Electrochemical Energy Storage
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

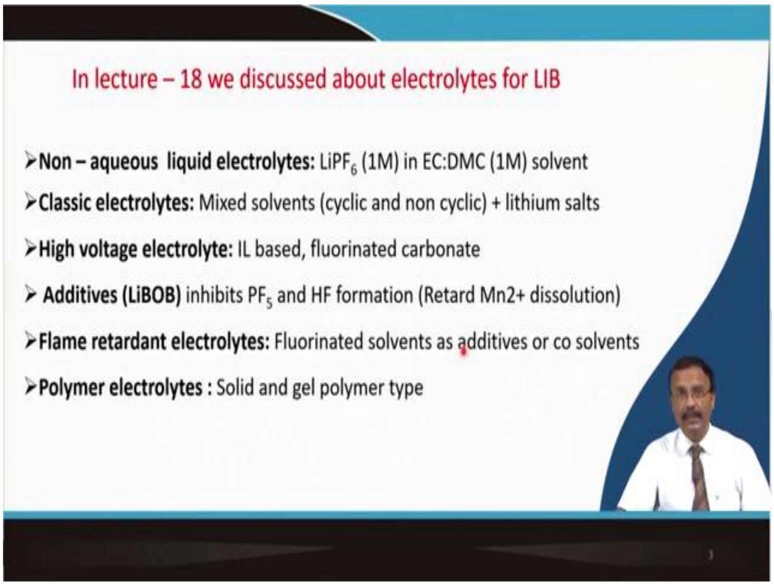
Module - 04
Basic components in Li – ion batteries: Electrodes, Electrolytes, and collectors
Lecture - 19
Current Collectors, Conductive Agents, Separator and Other Accessories

Welcome to my course Electrochemical Energy Storage. And, this is module number 4, where I am describing Basic Components in Lithium ion batteries, which includes Electrodes, Electrolyte, and collectors, separators. And, in this particular lecture we will be talking about Current Collectors, Conductive Agents, Separator and Other Accessories which are required to construct a commercial lithium ion cell.

(Refer Slide Time: 00:57)

So, the construction of a cell that will be described, then conducting agent what is their role; that, I will highlight followed by binder, then current collectors, separators, and also during cell construction you need to have tabs. So, that will also be introduced and what are the materials that usually we use.

(Refer Slide Time: 01:31)



Now, in lecture number 18, we discussed about electrolytes, which is an integral part of lithium ion battery. And, we told that non aqueous liquid electrolyte that is used. And, in most of the cell we use the salt component which is LiPF 6, usually we take one molar of this solution, I mean the salt and which is dissolved in a mixture of solvent. One is a cyclic type and another one is non-cyclic type. That, usually is 1 is to 1 volume ratio. This is not 1 molar, this is 1 is to 1 volume ratio of these two solvent and lithium PF 6 that is dissolved in it.

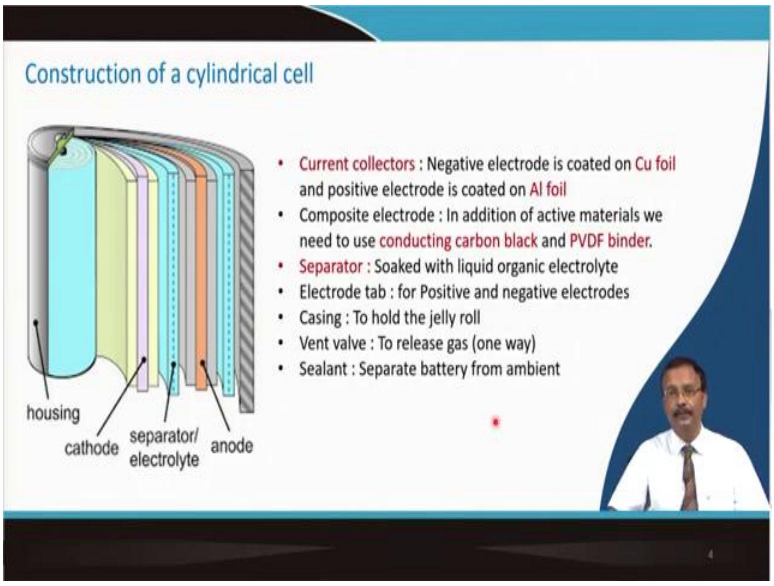
So, this is classic electrolytes, which use mixed solvent and you know that, what are the role of this mixed solvent, what are the role of the cyclic component, what are the roles of the non-cyclic component. Along with lithium salts which gets dissociated. Now, this kind of electrolytes that is good for low voltage lithium batteries, but when you consider high voltage, electrolyte required for high voltage lithium ion battery, then, usually one should use ionic liquid based electrolyte or fluorinated carbonate.

So, that has a higher flash point and certain advantages, which I described in my last class. Some additives are required typically LiBOB, that basically inhibits you remember that PF 6 PF 5 and hydrofluoric acid formation, if trace amount of water is there in the electrolyte. And, eventually it retards in case of spinel based positive electrode, the disproportionate reaction, Mn 3 plus if it is present it is converted to Mn 4 plus, which stays back in the electrode and Mn 2 plus that dissolute in the electrolytes. So, that dissolution is inhibited by this additives.

Apart from that fluorinated solvent as additive or as co solvent with carbonate based solvent, that is also used and they retard the flame. In case of thermal run out, then it will actually retard the flame propagation. So, that is also sometimes used. And in polymer electrolyte we talk two types; one is solid type where PEO or; PEO and oxide composite they are used. Along with the gel polymer where organic solvents are also used.

So, these are common for lithium polymer batteries. So, polymer forms an integral part the liquid electrolytes they form an integral part of commercial lithium ion cells.

(Refer Slide Time: 04:50)



Now, if you see the construction of a cylindrical cell, then you can see we have current collectors for negative electrode that is coated on copper foil. And, usually positive electrode, that is coated on aluminum foil. So, you know that this is your cathode material and this is coated on a current collector, and then you have separator, and then you have anode, then you have current collectors and everything is rolled.

So, we call it is a jelly roll and the separator is basically soaked, in fact the whole assembly is soaked with electrolytes. So, when I will talk about the construction of the cylindrical cell it will be clearer. So, this is the basic construction. So, apart from these main components, you know that there are housing, this housing that material will also have to be included and the connectors between the anode and cathode, integral part of this cylindrical cell.

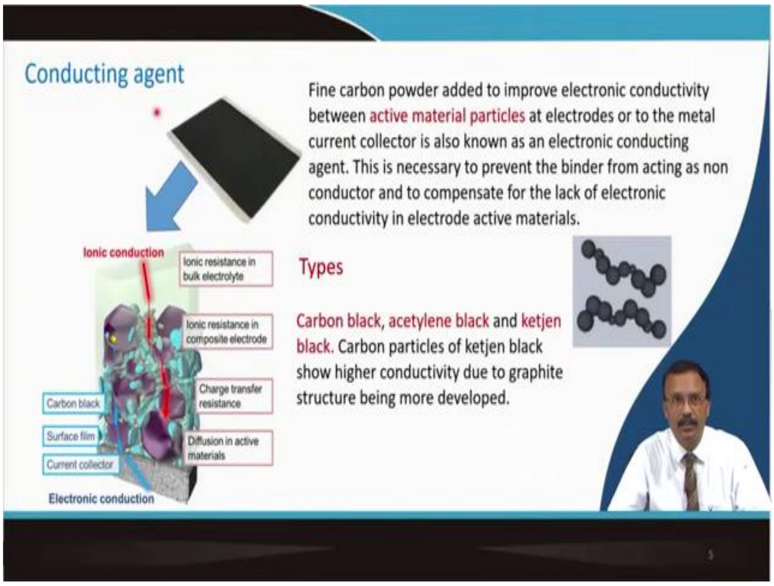
So, the composite electrode in addition to active materials, we need to use conducting carbon black and PVDF that acts as a binder. We need to use separator which is soaked with liquid electrolyte, organic based, then we need electric electrode tabs, for positive and negative electrode to take the electrons out. So, it acts as a connector.

Then we need casing to hold the so, called jelly roll. And, sometimes gases are formed you know that from electrolyte oxidation gas can form certain electrode material like, LMR or lithium cobalt oxide if you charge it at very high voltage oxygen comes out. So, there are various gaseous product. So, that will build pressure inside this cell, when they are hermetic sealed.

So, you need a vent valve somewhere a one way valve to release this gas pressure. And, exactly it is not known, that in the pressured condition how will be the charge discharge characteristics. So, that is one way to eliminate that we need to have a vent valve.

And of course, we need sealant that separate the battery from ambient, because you know moisture is one of the major concern, if you are using LiPF 6 with ECDMC. So, hydrofluoric acid can form they can lead to the manganese 2 plus dissolution. They can corrode the current collectors. So, you need a sealant so that this cell is detached from the ambient.

(Refer Slide Time: 07:52)



So, let us have a look of this composite electrode which is coated say on aluminum foil. So, the coating looks like this and it is a large long coating and winding machines are used to form the rolls, so that we will cover later.

So, if you look at this composite electrode, which is coated on the current collector then several phenomena that occurs here. You can see the carbon black and the active material, they are intimately mixed and the binder helps to hold this with the current collectors. And, also hold them together within this composite electrode.

Now, two types of conduction that you can see ionic conduction lithium comes in and then there are several reactions that takes place. So, ionic resistance in the bulk electrolyte is of our concern, that lithium should be moving quite fast. The viscosity is important, ionic conductivity of the ionic liquid is important, concentration of the salt is important. So, those kind of things already we have described in patches in earlier lectures.

Then, ionic resistance in the composite electrode that is of our concern it is not like liquid, it is a solid state. So, lithium diffusion through the bulk of the electrode which we can characterize basically from the EIS plot from the verb or tail that I defined in my one of my last classes. So, that is also important.

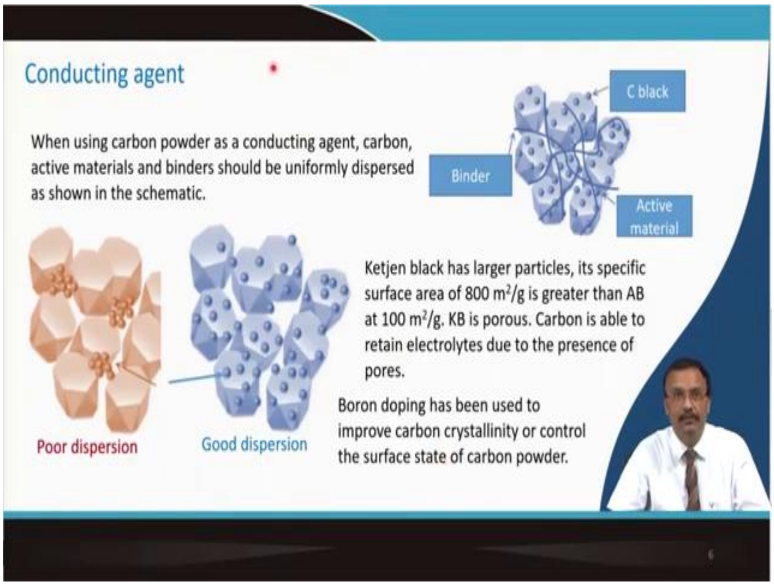
Then charge transfer, because it is coming as lithium plus and then it takes electron get reduced to metallic lithium. So, this charge transfer should be very smooth and we can also estimate what is the charge transfer resistance by Nyquist plot. That also I have hinted in my earlier classes. And, then diffusion in the active material, so diffusion is also important.

Carbon black takes care of the electronic conduction, because from the current collector actually the electron either towards this current collector or from current collector into the electrode material, that is important. So, homogeneous mixing is quite important. Then you have a surface film formation in the form of SEI layer it should be not; it should not be impervious to the lithium ion movement. So, those are the important consideration.

So, for conducting agent fine carbon powder that is added to improve the electronic conductivity between the active material particles, which are good ionic conductor or to the metal current collector. So active material particles at the electrode or to the metal current collector this is known as electronic conducting agent. And, this is necessary to prevent the binder from acting as a non conductor, because the binder which typically we use polyvinylidene fluoride. So, that is a non-conductor. So, the compensate the electronic conductivity this composites are made.

There are various types of this conducting agent, carbon black is one of them acetylene black or ketjen black. So, carbon particles of the ketjen black, they show higher conductivity. Due to their graphitic structure, layer structure. And, this is better although price is a bit high as compared to acetylene black or normal carbon black, but this is actually used in commercial batteries.

(Refer Slide Time: 11:58)

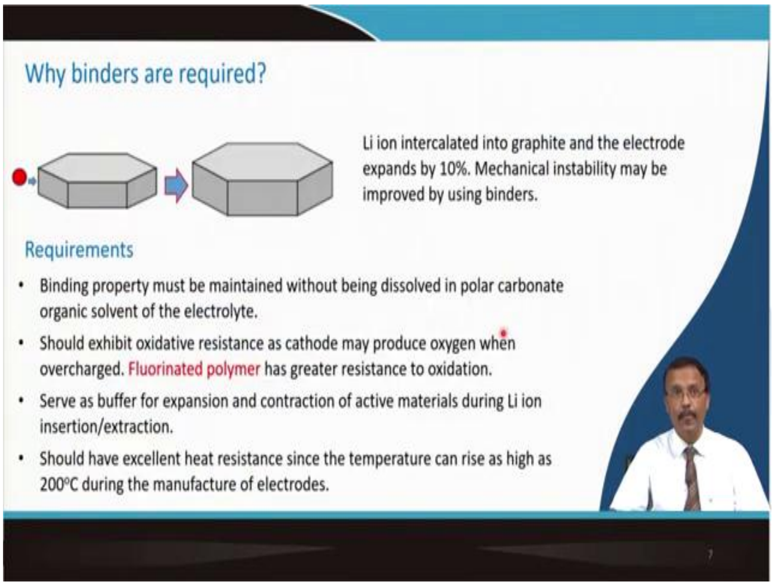


Now, this conducting agent when you use carbon powder, then carbon an active material and binder they should be of course uniformly dispersed something like this. You can see the binder particles they are polymer, the chain like this then carbon black, they are in the form of small globules, they are intimately mixed together with the relatively larger active material.

So, the dispersion is important between or among this binder, active material and this carbon black. And, this is a poor dispersion you see that they are getting agglomerated here and this is considered a good dispersion. So, if you compare with ketjen black has a larger particles and it is specific surface area is about 800 metre square per gram. And, this is basically little bit finer as compared to the acetylene black, which is 100 metre square per gram.

But, this KB although the larger relatively, if it is having a large particle size it is porous and this carbon can retain the electrolytes due to the presence of this pore. Sometimes we do boron doping to improve the crystallinity and to control the surface state of carbon powder. So, it is act is it is activity is basically improved.

(Refer Slide Time: 13:39)



Now, binder is actually required and why it is required it is clear to you now, because the active material, the conducting carbon and the binder they should be properly bonded to form the composite. And not only that, this composite also should have a strong bonding with the underlying current collector.

Sometimes we do tape casting and it is the industrial process to do the tape casting. But sometimes what happens that, tape casting they do not adhere the composite well into the current collectors. So, electrophoretic deposition I have shown earlier, that it is very effective to form a very strongly adhered layer.

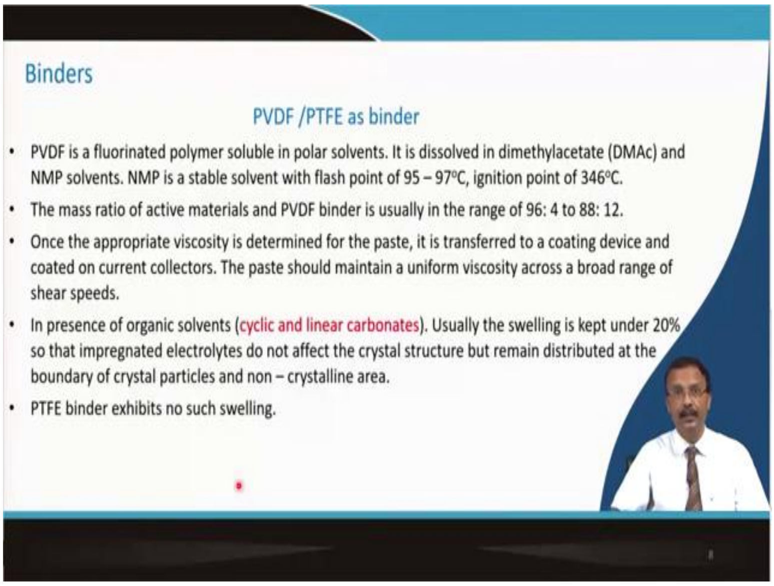
So, lithium ion intercalated into graphite and electrode expands by above 10 percent that also you know. So, mechanical stability this is improved it needs to be improved and for that, the binder is useful, it is a polymer base so it can buffer little bit the stress.

So, the binding property must be maintained without being dissolved in polar carbonate organic solvent of the electrolyte. So, that is one of the major criteria. So, if PVDF get dissolves in ECDMC, then the active particle will be disintegrated. So, that is not allowed.

And, you should exhibit oxidative resistance, because many cathode material they form oxygen you know cobalt oxide is one of them LMR is another oxygen is produced from the lattice. So, this oxidative resistance of this binder, they should be more particularly in case of overcharged, when you charge beyond 4 volt. So, fluorinated polymer they have usually greater resistance to oxidation. So, that is one of the reasons to use PVDF.

And, as I told it serve as a buffer for expansion and contraction of the active materials during lithium ion insertion or extraction. And, it should have excellent heat resistance, since the temperature can rise around 200 degree Celsius during not the operation but during the manufacturing, during hot calendering, which I will be describing later. So, temperature of the electrode you need to increase it for superior calendering to increase the tape density. So, it should withstand that.

(Refer Slide Time: 16:28)



So, sometimes PVDF binder is compared with PTFE kind of binder. So, PVDF is a fluorinated polymer soluble in polar solvent, it is soluble. So, usually this dimethylacetate and n methyl pyrrolidone these are the solvents to dissolve the PVDF and NMP is a stable solvent. So, it does not have it has a flash point around 95 to 97 degree Celsius. So, when you are drying the electrode before cell construction. So, ignition point is quite high as you can see 346.

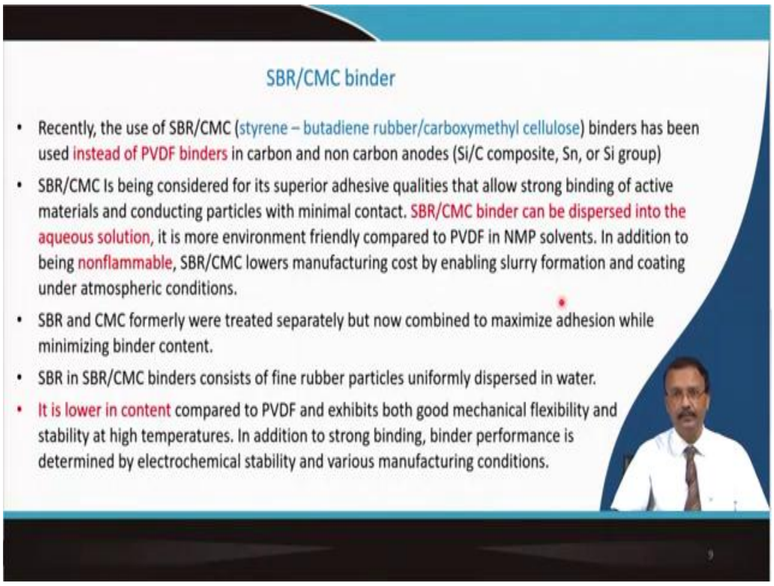
Usually, the mass ratio of active material and PVDF binder, that ranges like this. Active material must be larger, because for obvious reason your capacity depends on this. And, these are all stray elements, they contribute to the weight, but they do not do anything as far as the electrochemical reaction is concerned. And, it can vary from 88 is to 12.

So, once the appropriate viscosity is determined of the paste, it is transferred into a coating device is the tape casting unit. And coated on the current collector this ink, which constitute active material binder and conducting agent form some kind of ink and then it is tape cast. We will show how people do that, during cell construction.

Now, the paste should maintain a uniform viscosity across a broad range of shear speeds. So, the viscosity can be controlled for proper adhesion or proper laying out of this electrode. Now, the presence of organic solvents, you know that we use either cyclic or linear carbonates. Usually, the swelling is kept under 20 percent. So, that the impregnated electrolytes do not affect the crystal structure, but remains distributed at the boundary of the crystal particle.

You should not hamper the crystal structure of the active material, because you know that sometimes the graphite. For example, the solvated lithium, if it is inserted then there is exfoliation of the graphitic plane. And, PTFE is a binder that basically exhibits this kind of swelling. So, it is also considered as an alternative for PVDF binder.

(Refer Slide Time: 19:16)



Nowadays, this SBR which is styrene, butadiene rubber or carboxymethyl cellulose these binders are used instead of PVDF binder. In carbon as well as non carbon anodes; for example, silicon carbon composites or tin particle which form alloys, it has been used. And, this is considered superior adhesive quality as compared to your PVDF binder. So, that allows strong binding of active material and conducting particle with a minimal contact.

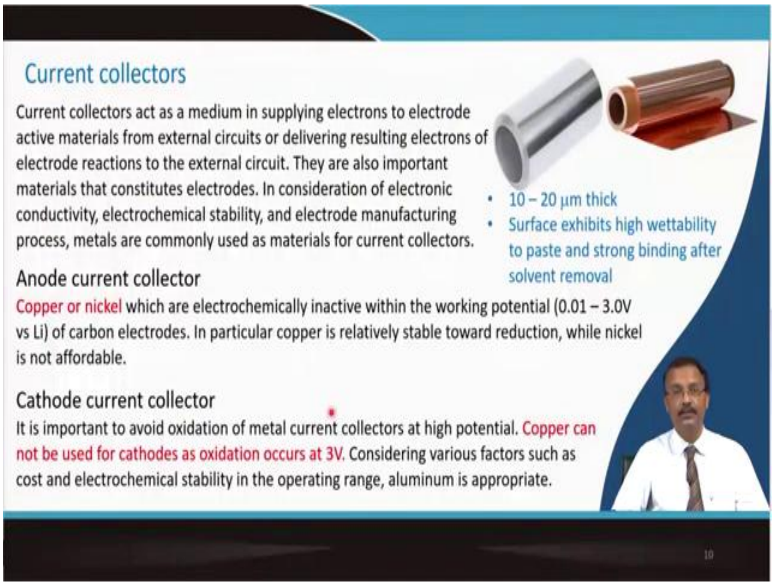
So, this binder can disperse in aqueous solution. Of course, you will have to dry it well because this should not remain in the battery during construction and afterwards, during cell characterization. It is more environmentally friendly than PVDF or NMP solvent this is carcinogenic. So, that therefore, this aqueous based binder is always good.

This is nonflammable and SBR, CMC that lowers the manufacturing cost also because PVDF is expensive. And, that enables the slurry formation and coating under atmospheric conditions. A dry room may not be required strong dry room. SBR and CMC, they were formerly treated separately, but now they are combined and maximize the adhesion of the electrode material on the current collector.

So, this SBR or this types of SBR, CMC combined binders. They actually consist of fine rubber particles, which is uniformly dispersed in water you know rubber is an elastomer and it is lower in content is required as compared to PVDF. So, you are gaining the gravimetric energy density, because the weight is relatively low.

And, it exhibits both good mechanical flexibility and stability at high temperature, that is also plus points. In addition a strong binding, binder performance is determined by the electrochemical stability as well. So, this electrochemical stability is quite good under various manufacturing conditions.

(Refer Slide Time: 21:53)



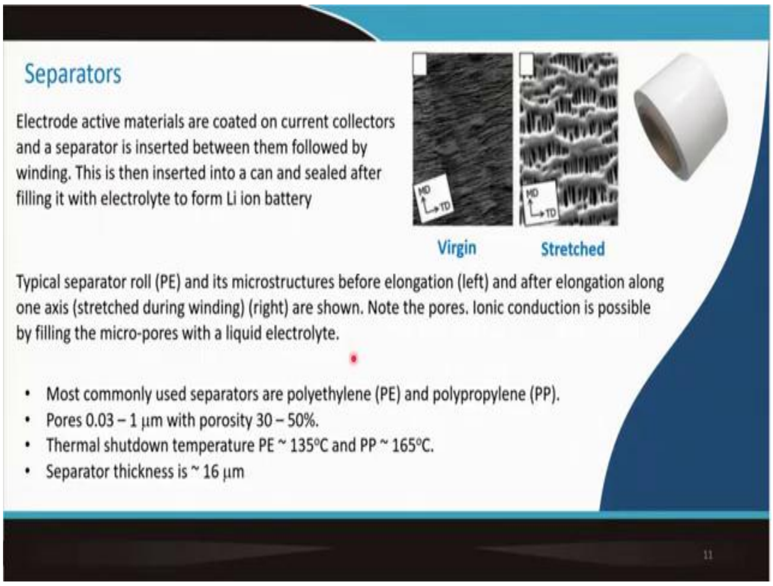
Now, the current collectors, that acts as a medium to supply the electron that you know. So, from the active material either the electron is coming from the external circuit or deliver the electrons during reaction to the external circuit during charge and discharge in two separate electrode.

They are actually important material that constitutes the electrodes. In consideration of electronic conductivity, electrochemical stability and electrode manufacturing process metals are usually used for current collectors. So, copper is used for negative electrode and aluminum is used for positive electrode usually they are 10 to 20 micron thick. And, the surface exhibits high wettability of the paste on top of it, and strong binding when the binders are removed.

So, copper and nickel are universal choice in this working potential they work copper 0.01 to 3 volt. So, it can safely be used as a current collector for the negative electrode, but beyond that it is not stable. And, nickel is not affordable it is expensive. And cathode current collector you know that it goes to 4 volt range. So, copper cannot be used. So, in that sense relatively lighter aluminum is used.

So, it is almost universal choice it comes like a roll as you can see and aluminum and copper they are universal choice for positive and negative electrode respectively.

(Refer Slide Time: 23:42)

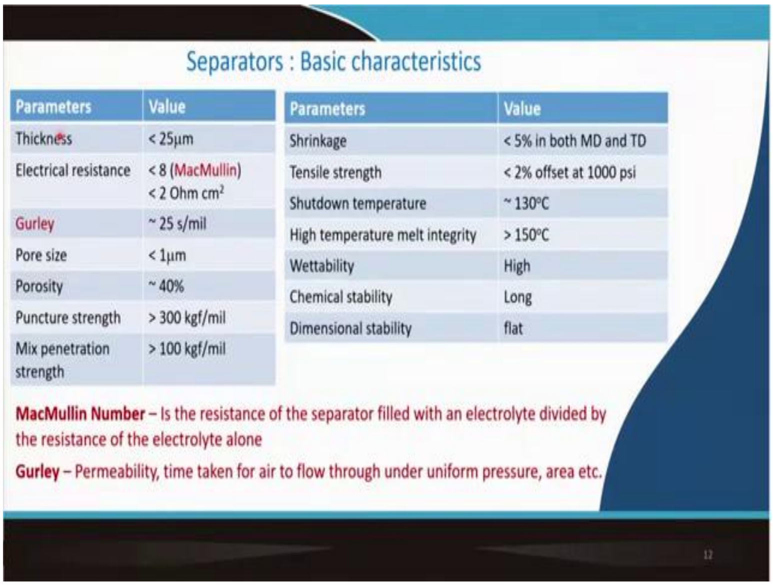


Now, the separator this electrode active materials they are coated on current collectors and in between there are separator inserted between them, and then you do the winding of the cell. So, this is inserted into a can and then sealed as you have seen in case of a cylindrical cell.

So, typical separator role is polyethylene and it is microstructure before elongation is something like this, you know that once you are rolling it, then it is stretched. So, after elongation in one axis stretched during winding they are having pores like this. So, ionic conduction is possible, by filling this micro pores with liquid electrolyte. So, that lithium can pass through.

So, most commonly used separators are polyethylene and polypropylene. So, pore size is typically 0.03 to 1 micron and the porosity is 30 to 50 percent, thermal shutdown temperature is 135 degree Celsius. So, if the temperature is raised then it will block the lithium ion passage by melting and the pores will be clogged. So, the connection will be disconnected between anode and cathode. And, usually the separator thickness is about 16 micron.

(Refer Slide Time: 25:15)

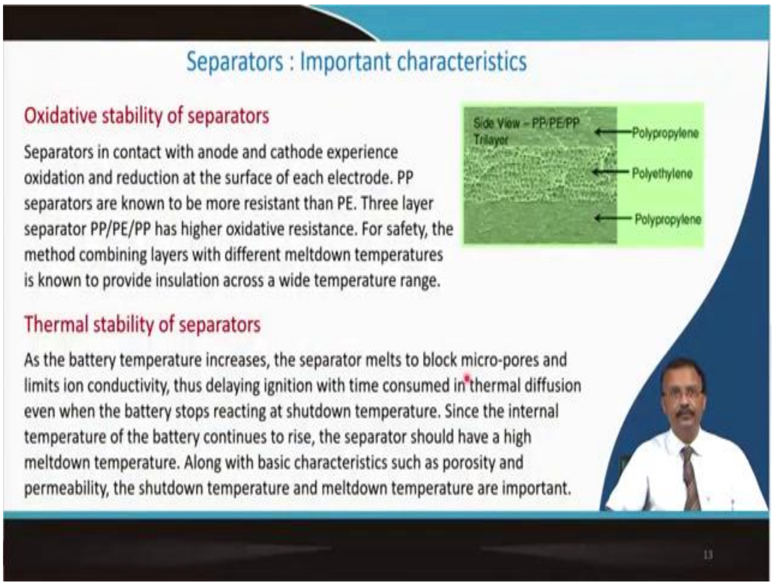


So, here are important characteristics thickness should be less than 25 micron; the electrical resistance is measured in terms of this MacMullin number. So, this is the resistance of the separator which is filled with an electrolyte divided by the resistance of the electrolyte alone. So, this number is the MacMullin number the corresponding electrical resistance is less than 2 Ohm centimeter square.

So, there is another thing which is Gurley. Gurley is the permeability that denotes the permeability time taken for air to flow through under a uniform pressure or uniform area. So, this number is also important usually it is about 25 second per mil 1000 time of an inch that is mil. Pore size is less than 1 micron, porosity is around 40 percent, puncture strength is important because you know that in case of dendrite formation it should not punctured, get punctured and leads to internal short circuiting. So, that is quite high 300 kg force per mil. And mix penetration strength, this is around 100 KGF per mil.

Shrinkage is less than 5 percent, tensile strength is less than 2 percent, shutdown temperature is important 130 degree Celsius. And, high temperature melt in integrity even if it melts it should not be just like a liquid the integrity is more than 150. Wettability is very high with the electrolyte, chemical stability is long and dimensional stability because we will have to wind it should not be scrambled. So, that is also quite good.

(Refer Slide Time: 27:12)



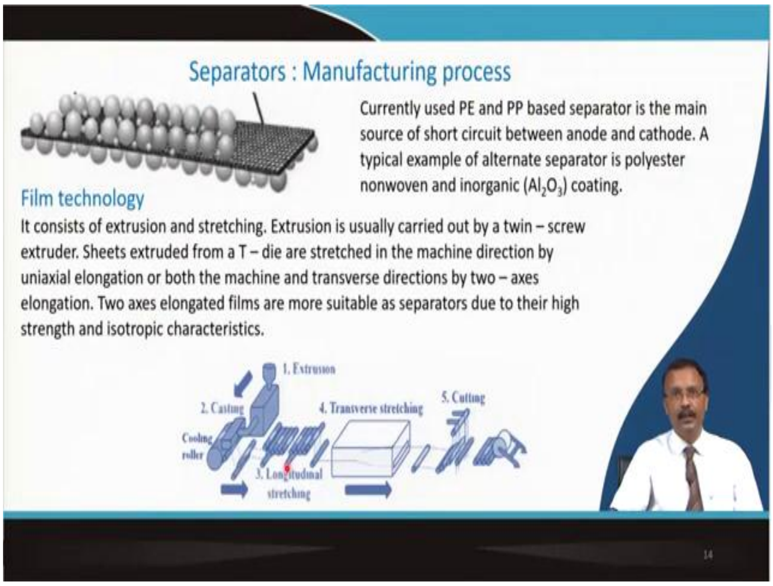
So, there are certain separators which are oxidative stability, step oxidative stable separator. And, this separators in contact with anode and cathode experience a oxidation and reduction at the surface of each of this electrode. So, your polypropylene separator are known to be more resistant then your polyethylene separator.

So, sometimes three layer separator as is has been shown, that is used polypropylene, then polyethylene, then again polypropylene. This has a higher oxidative resistance for safety the method of combining this layer with different meltdown temperature is important. And, that is known to provide the insulation across a wide temperature range.

So, the thermal stability of the separator that is important, as a battery temperature increases the separator melts and block the micro pores, which I just described and limits the ionic conductivity. So, that delays the ignition with time consumed in thermal diffusion even when the battery stops reacting at shutdown temperature.

Since, the internal temperature of the battery continues to be rise I mean it keeps on rising, the separator should have high meltdown temperature that is very important. Along with the basic characteristics such as porosity, permeability, the shutdown temperature and meltdown temperature, that is also very important for the separator.

(Refer Slide Time: 28:58)

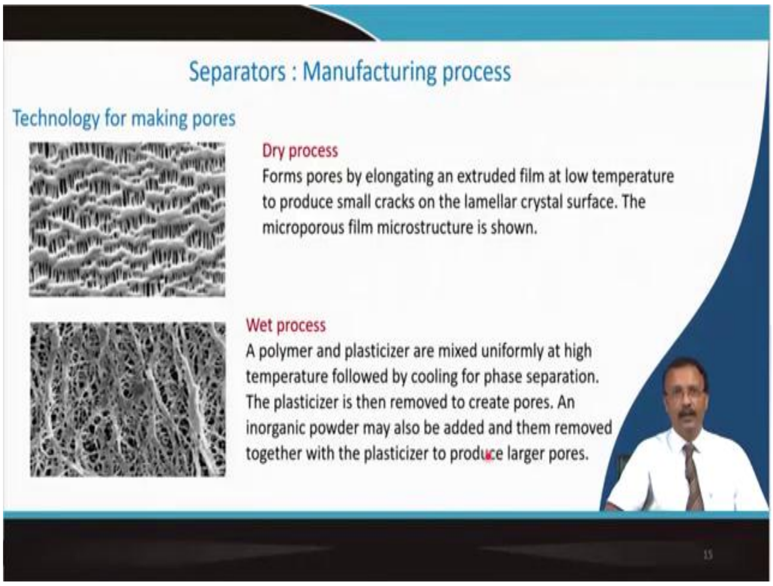


So, separator currently they are used polyethylene and polypropylene based separator that is a main source of short circuiting between anode and cathode. And, alternate separator could be a polyester nonwoven and this is coated with this aluminum oxide. So, these are considered to be stable, but this is all not actually commercially tried as such.

Now, there are several way that you can make this separator which are metres long. So, mainly extrusion is used; extrusion and stretching combined action. So, this is actually carried out by a twin screw uniaxial elongation, or both the machine and the transverse direction by two axes elongation. So, that you can see here; so, one is the longitudinal type and also the transverse type so it is extruded and this two axes elongation is more suitable, as a separator due to their high strength and isotropic characteristics.

So, they are extruded after casting this polymer you can see, that there are pulling roller and then they are stretched in both longitudinal direction as well as in the transverse direction by these two different types of dyes which is present. And, finally, they are rolled here in a spool.

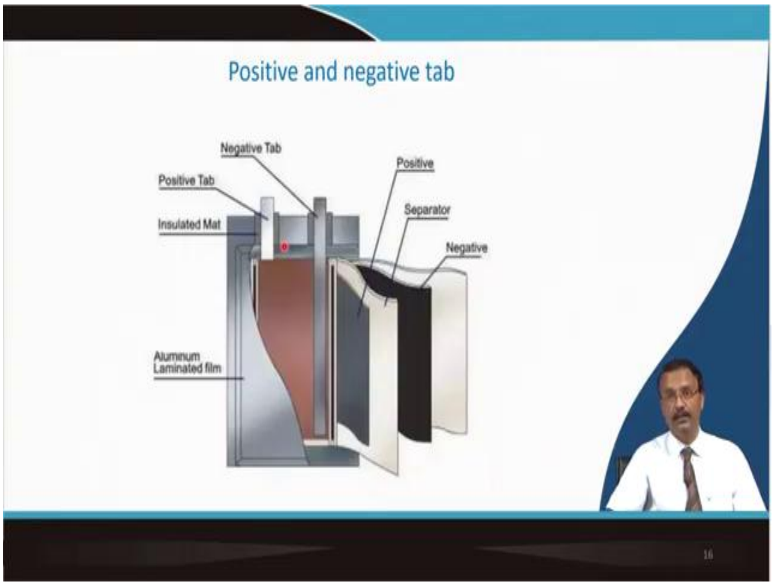
(Refer Slide Time: 30:44)



So, there are two different process of making this pore. The dry pores are by elongating the extruded film at low temperature and produce a small crack on the lamellar crystal structure. So, this is microporous film and this is the microstructure. And, also you have a wet process, where a polymer this polypropylene or polyethylene and plasticizer, they are mixed uniformly at high temperature followed by cooling for phase separation.

Now, the plasticizer is removed. So, once it is removed it creates pore like this inorganic powder may also be added and then removed together with the plasticizer to produce a larger pores.

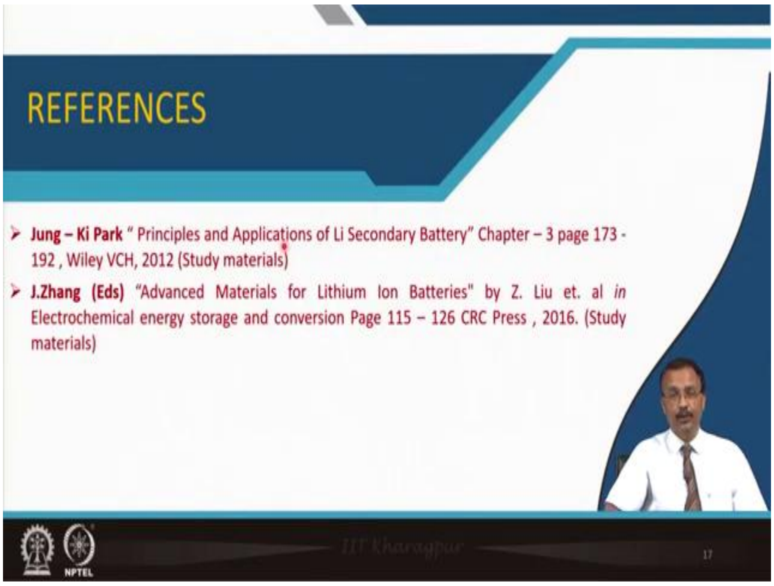
(Refer Slide Time: 31:36)



So finally, now this is a pouch cell typical pouch cell. So, instead of winding the jelly roll, here the stacking is done between your positive electrodes separator and negative electrode. And, then in order to take the connection out from the electrode you need to spot weld, this metal part which is known as tap.

So, you have positive tap for positive electrode and negative tap for negative electrode. Usually nickel tabs are used for taking the connection out from the pouch cell, it is clearly visible here. In case of cylindrical cell also spot welding is done. So, when I will describe the cell construction, it will be clearer to you that how exactly it is done.

(Refer Slide Time: 32:26)



So, these are the references the book by Park that is chapter 3, that is your study material. And, also the book by Zhang edited book the chapter by Z. Liu, that is important this 115 to 126, this you can read to clarify this ideas in a better way.

(Refer Slide Time: 32:55)

So, in this particular lecture we talked about type of conducting agents, their dispersibility issue wettability characteristics. Then, we talked about the binders, their functions, their characteristics, the types of binders, then we talked about the current collectors, aluminum and copper why they are used, because of their voltage stability.

Then separators; their function, their basic characteristics, their oxidative, and thermal stability, separator manufacturing also we have highlighted. You can go through the book chapters and read the relevant materials for a better idea. And, then finally, we talked about the tabs.

Thank you for your attention.