Advanced Ceramics for Strategic Applications
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Lecture - 33
Lithium Ion Battery (Contd.)

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The topic of this lecture, also is has lithium ion battery is basically a continuation of earlier lecture, we were discussing about the various aspects of lithium ion batteries, its importance, constructions, what the materials involved? and we wanted to discuss what are the alternative materials involved? or the possible materials, in addition to the anode which is normally the litheatedlithium interconnected graphite, and the cathode once again lithium intercalated cobalt oxide.

So, let us see whether we have alternative materials, and one can use a improved version of the batteries, and of course one can also see, whether less costly materials can also be used replacing cobalt.

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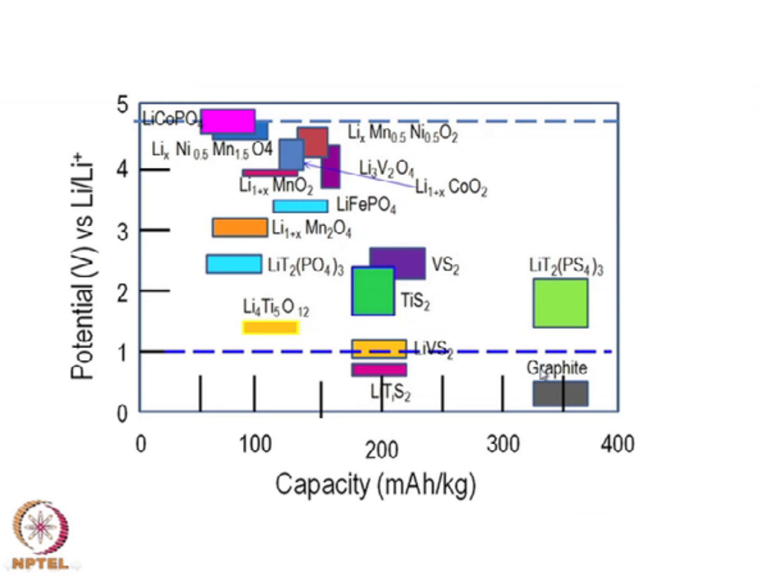

We discussed this particular figure, in which many different oxides are main different other compounds have been plotted, both in terms of the voltage and potential, which can be generated out of it, in terms of lithium and the capacity. So, there are large number of different material have been presented here, and has was mentioned earlier lithium cobaltiteis some there, then we have alternative materials material structures.

In fact we have discussed three different structures, one is the layer structure oxides cobalt oxide C O 2 is example of that, important member of that, and then we have fennel structure which is physically M n 2 O 4 structure, and the third one is a aloivein structure, the important example is L i F e P O 4 three different structures, and many of them have substitutions in them, they can be used or they have potentially, potentially they can be used from this diagram.

So, three member which are very important here, one is L i M n o 2, and then a variation of that with has some substitution have been made, with nickel and C O 2. C O 2 structure in this C O 2 structure C O has been replaced by partly manganese, partly nickel, and then you have L i F e O F e P O 4 structure, and this is M n 2 O 4 structure, others are not, although for theoretical purposes they are important, but there are not that important at this stage.

So, these 234 different compounds are being researched on extensively or additional one more compound, I will your attention to is L i 4 T i 5 O 12 L i 4 T i 5 O 12 this although has a very low voltage, in fact 1.5 volts are so. Also, capacity is not that high, but it has a different, it is important in a different context will discuss that also, at the later stage. So, these are few compounds which offer importance to us, and will see how they can be utilized in the lithium ion battery.

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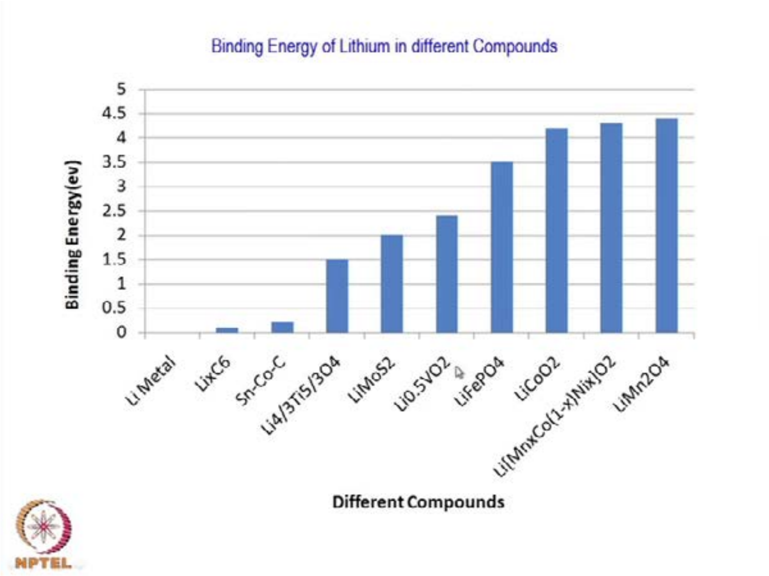

When, you are talking about this kind of compounds different compound, very first thing one is to find out, what is the binding energy? and that binding energy with the lithium actually provides idea of what kind of voltage, one kind expect, so in that context these are the different compounds, some of them have been plotted over there.

And lithium manganese oxide variety of the lithium manganese oxide has a highest binding potential, binding energy, and also has potential lithium cobalt oxide is here. So, they are quite comparable lithium iron phosphate a slightly lower the voltage, slightly low, and then you have here lithium titanium oxide, in fact it is actually lithium 4 by 3, titanium 5 by 3, oxygen 4, ok. So, if you multiply by 3, in fact it will be lithium 4, titanium 5, and oxygen 12, which was shown in the earlier picture is here, it is the same thing,

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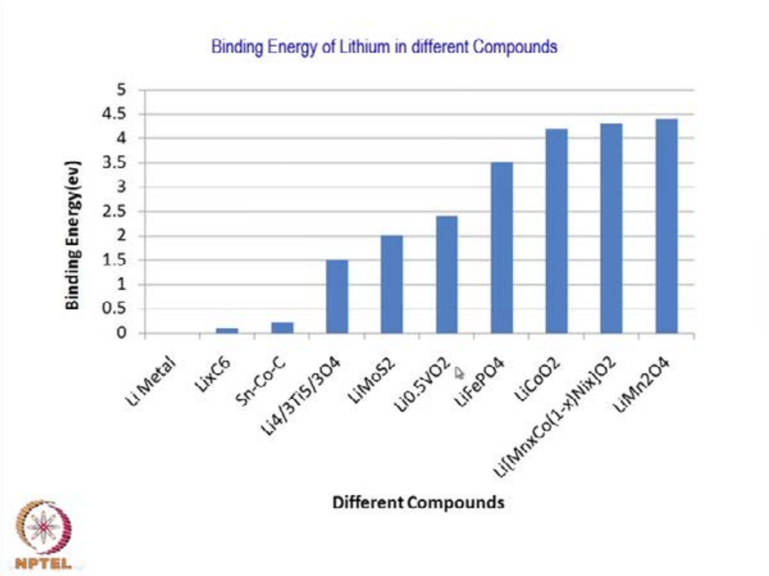

So, this is fairly low about 1.5 volts whereas, this is fairly high is about more than 4 volts, which is comparable to lithium cobalt oxide, so the binding energy are compared in this manner.

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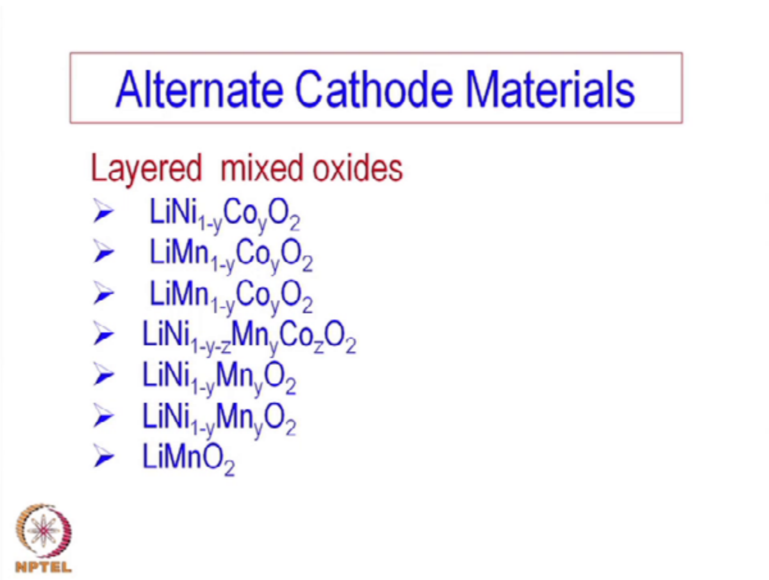

Now, considering all these we have particularly, if you talk about cobalt, or if you are concentrate, or attention primarily to oxides, and not likes sulphides and phosphides. These are phosphates, these are some of the oxides containing transition metal oxide, some transition metal oxide right, transition metal oxide has a role to play, because we have seen earlier in case of cobalt, there is a valences change from 3 plus to 4 plus or 4 plus to 3 plus, so obviously our attention has to be given are be paid to transmittal oxides.

So, these are some of the list of transmittal oxides, which helps potential application to replace cobalt oxide, and in the lithium and battery system. Now, of course all of them are not divide up cobalt, someone of them had been cobalt has been partly replaced by nickel, here partly replaced by manganese and its also partly, I think there is a repetition here, this can be this can be removed.

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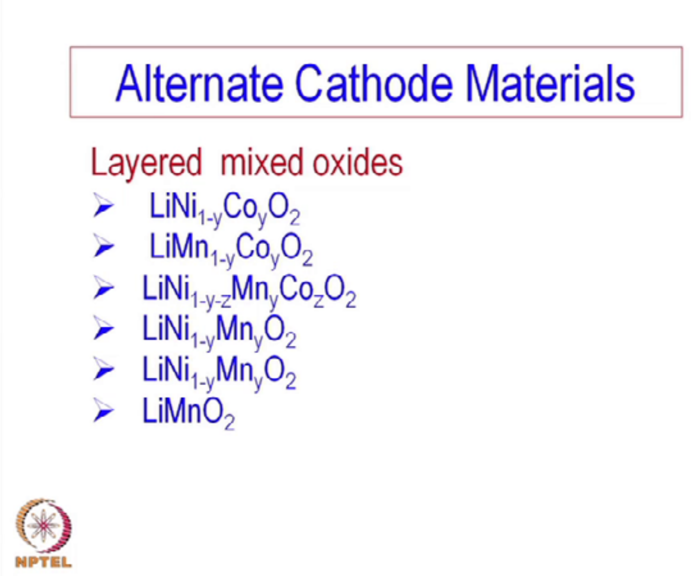

So, you have a because there has been basically an attempt to reduce cobalt. Cobalt as I mention, it is a costly or economic not economic material, so if you can replace completely replace or partly replace, that is the basic idea. So, here nickel cobalt has been replaced partly by nickel, partly by manganese, and also here partly by nickel, partly by manganese both, both nickel and manganese have been used. And here completely removed, cobalt have been completely removed both by nickel and manganese, and then also once again there is a mistake, I believe let me also remove that.

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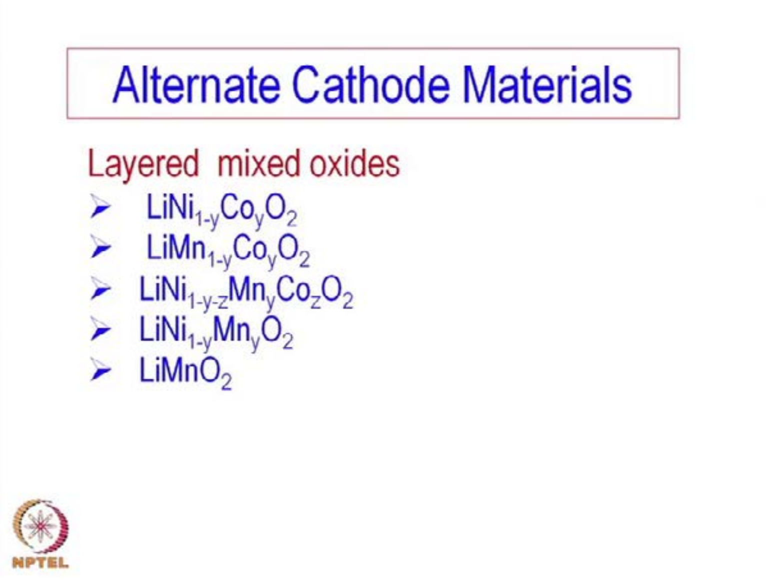

So, both nickel and cobalt have been replaced by cobalt has been replaced by nickel and manganese right, and here it is only manganese and this is of course, is a different, the same structure the M n 2 O 4, the M n 2 O 4 will have a spinal structure, but this is also a same structure ok, so these are some of the layers.

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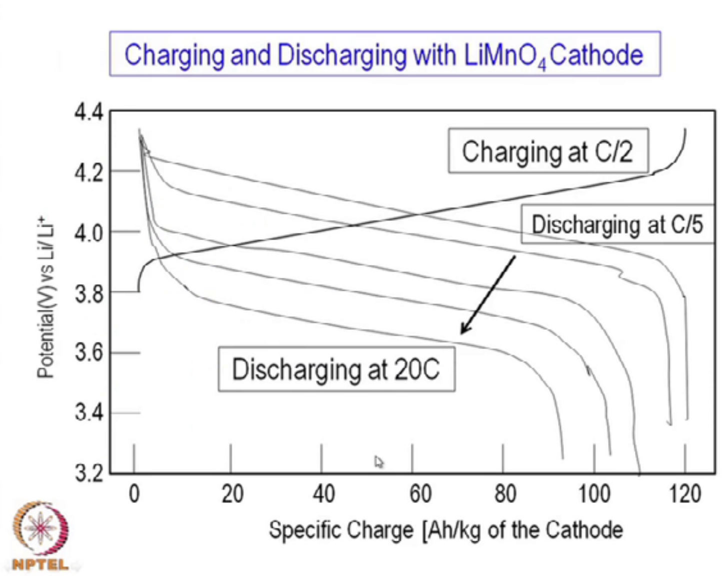

Next oxides and here this is the characteristics charge, charge discharge characteristics of the particular compound, which is spinal structure lethain lithium manganese 4, manganese 4 spinal structural, we have seen earlier. This is the charging characteristics of that, and these are the discharge characteristics under different conditions of discharging, now discharging is done normally, done at a rate of designated like C by 2 or C by 5 or 20 C know just to have a discussion on that.

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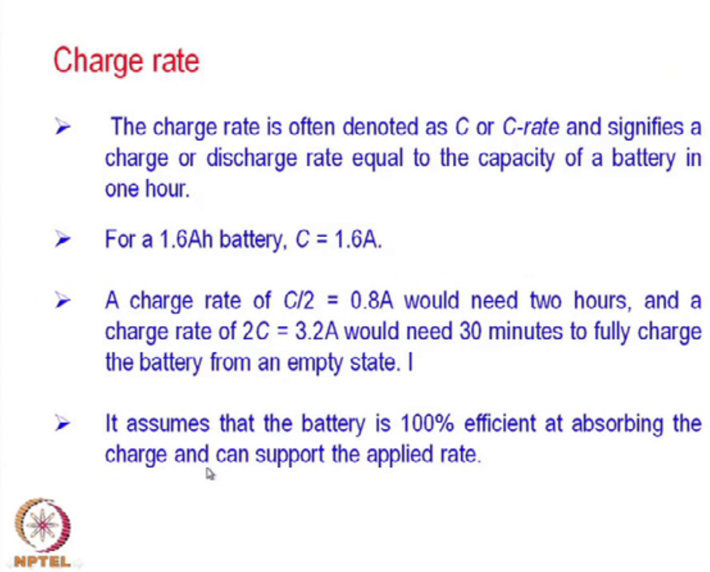

What we mean by this, this is what we call the charge rate or discharge rate, the charge rate is denoted as C or C rate, and signifies a charge or discharge rate, charge or discharge rate equal to the capacity of the battery in in 1 hour. For example, as you possibly you are aware, the capacity of a battery is normally given as ampere hour, that is the total amount of energy which it can accommodate. So, if you have a capacity of a particular batteries 1.6 ampere hour, the C 1 C it becomes 1.6 ampere, that means in 1 hour, 1 hour you charge it fully, or of discharge it fully at the rate of 1.6 amp.

So, if you draw current of 1.6 ampere over a period of 1 hour, then this is the total capacity of the battery, and this becomes then the C, a charge rate of C by 2 means actually 0.8 ampere, 0.8 ampere, half of 1.6 will be needed for 2 hours, and a charge rate of 2 C that means the double the value of the capacity, we have to charge 3.2 ampere would need 30 minutes half a minute to fully charged.

So, it is basically there rate at which the current is being drawn from the, from the battery or it is being introduced the charges, introduced battery or to recharge the battery, so that is what is known as C rate, it assumes that the battery of course, whenever we are doing it assumed the battery is 100 percent efficient at absorbing the charge, and can support the pled rate that means, if you charges it at a very fast rate. For example, 2 C or 10 C, 20 C that means your charging or discharging at a very fast rate, and the kinetics may not support it. So, the there may be a breakdown of the structure, so otherwise this can be done in fact, that is one of the criteria when it battery is tested, that is one of the criteria how fast one can discharge it? how can how fast or parameter? what is the rate of charge? what is the rate of recharging or discharge? and so on.

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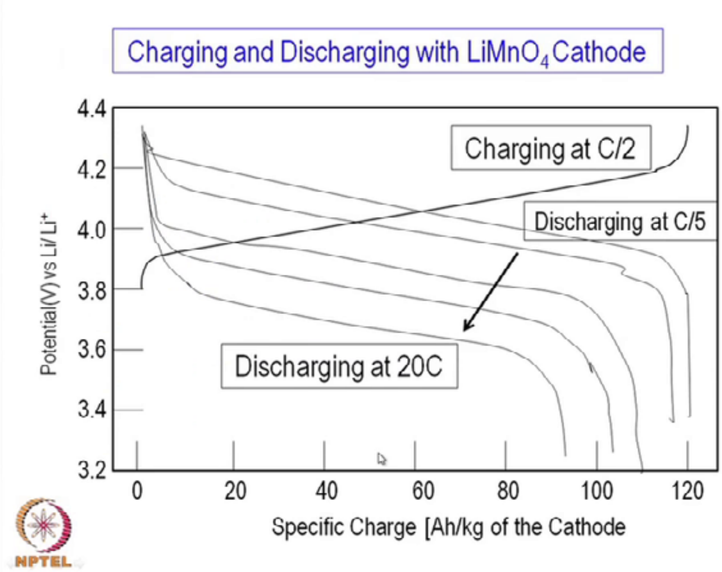

So, under this context to go back this particular curve, one can see the charging is done at C by 2 rate, half the total capacity, and discharging has been tried out, discharge have been tried out at C by 5 and in this increasing 20 C, 20 times the overall the capacity of the battery, and even then one can although the voltage will drop obviously, and charging rate increase, and then you can get a fairly high a specific charges.

So, M n O 4, so L i M n O 4 an alternative cathode material replacing L i C O 2, so these are the some of the typical experimental data, and which is been taken from literature of course, and the these are the possibilities, so one can charge it was very fast rate, as well as discharge fairly at a very fast rate, this is been discussed.

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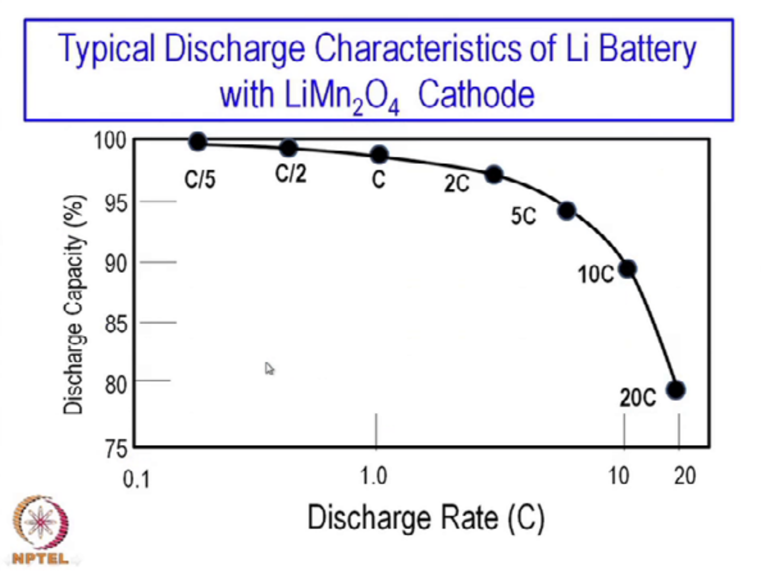

And the same thing once you plot as a discharge rate C, and the discharge capacity, so lower the discharge rate obviously, higher in the capacity what are the discharge rate the lower will be the capacity. So, we will have to find out at what rate, what will be the optimum condition on which the battery will be utilized? So, normally 2 C to 5 C not so low, so these are the typical again typical characteristics of the particular cathode material of course, in conjunction with the graphite graphite anode.

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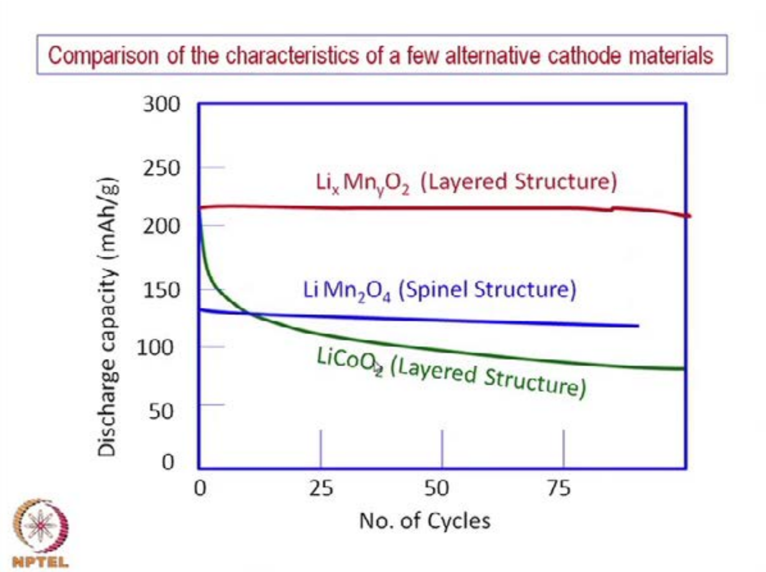

Here is a comparison of few different cathodes references is of course, the a L i C O 2 and the number of cycles, number of cycles initially of course, the there are discharge capacity is high. But, as a cycle say increases the slower although, we are talking about 300 600 cycle capability, but that is certainly it will get slower, and then gets stabilize. It does not continuously decrease, but compared to the initial capacity certainly the capacity is lower, even after about 50 cycles. So, that is the typical one will typical characteristics of the cobalt oxide cathode. Now, compared to that there are alternatives c r, which were are just discuss one is spinal type, one of them L i M n 2 O 4 is one of them.

And L i x M n y O 2 this is the same structure, only the cobalt has been replaced by manganese, and so far is the electrical characteristics is concerned of course, is quite good, that means it remains stable, is remains stable even, at the starting capacity for a long time on are no large number of cycles. The a a the L i M n 2 O 4 the spinal structure itself as a low capacity, but it is remains constant over large number of cycles. So, compared to lithium oxide is a certainly better in certain sense in this particular sense, at least so far the cyclability is concern. And the lower structure M n 2 if you replace cobalt by manganese, also a better property. However, there are certain disadvantages of course, so that these are not still commercially used, commercially the most important one is still the lithium cobaltite.

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The more promising of course is a L i F e P O 4, as mentioned orthorhombic structure, high thermal stability, in expensive, because iron and phosphorus are the two elements here. In addition to lithium environment-friendly are there is no cadmium or anything like that, and lead is also of course, not there and high capacity is 170 milliamps per hour which is quite high, and excellent cycle. So, this is another compound in a different crystal structure, a different structure with the having different structures characteristics.

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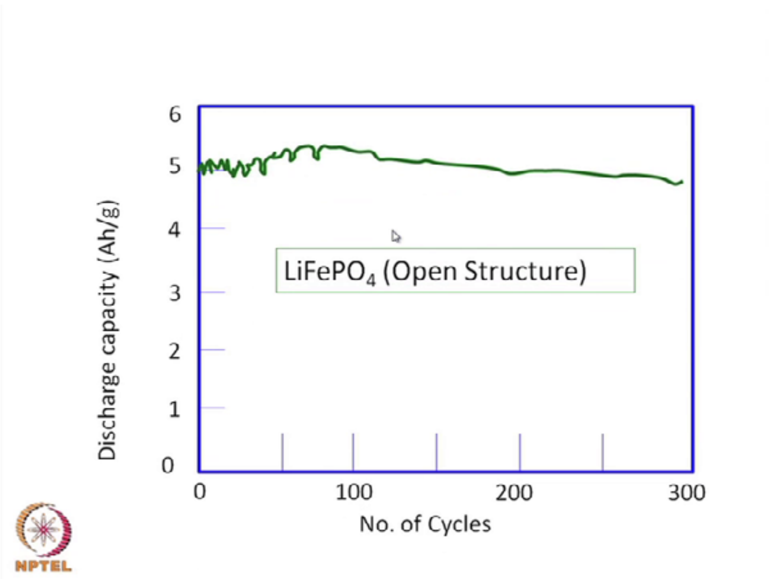

This is also a good material, and the typical discharge cycle relative curve is like this, here you can see about up to 300 hundred cycles more or less constant, in that sense this is one of the L i F e P O 4 lithium iron phosphate is one of the promising material, so far alternative to cobalt cobalt oxide.

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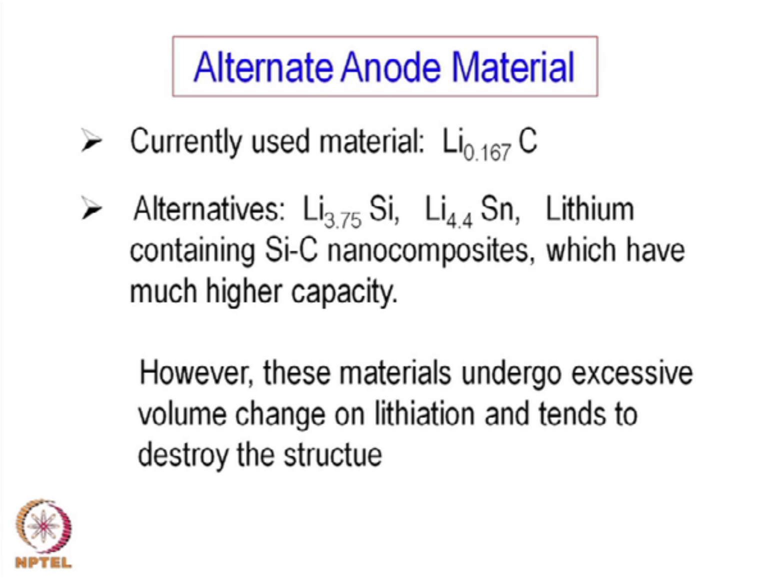

Now, there has been a lot of concentration, or research work is still going on on the alternate anode material, the so this is our current currently use material, either it is written in a different way, it is 1/6, it is actually L i C 6, alternative materials are in the same group. The group four elements is carbon, so these are either silicon, or the team lithium containing silicon carbon nano composite which also much higher capacity, that is see so, it is the same group same group element as carbon, oppose they do not have the same structure is different silicon, structurally different structure team is also different whereas, carbon is a different structure.

But, even then this material is to have some property of accumulating lithium, or intercalating lithium are as in case of carbon are however, this materials undergo excessive volume change on lithiation, and tense to destroy structure. This is one of the another very important criteria, this is another very important criteria for choosing the right kind of material. Now, whenever you are introducing lithium into the structure, it certainly there will be some expansion, because now compared to the origin material there will always some of volume change, and lattice parameter in will be increased, and as a result there will volume change.

So, this will volume changes certainly a very important criteria, or a problem for a actual practical application, so that has to need to consider, and it happens in all the intercalation compounds, but lithium cobalt lithium graphite is acceptable, but whereas the other thing is also need to the understood, how much one can accept volume change.

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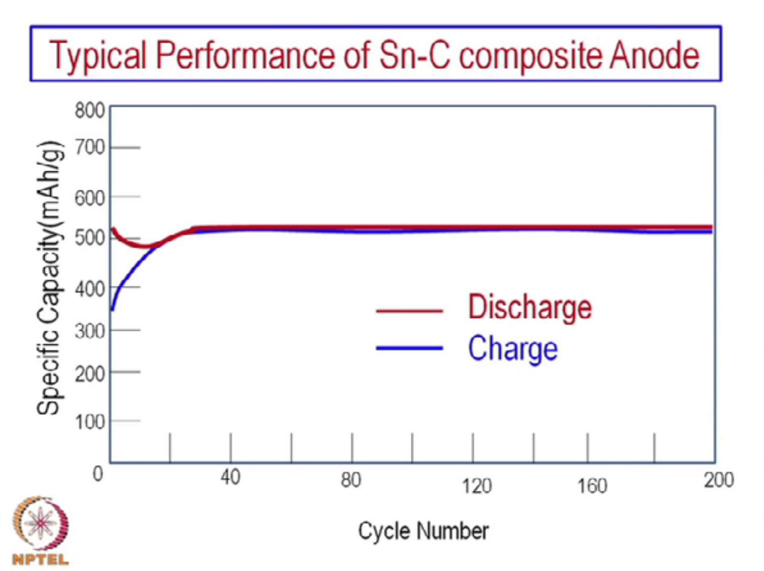

This is a typical performance of a tin carbon composite, and we have seen carbon anode, carbon graphite anode can be replaced by some other composites, including other metals. This is a very good, very good characteristics once again, very constant value of discharged discharge characteristic, there are exactly the same capacity, and it can extend up to 200 cycle quite easily, you can go beyond course.

So, this is a typical tin carbon composite anode, tin graphite composite of course, one is to also remember although we are talking about graphite, there are many is various kinds of carbon which can be used, and there are very I am not going to details of that, at depending on the preparation condition, depending on the morphology of material, the structure of the properties of battery, certainly change quite extensively.

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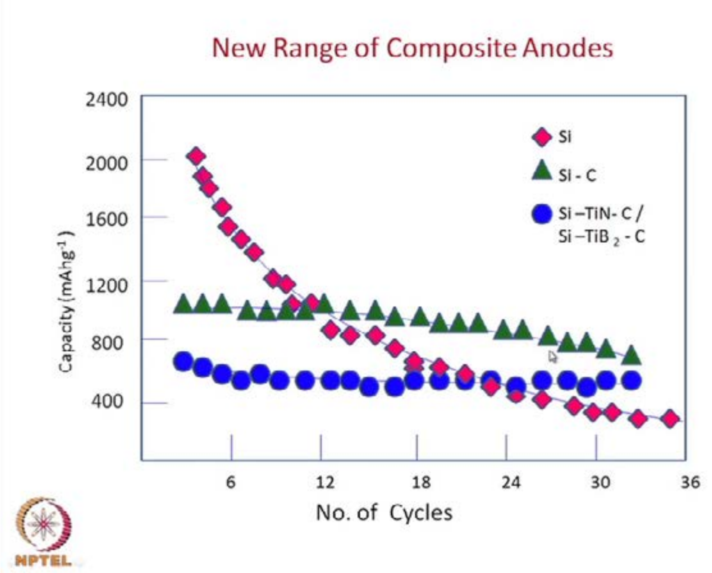

Now, are in addition to tin carbon there are other, but it was as just mentioned like silicon. Silicon is also a composite, the silicon the compound which can be directly used, or nano some kind of nano composites, actually, where graphite and silicon can be used together. Then, in addition to some more complex materials like silicon titanium, or nitride carbon composite, or silicon titanium diboride carbon composite. So, these are also can be used or can substitute the origin graphite, and these are, so these are some of the characteristics of course, for a limited period and one can see silicon, although it is a very high capacity you can see, range of this capacity is much much higher.

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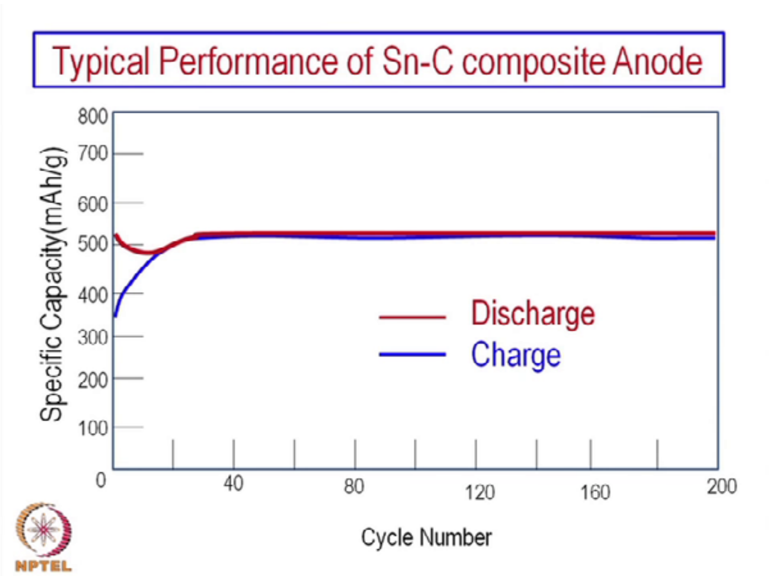

If you compared the earlier values 500, 400, 500.

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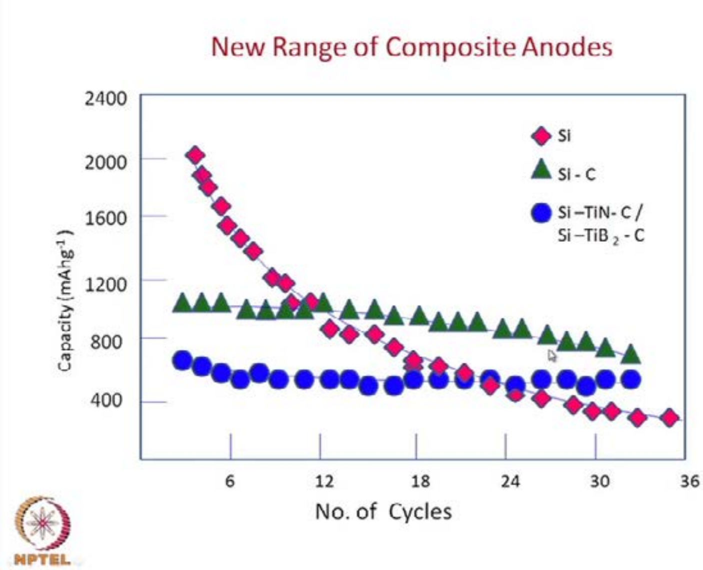

Here, silicon is a value of at lower initially a value of almost about 2000, but it slows goes down cycling, and stabilizes some around 400, 400 milliamps per gram whereas, if you take silicon carbon composite, this is happens sit yourself, so pure silicon although has a very high binding energy, and therefore, much better capacity, but then it drops off very sharp by cycling whereas, these two materials particularly the nano composites, silicon carbon, these are actually the nano composites of silicon carbon. They have a fairly stable capacity over large number of cycle, silicon titanium, carbide nitrate, carbide and titanium nitrate carbon and silicon titanate diborate carbon also can be used for this focus, and it has a lower capacity but, still stable with the cycling.

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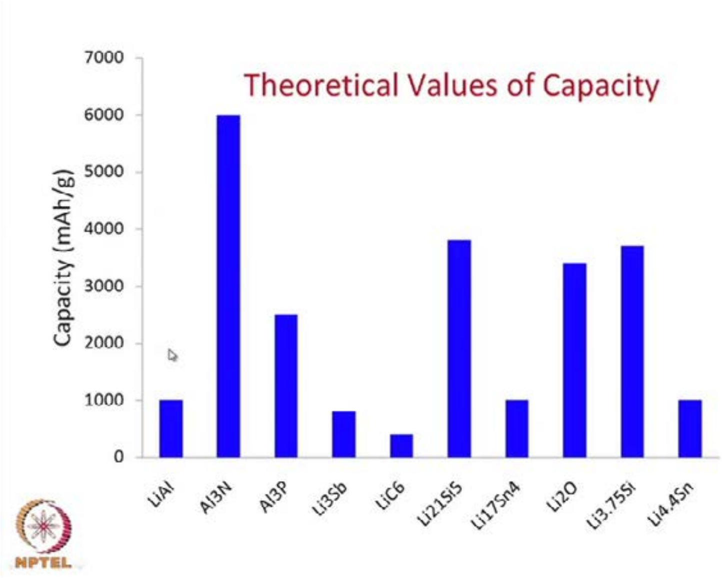

While, these are the when you talk about are different compounds, one also has to have a theoretical value of capacity, one can find out from binding energy, and these are different values and valuable capacity, theoretical value the capacity one can expect. Different kind of compounds is only tin, silicon lithium, lithium oxide, lithium, and this is against tin and so. Silicon carbon L i 6, this is the currently used compound. Compared to that one can see, the capacity is much much higher, compared to much much higher compared to a L i C 6.

So, the other materials are much higher compound, where capacity is but these are all theoretical value is, so when somebody is screening, screening the different material, one can look at theoretical capacity. But, many of them are practically not feasible, really not feasible, and thats why and a L i C 6 is still a material of interest for the practical devices. So, however many research is going on different other compounds, as well so these are some of the results of that based occasion.

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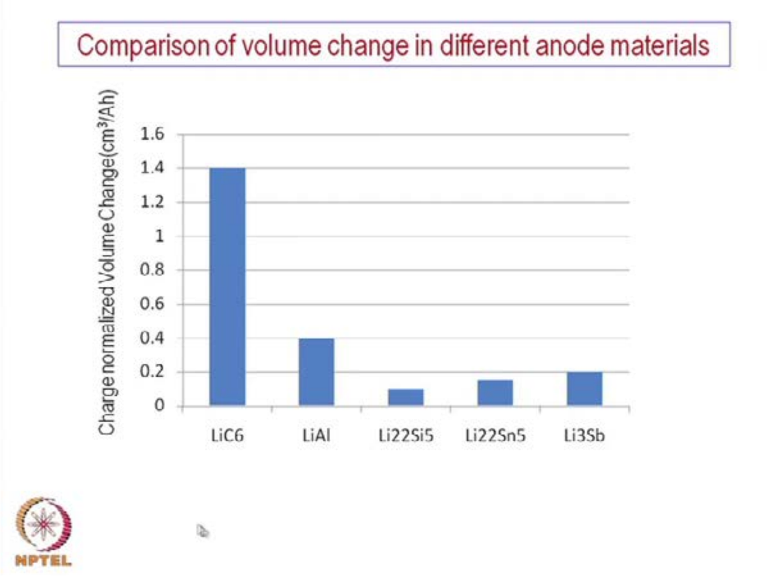

One of the problem, so the as once again as a mention the volume change, in a L i C 6 is fairly large volume change, but that is acceptable whereas, lithium aluminum and these are lower volume. But, even then there are because of some other problems, because of some other problems, they have not been used so far or being investigated or investigation stage only.

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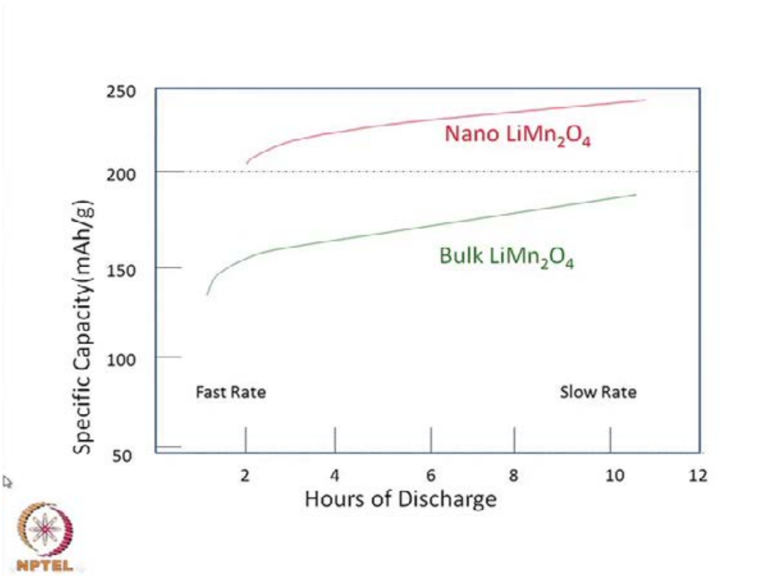

Nano impact is there, in fact is that material in very very important, one of the major investigation research, or still impressed is in the area of nano, whether are the materials can be used in the nano powder form, and they have some effect on that. And here only case of particular spinal type of compound, the A l i M n 2 O 4 if you prepared in the micro bulk in the sense, micro fine powders, and these are nano fine powders, you can see a significant increase in the capacity, specific capacity here once again it increases almost a by 50 percent more,ok.

So, in fact most of the research is going on here, what is the effect of nano materials, or nano structured materials in improving the properties of the lithium acts, this is one example where nano materials of some important properties.

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This is where once again is being taken from literature here, they are this is how the construction of the cells are met? you have seen large number of coin cells, sometimes called as button cells, or and very thin cells, just like a metal tablet, and but it contains a large number of components, thats the reason why you showing this? this is the top cover which is top stainless steel cover, which acts as a negative terminal, we have a installation ring, a insulation gasket normally teflon ring, and this is the top cover and this is the bottom casing.

So, these two in between you have large number of thin layer sheets or thin layers, or this as your positive electrode, that is lithium cobalt cobaltite, and that is the cathode, and and this is the negative electrode. So, this is basically this is the single cell, you have a separator, a very thin separator containing the electrolyte, this is the layer very fine layer of graphite, and this is a cathode layer a positive electrode, and they are all sandwiched between these two casing sand, this is the electrolyte sorry that this is the liquid electrolyte soaked, or the one porous material soaked in the electrolyte.

So, this sandwich structure actually forms the cell, and these are actually a stainless steel spacer, this is a spring and finally, through this is connected to the top layer, this becomes the negative terminal, this becomes the positive terminal, and in between we have an insulators, insulating gasket which separates the top cover electrode, electrical separates top cover and bottom casing, thats out one makes a coin cell which is extensively used in many electronic gadgets, and electronic device. As in addition of course, one thing which will also mention all this things are actually produced in powder for a, whether it is a lithium graphite or lithium cobalt, both of them are prepared in actually in the powder form.

So, they are coated there coated runs substrates normally, and this side is a copper fall and the on the other side there is a aluminum foil, so there actually screen printed, screen printed on this, so basically materials are in the form of powders, so it is not informal discs or any plates. So, their powders coated on some substrates, so therefore nano powders has a very important fact, because nano sized powders increases or decreases the number the the electron the lithium mobility, or in fact increases a lithium mobility, the interaction distance becomes finer and therefore, there is a enhancement properties.

So, since we are talking about powders only in the solid state, so certainly the nano powders is of much finer, much larger specific surface area, so the interaction becomes better, and the charge transport becomes much faster. So, that is one of the considerations and that is what we call the coin cells. The another there are very different kind of sets of the lithium cell, like many other rechargeable batteries, a standard kind of battery here a cylindrical here the of course, there are produced in a completely different manner,this is a similar to typecasting process, very similar to typecasting process.

So, there are roles, roles of the different three different sets, one is the cathode and anode and the separator, so all of them rolled together, and then in the form of coil put in the form of cylindrical cells, that is a different reason these are not discrete, discrete seats, but there are in the continuous seats which can be rule together to form a second, so that is how the cylinder cell.

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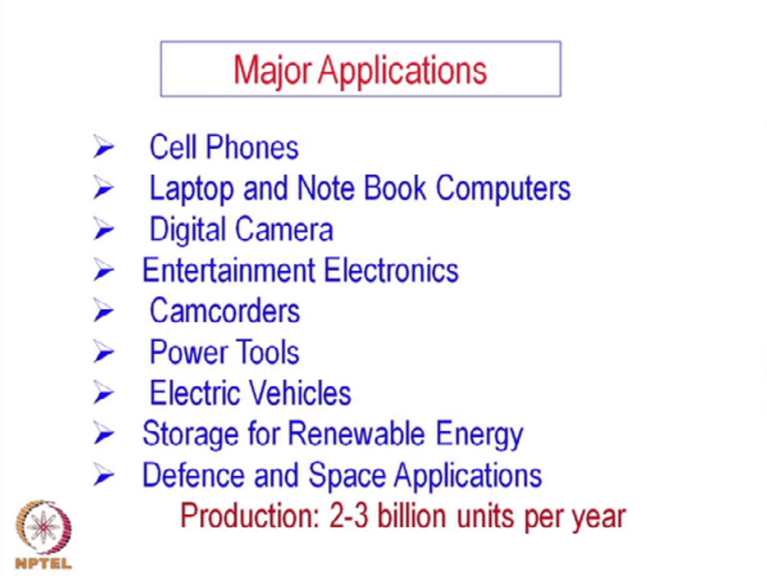

Well with all these let us come to our discussion of a major applications, and I am sure most of you are familiar with that cell phones, one of the largest applications are different forms of cell phones are i phones, i pods, and all kinds of electronic gadgets and communications. So, one our import material the laptops and notebooks computers almost, all computers particularly, laptops and notebooks do have in this lithium ion batteries, rechargeable battery, that it one of the very important component of the system, the digital camera almost all digital camera equal as a battery.

And they are all rechargeable battery, earlier rechargeable batteries were nickel cadmium now, they have been replaced by lithium batteries, many electronic entertainment electronics also requires lithium batteries, camcorders thats also requests the lithium batteries, these are all low power application we not drying very large currents. So, the rate of discharge is relatively low and however, if you go to rest of the application the rate of discharge and the power capacity is a is very high.

For example, were talking about power tools, power tools reverted larger energy but, it can be made out of a lithium batteries, then the most important driving force for development, the for the development of lithium batteries is here, it is the electric vehicles, hybrid vehicles. Hybrid vehicle are prototypes are they are already, so the main driving force currently, for development of the lithium ion battery is the electric vehicles for the future, and how much is a and the requirement is completely different compared to the current range of applications, where you are requiring only lower discharge rates, here you need very very high discharge rates, and total capacity also have very large, so that the range of the vehicle can be increased to a reasonable extent.

So, from that you need a completely different materials, as well as different structures, structure of powders are not the crystal structures, but the morphology of material and in that context, nanotechnology is playing a very very important role. So, nanotechnology particular nano powders of different shapes, and sizes of the same material may be lithium cobalt or graphite, or other or the spinal cell the all even structure as they phosphates iron phosphates, and so on. They are primarily concentrating the research is primarily concentrating their research, is primarily concentrating the morphology of the powders, how the morphology of the powders can influence the property?

So, not only the crystal structure but, the morphology of the powders fineness, the shape size surface area, all of them are very important role to play, in looking at are in the performance level. The other area, this is also same form fuel talking about the defence and space applications, because here densities very high per kg of material, you have a very large energy density, come a much larger than any other form of battery and therefore, space application is a very important application. Where you need space breakers, and weight is a very poor consideration there in defence also here are some of the applications, particularly missile applications want you have a tremendous importance of lithium battery, because one of the major driving force is the power to weight ratio is a very high, power to weight ratio and therefore, is all these applications air bone, air bone systems whether is missile, whether it is spacecraft or satellite all this, and have a very important application areas for lithium ion batteries.

However, another important area which is coming up is because of the renewable energy, we are generating a lot of power through a renewable source either solar, or wind, or wave, and so on. So, in this storage is a very important issue, there storage of batteries. There are many different forms of storing the electrical energy, but lithium battery once again is a very efficient storing device, and the lithium they are also important for as the storage for renewable energy, so lithium batteries along with solar energy is a very good combination, a very good combination for generating power and storing it for the off periods.

So, these are the important areas and thats the reason, this is one of the most active a area materials research, so far or at this point of time, current production level about 2 to 3 billion units per year, which is a very high compared to many other batteries, fairly large number, so this is a so far the applications are concerned.

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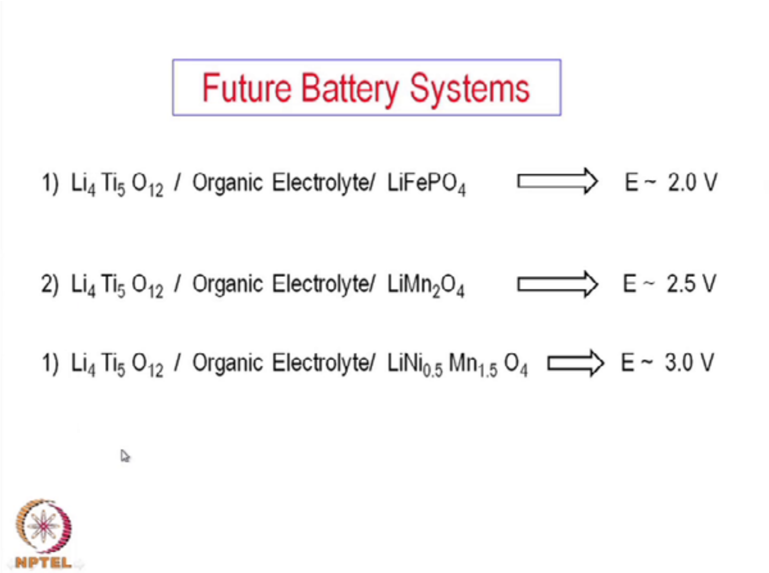

Finally, we will come to what are the in future directions, future directions and very interesting, there are two aspects as a mention, so the developments are concerned one is of course, the anode and cathode material, and also the organic electrolytes. A lot of research is going on, whether the electrolyte can be replaced by some other organic materials a better materials, but I am not discuss here that kind of work, what I want to point out here are we have discussed, this is as the cathode material.

And we have seen some of the results where graphite has been used as the anode material, but there is a possibility in this, also is a is a cathode material, this is also a cathode material which can replace lithium cobaltite, but voltage is very low is about 1.5 volts, or so compared to graphite people compared with graphite and this becomes cathode, then the voltage is about 1.5 volts whereas, compared to graphite this is a voltage of about a 4 volts very close to 4 volts or 3.5 volts or, so. Since, the mechanism of both the materials the lithium intercalation is more or less same, they attempts now being made, whether this can be used as one of the electrodes and or anode.

So, this can be used as one of the anodes, so here which the material which was material originally developed, and the cathode material now being used as a anode material. So, this becomes are also completely replace graphite, and this becomes your anode, and this becomes cathode, electrolyte remains same. So, this kind of a system with the new a voltage about 2 volts which is much lower than 4 3.5 volts normally available its lithium battery but, still a interesting systems or still an interesting system and a lot of research is going on in this kind of, with this kind of material, 2 volts is low so the capacity will be reduced but, the materials are very abundantly available.

One is titanium iron phosphate, so it is not restricted by the widely non availability of cobalt of course, graphite is an abundantly available material but, is has some other problems. So, this is one system which is being tried out for the future systems and of course, the charge discharge characteristics is important what, so although it is a lower EMF open circuit voltage, but still this can be an attractive system to start or to get, then you have a another system again the same material but, here the cathode is replaced the same anode but, the cathode is replaced so you have about 2.5 volts, it is so that the voltage can be increased some extent.

So, instead of lithium phosphate, iron phosphate, the cathode can be lithium manganese and it will spinal structure but, the anode is same, so you have a possibility of increasing the voltage from 2 to 2.5, there are more system which is also being thought of places once again the same anode, so the anode is being common, the cathode instead of manganese only manganese only, iron phosphate, we have the this manganese been replaced by partly nickel, so lithium nickel manganese and that leads voltage of about 3 volts. So, these are some this system can be tried are being tried out, and to think that these are possibilities for the future, the most important any of these there is no cobaltin it, so the cobalt in one of these bottle necks and that can be avoided in all systems, and the volume change of the graphite, volume change of the graphite is can also be avoided, here are one is a there are volume change of graphite, can be avoided here.

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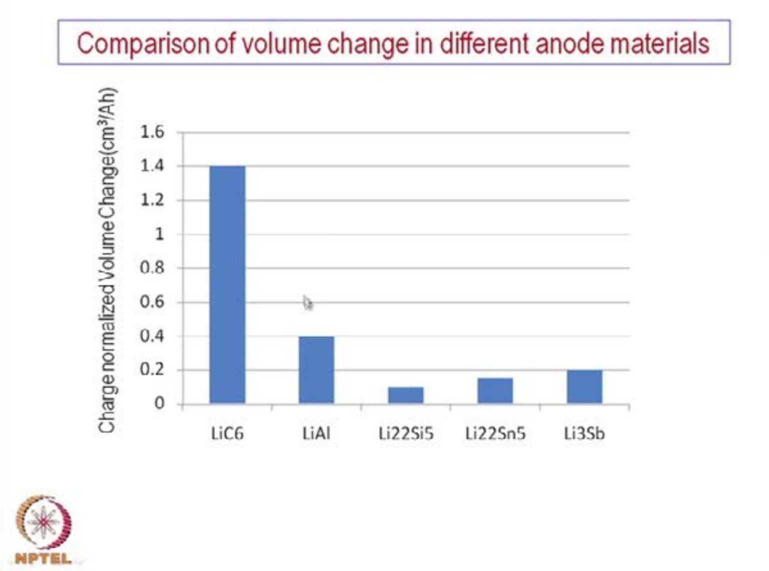

One sees the earlier curve, the volume change of the graphite is quite large, so that can be avoided.

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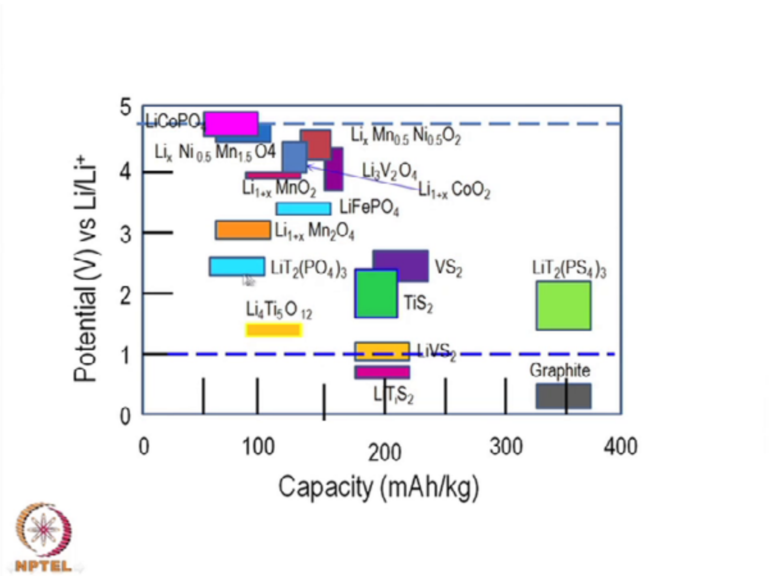

And if you go back to our earlier diagram, of possibility of different materials like this, here is this mentioned earlier, that this is which is been originally thought of cathode material compared to the graphite. Now, we are talking of this becomes your anode, and all these materials here can be used as the cathode material, so you can see, here is your lithium iron phosphate compared to this, so this becomes a voltage here, this is a 1.5 volts this is close to about 3.5 volts, so it becomes somewhat 2 volts or 2.5 volts.

Then you have a this one, this one is, and this couple is another one, and this couple is another one, this one, and this one, so this is another interesting direction in which this is going on, so it started with the graphite and lithium cobaltite. Now, we are talking about different couples, different systems, different cathode and different anode.

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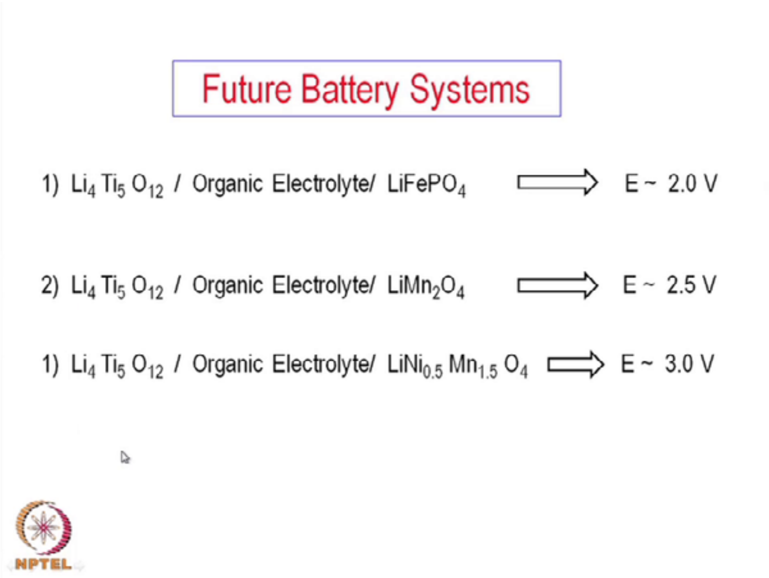

And so this is what actually, the development is this is three systems on which the work is now is current on, and maybe some of them useful for the future generation batteries, and future applications as a mention. The future application the driving the main driving force is high power application, the low power application is more or less saturated, the electronic application but, it is now the high current applications or highly discharge application which are off importance.

So, with this we complete our discussion on a battery, the lithium ion battery, and also the system is related to energy technology earlier we have discussed, the fuel cell, then we have also discussed how the hydrogen can be produced? using the advanced materials, some of the electrical properties of the materials, and now we have just completed the discussion on lithium ion battery, as you can see there are many many different oxides, and carbides, as well as borides and types or nano composite's, which can be very conveniently used for the systems. So, its materials research which is actually the key to the success of this energy technology systems, with this will come to the end of this lecture.

Thank you for your attention.