Electrochemical Energy Storage
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Module - 06
Sodium ion rechargeable cell
Lecture - 28
Electrolytes: Roles and Requirements, Organic Electrolyte, Ionic Liquid Electrolyte, Polymer Electrolytes

Welcome to my course Electrochemical Energy Storage and this is module number 6, we are talking about Sodium ion rechargeable cell. This is lecture 28, where I will be describing the Electrolytes, their Role and Requirements for sodium ion batteries, mostly Organic Electrolytes are used like lithium ion batteries; then Ionic, Liquid Electrolyte and also Polymer Electrolyte.

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So, first I will describe the general characteristics of the electrolyte including the salt and solvent that is used; the conductivity of the electrolyte, at what range that is desired, what is the stability window that is fixed by the used anode and cathode material and the HOMO LUMO band of the electrolyte in between.

Then what kind of electrolyte additives are used, basically to expedite the film formation or due to I mean to impart the flame retardant and then ionic liquids whatever so far have been tried for sodium ion batteries and then what is the status of the polymer electrolytes.

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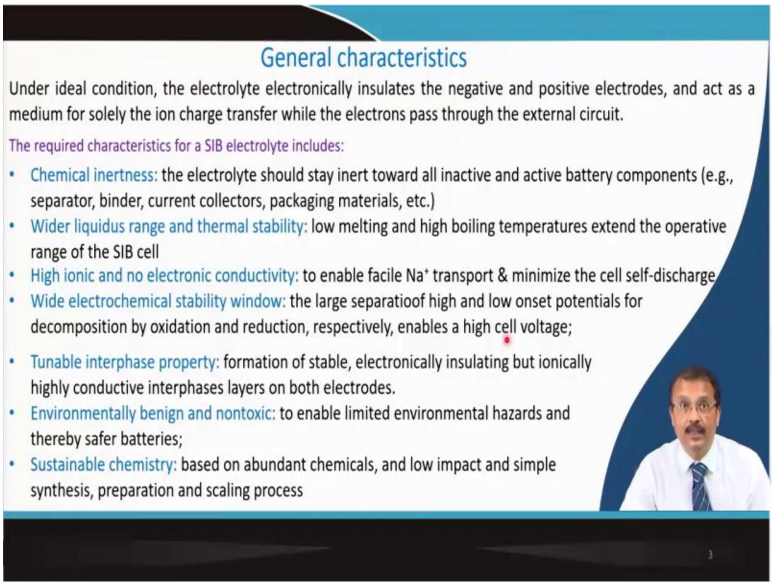

So, as you know under ideal condition, electrolyte is electronically insulate the negative and positive electrodes and act as a medium for solely for the passage of ion charge transfer while electron pass through the external circuit. So, same thing whatever we talked about for lithium ion batteries. The requirement characteristics of the sodium ion battery, it is some kind of recapitulation already what you know, when I talked about it for lithium ion batteries.

First one is chemical inertness, electrolyte of course should stay inert all inactive and active battery components, like separator it should not react with the binder that you are using, it should not dissolve the binder; current collector it should not attack, packaging material you know by this time that, we need to hermetically seal the battery in having different types of form factors.

So, it should not react with that. Wider liquidus range and thermal stability, it should not get solidified; the solidus line and liquidus line and the mixed electrolyte eutectic formation that already we talked about, while I was discussing for lithium ion batteries. So, similar things are valid also here; low melting and high boiling point temperatures extend the operative range as you know for lithium ion batteries as well as for sodium ion batteries.

High ionic and no electronic conductivity, already we talked about it; wide electrochemical stability window that is important, so that the anode should not get the reduced product, precipitate on it or electrolyte should not oxidize to affect the positive electrode material. Tunable interphase properties; that means formation of a stable electronically insulating; but ionically high conductive interphase layers on both the electrodes, particularly the negative electrodes.

And positive electrode even if it forms, it should not get dissolved and come back to the electrolyte itself. It should be environmentally benign and non-toxic, needless to say that and they should have a sustainable chemistry beyond, I mean based on the abundant chemical. So, you should not use a very expensive or a obscured kind of or the process should be relatively simplified; you mix it and prepare it for your own purpose and it should be of course be scalable.

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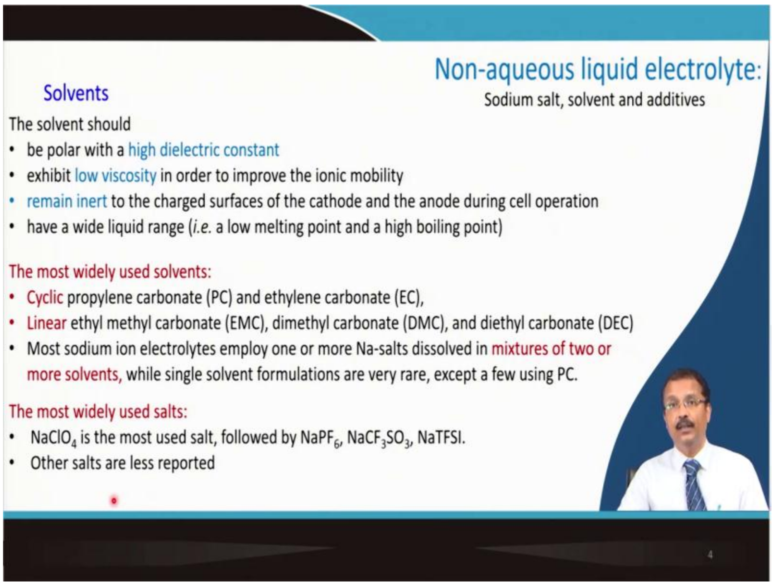

So, here also we will use non aqueous electrolyte; because you know both lithium and sodium they are very prone to attack by this moisture content. So, the solvent should be polar with a high dielectric constant; you know the EC DMC we talked about it. It should exhibit low viscosity to improve the ionic mobility; then remain inert, particularly to the charged surface of the cathode and the anode during cell operation.

So, then they the structure is stabilized and destabilized right, when the charging is taking place, then sodium is taking out from the crystal lattice and there are lot of phase transition can takes place depending on what type of positive electrode that you are using. So, it should remain inert, it should not attack the electrode materials and it should have a wide liquid range; that is a low melting point and high boiling point.

So, that is very important, because you will have to use the battery in different kinds of environment. So, maybe hot summer days in Rajasthan 46 degree Celsius or very cold chill day in the Himalayan area; if the batteries are used, so then it should remain liquid of course in the low temperature.

The most widely used solvents, they are basically same; what I described earlier, cyclic type propylene carbonate and ethylene carbonate or linear type ethyl methyl carbonate EMC or dimethyl carbonate or di ethyl carbonate, so DEC and DMC.

Most sodium ion electrolytes employ one or more sodium salts dissolved in a mixture of two or more solvents. So, two types of sodium salt, some of the reports I have found; but it should be a mixture of the solvent, solvent should be of the mixed type, because we talked about the electro eutectic point and elaborately discussed it during, while I was discussing the lithium ion battery cases.

So, most widely used salts are sodium perchlorate and sodium PF 6 or NaCF 3 SO 3 or NaTFSI they are used and other salts are relatively less report, because this technology is not yet well ripened.

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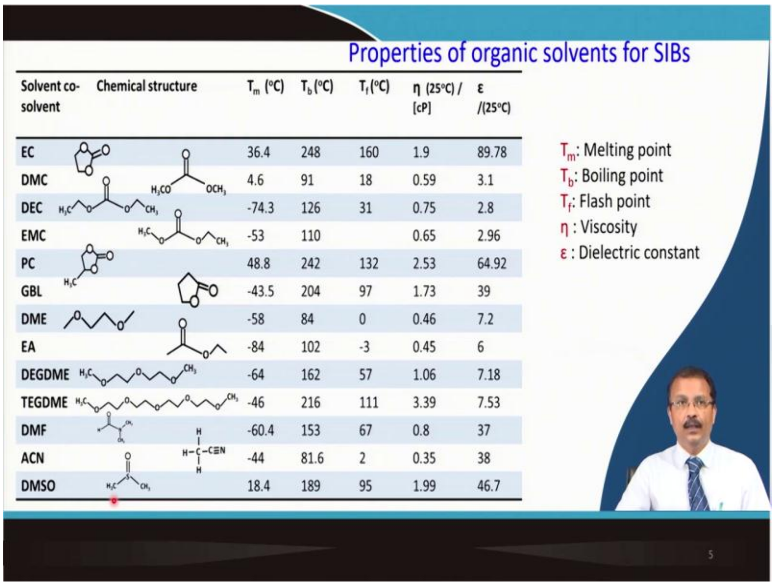

So, this is a standard characteristics, so for reference it is very important to you. And these are the solvent and co solvents all are tabulated here with their chemical structure and melting point you can see; boiling point, freezing point, viscosity at room temperature of course, and the electric constant.

So, that will help you to mix this solvents together and this is very important; this organic solvents particularly the cyclic and linear type of solvent use it along with the sodium ion salt, that is very important to get a stable electrolyte.

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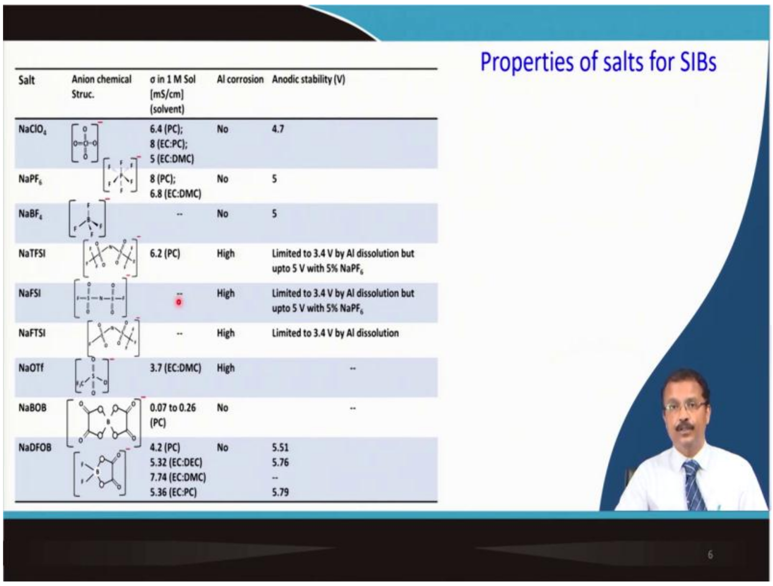

The salt properties also I have tabulated here; different types of salt that you can see whatever I just mentioned with their anion chemical structure and more importantly what is the conductivity that you can get. So, this conductivity of 1 molar of Sol at different fraction of this solvents that is given and whether they have any corrosive effect; corrosive effect on the current collector the metal if they attack, that is also important to be considered.

And anodic stability at what voltage, up to what voltage it is stable that is also important, it should not get oxidized. So, this oxygen gas will evolve and that will attack the electrolyte and there will be thermal run out, so you know that. So, that is to be avoided. So, accordingly judiciously we will have to select the salt.

But as I said in case of lithium ion battery this 1 molar of LiPF 6 in EC DMC or EC DEC. Aame thing here for sodium ion battery, either sodium NaPF 6 or sodium perchlorate in EC DMC or the cyclic and linear type of solvent, whatever I have mentioned here. So, not much choice; not much choice, people only follow this kind of typical composition.

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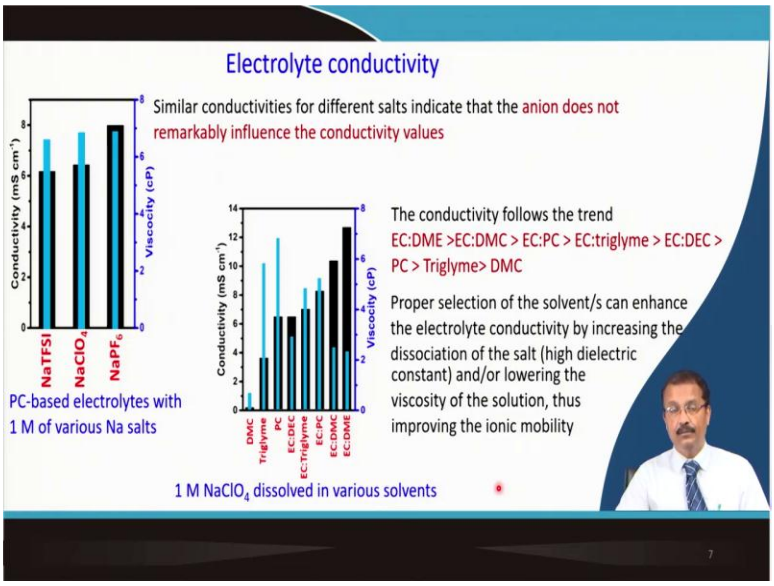

Now, a conductivity you see, this is quite interesting. If you take a PC based electrolyte with 1 Molar of various sodium salt; here the black part, this black part is the conductivity. So, the conductivity remains like this, if you take NaTFSI of course, it is having a relatively lower conductivity in millisiemen per centimeter and sodium perchlorate is relatively better.

But you can see NaPF 6 is about 8 millisiemen per centimeter. And the viscosity, this viscosity is given in the same histogram. So, the viscosity should not be increased much that, will reduce this thing, the mobility of the sodium ion. So, similar kind of conductivities for different salts, more or less similar kind of conductivity; that indicates that anion does not remarkably influence the conductivity values, but if you see the mixture of the solvent, then you have a clear cut trend.

So, EC DME and compare with DMC. So, here DMC you can see conductivity is very low, sorry this is the viscosity part; conductivity is also very low and then you go progressively with EC DME, which is the maximum one here and viscosity also reasonably low and EC DMC also it is there with a reasonably high conductivity.

So, you do not have much choice in this to select the salt and solvent combination and the true two controlling factors are one is the viscosity should be low enough and second one is the conductivity should be reasonably high. So, proper selection of the solvent can enhance the electrolyte conductivity by increasing the dissociation of the salt. So, high dielectric constant is important or lowering the viscosity of the solution to improve the mobility.

So, I think that you now understand the role of this salt and solvent in controlling the viscosity and electronic ionic conductivity of the electrolyte.

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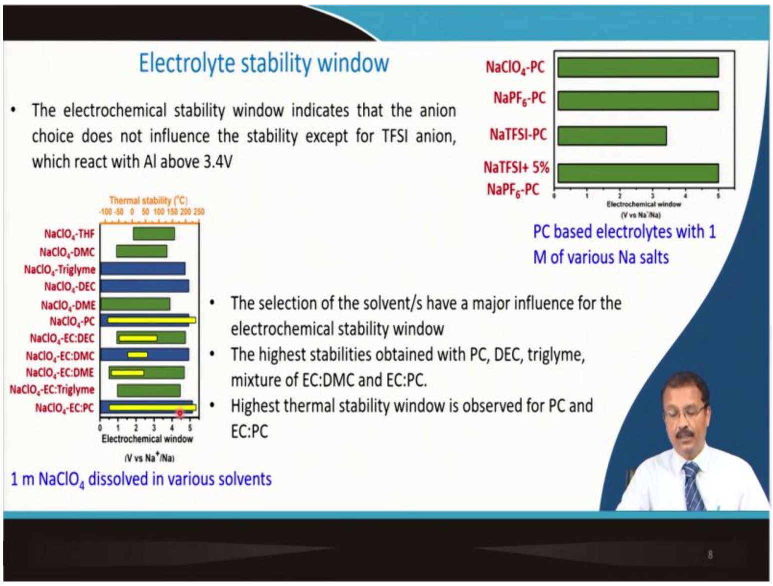

Now, the stability window is important, the electrochemical stability window that indicates that anion choice does not influence the stability, except for TFSI anions, which react with aluminum about 3.4 volts. So, if you study this, it is actually 1 molar sodium perchlorate that is dissolved in various solvents. So, the solvents are here this is given and this part is the electrochemical window.

So, it has a wide electrochemical window sodium perchlorate N a c EC and PC polycarbonate; but this is having a very low kind of electrochemical window and this yellow part is the thermal stability. So, you should have a good thermal stability and wide electrochemical window. So, the PC based electrolyte is giving a good characteristic. So, this has been compared with various types of sodium perchlorate salt and this is plotted with the electrochemical window.

So, as you can see that this one is good, this two are good, it is slightly less, NaTFSI PC that is having a very shorter window. So, the selection of solvent have a major influence for the electrochemical stability window as well; earlier we saw the electronic conductivity and viscosity also is more or less controlled by the solvent. And the highest stability is obtained with PC DEC, then triglyme, mixture of EC DMC or EC and PC. So, highest thermal stability window is observed for PC and EC is to PC.

So, these are good guideline for you to select that what kind of solvent, what kind of salt that we will use; not only to control the ionic conductivity and viscosity, but also the electrochemical window, the voltage range that basically the HOMO LUMO band, the voltage range that you can operate it with and also the thermal stability of this electrolyte solution.

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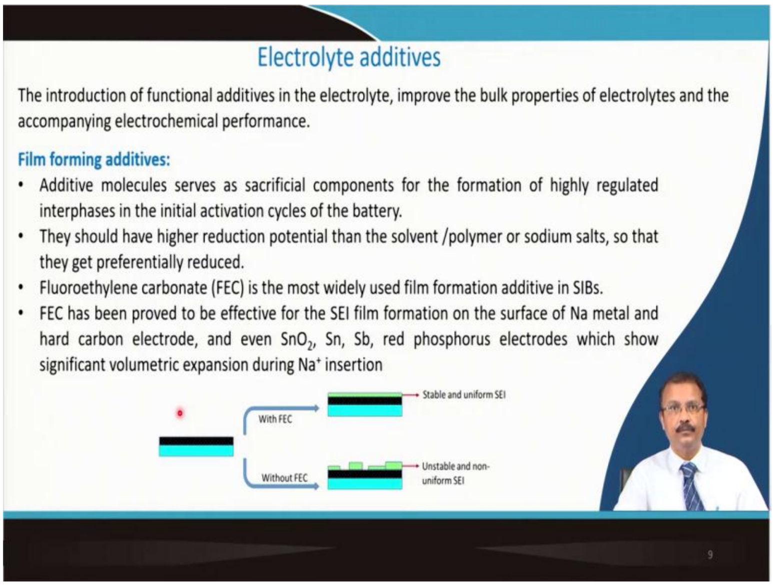

Some case you add the functional additives to the electrolyte and that is to improve the bulk properties of the electrolyte and accompanying electrochemical process, this also was introduced for lithium ion cells. So, there is a film forming additive as you can see that, FEC is the best one.

So, without FEC the form, this is the current collector, this is your negative electrode and this one is your unstable kind of SEI that forms. So, you should not expose this electrode further. So, you should have a stable and uniform SEI.

So, this molecule serve as a sacrificial components for the formation of a high regulated interphase in the initial activation cycles of the battery; you remember that when you construct a cell, then forming cycles are important, where you basically grow the SEI layer, you know the reversible capacity, you know the irreversible capacity and then accordingly you construct the cell, you design your cell in that way.

So, they should have very high reduction potential than the solvent or polymer or sodium salt, so they are they get preferentially reduced. Fluoroethylene carbonate, that is a FEC; this is the most useful one and it has been used for SIB as well as in LIB also and this has been proved to be effective for this SEI film formation on the surface of sodium metal and also hard carbon electrode and even the conversion type of anode SnO 2 or alloy type of material Sn, Sb, red phosphorus, so this is a quite good and effective electrolyte additives that one can think of.

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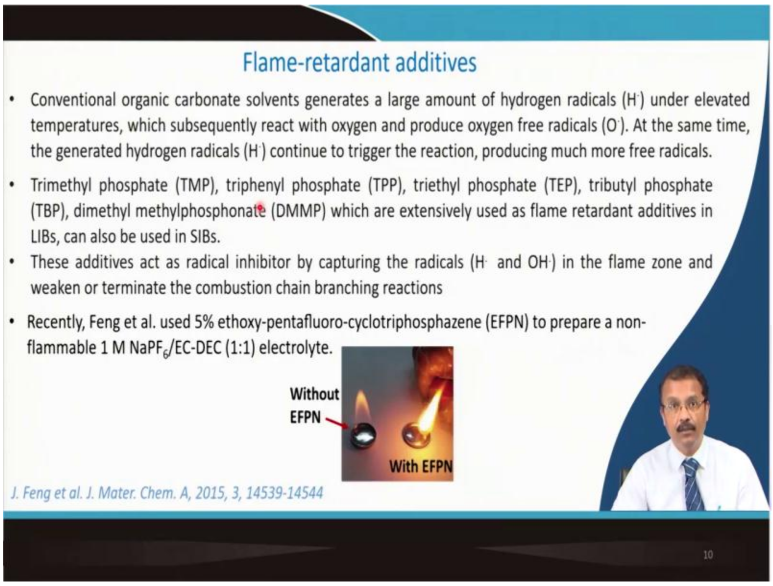

Then for sodium ion battery, since the melting point is quite low for sodium metal case, flame retardant additives they are very useful. So, conventional organic carbonate solvents that, they basically generate a large amount of hydrogen radical, particularly at high temperature that, reacts with oxygen and produce this oxygen free radicals. At the same time the generated hydrogen radicals continue to trigger this reaction and that produces more free radicals.

So, this trimethyl phosphate TMP or triphenyl phosphate, triethyl phosphate, tributyl phosphate, dimethyl methylphosphophonet, DMMP; these are extensively used for the flame retardant additives in LIB and they can also be used in case of your sodium ion batteries.

So, this additives acts as a radical inhibitors. So, they basically capture the radicals H and OH types in the flame zone and weaken the terminate, either they weaken it or terminate this combustion chain branching reactions.

So, they are indeed very effective. So, this paper is quite good one. So, this fellow Feng used about 5 percent of ethoxy pentafluoro cyclotriphosphazene, which is abbreviated as EFPN and prepare a non-flammable 1 molar sodium PF 6 that is the salt in EC DMC 1 is to 1 electrolyte.

So, as you can see that with this PFN, this is not flammable as compared to bare EFPN kind of additives. So, I would like you to go through this journal paper to know more about this additives.

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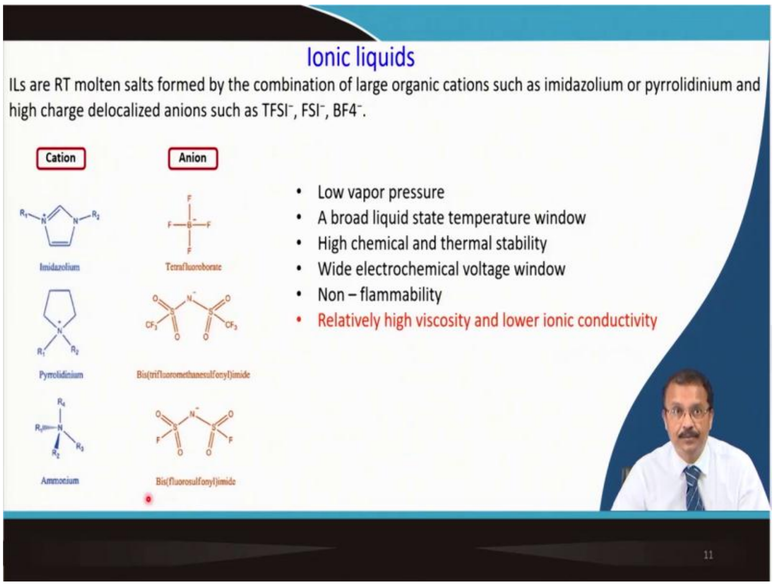

Ionic liquids you know that, at room temperature their molten salts that is formed by combination of large organic cations; imidazolium is one of them, pyrolydinium, pyrrolidinium, and high charge delocalized anions like TFSI and or FSI or BF4. So, same like lithium ion battery and this is the structure of cation and anion and they have low vapor pressure, a broad liquid state temperature window, high chemical as well as thermal stability.

And wide chemical electrochemical voltage window, they are non-flammable; but the problem similar to the ionic liquid that we use for lithium ion batteries, its viscosity and relatively lower ionic conductivity. So, that remains a major problem.

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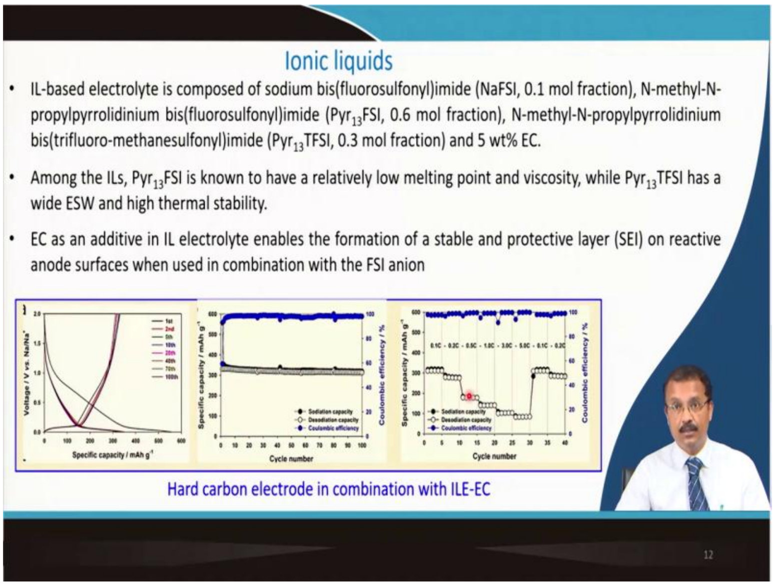

So, this sodium bis fluorosulfonyl imide which is abbreviated as NaFSI, small fraction point 1 mol fraction in N methyl N pyrrolidinium and bis fluorosulfonyl imide, which is abbreviated as Pyr 13 FSI, 0.6 mol fraction and N methyl N pyrrolidinium bis trifluoro methyl sulfonyl imide, this is P y r 13 TFSI and 5 weight percent of EC.

So, this are the popular ionic base liquid which people have tried and you have studied with sodium ion battery. So, among the ionic liquids, this composition; this Pyr 13 FSI that is known to have a relatively low melting point and viscosity and this TFSI based has wide electrochemical stability window and high thermal stability.

So, sometimes EC also is add added in this ionic liquid as additive to basically enable the formation of a stable protective layer SEI on reactive anode surface, when used in com combination with FSI types of anion. And this is some results taken from the literature report and this coulombic efficiency, sodiation and dissodiation they are quite impressive and this is used with hard carbon electrode and a combination of ionic liquid base electrolyte and EC as a additive and the rate performance is also quite good.

So, people are studying this ionic liquid, mainly because that when he will go for the high voltage sodium ion positive electrode; then certainly to retard the electrolyte oxidation because of this high voltage, then ionic liquid is the only answer.

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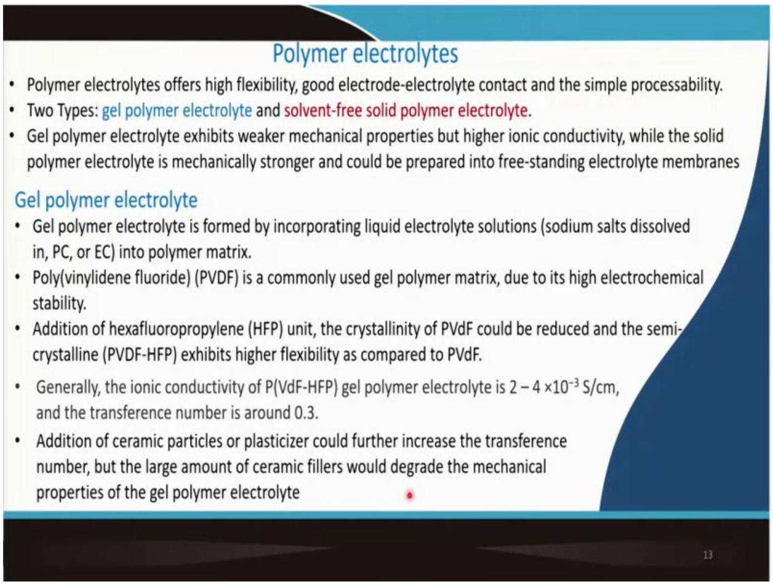

Polymer electrolyte people have started using it, mainly they are two types; one is the gel polymer electrolyte, and another one is a solvent free solid polymer electrolyte, exactly the same what we described in case of lithium ion battery. So, this gel polymer electrolyte that actually exhibits a weaker mechanical properties; but flexibility is quite good, it has good electrode electrolyte contact and processing is quite simpler.

So, but mechanical property is a bit weak; but conductivity is higher, because you are using the organic solvent also. And solid polymer electrolyte that is on the other hand mechanically stronger; you can prepare it in the free standing film as well as a membrane.

So, they have relative advantages and disadvantages. So, in case of gel polymer electrolyte, this is formed by incorporating a liquid electrolyte solution, which is sodium salt dissolved in a cyclic and linear types of solvent into a polymer matrix.

So, PVDF is taken as that polymer matrix. So, that is used as a gel polymer matrix due to its high electrochemical stability. Then addition of this HFP unit, that is hexafluoropropylene crystallinity of PVdF could be reduced and the semi crystalline PVDF HFP exhibits a higher flexibility as compared to the sole PVdF.

Ionic conductivity this electrolyte is about 2 to 4 into 10 raised to minus 3 Siemens per centimeter is not that aggressive; because had it been in minus 2 range, it would have been better. Transference number is about 0.3; I hope that you know what is transference number.

Addition of ceramic particles sometimes or some kind of plasticizer that could further increase the transference number; but large amount of ceramic fillers would eventually degrade the mechanical properties of the gel polymer electrolytes.

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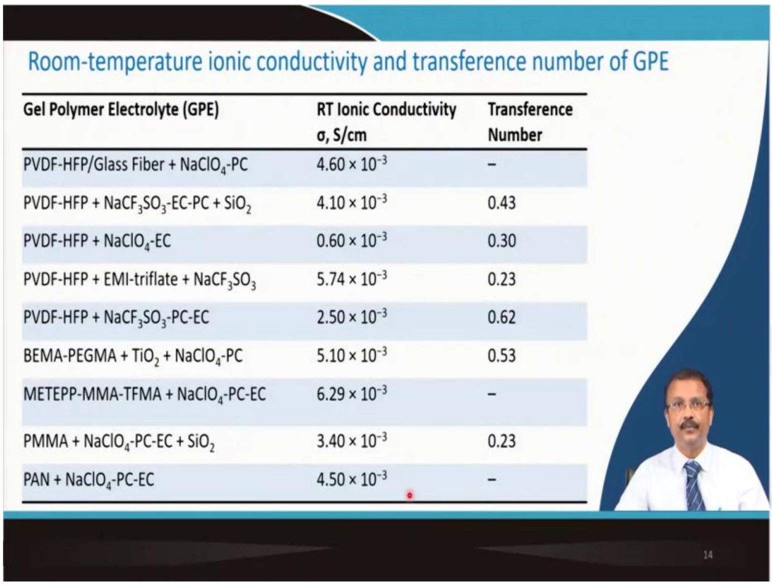

Gel Polymer Electrolyte (GPE)	RT Ionic Conductivity σ, S/cm	Transference Number
PVDF-HFP/Glass Fiber + $NaClO_4$-PC	4.60×10^{-3}	–
PVDF-HFP + $NaCF_3SO_3$-EC-PC + SiO_2	4.10×10^{-3}	0.43
PVDF-HFP + $NaClO_4$-EC	0.60×10^{-3}	0.30
PVDF-HFP + EMI-triflate + $NaCF_3SO_3$	5.74×10^{-3}	0.23
PVDF-HFP + $NaCF_3SO_3$-PC-EC	2.50×10^{-3}	0.62
BEMA-PEGMA + TiO_2 + $NaClO_4$-PC	5.10×10^{-3}	0.53
METEPP-MMA-TFMA + $NaClO_4$-PC-EC	6.29×10^{-3}	–
PMMA + $NaClO_4$-PC-EC + SiO_2	3.40×10^{-3}	0.23
PAN + $NaClO_4$-PC-EC	4.50×10^{-3}	–

So, this room temperature ionic conductivity we will compare along with the transference number of this gel polymer electrolyte, there are several gel polymer electrolytes that people have studied. And you can see here the conductivity range is not improved much; there is not anything available, which is having a dramatic change in the order of magnitude.

So, still further research is required to understand it and gel polymer electrolyte it will be particularly useful for flexible kind of sodium ion cell, which is not part of this course anyway. But that is also an interesting area of research, where you can have a not a stiff battery; but a flexible battery which you can wrap it, you can make a fiber kind of thing. So, that is a very very interesting area, which is emerging in last decade. So, that also is quite useful.

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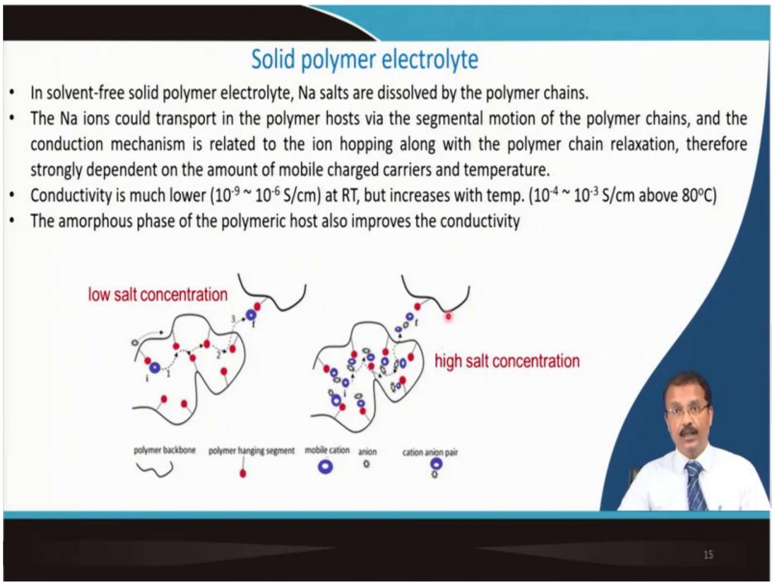

So, solid polymer polymer electrolyte, this is solvent free solid polymer electrolyte, sodium salts are dissolved in the polymer chains. The sodium ions could transport in the polymer host via a segmental motion, segmental motion within the polymer chain. So, polymer chain relaxation takes place; therefore they strongly dependent on the amount of mobile charged carrier and also temperature is involved.

In my non-metallic material course, I have a detailed description about the basic polymer structure. So, if it is I am sure that is available. So, I would like you to just go through those five lectures in module 1 of my non-metallic material courses, so that this segmental motion or the type of the polymer structure that will be clear to you. So, conductivity in this case you see it is quite low 10 raised to minus 9 9 to 10 raised to minus 6 at room temperature.

And increase with temperature. So, if you go above 80 degree Celsius, it just increases. So, still it is a long way to go and to control this polymer hanging segmental motion and how to control this mobile cation through this. So, that part needs to be better engineered, before you can use this polymer electrolyte in sodium ion battery.

So, this is not in a stage of commercialization anyway; but even as a part of a research, first we will have to reduce the conductivity substantially, because 10 raised to minus 3 and 10 raised to minus 6 at room temperature is a huge difference. So, the amorphous phase of the polymeric host that also improves the conductivity. So, we should have a semi crystalline polymer and we should have the control on the amorphous phase in the polymer to improve its ionic conductivity, sodium ion conductivity.

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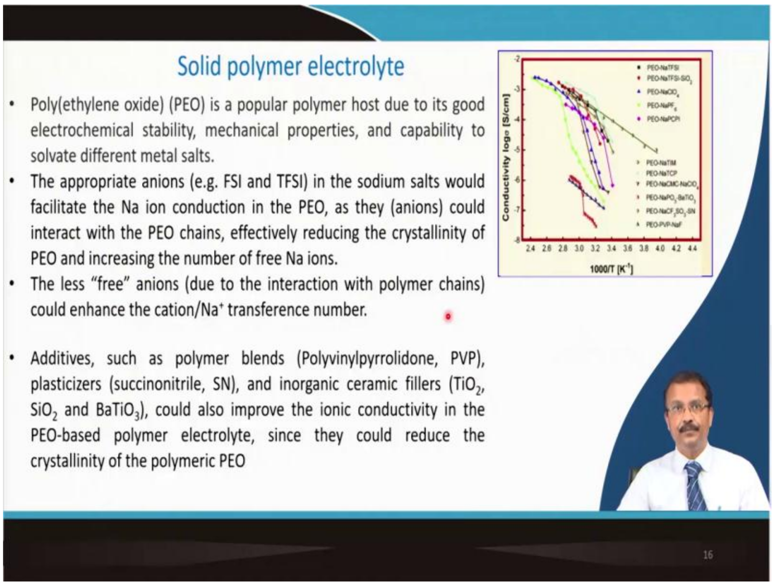

So, this solid polymer electrolyte there are lot of research that is going on; you can see here the conductivity versus temperature plots, temperature is increasing in this way and this is a number of different types of polymer based electrolyte. So, out of that, this PEO polyethylene oxide, this is a polymer which is a popular choice, mainly due to its good electrochemical stability and other mechanical properties and it can solvate various types of metal salts.

Appropriate anions that is FSI or TFSI in the sodium salt would facilitate the sodium ion conduction in PEO as basically this anion could interact with the PEO chain effectively reducing their crystallinity and PEO and increase their number of free sodium ion for proper movement. The less free anions due to interaction of this polymer chain could basically enhance the cation is to sodium cation, I mean the sodium ion transference number.

So, polymer blends that is PVP or plasticizer, that is succinonitrile and inorganic ceramic fillers which is T i O 2, sometimes they have used or silicon dioxide even barium titanate is also used; that basically found to improve the ionic conductivity in the PEO base, that is the I mean mostly studied polymer based electrolyte. And basically all this addition they what they do is to reduce the crystallinity of the polymeric PEO.

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So, this is your study material, this is a quite good description you will find in this two particular publications and this also is a good review article, that one should go through.

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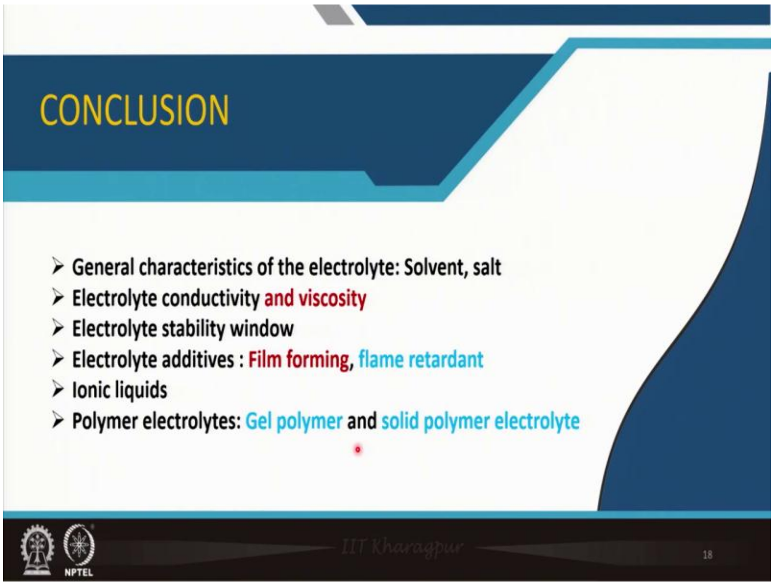

So, in this particular lecture, we talked about general characteristics of the electrolyte; mainly their salt and different solvents including cyclic and the linear one. Electrolyte conductivity and viscosity, interrelation with the solvent and the salt that we talked about; then electrolyte stability window also with solvent and electrolyte the salt in the electrolyte that was talked about.

The actual role of FEC as a film forming agent or several flame retardant additives in the electrolyte that was introduced. Ionic liquid work is coming up for sodium ion battery as well, but they are not yet well established. And gel polymer electrolyte some work has been done and solid polymer electrolyte that will be very much needed for flexible battery for energy storage. So, the latest things I have described.

Thank you for your attention.