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

Module - 05
Characteristics of commercial lithium ion cells
Lecture - 23
Major Characteristics of Commercial Li ion Cells: Cell Performance, Degradation Phenomena

Welcome to my course Electrochemical Energy Storage and we are now in module number 5, where I am describing the Characteristics of commercial lithium ion cells and this is lecture number 23, where I will describe the Major Characteristics of Commercial Lithium ion Cells: the Cell Performance and Degradation Phenomena.

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One thing that is quite clear. You know that although we some of the groups we working on lithium ion batteries. In India we do not have any company who really makes. There are few who are trying to make or established a process line to prepare this lithium ion cell which is so important you cannot import the lithium ion cells.

So, here we will look at the what are the companies and which kind of cell and battery pack model they actually sell it to us, but honoring this Make in India initiative I am very much interested to see that we have lot of lithium ion battery manufacturer in our country. So, this is just a passing remark I felt that I should share with you.

Half cell characteristics of the negative and positive electrodes for determining the nominal voltage that is important. I should select the positive and negative electrode as well as the electrolyte. The same old figure which I have described. So, many times that the HOMO-LUMO band there should be larger the differences should be larger than the chemical potential of cathode and anode the VOCs is related to that. So, that must be taken care of.

And then we will talk about the characteristics of some commercial cells. And I have given the references here. And you can go to their website and you can you are now in a position to understand the what is nominal voltage, what is the energy density, what is capacity what is power density, what are the different shapes of cells, what are the typical applications, what are the chemistries that is involved in making the cell everything.

If you go through the previous lectures along with the fundamental part which I have touched, so, that you can understand that what are the science behind this kind of requirements. I am pretty sure that you will be able to understand that in what way these companies are selling the cells throughout the globe.

So, the characteristics of some of the commercial cells that I will introduce, then the cell performance evaluation that is important the capacity, the discharge characteristics, the temperature characteristics, the energy and power densities. So, that how to evaluate that or what to evaluate, so, that will be talked about.

And then how do they charge the commercial cell? So, charging and is not that simplified discharging is even more complicated that is guided by the application that is for you are looking for this cell. So, I have made no attempt about the discharge, but I leave it on you on imagination that what kind of the discharge profile that you may have in your application.

Sometimes you need to accelerate sometimes you need to have a constant cruising speed sometimes you want to de accelerate, so, the discharge current will vary and how it will affect your standard discharge profile that usually in laboratory you measure in a constant current. So, that is a matter of study. So, that is not attempted here.

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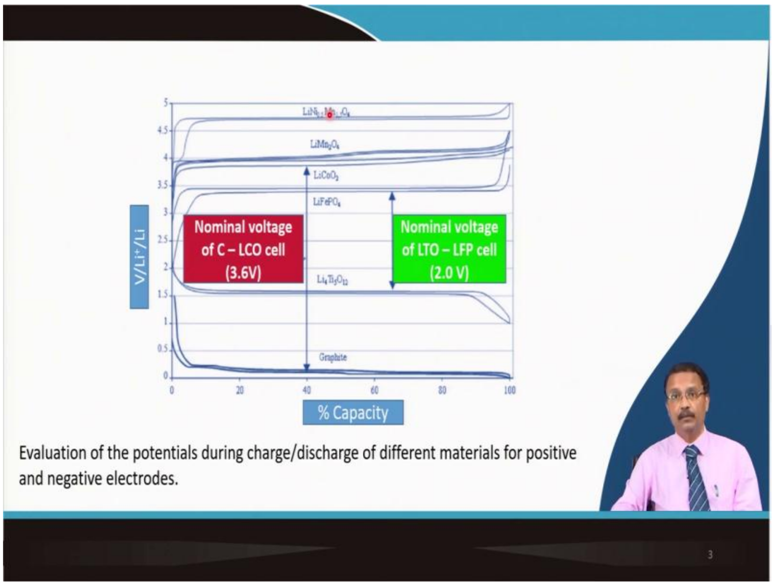

Now, if you see the different types of voltage profile this is the charge part and again from here we are discharging. So, this is you know that initially we apply a constant current and for charging and then put a load back and discharge again through it constant current. So, if you see the profile initially this is kind of charging profile goes like this and then you discharge like this.

So, the time that you calculate from here where the charging completed and discharging ends, so, that time you need to calculate the capacity which is I into T. So, that is quite straightforward. So, here the charge and discharge is not elongated, but it is again going back here.

So, there are 5 volt cathode which is LiMo. There are 4 volt cathode which is spinal based lithium manganese oxide, around 3.6 volt cathode which is lithium cobalt oxide and then around 3.6 volt slightly higher 3.9 3.8 volt lithium cobalt oxide and this is about 3.5 volt and then you have the capacity profile the voltage profile sorry the voltage profile for LTO and graphite.

So, LTO you can use with any of this cathode, but if you use it with say LFP then you get voltage is in 3.5 volt range it is around 1.5. So, you will get nominal voltage around 2 volt. But if you use graphite with say lithium cobalt oxide you will get 3.6 volt. If you use graphite with this one you will get much higher voltage. So, that is the potential if you do in the half cell configuration you have a quite good idea that what kind of voltage you will be getting in the half cell configuration right. But this is not all.

I mean you will have to select that this anode and this cathode whether it fits my criteria which I have told earlier the HOMO-LUMO band one and also upon charge and discharge whether the volt the whether the crystal structure is stable enough. So, during charging for example, lithium cobalt oxide if you over charge it oxygen evaluates evolve from the cathode.

So, that is a problem, in layered type of material if you extract more lithium then the structure collapses. A lot of problems are there and part of this problems I have tried to introduce when I was talking exclusively on the positive material negative material electrolyte in the earlier part of the course so, that you must keep it in mind.

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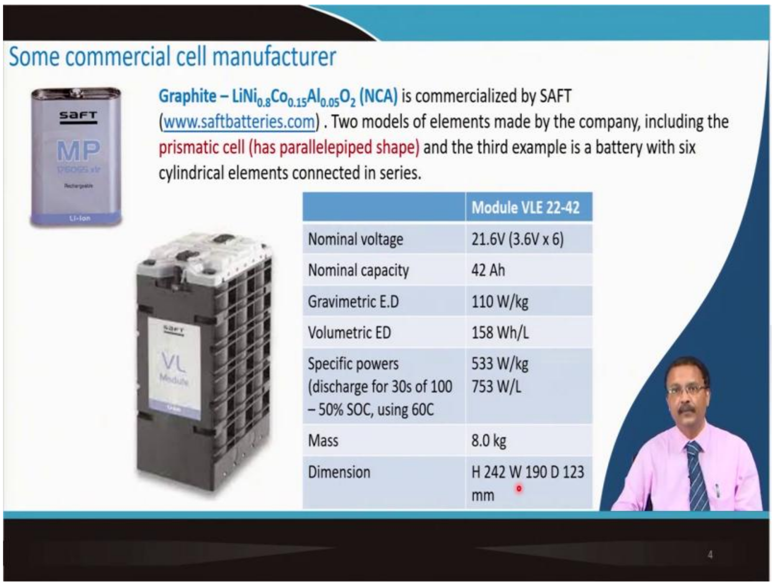

So, some commercial cell manufacturers for example, the SaFT Company, I have given the website of them. They use this graphite and you remember NCA. This is basically lithium nickel cobalt and aluminium is dope to increase the stability. Here nickel is in plus 2 valence state and cobalt is in plus 3 valence state. So, here is a 2 electron transfer that is why 80 percent of nickel is there and here it is a 1 electron transfer from plus 3 to plus 4, here it is plus 2 to plus 4. So, this is a quite good commercial material NCA.

And this is commercialized by SAFT and modules also have been developed along with the single cell. So, as you can see they usually work with the prismatic kind of cell which is having a parallelepiped kind of shape and they also make cylindrical cell 18 650. So, this is the module. They have made with 6 cylindrical cell.

So, there are variety of this kind of cell or this kind of model they usually sell for commercial purpose. Now, you know the nominal voltage is 21.6 volt; that means, 6 cylindrical cell and this is about 3.6 volt. So, they get 21.6 volt. So, remember that this is always in the even number for making this module and this is a typical module taken from their website.

Nominal capacity you can get 42 ampere hour that tells that you can get 42 ampere current for 1 hour. You will get 84 ampere hour if you have reduced the C rate or forget about it this is the nominal capacity. Then gravimetric energy density is about 110 watt per kg that you need to know because if you are going for a electric mobility then you need to know that 1 kg of the battery what kind of energy that I will get.

So, this is sorry this is power density this is power density because or I have made a mistake it could be watt hour per kg. So, please check it. So, there is something wrong here. And volumetric energy density is watt hour per litter that is the space that it is taking. Specific power of discharge that must be specified by the manufacturer, you can see here the discharge for 30 second of a 100 to 50 percent of SOC using 60C.

So, you can enormously drain current, but not for indefinite time. And for this module what is the energy and power density you are getting for that? Typical mass for this module is 8 kilogram and dimension you can see height, width and depth. So, this is the kind of thing you will look for when you are interested to purchase a battery module.

So, 42 hour with this kind of specific power discharge whether it suits your application wherever you want to put it maybe that is in a scooter or wherever with 21 volt or 42 ampere hour this application is suitable for your purpose. So, accordingly 1, 2 you can order from them and basically they serve the defense people for their typical applications.

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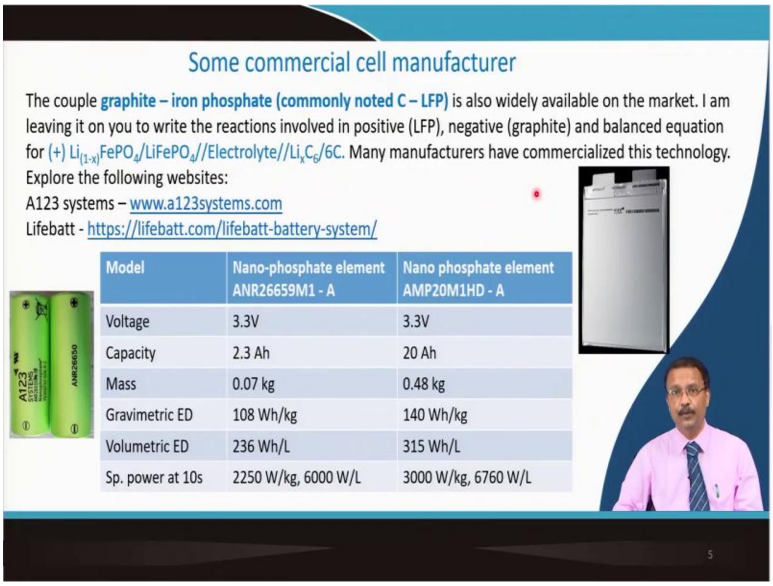

Another one is graphite and iron phosphate and they are cheap material as you can understand iron phosphate is cheaper one of the cheapest cathode material and graphite is also available plenty. It is widely available in the market. But as you can see it is 3.6 volt 3.3 volt around you will be getting with graphite.

And I am leaving it on you that how to actually write the cell equation when it is getting charge, what is happening to lithium iron phosphate, how much lithium is taking out and during discharge how much is going back and then you can calculate the theoretical capacity of it.

One of the examples or a couple of examples I have already referred in the earlier classes. So, please go ahead and do that. I may ask as part of the assignment problem that, if you have this kind of configuration then assuming that you can take out the whole lithium out of it, what is the capacity of the full cell that you will be getting. So, do this practice and that will clarify certain ideas of yours.

Many many manufacturers they have commercialized this technology and you can explore these two sites A123 system. As I remember that A123 is now bankrupt, but someone else has purchased them. I forgot the name of that particular Chinese company and Lifebatt they also have the details of the cell that they manufacture and sell. It is basically cell level. A123 makes both cylindrical cell as well as the pouch cell. The fabrication of both of them I will be covering in next two classes.

You can see now, the what is the voltage per cell that you get capacity. For cylindrical cell the capacity is certainly low because you have a smaller area of the jelly roll, but this is flat one and you can stack a lot of electrodes. So, capacity is 20 ampere per hour. Mass is of course, this is much lighter as compared to this one. You have gravimetric energy density. You have volumetric energy density and specific power at up to 10 second how much you can get out of it these actually are specified by the cell manufacturers.

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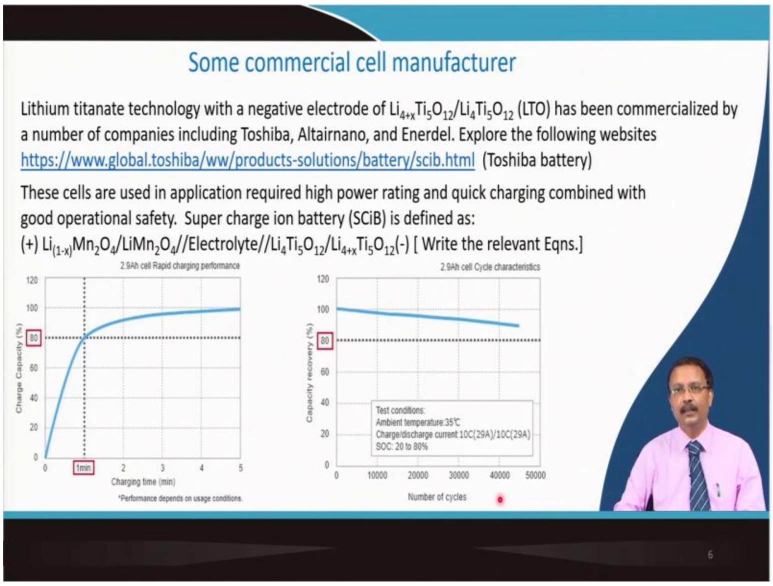

Now, another company probably Toshiba they are building a firm in somewhere in Gujarat in our company in our country and they have this technology. You see that it is LTO based technology. They have commercialized using lithium titanate technology and number of companies they adopt this.

And this LTO based technology what it does? If you use it with a spinal base material which is stable this one is also very stable. So, you can charge this cells at very very fast rate. You can see within 1 minute you have almost 80 percent of the cell capacity and within 5 minutes is a 100 percent cell is charged and this capacity fading is also reasonably good and see the number of cycles 40000 they are reporting.

This data we have gotten from their website and we can purchase one of two cells from A123. In fact, I have done it and I can test it in my laboratory that whether they are telling the truth and surprisingly this is truth because they could they can build a lot of good quality cell. I had an opportunity to visit ITRI in Taiwan, but unfortunately you know that they will never tell you how exactly they are manufacturing the cell.

All the procedure etcetera. In fact, I spent about one month there just to learn how to get a good quality of battery, what is needed to get a good quality of the battery like this capacity balance irreversible and reversible capacity balance and then to go for the tap density and mix the different types size range of the electrode material to have good packing density.

All the engineering things as a part of the project that was very clear to me, very clearly they could tell it to me.

But once I asked that I will have to see that in what way exactly you make this cylindrical cells with such a good performance they donate it a couple of cells to me. I tested in my laboratory, but they tell that this is not allowed. So, this is still a secrete that how exactly they make quality cell. So, this is one of the chemistry at least we know that Toshiba uses and very good quality cell they can make and sell in the market.

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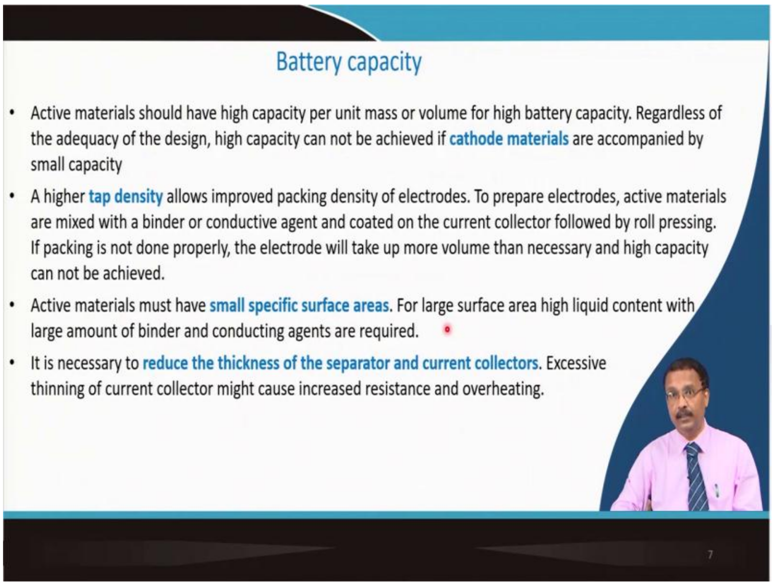

So, you know that this is the heart of the thing. Material is the heart of the lithium and battery technology. You need to know different types of material, how they can be utilized to get good quality of the battery, not only that you will have to be master on making the cells.

So, engineering aspect is also important. You will have to operate very sophisticated equipment where the your workmanship also matters to make a cell. If I make a cell in my laboratory it will be having worst performance. But my best PhD student when they are making the cell that is wonderful, make using the same material and everything so; that means, this experience and workmanship that is also important.

So, active materials should have high capacity per unit mass or volume of high battery capacity regardless of the adequacy of the design high capacity cannot be achieved by cathode material. So, we are looking for high capacity material and LMR is one of them lithium manganese rich you can see we can go up to 300 milliampere hour per gram.

A high tap density what I was talking about that to pack it in a electrode material you need to have a good packing efficiency. So, that is important. So, the tap density requires size of different types of active material. So, that the packing efficiency is good when you do the casting followed by hot cal calendaring. I will be explaining it to you. So, that is important.

Active material they must tell small specific surface area. For large surface area high liquid content because, you will have to wet it with the electrolyte, large amount of binders and conducting agents will be required. I am pretty sure that the nanotechnology, nanotechnologies they are not they will not like my observations because finer the particle smaller is the diffusion length. So, it is good.

But in practical sense whatever we have found that if you have a very fine particle it itself gets agglomerated and due to its higher specific surface area its very reactive, lot of dangling bonds are there. So, very reactive towards electrolyte reaction forms the ACI layer and then ACI layer disintegrates, fresh surface is exposed. So, thicker ACI layer forms a lot of trouble. So, you need to have a balance between this two.

It is necessary to reduce the thickness of the separator and current collector. Excessive thinning if you do of the separator then if then right forms on the graphite because if you do not match the p y n ratio then you have lot of lithium and this lithium will get precipitated on the positive sorry negative electrode surface form the dendrite and if your separator is thin it will puncture it and internal short circuit will take place.

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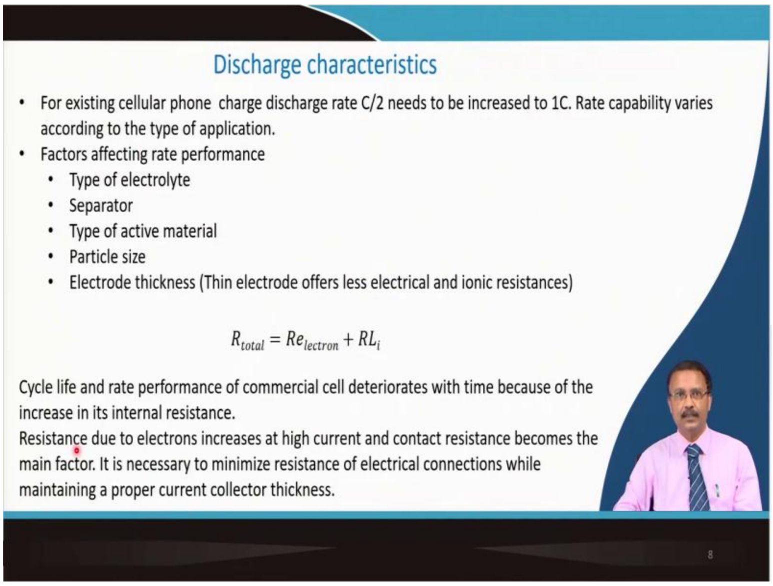

So, discharge characteristics for existing cellular phone charge discharge characteristics rate is C by 2 and that needs to be increased to 1C. So, the rate capital varies according to the types of applications. So, if my application wants for say 5 z, I need 3 3C kind of discharge then you will see your battery in the mobile phone that is not performing well. So, you need to improve the quality of the battery.

I know the Apple they never disclose what kind of battery they use and this is one of the best quality battery I have ever found in my phone that is running for say three years continuously without any problem of cycle ability. So, type of electrolytes that is important, separator is important, type of active material is important, particle size is important and electro thickness is important.

So, all this you know separator, thickness is important, active material quality is important, particle size as I said that is important. So, this kind of total resistance that is coming from electron and that is coming from lithium ion. So, ionic and electronic resistance that constitutes the total internal resistance of the battery.

$$R_{total} = R_{electron} + R_{ionic}$$

The cyclic life and rate performance of commercial cell that is deteriorates with time because of the increase in this internal resistance due to a variety of efforts, ambient is one of them. So, they are prepared the electrolyte for use in Canada. You import that cell and using it in Rajasthan in the summer time at 46 degrees Celsius. This wide temperature difference it has not been if it has not been taken into account then your cell performance will be bad.

Resistance due to electron increases at high current rate that is obvious at high charge discharge rate and contact resistance become the main factor because you will see that the tab is connected with your current collector. So, that contact resistance is important. So, it is necessary to minimize the resistance of electrical connections while maintaining a proper current collector thickness. That is also equally important. Very thin current collector you take then you may face problem.

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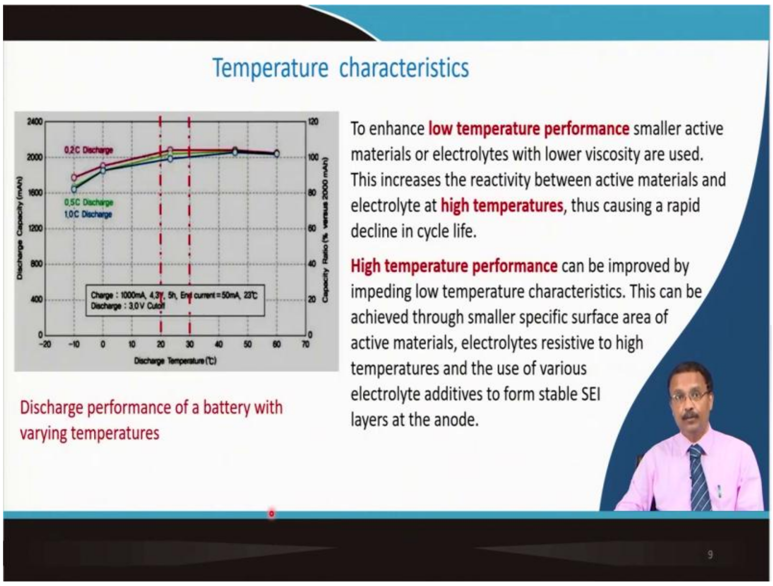

Temperature characteristics I was saying it that you see that it has been tested at low temperature this particular battery and then room temperature range where it gives the discharge capacity in milliampere hour, it is quite good and high temperature is slightly deteriorated.

So, to enhance the low temperature performance smaller active material is preferred and electrolyte with lower viscosity is preferred because if the viscosity increases once you reduce the temperature then lithium ion mobility will be affected. The increase in the reactivity between the active material and electrolyte at high temperature that is more important because they can react relatively with high vigo. So, that causes a rapid decline in the capacity.

So, high temperature performance that can be improved by impeding the low temperature characteristics, it is already less viscous of course. And as you know that I have described that smaller specific surface area of the active here is maybe important. So, the particle size is relatively large. Electrolyte resistive to high temperature and thus use various electrolyte additives to form a stable SEI layer.

So, a lot of modification you need to do if you take the if you have to expand the window and that is one of the problem that is why we need indigenous company because those battery should serve our country. So, they should be made according to our country's specification. Not always good quality battery if you are getting from outside particular, particularly for the cold countries that may not be good to serve the purpose what you are looking for.

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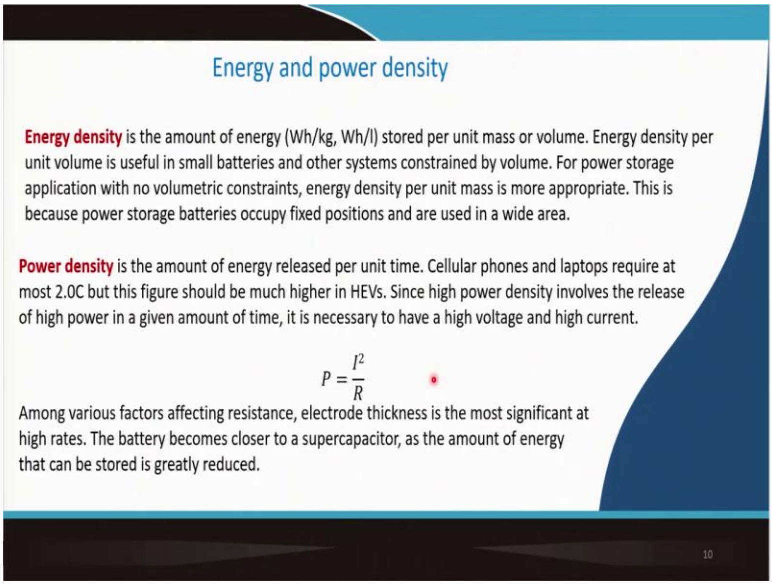

Energy density and power density by this time you know that amount of energy it is stored per unit mass or volume. So, energy density per unit volume is useful for small batteries and other system constrained by volume. For power storage application does not matter the volume constraints, but the energy density plays a measure role.

In case of power density this is the amount of energy released per unit time. For example, cellular phones and laptops require at 2C, but this figure should be much higher in case of hybrid electric vehicles that I talked about. Since high power density involves release of high power in a given amount of time it is necessary to have a high voltage and high current. So, power is I square by R.

So, among various factors affecting resistance, electrode thickness is most significant at high rate. So, thinner electrode is required. The battery becomes closer to a super capacitor as the amount of energy that can be stored is greatly reduced or high power density applications I will flood the battery with a lot of electrolyte, but use thinner electrode material as a thumb rule.

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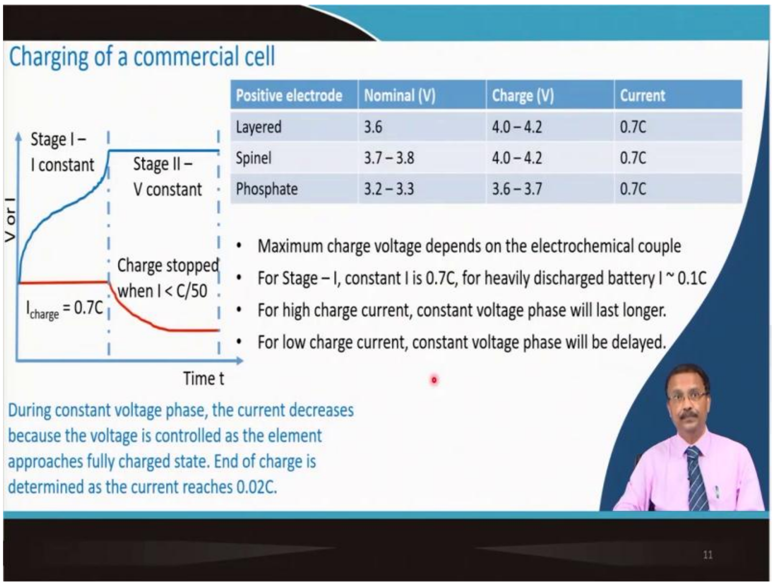

So, charging of commercial cell that is quite important and this is the profile that is followed. So, here I have recapitulated. This based on the positive electrode material and their nominal voltage. You see the charge voltage is specified here and usually during charging a constant current charging point C rate is actually preferred.

So, you can see that a constant current C C mode where the voltage during charging it increases and reaches here. So, maximum charge voltage depend on the electrochemical couple whatever negative electrode you are using with this positive electrode. So, this is your stage number 1, constant current is applied, but if you are using a heavily discharged battery which death discharge is quite high then you start with lower current.

So, it will take a little bit longer time for you to reach this voltage of course, you can understand it from the rate. For high charge current constant voltage phase will last longer. So, if you are using a high charge current then this will very quickly reach to the desired voltage limit. So, this time here will be relatively small. So, stage 2 this time will be prolonged and here this current you will find when it reaches constant voltage then this current will drop down.

So, when the current is dropped down to a level of 0.02C then you stop it. So, then the battery is fully charged. So, for low charge current the constant voltage phase will be delayed because already you are taking time to reach this voltage because the current is low.

So, this part will be achieving this part will be significantly delayed and you will see the current will remain constant, voltage is yet to be achieved. So, it will take time to achieve this voltage and then this will start. So, during constant voltage phase the current decreases as you can see here because of voltage is controlled as the element approaches is fully charged state and as I said the end of charge is determined when the current reaches 0.02C.

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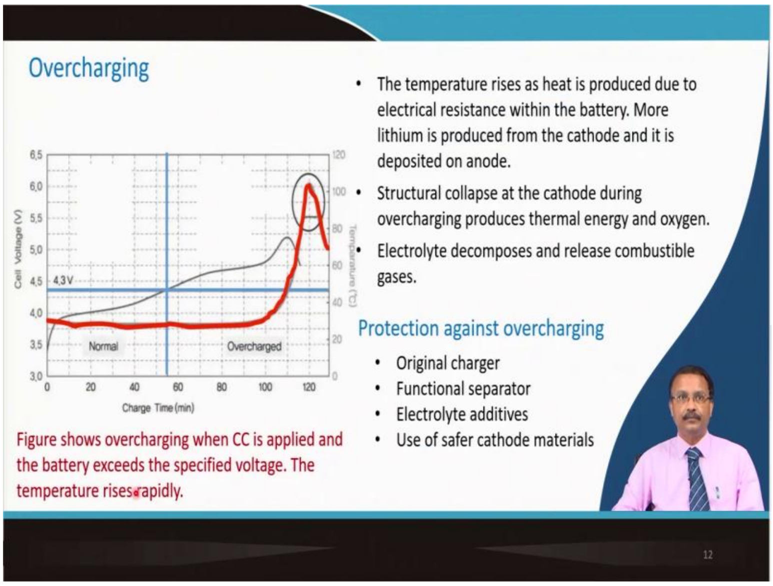

Overcharging is having a problem. The temperature rise as the heat is produced due to electric resistance within the battery. So, more lithium is produced from the cathode.

Because you are overcharging it and it is deposited on the anode. So, electroplating takes place if you cross the voltage limit.

So, all the charger that you use in your mobile phone it has this capability that it will not go it knows that what type of chemistry is there with your battery. So, it knows that it should not cross that voltage limit which is specified for the battery. So, you can understand now that not all chargers even if you can fit it in your mobile phone you should not use any kind of charger for your battery, you should only use specified original charger to charge this material and this is the reason.

If it goes temperature is raised and due to the electrical resistance within the battery more lithium is produced from the cathode and it is deposited on the anode. So, structural collapses also can take place. For example, lithium cobalt oxide you are not allowed to take beyond 0.5 mole percent of lithium out of the lattice.

So, it overcharging produces the thermal energy and oxygen that oxygen can oxidize your electrolyte can be decomposed and heat is generated. So, if the electrolyte is having lower flash point it can catch fire even. So, it can create combustible gases. So, this will destroy the battery.

So, the original charger is used functional separator. As I have mentioned the separator plays a major role as the temperature is increased its clogged the ports, but it is not disintegrated. So, it blocks lithium. Electrolyte additive as you can remember that what type of electrical electrolyte additives that is added for this purpose.

So, in the assignment you can expect question that out of 4 5 materials which you will prefer for additives that to reduce the thermal runaway condition in lithium ion batteries. So, you will have to remember those names which I covered in my earlier classes and use of safer cathode materials that is always welcome.

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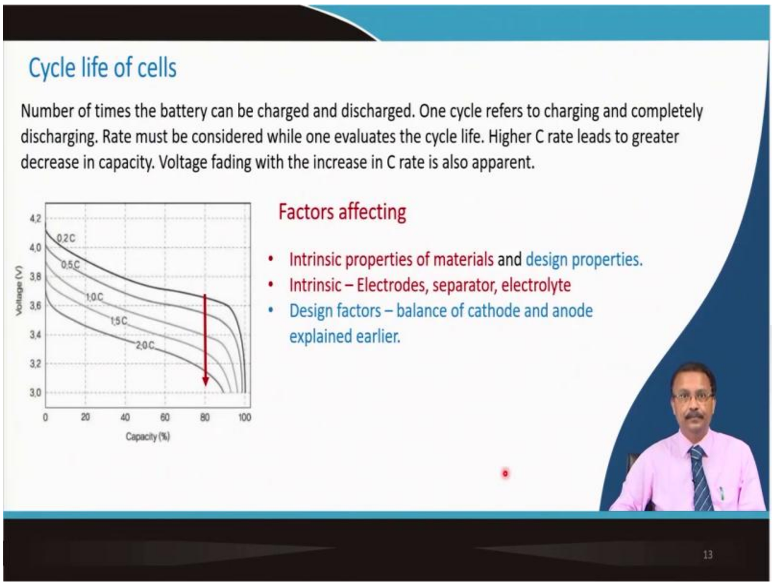

Cycle of life of the cell: you know that it is only the rate that is important. If you increase the rate of course, the capacity will be progressively reduced and that is known as the capacity fading with the current increment, but also the voltage fades. You know at this capacity if you are doing it at 2C rate discharge then your voltage is here 3.1 otherwise it should be 3.6. So, both voltage and capacity fading you can achieve when you increase the C rate.

So, the controller C rate is really important and the factors that affect that is intrinsic property of material and also the design property. You will have to properly design the electrode mass balance charge balance between the two electrode in the full cell. Intrinsic electrode separator electrolyte that also plays a major role and as I said the balance between the charge between anode and cathode.

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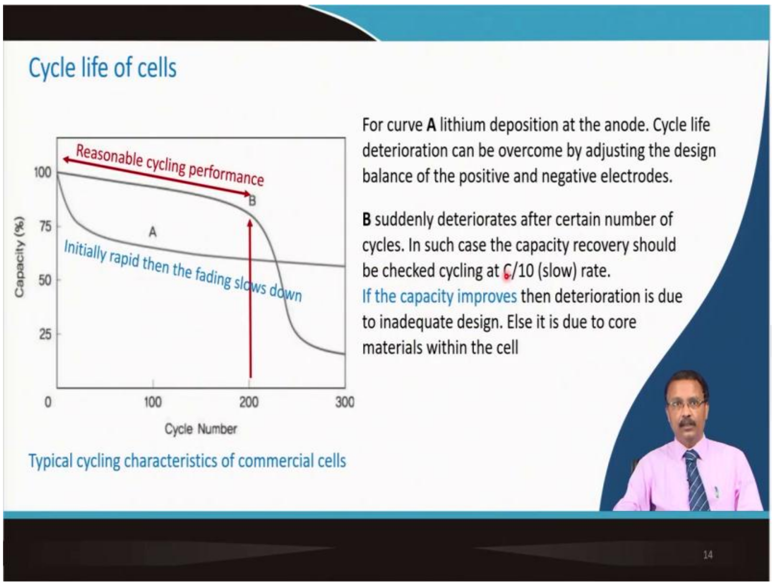

So, in the cyclability we will find two different types of profile. One as you see its it was reasonably good and then suddenly at one particular cycle number it drops down. This is better. Initially it goes down because of the SEI formation, but after that it is this rate is relatively less and it is perform more or less ok. Although the capacity percentage is not ok because after 300 cycles no good cell will allow you that capacity falls down as low as 50 percent, but had it been here around 85 percent it would have been good.

Anyway, so, for curve a lithium deposition at the anode cycle life deterioration can overcome by adjusting the design. So, balance is important that is for this one this is due to the balancing of the capacity, but when it suddenly deteriorates after certain number of cycles the capacity recovery should be checked that whether at lower rate again it goes back to its original value.

If the capacity improves then the deterioration is due to inadequate design else it is due to the core material problem with the cell. If you come across with this kind of thing then probably delimitation also can take place. You are using a metal alloy base anode which is pulverized or delaminate and then suddenly it goes back. If that is the case then it will never at low current rate it may or may not go back to the original value. So, this you should keep in mind.

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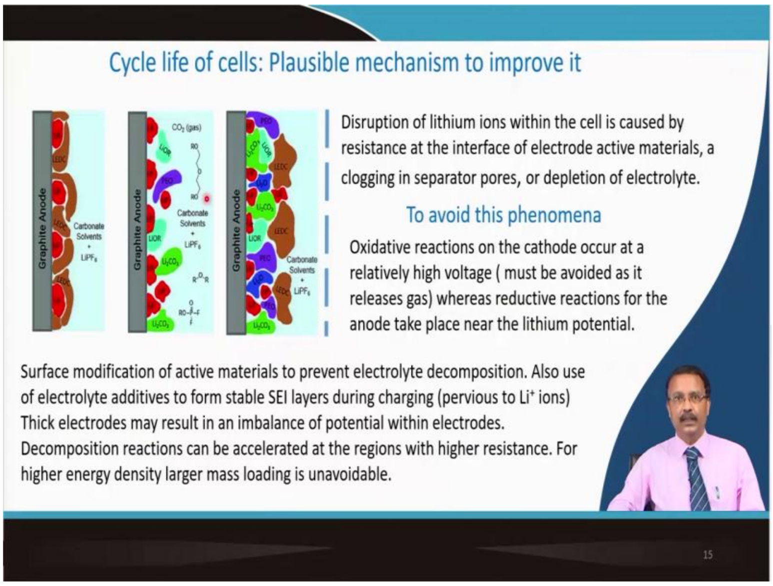

Cycle life of cells: this is related to a SEI formation. Disruption of lithium ions within the cell that is usually caused by the resistance at the interface of the electrode active materials, and clogging of the separator pore, or depletion of the electrolytes. So, if you want to get rid of this problem oxidative reaction on the cathode occur at relatively high voltage.

You remember if I go beyond the certain voltage then oxygen evaluates from your positive electrode material and that causes the electrolytic oxidation and reductive reduction also takes place in the anode near the lithium potential when you are very close to 0.

So, surface modification of the active that is one way to prevent the this electrolyte decomposition and also for electrolyte additives to form a stable SEI layer during charging previous to lithium ions and thick electrode may result an imbalance potential between the electrodes.

Decomposition reaction can be accelerated at the regions with higher resistance for higher energy density larger mass loading is unavoidable. You will have to take larger mass loading and then the energy sorry, resistance will go up of the electrode material as compared to very thin electrode. So, it is almost unavoidable.

Now, once someone is mastering about the cell manufacturing they will never tell you about these details that what are the additives they are using, what kind of electrode mass balance that they are doing, what kind of tap density they are using, what kind of calendaring they are doing whether it is cold or hot cat calendaring, what kind of electrolyte mixing they are doing. You know one is a cyclic and linear part of the solvent that is used along with the lithium salt and some additives also you can add LIOB.

So, this recipe they are patented and no commercial cell manufacturer will never tell you in their website that what chemistry they are using, but searching different literatures and things like that I have compiled this lecture, where you will get a vivid idea that what are the problematic regions and how to overcome that. So, you have all the weapons with you, but to get a recipe of your own you will have to work on your own.

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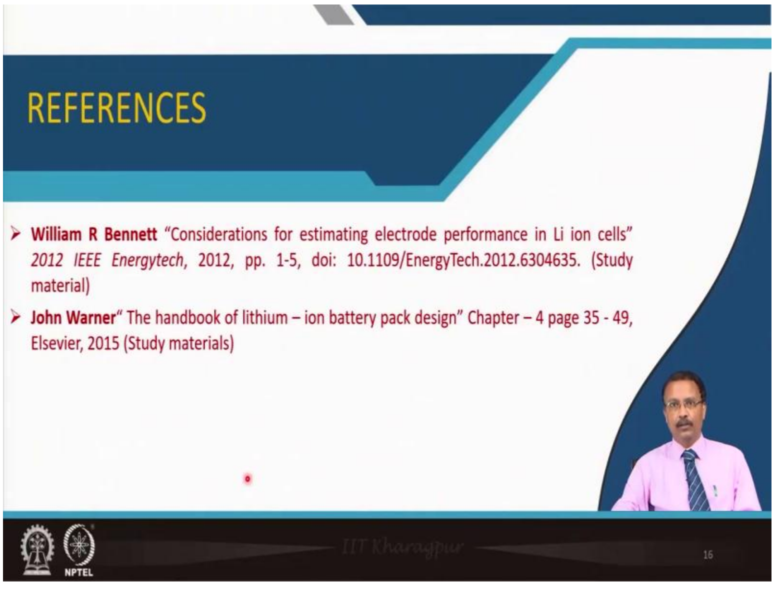

So, this is a reference by Bennett, Consideration of estimating electrode performance that is one and the handbook of the lithium ion battery pack that is also equally important and most of this have been taken by this to lecture material.

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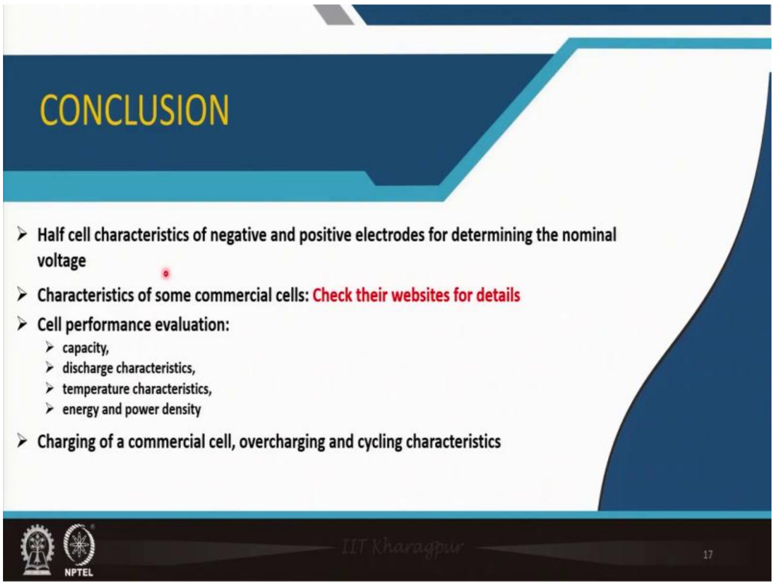

And also as I said go to the website and see their application notes to know more about these batteries. Half cell characteristics of negative and positive electrodes for determining the nominal voltage that is important. Characteristics of some of the commercial cells and I will strongly urge you to go to their website and have a look different types of battery.

If chemistry is available what are the performance that they are getting, in their application load, how they do the mass balancing how they connect the cells although I will explain it in more details when I will be talking about the model manufacturing. So, cell performance evaluation is important.

So, that includes capacity, discharge characteristics, temperature characteristics, energy and power density they do that and then they find all the cells ok for selling it. So, these are the four things that any commercial manufacturer they usually do. And what are the technique for charging of a commercial cell, what happens when you overcharge it and also the cycling characteristics.

Thank you for your attention.