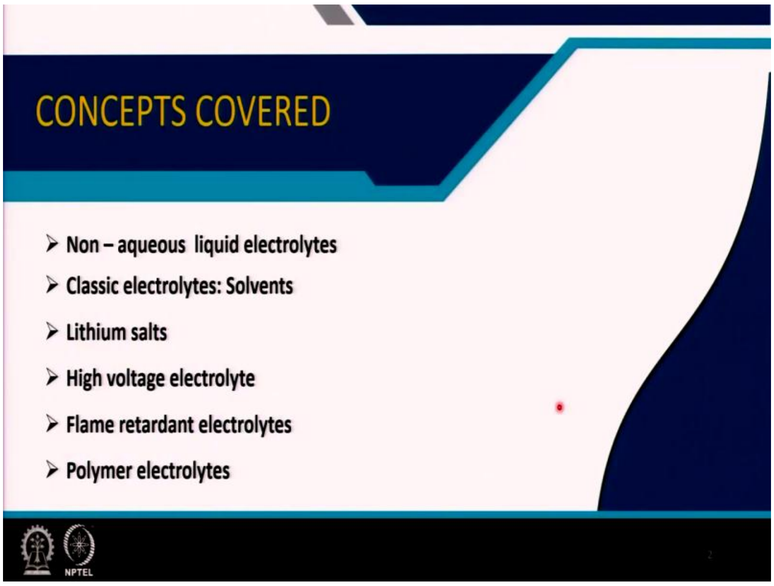

CONCEPTS COVERED

- Non – aqueous liquid electrolytes
- Classic electrolytes: Solvents
- Lithium salts
- High voltage electrolyte
- Flame retardant electrolytes
- Polymer electrolytes

So, first we will talk about non-aqueous liquid electrolytes, then classic electrolytes, what is used in commercial batteries including the solvents and the salts various types of lithium salts. Now, in order to increase the energy density of the battery you need to use the high voltage cathode material. So, the existing classic electrolyte classical electrolytes that is that may not be sufficient. So, high voltage electrolyte people are trying to develop. So, we will talk about it.

And, initially I talked about the flammability of this kind of electrolyte so that catches fire if the battery malfunctions particularly if the dendrite forms or if there are internal short circuit then heat lot of heat is generated. So, that actually causes the electrolyte to catch fire. So, certain flame retardant electrolyte that we will also discuss and finally, polymer base electrolyte we will talk about.

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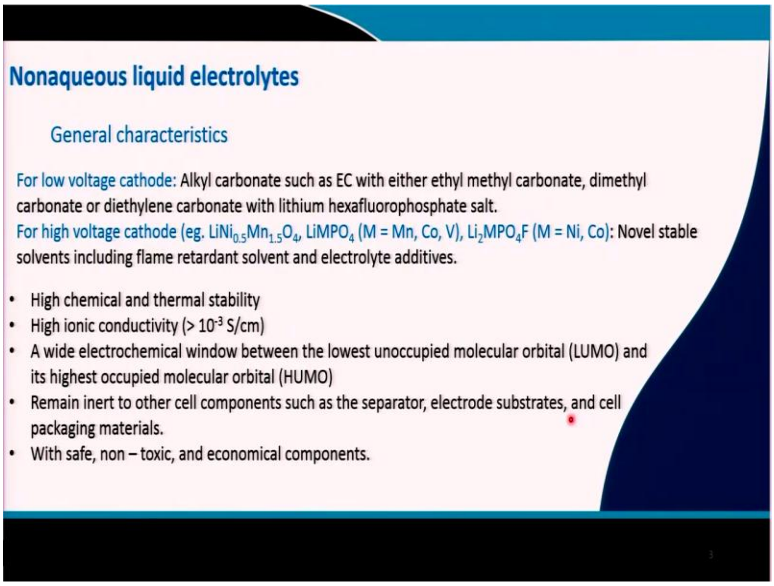

Nonaqueous liquid electrolytes

General characteristics

For low voltage cathode: Alkyl carbonate such as EC with either ethyl methyl carbonate, dimethyl carbonate or diethylene carbonate with lithium hexafluorophosphate salt.
For high voltage cathode (eg. $LiNi_{0.5}Mn_{1.5}O_4$, $LiMPO_4$ (M = Mn, Co, V), Li_2MPO_4F (M = Ni, Co): Novel stable solvents including flame retardant solvent and electrolyte additives.

- High chemical and thermal stability
- High ionic conductivity ($> 10^{-3}$ S/cm)
- A wide electrochemical window between the lowest unoccupied molecular orbital (LUMO) and its highest occupied molecular orbital (HUMO)
- Remain inert to other cell components such as the separator, electrode substrates, and cell packaging materials.
- With safe, non – toxic, and economical components.

So, there are two different categories of the cathode material one is low voltage cathode and as I said another one is a high voltage cathode. So, for lithium ion battery we mostly use non-aqueous liquid electrolyte. So, it is organic base electrolyte.

So, for low voltage cathode, usually alkyl carbonate prominent among is ethylene carbonate with ether ethyl methyl carbonate or dimethyl carbonate or diethylene carbonate is that is the solvent that is used with lithium hexafluorophosphate salt.

So, that is quite standard and most of the commercial batteries they use it. Now, for high voltage cathode which I have introduced that LMnO then our LMr type of cathodes, then lithium, manganese, cobalt, vanadium, phosphate which are having more voltage as compared to iron based lithium iron phosphate or also Li 2 MPO 4 F this is another type of high voltage cathode.

So, some novel stable solvent including the flame retardant solvent and certain electrolyte additives they must be developed. So, we will investigate that what is the status of this kind of high voltage I mean electrode electrolyte which is required for high voltage cathode material in other words high voltage batteries.

So, the characteristics that is required is high chemical stability and thermal stability. Then conductivity should at least be 10 raised to minus 3 Siemens per centimeter for effective lithium ion transport.

A wide electrochemical window between the lowest unoccupied molecular orbit orbital which is LUMO and the highest occupied molecular orbital that is HUMO, so that eg should be quite large so that it can accommodate the voltage otherwise you know that the anode will get electrolyte will get reduced on anode or oxidized on cathode.

It should remain inert to other cell component like separator, like electrode substrate which is current collector or the cell packaging material because so far we are only talking about the lithium ion cells, but it will have to be packaged in the form of either a cylindrical or a coin cell or a pouch type of cell or a prismatic cell.

So, even if the this electrolyte is cased in between so it should be inert to the cell component as well and it should be safe of course, non toxic and economically viable because of the battery it is most important thing is all your anode cathode etcetera whatever you are using if it is very expensive then no one will purchase your battery.

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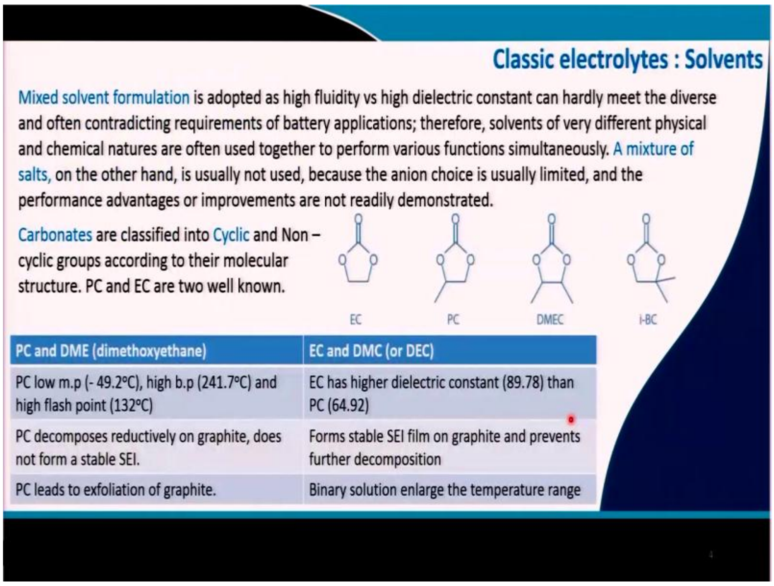

Classic electrolytes : Solvents

Mixed solvent formulation is adopted as high fluidity vs high dielectric constant can hardly meet the diverse and often contradicting requirements of battery applications; therefore, solvents of very different physical and chemical natures are often used together to perform various functions simultaneously. A mixture of salts, on the other hand, is usually not used, because the anion choice is usually limited, and the performance advantages or improvements are not readily demonstrated.

Carbonates are classified into Cyclic and Non – cyclic groups according to their molecular structure. PC and EC are two well known.

PC and DME (dimethoxyethane)	EC and DMC (or DEC)
PC low m.p (- 49.2°C), high b.p (241.7°C) and high flash point (132°C)	EC has higher dielectric constant (89.78) than PC (64.92)
PC decomposes reductively on graphite, does not form a stable SEI.	Forms stable SEI film on graphite and prevents further decomposition
PC leads to exfoliation of graphite.	Binary solution enlarge the temperature range

So, we need to have a mixed solvent formulation that is adopted it is not a single solvent that is required for high fluidity and high dielectric constant. So, one component should have higher fluidity and high dielectric constant and that hardly can meet the diverse and often contradictory requirements of the battery applications.

So, solvents of very different physical and chemical nature they are often mixed together to perform various functions simultaneously. So, a mixture of salt on the other hand is usually not used because the anion choice is usually limited and the performance advantage or improvement are not readily demonstrated.

So, solvent is a mixed type of solvent, but the salt is usually one component salt that is used because of the complicacy of introducing two different types of anion. So, this actually use carbonates they are classified either cyclic type and non-cyclic group according to their molecular structure.

So, this polycarbonate and ethylene carbonate PC and EC they are quite well known and this is their molecular structure along with other cyclic carbonate. So, PC and DME that is dimethoxyethane and EC and DMC that or DEC they are use. So, you can have PC at low melting point about minus 49.2 and high boiling point and it is having high flash point.

And, it decomposes reductively on graphite, so, that is another problem and does not form a stable SEI and this leads to exfoliation of graphite because you remember these two were important. We talked about it one problem is the decomposition of this electrolyte on the anode surface and second is the solvated lithium if it intercalates together so, that will exfoliate the graphite.

So, if you compare this PC with EC base mixture it has high dielectric constant than PC. So, that is one good signature and it forms a stable SEI on graphite and decomposition is also retarded, and binary solution enlarge the temperature range. So, the applicability the temperature is pretty large.

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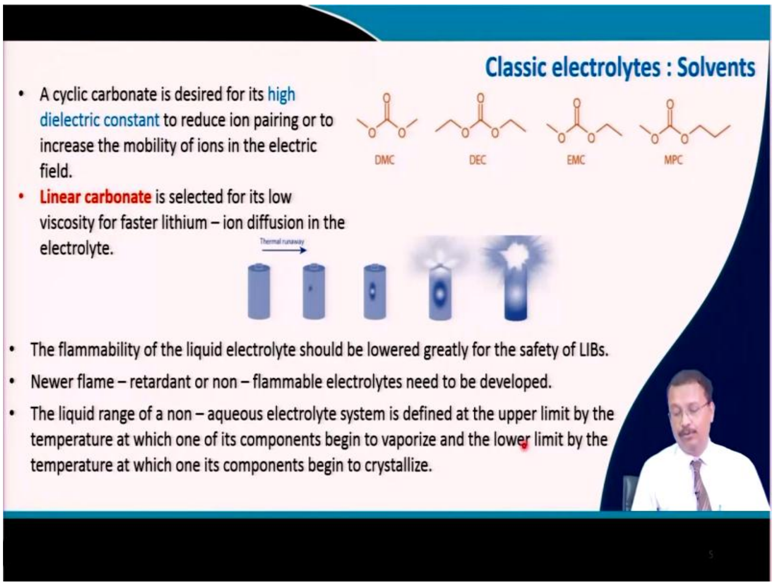

Classic electrolytes : Solvents

- A cyclic carbonate is desired for its high dielectric constant to reduce ion pairing or to increase the mobility of ions in the electric field.
- **Linear carbonate** is selected for its low viscosity for faster lithium – ion diffusion in the electrolyte.

- The flammability of the liquid electrolyte should be lowered greatly for the safety of LIBs.
- Newer flame – retardant or non – flammable electrolytes need to be developed.
- The liquid range of a non – aqueous electrolyte system is defined at the upper limit by the temperature at which one of its components begin to vaporize and the lower limit by the temperature at which one its components begin to crystallize.

So, a cyclic carbonate is desired for its high dielectric constant for example, EC that is to reduce the ion pairs or to increase the mobility of the ions in the electric field. And, along with that always one uses a linear carbonate and there are several examples the DMC, DEC, EMC and MPC which part of it I show that you see DMC is used here, DME is used here.

So, that those are linear carbonates that is selected for its low viscosity and that leads to faster lithium ion diffusion in the electrolyte. Now, the flammability of the liquid electrolyte should be lowered for greatly I mean considerably it should be lowered for the safety of LIB.

Otherwise if there is any thermal run away as you can see in the battery if there is a hot spot and then it cannot dissipate that heat so, there will be thermal run away and then finally, it can catch fire. It will reach this electrolyte will reach the flash point and it will catch fire.

So, newer flame retardant and non flammable electrolytes need to be developed so that to get rid of this kind of behavior and remember in a battery module you have several cells. So, one catches fire even if the other one is not thermally runaway has not taken place, then also it is detrimental for the whole battery pack.

The liquid range of a non aqueous electrolyte system is defined at the upper limit by the temperature at which one component begins to vaporize and the lower limit is also important at which one component become begin to crystallize. Because it is not only internal short circuit you will have to use the battery in a wide temperature range.

So, there is a possibility for flammability of the electrolyte in one hand if the temperature is raised; at the same time when the battery is used at relatively lower temperature then lithium ion conductivity will also be deteriorated at the same time the liquid electrolyte also can be solidify. So, a mixture is needed.

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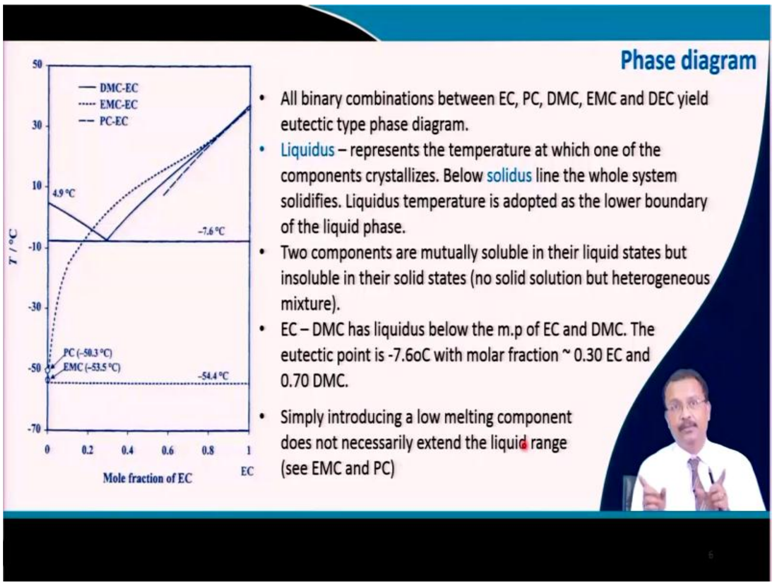

Phase diagram

- All binary combinations between EC, PC, DMC, EMC and DEC yield eutectic type phase diagram.
- Liquidus – represents the temperature at which one of the components crystallizes. Below solidus line the whole system solidifies. Liquidus temperature is adopted as the lower boundary of the liquid phase.
- Two components are mutually soluble in their liquid states but insoluble in their solid states (no solid solution but heterogeneous mixture).
- EC – DMC has liquidus below the m.p of EC and DMC. The eutectic point is -7.6oC with molar fraction ~ 0.30 EC and 0.70 DMC.
- Simply introducing a low melting component does not necessarily extend the liquid range (see EMC and PC)

So, we will try to understand in the form of a phase diagram how really it works. So, all binary composition between your EC, PC polycarbonate or dimethyl carbonate or EMC and DEC they all have a eutectic kind of phase diagram that you can have. So, I can define a liquidus line that represent the temperature at which one of the components crystallizes.

So, if this is liquid then if you cross this line so, one of the component of the electrolyte that will start to crystallize and there is a solidus line. So, below this solidus line the whole system solidifies. Now, the liquid temperature is adopted the liquidus temperature has a lower boundary of the liquid phase and two component which are mutually soluble in their liquid state here, but insoluble in their solid state. So, if they are does not form any solid solution so, they form a heterogeneous mixture here.

So, we have compared three different mixture EC DMC and this has a liquidus as you can see the liquidus below the melting point of your EC. So, the melting point of EC is quite large and the liquidus this liquidus is below EC. And, this EC – DMC, if you compare EC DMC has a liquid liquidus below the melting point of EC and DMC. The eutectic point is about minus 7.6 degree Celsius as you can see in this view graph.

And, with a molar fraction roughly about here it is around 0.3. So, simply introducing a low melting component. So, these components are quite low melting that does not necessarily extend the liquid range. So, you can compare the this EMC and PC. So, EMC and PC if you compare, so, that does not necessarily introducing this part that does not necessarily extend the liquid range.

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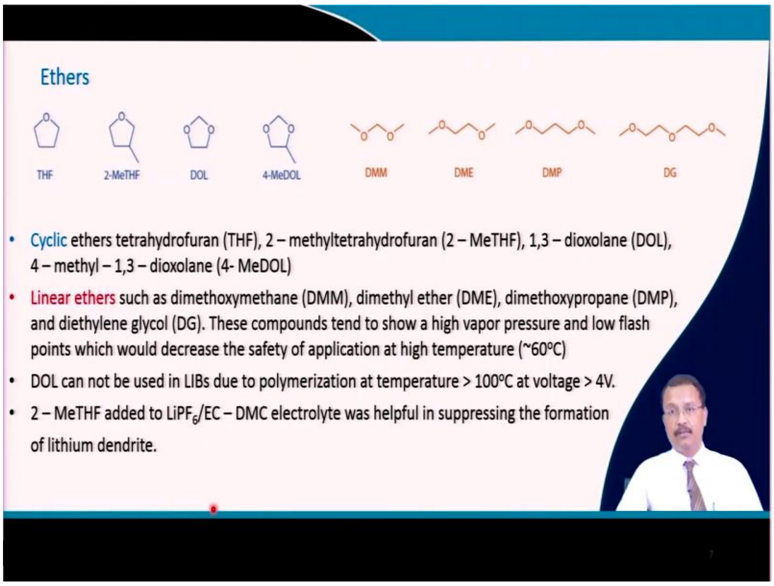

Ethers

- Cyclic ethers tetrahydrofuran (THF), 2 – methyltetrahydrofuran (2 – MeTHF), 1,3 – dioxolane (DOL), 4 – methyl – 1,3 – dioxolane (4- MeDOL)
- Linear ethers such as dimethoxymethane (DMM), dimethyl ether (DME), dimethoxypropane (DMP), and diethylene glycol (DG). These compounds tend to show a high vapor pressure and low flash points which would decrease the safety of application at high temperature (~60°C)
- DOL can not be used in LIBs due to polymerization at temperature > 100°C at voltage > 4V.
- 2 – MeTHF added to $LiPF_6$/EC – DMC electrolyte was helpful in suppressing the formation of lithium dendrite.

So, ether is also used. So, cyclic ether tetrahydrofuran or methyltetrahydrofuran or dioxolane DOL they are used along with that along with this cyclic ether. Linear ethers thus such as DMM or DME or DMP and diethylene glycol which is DG they are also used. Now, these components tend to show a higher vapor pressure.

So, the boiling point is low and low flash point and that actually would decrease the safety operation particularly at high temperature. So, DOL cannot be used in lithium ion battery due to polymerization at a temperature about 100 degree Celsius at voltage about 4 volt. In comparison, this 2 – MeTHF that is added to LiPF 6 and EC DMC this one is a cyclic one and this is a linear part. This is considered to be helpful in suppressing the formation of lithium dendrite.

So, as such the mixture of cyclic and linear ethers may not be that efficient, but this component this ether component if you add with conventional liquid electrolyte so, that may be helpful particularly if lithium metal is used as in lithium polymer batteries. So, that will suppress the dendrite formation which I described as a part of my earlier lectures.

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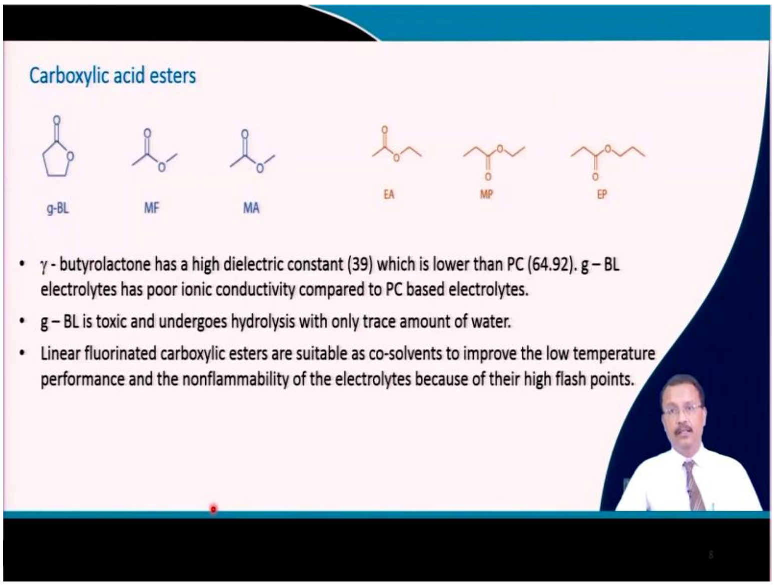

Carboxylic acid esters

- γ - butyrolactone has a high dielectric constant (39) which is lower than PC (64.92). g – BL electrolytes has poor ionic conductivity compared to PC based electrolytes.
- g – BL is toxic and undergoes hydrolysis with only trace amount of water.
- Linear fluorinated carboxylic esters are suitable as co-solvents to improve the low temperature performance and the nonflammability of the electrolytes because of their high flash points.

Esters are used for example, this gamma butyrolo butyrolactone it has higher dielectric constant about 39 which is lower than PC and this g-BL this one that has poor ionic conductivity compared to PC based electrolyte. So, this is also toxic and it undergoes hydrolysis if there is a trace amount of water in the electrolyte.

So, linear fluorinated carboxylic esters they are actually suitable for the co solvents to improve the low temperature performance of the electrolyte and the non flammability of the electrolytes and this is because of their high flash point. So, in that consideration this can be used.

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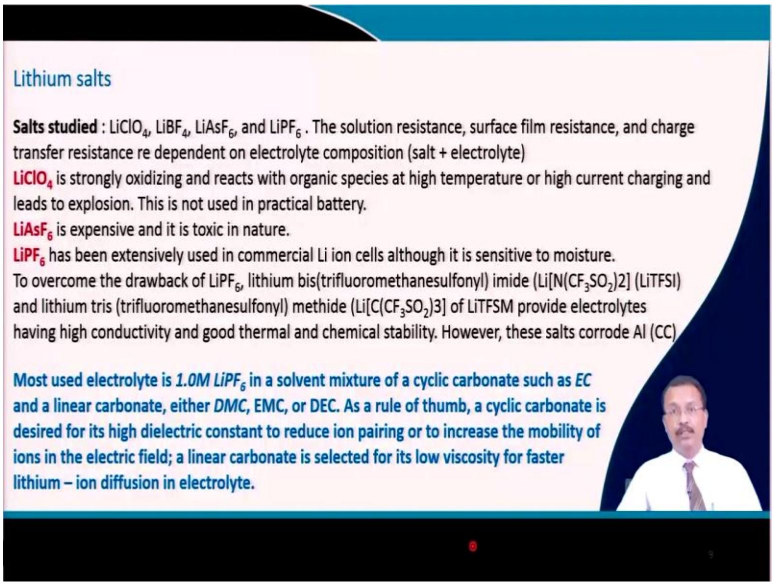

Lithium salts

Salts studied : $LiClO_4$, $LiBF_4$, $LiAsF_6$, and $LiPF_6$. The solution resistance, surface film resistance, and charge transfer resistance re dependent on electrolyte composition (salt + electrolyte)

$LiClO_4$ is strongly oxidizing and reacts with organic species at high temperature or high current charging and leads to explosion. This is not used in practical battery.

$LiAsF_6$ is expensive and it is toxic in nature.

$LiPF_6$ has been extensively used in commercial Li ion cells although it is sensitive to moisture.

To overcome the drawback of $LiPF_6$, lithium bis(trifluoromethanesulfonyl) imide ($Li[N(CF_3SO_2)2]$ (LiTFSI) and lithium tris (trifluoromethanesulfonyl) methide ($Li[C(CF_3SO_2)3]$ of LiTFSM provide electrolytes having high conductivity and good thermal and chemical stability. However, these salts corrode Al (CC)

Most used electrolyte is *1.0M $LiPF_6$* in a solvent mixture of a cyclic carbonate such as *EC* and a linear carbonate, either *DMC*, EMC, or DEC. As a rule of thumb, a cyclic carbonate is desired for its high dielectric constant to reduce ion pairing or to increase the mobility of ions in the electric field; a linear carbonate is selected for its low viscosity for faster lithium – ion diffusion in electrolyte.

Now, if you consider now the solvent sorry the solute part the lithium salt that is being used, so, lot of salts have been studied including lithium perchlorate LiBF 4 or LiAsF 6 and LiPF 6. So, the solution resistance, surface film resistance, and charge transfer resistance are actually dependent on electrolyte composition. So, electrolyte means that you have the salt and the solvent.

So, all this thing because as you can understand the decomposition of the electrolyte, formation of SEI layer that actually influence the performance of the battery sometimes in a positive way because you do need SEI formation. Sometimes this is detrimental for the use because if the SEI itself is not pervious to the impervious to the lithium ion diffusion.

So, if you compare this that lithium chlorate this is strongly oxidizing and that react with the organic species at high temperature or high current charging current, so, that can lead to explosion. So, therefore, this these are this lithium perchlorate salt they are not used in practical battery and this material is good, but it is very expensive and arsenic is toxic in nature.

So, you are actually left with LiPF 6 and this in fact, has been extensively used in lithium ion battery, but this is sensitive to moisture. So, to overcome the drawback of LiPF 6 there are several additives like LiTFSI and lithium tris trifluoromethanesulfonyl methide which is abbreviated the formula is this and abbreviated as LiTFSM, that actually provides electrolyte with high conductivity and good thermal and chemical stability.

So, the problem of these salts is that that if you add it with LiPF 6 with EC-DMC combination it will corrode the current collector aluminum. So, most used electrolyte in commercial batteries they are 1 molar LiPF 6 in a solvent mixture of a cyclic carbonate such as EC and a linear carbonate either DMC or EMC or DEC.

So, as a rule of thumb a cyclic carbonate is desired for its high dielectric constant to reduce the ion pairing or to increase the mobility of the ions in the electric field. And a linear carbonate is selected for its low viscosity for faster lithium ion diffusion in the electrolyte.

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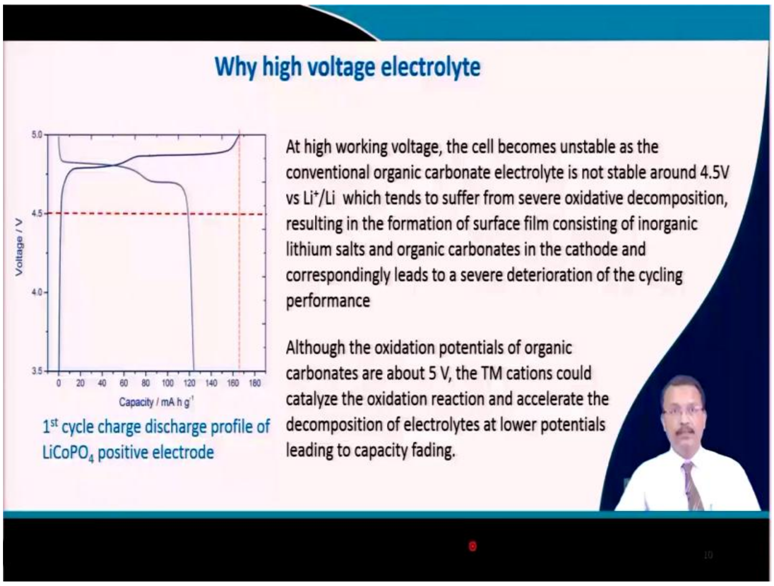

Why high voltage electrolyte

1st cycle charge discharge profile of $LiCoPO_4$ positive electrode

At high working voltage, the cell becomes unstable as the conventional organic carbonate electrolyte is not stable around 4.5V vs Li^+/Li which tends to suffer from severe oxidative decomposition, resulting in the formation of surface film consisting of inorganic lithium salts and organic carbonates in the cathode and correspondingly leads to a severe deterioration of the cycling performance

Although the oxidation potentials of organic carbonates are about 5 V, the TM cations could catalyze the oxidation reaction and accelerate the decomposition of electrolytes at lower potentials leading to capacity fading.

So, high voltage electrolyte is required as I have told. So, at high working voltage the cell becomes unstable as the conventional organic carbonate electrolyte that is not stable beyond 4.5 volt. So, if you go beyond 4.5 volt, the electrolyte itself is not very stable and it tends to suffer severe oxidation.

You remember that experiment that I showed you that at higher voltage in gold lithium with the organic electrolyte the one of the examples that I cited, then at higher potential they are prone to oxidative decomposition and they form the surface film which consist of inorganic lithium salt and organic carbonates in the cathode.

So, it is some kind of cathode electrolyte interface layer and that leads to severe deterioration of the cycling performance.

So, it is not good to have an SEI layer formed on the cathode surface. In some instances it dissolves back in the electrolyte and sometimes it leads to the deterioration of the performance of the cycling performance of the cathode itself. So, oxidation potential of organic carbonate are about 5 volt that is the usual range, the transition metal cation which is there in the cathode part that catalyze actually this oxidation reaction and accelerates the decomposition of the electrolyte at relatively lower potential.

So, even if the HOMO LUMO band you can see that is large enough and theoretically it is suitable for 5 volt up to 5 volt it is stable, but most of the cathode material they have transition metal cation which acts as a catalyst and they are responsible for the decomposition.

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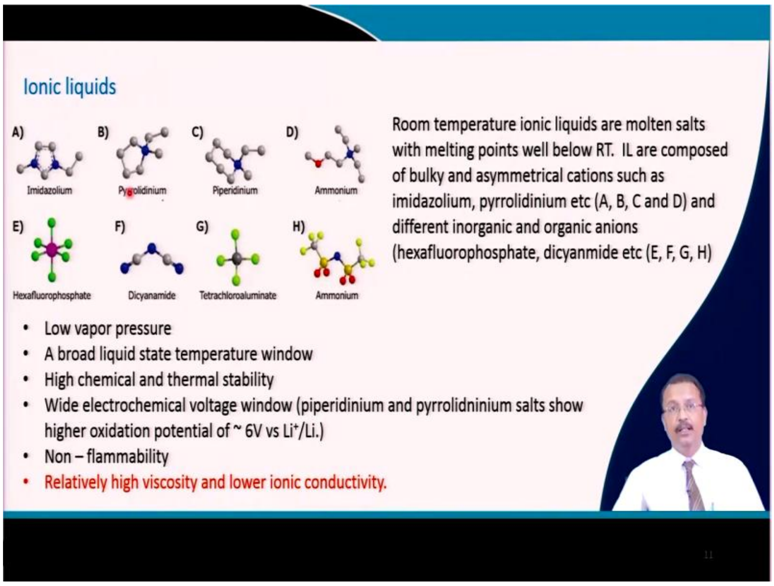

Ionic liquids

Room temperature ionic liquids are molten salts with melting points well below RT. IL are composed of bulky and asymmetrical cations such as imidazolium, pyrrolidinium etc (A, B, C and D) and different inorganic and organic anions (hexafluorophosphate, dicyanmide etc (E, F, G, H)

- Low vapor pressure
- A broad liquid state temperature window
- High chemical and thermal stability
- Wide electrochemical voltage window (piperidinium and pyrrolidninium salts show higher oxidation potential of ~ 6V vs Li^+/Li.)
- Non – flammability
- Relatively high viscosity and lower ionic conductivity.

So, ionic liquid they are actually being tried. So, room temperature ionic liquids are basically molten salt with the melting point that is well below the room temperature. So, they are liquid in nature. So, these particular salts they are composed of a bulky and asymmetrical cations.

So, some of the examples are showing are shown imidazolium pyrrolidinium etcetera this is shown A, B, C, D this one and different inorganic or organic anions part. So, for example, hexafluorophosphate or dicyanamide, so, this E, F, G, H these are the organic or inorganic anion that is attached with the bulky asymmetric cation.

So, these salts have usually lower vapor pressure. So, that is not a problem for a high boiling point. A broad liquid state temperature window is available. They have sufficiently large chemical and thermal stability and wide electrochemical voltage window. So, this piperidinium and pyrrolidinium salt they actually show the oxidation potential about 6 volt.

So, that is quite safe to use and they are also non-flammable. So, but the problem is this salts have high viscosity and relatively lower ionic conductivity. So, that kills the property of the battery if you start to use ionic liquid particularly at room temperature; if you increase the temperature then the battery will start to perform well, but at room temperature or below room temperature ionic liquid performance is not that good.

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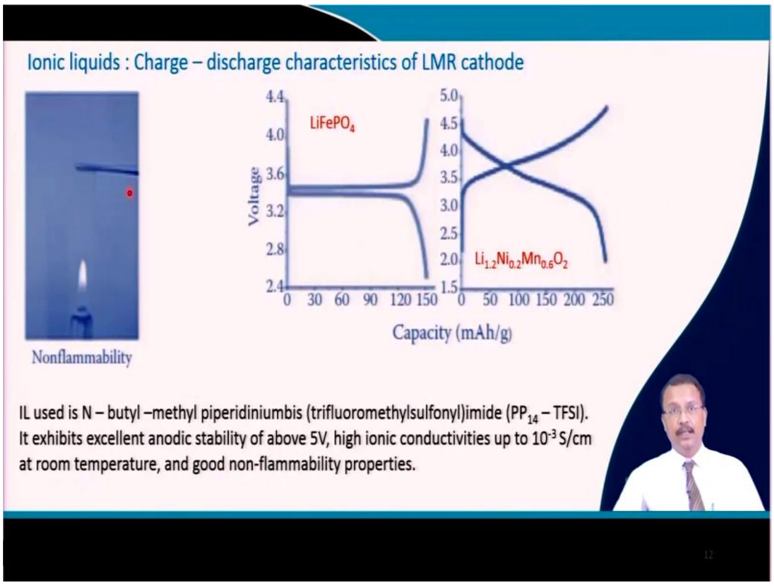

Ionic liquids : Charge – discharge characteristics of LMR cathode

IL used is N – butyl –methyl piperidiniumbis (trifluoromethylsulfonyl)imide (PP$_{14}$ – TFSI). It exhibits excellent anodic stability of above 5V, high ionic conductivities up to 10^{-3} S/cm at room temperature, and good non-flammability properties.

So, this is the typical charge discharge characteristics of an LMR Lithium Manganese Rich cathode. So, you know that this is this operates at high voltage as compared to lithium iron phosphate. This ionic salt base electrolyte they have reasonably good non flammability.

So, this ionic liquid that used in N-butyl-methyl piperidiniumbis trifluoromethylsulfonyl imide which is PP 4 14 TFSI. So, that exhibits excellent anodic stability about 5 volt range and high conductivity up to 10 to the power minus 3 Siemens per centimeter at room temperature and good non-flammable properties. So, various combinations people are trying to develop this.

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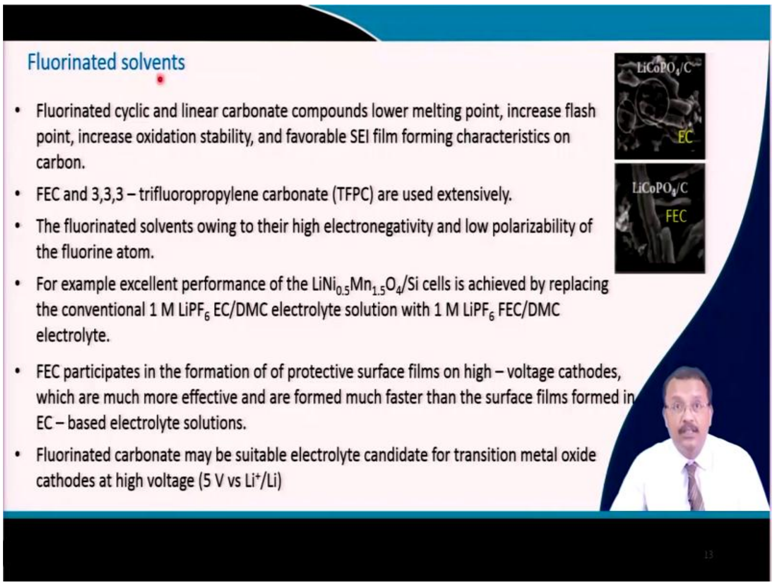

Fluorinated solvents

- Fluorinated cyclic and linear carbonate compounds lower melting point, increase flash point, increase oxidation stability, and favorable SEI film forming characteristics on carbon.
- FEC and 3,3,3 – trifluoropropylene carbonate (TFPC) are used extensively.
- The fluorinated solvents owing to their high electronegativity and low polarizability of the fluorine atom.
- For example excellent performance of the $LiNi_{0.5}Mn_{1.5}O_4/Si$ cells is achieved by replacing the conventional 1 M $LiPF_6$ EC/DMC electrolyte solution with 1 M $LiPF_6$ FEC/DMC electrolyte.
- FEC participates in the formation of of protective surface films on high – voltage cathodes, which are much more effective and are formed much faster than the surface films formed in EC – based electrolyte solutions.
- Fluorinated carbonate may be suitable electrolyte candidate for transition metal oxide cathodes at high voltage (5 V vs Li^+/Li)

Fluorinated solvents they are also useful. So, for example, fluorinated cyclic and linear carbonate compounds lower the melting point and increase the flash point increase the oxidation stability and favorable SEI formation is possible on carbonaceous electrode. So, this FEC and 3, 3, 3 trifluoropropylene carbonate which is abbreviated as TFPC they are used extensively.

This fluorinated solvent owing to their high electronegativity and low polarizability of the fluorine atom they showed excellent performance in this high voltage cell and this is you know the high voltage and silicon as an anode that is also quite novel. So, people have replaced this traditionally EC DMC based electrolyte solution with LiPF 6 and with FEC and DMC. So, this performs well.

So, this FEC that participates in the formation of a protective surface film on high voltage cathode which is much more effective and formed much faster than the surface film formed in EC based electrode. So, the that formation is quite effective. So, this is the example that has been shown that is that forms a quite stable film.

So, the fluorinated carbon this is suitable for electrolyte candidate for transition metal oxide which operates beyond 5 volt regime.

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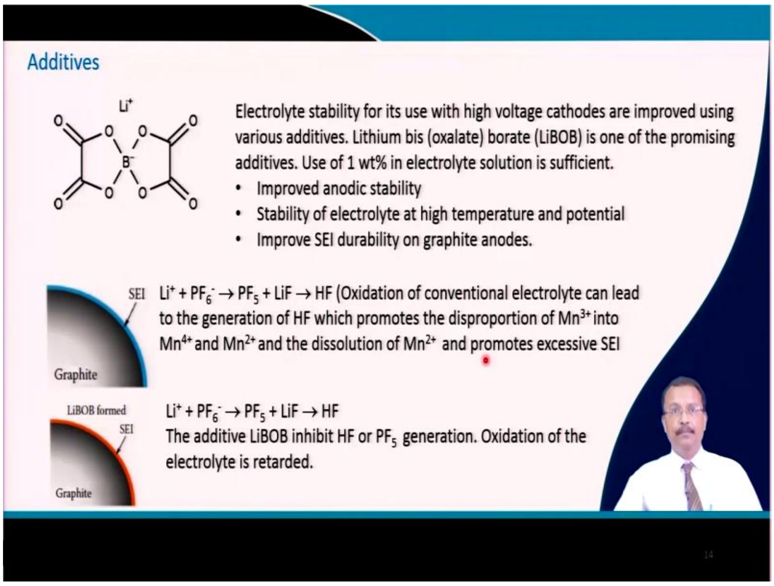

Additives

Electrolyte stability for its use with high voltage cathodes are improved using various additives. Lithium bis (oxalate) borate (LiBOB) is one of the promising additives. Use of 1 wt% in electrolyte solution is sufficient.

- Improved anodic stability
- Stability of electrolyte at high temperature and potential
- Improve SEI durability on graphite anodes.

$Li^+ + PF_6^- \rightarrow PF_5 + LiF \rightarrow HF$ (Oxidation of conventional electrolyte can lead to the generation of HF which promotes the disproportion of Mn^{3+} into Mn^{4+} and Mn^{2+} and the dissolution of Mn^{2+} and promotes excessive SEI

$Li^+ + PF_6^- \rightarrow PF_5 + LiF \rightarrow HF$

The additive LiBOB inhibit HF or PF_5 generation. Oxidation of the electrolyte is retarded.

So, certain additives are added. So, electrolyte stability for the use with high voltage cathode they are improved by various types of this additives. Lithium bis oxalate borate which is abbreviated as LiBOB that is one of the promising additive very small amount of is required only 1 weight percent because anything you add that will add up to the weight of the battery and reduce the gravimetric energy density of the battery.

So, it improves the anodic stability and stability of the electrolyte at high temperature and potential and third, it improves the SEI durability particularly on the graphite anodes. So, this SEI layer is formed something like this it happens that lithium ion and PF 6 they are dissociated. So, it forms PF 5 and form LiF.

So, this hydrofluoric acid this oxidation of conventional electrolyte can lead to the generation of hydrofluoric acid that promotes this disproportion of manganese into manganese 4 plus and manganese 2 plus and dissolution of manganese 2 plus and promotes excessive formation of SEI. So, that is a common clause and we talked about this disproportion reaction particularly when you are using the spinel material at lower potential limit.

So, LiMn 2 O 4 at 3 volt range you have if you deep discharge it then the formation of this disproportionate due to the disproportionate reaction and dissolution of manganese this is expedite by this cause the formation of HF because of the presence of a small moisture so, that expedite this process.

So, when you add this LiBOB that inhibits this HF or this PiF this generation so, the oxidation of the electrolyte is grossly retarded by this process. So, in that way it is quite useful.

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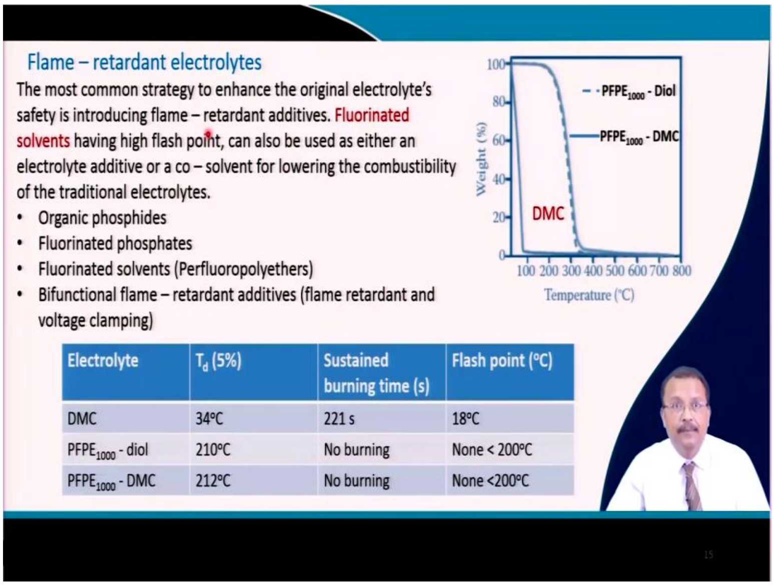

Flame – retardant electrolytes

The most common strategy to enhance the original electrolyte's safety is introducing flame – retardant additives. Fluorinated solvents having high flash point, can also be used as either an electrolyte additive or a co – solvent for lowering the combustibility of the traditional electrolytes.

- Organic phosphides
- Fluorinated phosphates
- Fluorinated solvents (Perfluoropolyethers)
- Bifunctional flame – retardant additives (flame retardant and voltage clamping)

Electrolyte	T_d (5%)	Sustained burning time (s)	Flash point (°C)
DMC	34°C	221 s	18°C
$PFPE_{1000}$ - diol	210°C	No burning	None < 200°C
$PFPE_{1000}$ - DMC	212°C	No burning	None <200°C

There are certain flame retardant electrolyte. The most common strategy to enhance the original electrolyte safety is introducing this flame retardant additives and usually fluorinated solvent have high flash point that can also be used what I told in couple of slides back. This can be used either as electrolyte additive or a co-solvent for lowering the combustibility of the traditional electrolyte for both the purpose it can serve.

So, usually organic phosphides fluorinated phosphates, then fluorinated solvents, bifunctional flame – retardant additives they are used. So, if you can use this electrolyte DMC or PFPE 1000 with diol you can see the decomposition temperatures they are pretty high here and burning is avoided and flash point is quite large. So, these flame retardant electrolytes they play a major role as far as the safety of the lithium ion battery is concerned.

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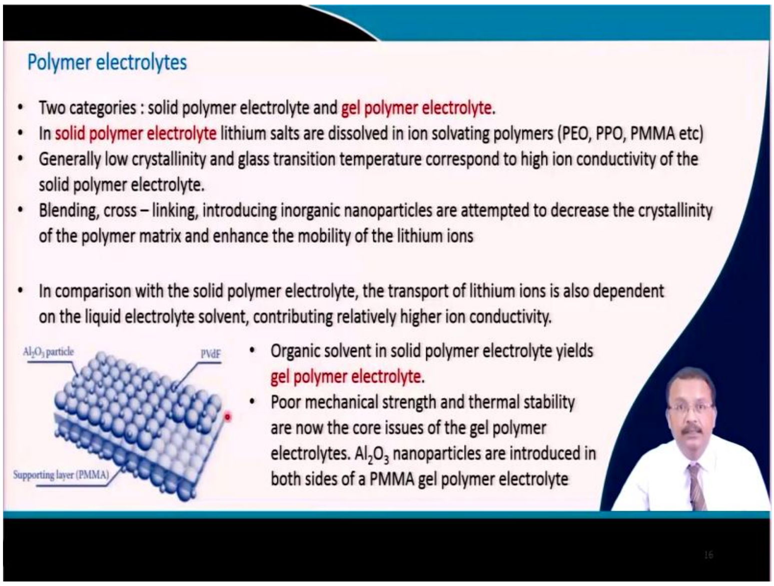

Polymer electrolytes

- Two categories : solid polymer electrolyte and gel polymer electrolyte.
- In solid polymer electrolyte lithium salts are dissolved in ion solvating polymers (PEO, PPO, PMMA etc)
- Generally low crystallinity and glass transition temperature correspond to high ion conductivity of the solid polymer electrolyte.
- Blending, cross – linking, introducing inorganic nanoparticles are attempted to decrease the crystallinity of the polymer matrix and enhance the mobility of the lithium ions

- In comparison with the solid polymer electrolyte, the transport of lithium ions is also dependent on the liquid electrolyte solvent, contributing relatively higher ion conductivity.

- Organic solvent in solid polymer electrolyte yields gel polymer electrolyte.
- Poor mechanical strength and thermal stability are now the core issues of the gel polymer electrolytes. Al_2O_3 nanoparticles are introduced in both sides of a PMMA gel polymer electrolyte

In case of polymer electrolytes there are two categories one is solid polymer electrolyte and gel polymer electrolyte. In case of the solid polymer electrolyte lithium salts are dissolved in ion solvating polymer like PEO or PPO or PMMA. So, lithium salts are dissolved there.

So, generally the low crystallinity and the glass transition temperature correspond to high-ion conductivity of the solid polymer electrolyte. The conductivity is not that great as compared to the conventional organic liquid phase electrolyte, then several aspects like blending cross linking introduction of the inorganic nanoparticles those things are attempted to decrease the crystallinity of the polymer and enhance the mobility of the lithium ion.

In case of in comparison to this kind of solid polymer electrolyte with inorganic nanoparticle the transport of lithium that is also dependent on the liquid electrolyte solvent contributing relatively higher ionic conductivity. So, organic solvent in solid polymer electrolyte yields a gel polymer electrolyte.

So, poor mechanical strength and the thermal stability these are now the core issues of the gel polymer electrolyte. So, as you can see that this is a supporting layer of this PMMA and then you have alumina particle and this is bounded by this PVdF. So, this kind of polymer based electrolyte that has been found fruitful for lithium polymer batteries.

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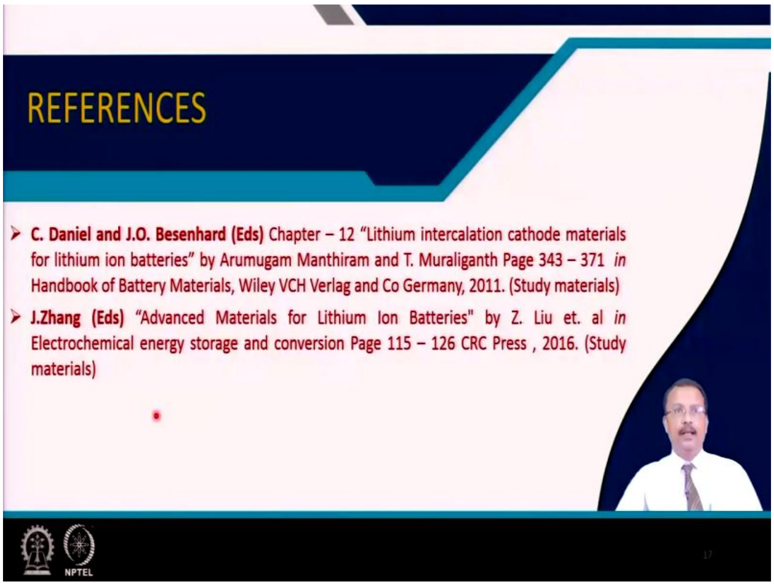

REFERENCES

- **C. Daniel and J.O. Besenhard (Eds)** Chapter – 12 "Lithium intercalation cathode materials for lithium ion batteries" by Arumugam Manthiram and T. Muraliganth Page 343 – 371 *in* Handbook of Battery Materials, Wiley VCH Verlag and Co Germany, 2011. (Study materials)
- **J.Zhang (Eds)** "Advanced Materials for Lithium Ion Batteries" by Z. Liu et. al *in* Electrochemical energy storage and conversion Page 115 – 126 CRC Press , 2016. (Study materials)

So, the study material for this is again the chapter 12 for this book Lithium intercalation cathode materials and lithium battery. So, and second one is the advanced material for lithium ion battery. So, this two are the study materials for this particular particularly this book along with the intercalation compound there are description for the polymer based electrolyte as well.

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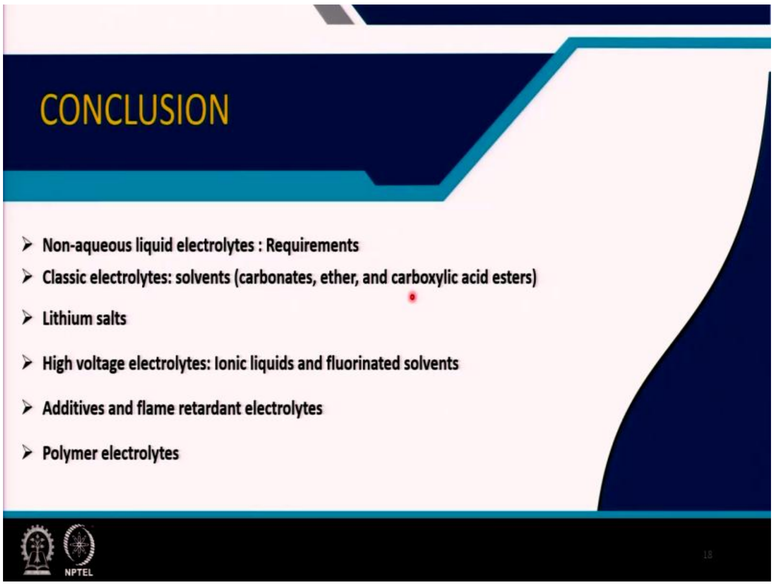

CONCLUSION

- Non-aqueous liquid electrolytes : Requirements
- Classic electrolytes: solvents (carbonates, ether, and carboxylic acid esters)
- Lithium salts
- High voltage electrolytes: Ionic liquids and fluorinated solvents
- Additives and flame retardant electrolytes
- Polymer electrolytes

So, in this particular lecture we introduce the non aqueous liquid electrolytes, what are their requirements. Then we introduce the classic electrolytes, the solvent which is which could be carbonate, ether and carboxy acid carboxylic acid esters. And, lithium salts various types of lithium salts were introduced and this LiPF 6 proved to be the best one so far.

Then we talked about the high voltage electrolyte in particular the ionic liquids and fluorinated solvents, and role of various additives and flame retardant electrolytes that were introduced and finally, a brief description of polymer base electrolytes was considered.

Thank you for your attention.