

Advanced Ceramics for Strategic Applications
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Lecture - 32
Lithium Ion Battery (Cont)

Welcome, today's topic is lithium ion battery. This is also a energy technology related subject. We are all here, the importance of rechargeable battery in our daily life as well as the industrial electronics, including computation. And, in the of the microelectronics, micro batteries are essential for driving the systems, and in some of these batteries are energy systems, advance ceramic has a very important role to play. So, we have chosen this particular topic to demonstrate that aspect.

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Lithium Ion Battery

- It is a rechargeable electro-chemical battery.
- Energy Storage Device
- Conversion of Chemical Energy into Electrical Energy and vice versa
- Energy conversion and storage takes place in the same compartment.



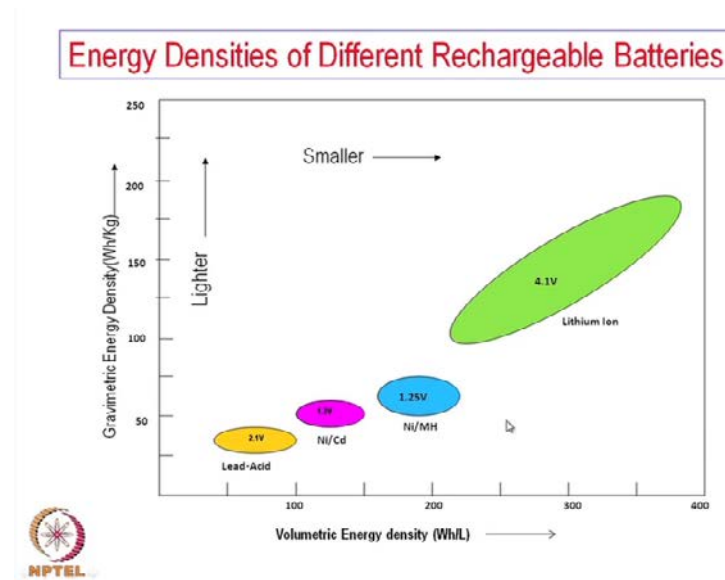
Obviously we understand, what is a lithium battery? as just mentioned, it is a rechargeable electrochemical battery. Earlier, we have consider we have discussed, some of the electrochemical systems, including fuel cells, which is basically a energy conversion device. Here, we are talking about another energy systems; an electrochemical device once again and it is; however, a rechargeable system comparable to any other rechargeable systems, like lead acid battery, nickel cadmium battery and so on. So, lithium ion battery is one of the latest system, in that series and it has, its many important advantages over others.

So, that is what we want to discuss today, it is a energy storage device, as a any other rechargeable battery, it can be charged with electrical energy; and that energy can be stored in the system, which can be once again can be utilised, whenever you need that. So, it is also a energy conversion device, conversion of chemical energy into electrical energy and vice versa; is not a one way process were not is not a primary battery.

So, it is not only the conversion device, for the chemical energy into electrical energy but, the reverse is also possible, that can convert the electrical energy into the chemical potential; and the same energy can be stored in system and that is why, it is a rechargeable battery, energy conversion on storage takes place in the same compartment; obviously, for any other rechargeable battery, the same systems can be used for storing the energy, as well as for discharging it or utilising it, for some of the purpose, so that is basically lithium ion battery.

We will see, why it is called lithium ion battery; it is lithium ion is the basic mobile species in this whole system; and that is the charge carrying species and therefore, it is called lithium ion battery. So, it is the movement of the lithium ion, which either stores the energy or we can get the energy back, for practical system. So, these are the reason, why it is called lithium ion battery.

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Well, if we compare some of the specific characteristics of few rechargeable battery, which we can think of or which is in use for many practical devices and for longer time. We can compare the galvanic energy density, in this case the energy density is nothing but how much energy one can store a per kilogram of the battery weight? So, that is an important criteria, when you are comparing the rechargeable batteries with each other. And so, in the vertical axis, we have a energy galvanic, energy density watt hour per kg, that is the total energy density. And, on this side it is the volumetric energy density. So, this is per unit weight and this is x axis in the per unit volume.

So, what will be the overall size of the battery and what will be the density of the battery, and if we compare four types of rechargeable battery, which are quite industrially important or technologically important, this first one is about lithium acid; lead acid battery, which is extensively used. These days for many different, you can use for many different, many decades and one of the most used battery. Today, in addition you have nickel cadmium battery; that is also extensively used in some of the systems. And then, nickel metal hydrate battery; these are the and then we have compared the lithium ion battery.

So, lead acid battery the nominal voltage about 2 V 1.2 0.1 volts, here nickel cadmium is less is about 1.2 volts whereas, nickel metal hydride is 1.25 volts, of course this voltage depends on the particular reactants, we use and the energy of the reaction involved with

free energy of the reaction, chemical reactions involving in each of these batteries compared to that, lithium ion battery has a very relatively high voltage about 4 around 4 volt, and however, the more important consideration, here is the energy density; energy density is very low, in case of lead; as lead is a very highly a dense material, its densities is very high.


So, the amount of power, you can generate amount of power. You can draw, from this kind of a system is very poor is about less than 50 51 hour per kg. And, nickel cadmium slightly better is slightly above 50 is about 70 75 and the voltage of course is still low, and that also bearing, how much energy density one can get in addition to the density of the components? and then you have nickel metal hydride battery once again its voltage is low, and the maximum energy density can get a gets around 70 75 less than 100 whereas, if you take lithium ion battery; this is on this part of the diagram, so you have very high energy density of the order of 150 to 200 volts watt hour per kg.

So, it is lighter for the same amount of energy to be stored or to be derived from that, and it is also smaller. So, it is basically a miniaturised power house, compared to many other batteries; it is really a very miniaturised store house of energy and therefore, it is so very important in current days of micro electronics. So, that is the main advantage and that is the main driving force, why lithium ion batteries are important and one should understand, its mechanism of cooperation, the materials to be used and what are the alternatives materials? So, that is what, we are going to discuss in this class.

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Typical Characteristics of Different Rechargeable Batteries

Ni- Cd <ul style="list-style-type: none">➤ 1.2 V, 500 Cycles➤ Inexpensive➤ Low energy density➤ Memory effect➤ High self discharge (15-20 %/month)➤ Toxic	Ni-MH <ul style="list-style-type: none">➤ 1.4 V, 600 Cycles➤ Low capacity➤ High self discharge (20-30 %/month)➤ Reduced memory effect,➤ Less-toxic
Lithium Ion <ul style="list-style-type: none">• 3.5V, 2000+ Cycles• Higher energy density (150 -200 Wh/kg)• No memory effect• Low self discharge (5-10 % / month)• Less Toxic.	



Well, if you have specific comments, so where is the different systems? We have just consider, and nickel cadmium is 1.2 and 500 cycles, the life we did not consider in the earlier slide; so the life is also very important, the cost is also important, and this is about nickel cadmium 1.2 volts and approximate life is about 500 cycles, is in inexpensive nickel and cadmium not that costly but, it certainly costlier than lead acid batteries but, it less costly than the other two low energy density; that we have already discussed. Memory effect; it has during its charging and discharging; it has some problem and it memorises, what has happened in the earlier cycle?

So, a high self discharge, that is also another very important criteria for any battery. If it is not in use, whether there is any deterioration of the of the battery; that means whether it is losing the store energy and that is what, we call the self discharge and the rate of discharge, self discharge is about 15 to 20 percent per month.

And particularly, for cadmium is a toxic material and that is one of the disadvantages of this system, if you take the other system that is nickel metal hydride, then the voltage is about 1.4, of course it varies in any system, it varies earlier, it was shown, 1.25 its 1.4 that can happen from the way, it has been prepared although the materials are same but, the previous condition on the morphology of the system and so on.

To change some of these parameters, the life is about 600 cycles, a low capacity a high self discharge, once again it was higher the rate of discharge, self discharge or self life is


less or 20 30 percent per month. So, that is another disadvantage. About this battery, reduced memory effect and less toxic, because it is not cadmium or lead. So, it is less toxic in comparison, if you have a lithium ion battery, although the theoretical voltage is about a 4.1 volt, the normal voltage in reality is about 3.5 volts but, the life is very large or very long compared to 500 to 600 cycles; we have about 2000 cycles plus, so that is a very attractive feature and then, we have a higher energy density.

That, we have already seen in earlier slide. That is the highest 150 to 200 watt hour per kg, that we have already mention, no memory effect that is an advantage. And, low self discharge is 5 to 10 percent per month, compared to more than around 20 percent or rechargeable batteries and less toxic; of course, although its less toxic, there is some problem. We will discuss that later, the some of the chemicals used are not very safe. So, safety is certainly an issue, which has not been mentioned here but, even then because then advantages is much more and it compensates the other disadvantages points.

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Working Principle and Functional Materials

- Both anode and cathode are Lithium intercalated materials with sufficient Electronic Conductivity.
- Anode: Lithium intercalated graphite (LiC_6)
- Cathode: Lithium intercalated LiCoO_2 (Li_xCoO_2)
- Electrolyte (Liquid): Alkyl Carbonate + LiPF_6
[Solution of LiPF_6 in a mixture of Ethylene Carbonate and Di methyle Carbonate (EC-DMC)]



Well, the working principal at the materials, used functional materials are relatively simple, is not that complex. Both anode and cathode are actually lithium, intercalated materials will sufficient electronic conductivity. Of course, any battery system, whether it is cathode, anode or the electrolyte must have sufficient conductivity, electrical conductivity and therefore, whether anode or cathode, when it is used in the system, it must have an electronic conductivity.

Since, lithium is the charge carrying species in this case, and the active species show both anode and the cathode, must have must get some interaction; it should interact with the lithium, and in this case a very simple interaction is a both this both the anode and the cathode; are actually intercalated compounds. Intercalation is a phenomena, in which some of the solids, some of the solid this particular type of structures can accommodate can accommodate, some others ionic species into the structure, without disturbing the structure itself.

So, there are the there are some are the crystallographic pores, which can be filled up, which can be filled up with some mobile species likely lithium in this case. So, it is called lithium intercalation. Normally, the layered structures have a property of intercalation between the layers.

You have a less ionic bonding, and those layers can be slightly distorted, slightly can be moved apart and in between certain ionic species, can come in, so that is what, is known as the intercalation or sometimes also called insertion; these are the insertion compounds, in which lithium can be intercalated or inserted into the structure of the solid material, that two active materials here; the anode and the cathode both are intercalated lithium intercalated compounds; one is very simply graphite; graphite as you all know, that it has a hexagonal structure, it is a layered structure, and in between when the layers, we have a very weak bond and the bond and those layers can be filled up with certain amount of lithium ions. So, that is what, we call the lithium intercalated graphite.

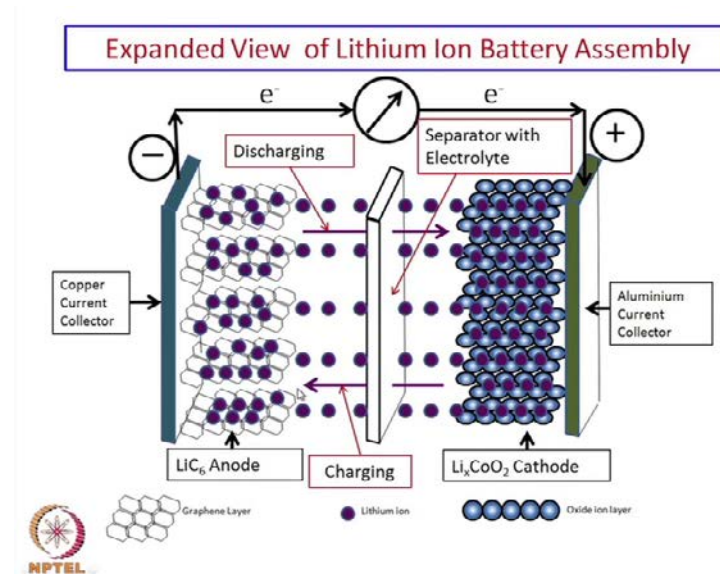
So, that is used as the anode, and the cathode is also another intercalated compound but, not graphite, it is oxide, it is lithium cobaltite or lithium cobalt oxide. So, a variable quantity either it can be presented $LiCoO_2$ or Li_xCoO_2 , x is variable. So, variable quantity of lithium can go into the structure and accommodate it. So, on both the sides, whether it is anode or the cathode, both have the property of intercalating lithium ions.

And, that is how there is a reversible reaction? and lithium can move in both the directions, under different conditions the electrolyte of course, both these two both anode and the cathode are solid materials, however it is not an all solid state battery, it is not an all solid state battery, so it is the electrolyte. Of course, is a liquid one, so the electrolyte is liquid and it is basically a solution of lithium phosphofluorite $LiPF_6$, in some alkyl

carbonates alkyl carbonates are like this, it is a mixture of solution of this compound LiPF_6 in a mixture of ethylene carbonate and di methyl carbonate.

Normally, it is referred to as EC-DMC. So, in a solution of EC-DMC, you have some in a solvent of EC-DMC, you have a solute like LiPF_6 , so that is the compound, which is used as the liquid electrolyte and; obviously, this has a lithium ion conductivity. So, lithium can have a very high conductivity in this particular liquid electrolyte. So, these are the three major components, the active components of a lithium ion battery.

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The details, if we go to the details of the structure, and the working principal; it looks like this. You have as I said, this is the anode side, the anode is a LiC_6 and the cathode is Li_xCoO_2 , so this both of them has a layered structure, as we know graphite has a layered structure. So, these are the graphite sheets hexagonal, this one sheet and another sheet, another layer, there are five different different layers in between the layers. The space between the layers, the lithium being a very small diameter or small radius, ion can go in and sits there and it remains stable.

So, you form the maximum quantity of lithium, that you can introduce is about a for 6 carbon atoms, there will be only one lithium atom, so that is the maximum amount, one can introduce in this structure, so that is the solid cathode material, sorry the anode material. This side is the anode material and this side is the cathode material; cathode

material is basically a cobalt's oxide CoO_2 and, in which lithium again is intercalated, these are the CoO_2 layers, these are layers.

I will see some of the detailed, little expanded view of this, later on. And in between, the layers lithium ion can go in and sits there. So, if there will electronic exchange, so when discharging, in the during the discharge lithium ion from the anode goes to the cathode side, so the electron gets transferred here. Alright so, lithium is ionised metal state to negative, positively charged state, and electron gets injected into the outer socket. So, electron flows in this direction and lithium flows in this direction. So, that is the way that is a normal thing or discharge. However, you want to recharge, you have to charge the system, then the lithium have to be pushed back to the system.

So, by applying an EMF from the outside lithium from the cathode is pushed back into the anode side. So, when it is gets saturated with lithium, the charging is complete, once again if you it can discharge, by connecting it to a load or driving some current from the system.

So, that is what, we have basically the lithium ion goes back and forth, from the anode to the cathode or cathode to the anode and by this process; it can either discharge or charge the electrolyte is as, I mention is basically liquid electrolyte a LiPF_4 , LiPF_6 dissolve line cdm c and that is taken, there is a that is taken in this felt, is actually separate with electrolyte, separated is a porous separator, basically felt organic felt kind of material and that is soaked in the liquid electrolyte and that is, how the electrolyte is there the expansion is not separated out, actually it is compact. There is hardly in space between this, we will see, how exactly is fabricated but, it has been expanded for clarification.

So, are you have a this is the electrolyte or electrolyte containing a porous material, here a flexible porous material, otherwise the solid; that is solid and these of course, thin not a very bulk material is fairly thin, in the form of thick films will see, how exactly it is manufactured? and then, you have a current collector on this side, which is aluminium metallic aluminium and a metallic copper on the other side. In the anode side, a metallic copper as the current collector. So, this is basically for proper contacts with the both anode and the cathode. So, this is basic simple construction or the structure of a battery assembly or battery system. So, these are lithium ions, this violet ions are lithium ions;


these are the hexagonal blocks are basically, the carbon blocks and then you have C O 2 blocks on this side.

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Discharging/ Charging

➤ Discharging Process (Spontaneous)

- Anode:
$$\text{Li}_x\text{C}_6 \rightarrow \text{Graphite} + \text{Li}^+ + \text{e}^-$$
- Cathode:
$$\text{CoO}_2 + x\text{Li} + x\text{e}^- \rightarrow \text{Li}_x\text{CoO}_2 \quad (\text{Co}^{4+} \rightarrow \text{Co}^{3+})$$



The reactions, which are taking place during discharging and charging, this is the discharging process; this is spontaneous process; that means, as long as the anode is fully saturated with lithium, and if you have a load has been attached or current is drawn, immediately lithium will come out of the cathode side, and go into the, sorry lithium will come out of the anode; that means, the graphite and go to the cathode. So, the two reactions, which takes place at two different places, at the anode and the cathode are like, this is quite understandable.

You have a different percentages or different concentration of lithium, within the graphite block and that changes ionises lithium, becomes lithium plus and then, one electron is gets injected into the current collector and then to the external circuit. So, these are separated out lithium goes through the electrolyte and goes to the cathode. So, in the cathode, it reacts with the cobalt oxide cobalt oxide structure. So, a very will percentage or a very will amount of lithium comes in plus electron, x amount of electron, x quantity of electron and that forms, this comes from the external circuit, this comes through the electrolyte.

So, they join together or the interface, the becomes lithium ion, and then finally it goes to the structure. Now, this lithium electron; additional electron, which comes in into the


system, actually changes the valency of the cobalt. So, that is how it is actually accommodated into the structure, because cobalt is a very variable valency and therefore, cobalt plus a cobalt 4 plus changes to cobalt 3 plus. So, depending on the number of electrons is adsorbed, the number of lithium ions gets this; that means, more and more discharge takes place, more and more cobalt 4 plus converts to cobalt 3 plus. So, that is another way around the structural change, which takes place into the system of a cobalt oxide or the cathode structure. So, this is what happens in the discharge process; that means, when the current is drawn from the battery.

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Discharging/ Charging

➤ Charging Process (Non-Spontaneous)

- Anode:
 $\text{Graphite} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_6$
- Cathode:
 $\text{Li}_x\text{CoO}_2 \rightarrow \text{CoO}_2 + x\text{Li} + xe^- \quad (\text{Co}^{3+} \rightarrow \text{Co}^{4+})$

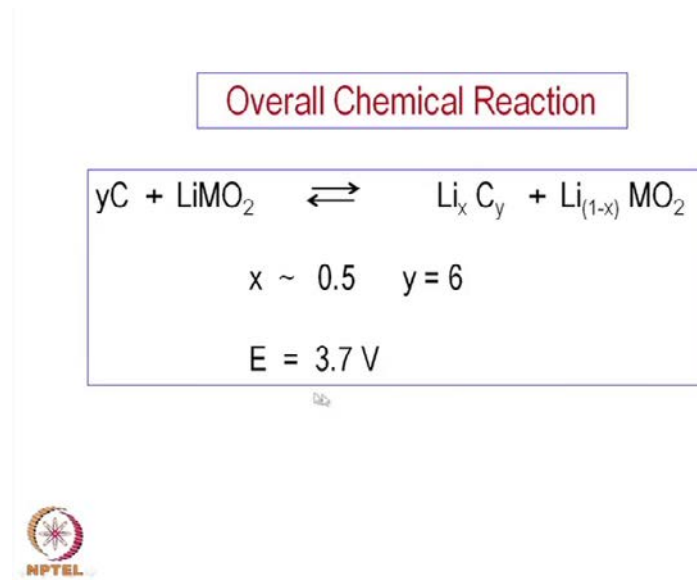


And, next one will be charging stage. Just, the reverse will take place, this is a non spontaneous, which means you have to apply energy, you have to provide energy in the form of an electrical energy from the outside. So, in the anode side with the reverse reaction takes place graphite plus x L i 4; it gives rise to and absorbs the electron, and finally, converts back to a L i x C 6. So, this is the charging process, and in the same manner or the reverse manner, what happened in the discharge case, in the cathode we have a L i x C o O 2 Converts to C o O 2, and x L i and this is a liberated out. So, this C O 3 plus again gets converted to C O 4 plus.

So, there is a valence change, there is a valence change of the cobalt ion and that takes place through the intercalation step. So, one only, when lithium comes in and there is an exchange of electron between, the lithium and the cobalt, and that is how the cobalt gets

changed from a trivalent state to a tetravalent state? So, depending on the number of electrons more, and more cobalt ion convert itself to a high valent state material high valent state species. So, that is the charge.

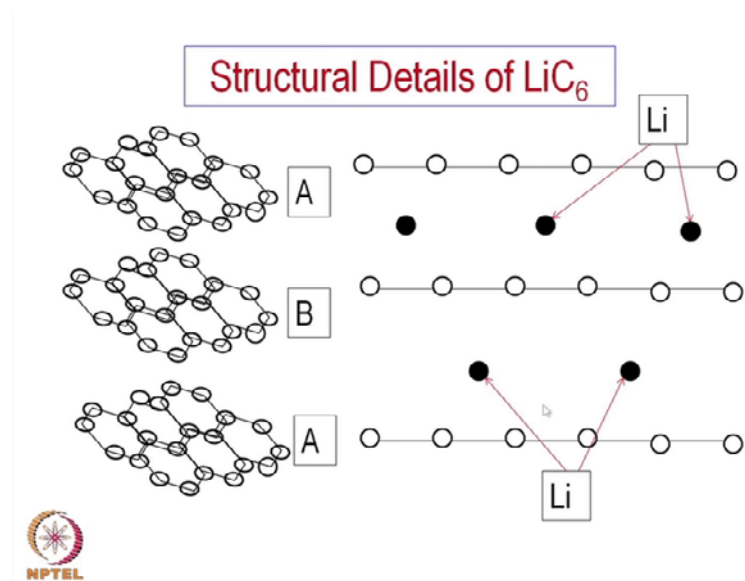
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Well, one can write the overall reaction in this manner, in a slightly different way of course. So, why atoms of carbon and lithium MO_2 , M stands for cobalt here, it can be seen later on, M can be cobalt, it can be manganese, it can be nickel and so on. So, that is why a generalised formula has been used. So, $Li_x C_y$ and $Li_{1-x} MO_2$, so a Li goes to the MO_2 structure and also partly closed carbon structure.

So, this is what happens or this takes value of X is about 0.5 and y is 6 y means number of lithium ions the ratio of the lithium to the carbon atoms, that is about 1 is to 6, where as x amount of lithium, which can go in to the oxide structure, is about 5.5 atoms per 1 mole of oxide and the voltage is about 3.7 volts, that is the normal voltage one gets.

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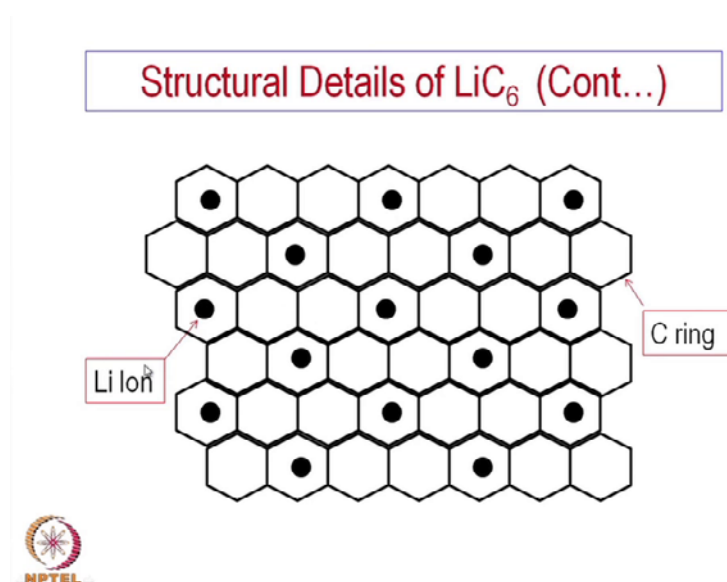
Now looking at the structure, we have already seen or we have already mentioned that the, it is a intercalated compound, it a lithium intercalated graphite compound. So, what actually happens, so far the structure is concerned is very simple. A way to assume that, lithium just goes into the lattice sites, or the in between the two layers, and that is what have been shown here, these are the layered structure of hexagonal structure of graphite, as you know is you remember the structure of graphite.

Actually it is a A B A A B stacking, means this is A layer, this is B layer and then, you have A layer once again. So, these and these are equivalent whereas, this is a bout 120 degree rotated in one particular direction on the plane. So, these are planar structures as such and the and the stacking in terms of the crystallographic stacking is A B A B stacking, that is why this A B and A has been mentioned.

Here, if you take a kind of section along the vertical direction, so this is one layer. So, this is the horizontal section or the planar view and is the vertical or a leaf kind of elevation, one can say this is elevation; that means, this is one layer of graphite, this is another layer of graphite, and this is a 3rd layer of graphite. So, corresponding to these 3 layers, here and in between the lithium goes now, from the structure, it is been from the LiC_6 or every 6 atoms of of carbon, there is only 1 lithium that is, the structural requirement and one cannot use more than the lithium.

So, once that is satisfied, then it is fully charged. So, lithium goes there and sits here and in between the structures and you can see, all the sites all the sites are not really occupied by the lithium, it is the alternate sides. If you take this Square, here in the elevation becomes square or a rectangle, so this is occupied, this is not occupied, this is occupied and this is not occupied on the both. This reaction, if this is occupied, next one not empty and only the adjoining one or the neighbouring one is occupied. So, alternate even in the vertical direction alternate sides are occupied. So, these are the lithium ions that is, how otherwise, if you want to push more lithium into the system, the structural will break down. So, it cannot stand.

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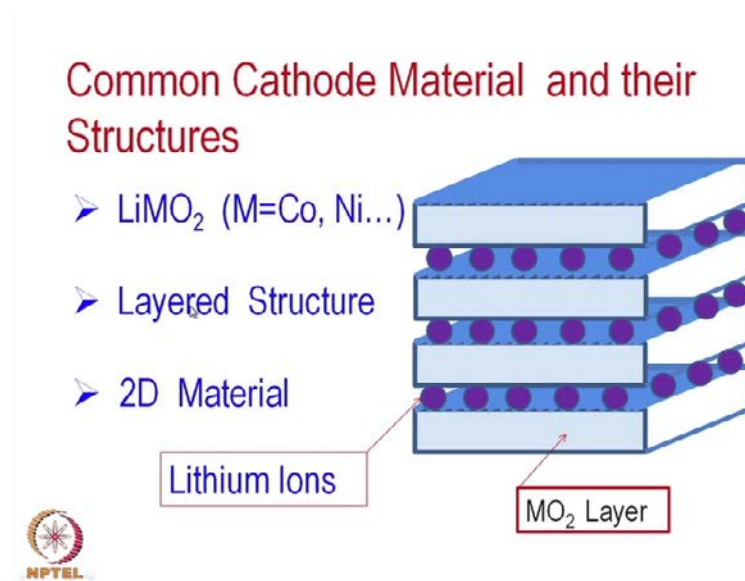


In the another view, you will get a much better picture, you can see. This is the horizontal view of one particular layer and these are the hexagons; and these are the positions of lithium ions; and these are the positions of lithium ions and you can see a in this along the horizontal things. Every 3rd every 3rd hexagon is actually occupied, every 3rd hexagon is occupied and here this is in vertical direction, and vertically one can say one layer is off, then the second layer is occupied.

So, if this layer is occupied, then this layer the next hexagon is not occupied or if you take this action one one one axis like this diagonal axis, you will see also that every 3rd hexagon is actually occupied. So, along this this is a every 3rd and this also every 3rd along the horizontal axis also a every 3rd axis 3rd one is occupied right. So, it depends

on the structure, and it has to anyway maintain and 1 is to 6 ratio. So, the other way also if you take 7 hexagon around, which out of 7th 1 only occupied, all the other 6 is empty. So, that happens in each case, surrounding each lithium. Actually, there are 6 empty hexagonal structure or hexagons, that happens everywhere, so that is how it is actually maintained, this is a saturated under the saturated situation, how the lithium ions are distributed in the graphite structure.

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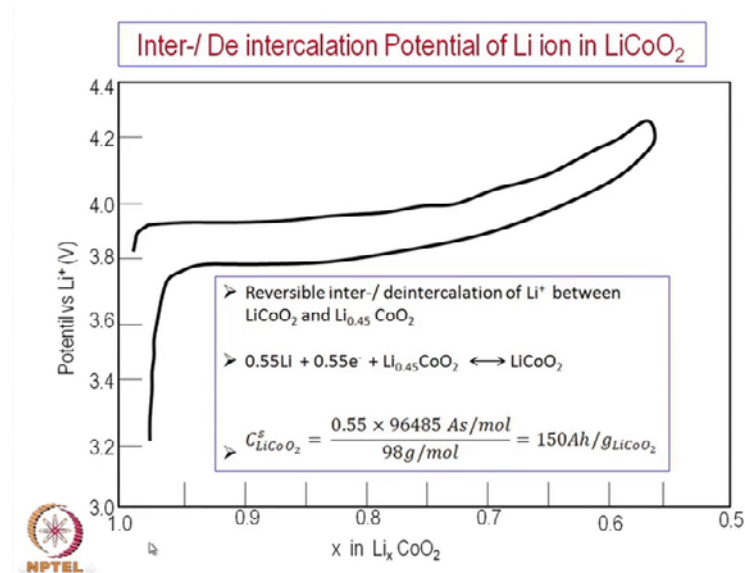


Well, if you look at the similar thing, for the C O_2 , the cathode material once again, it is been written as M stands for cobalt nickel and manganese. So, you have a layered structure here. So, these are C O_2 layers; these are C O_2 layers blocks. One can say, these are and in between the blocks, it has a similarity of the graphitic structure but, it is not a hexagonal structure, it is a different structure; it is basically a rhombus metal structure, and so these layers are C O_2 layers and in between C O_2 layers are in between these are lithium ions. So, it is the it is not only a layered structure, it is called a 2D material; this particular structure as a 2D 2 dimensional recreation or intercalation, exactly same way as graphitic layer, you have 1 layer of lithium and that layer between themselves forms a two-dimensional layer, so it is a planar structure.

The lithium ions can move in both the directions, it can move in this direction x as well as y direction but, it cannot move in the z direction z direction, these layers is obstructing. So, the movement or the mobility is actually in both directions x and y

directions, and that is why, it is a two dimensional material two dimensional intercalation material. So, this is a typical structure, of course, it is a schematic view; it is not an exact view. So, it is a schematics of the cathode material and the structures right, how the lithium can go in...

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One can calculate, what will be the theoretical density? and by a kind of cyclic volt meter experiment, electrical experiment, and this is the potential versus lithium ion and that going to the details. This is a typical intercalation intercalation curve; that means, basically the intercalation is taking place by an electrochemical means... So, how much is the potential, you have to apply to introduce, how much x quantity of lithium into the system. So, as I mentioned, the maximum one can introduce about 0.5 x is about 0.5 not one, so normally it is about 0.452 0.5 and that is why, the x value here is 0.5 and these are the potential, you use to introduce introduce, as you increase the potential more and more lithium goes in, and then as you reduce the potential on the more and more lithium comes out.

So, by this intercalation experiment, which shows the intercalation or de intercalation potential of lithium ion into a Li_xCoO_2 structure. So, Li of course, it should be Li_x . So, one can write also, Li_x , so x value is about 0.5 and one can calculate, from these potential, the reversible intercalation and deintercalation lithium ion between LiCoO_2 . And, let us say $\text{Li}_{0.5}\text{CoO}_2$, if you start with 0.5 and then goes to 0.55. So, this is


what happens, you make a lithium LiCoO_2 and then, one can calculate, what is total amount of energy? Which can be stored? and Whereever energy can be stored in to the gram of lithium cobalt oxide lithium cobalt, it so per gram.

One can theoretically, from this curve one can find out and this is the ampere second or the ferret, then and then per 98 gram, which is the mole. So, you can find out, what is the theoretical value of energy? which can be stored into the system by from this electro chemical potential curve?

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Properties of LiCoO_2 Cathode Material

- Layered rhombohedral structure of CoO_2 framework with intercalating Li^+ ions
- Large c parameter facilitating the to and fro motion of the Li^+ ions
- High working potential of ~ 4.0 V giving a high energy density (150 - 200 Wh/kg)
- Specific gravimetric capacity ~ 120 -130 mAkg⁻¹
- Good cycleability (charging – discharging)
- Less capacity fade out

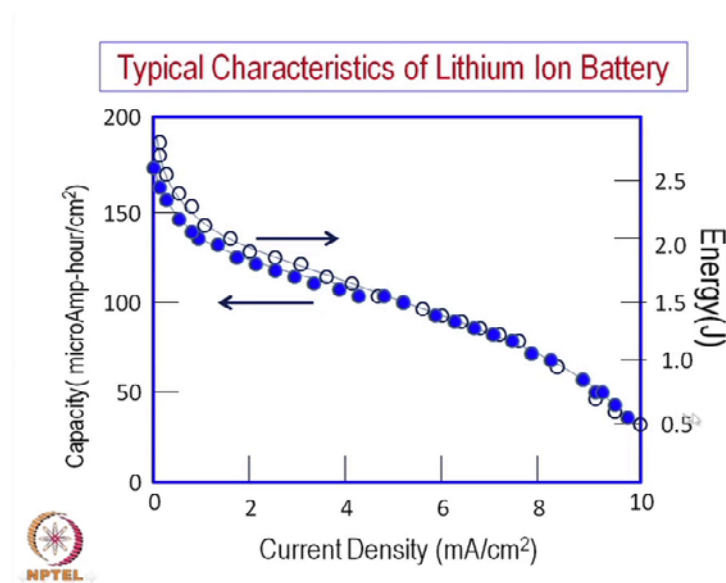


Well, some typical properties of lithium cobaltite, as the frame work with intercalating lithium ions, that as I mentioned, the layered from little structure of CoO_2 framework with intercalation of lithium ions.

Lithium ions, that is the basic feature of lithium cobalt cathode, it is the largest c parameter facilitating to and fro, most of the lithium ions that is also structural feature of the that are doing pictorially soon in an earlier slide. And it is a high working potential that also mention about 0.4 about 4 V giving a higher energy density of 150 to 200 watt per hour kg. Specific gravimetric capacity, is the milliamps per centimetres per kg. Here are given 120 to 130 mA per kg, and good cycle ability, charging discharging is already mentioned about 600 cycles.

One can stand, material and less capacity fade out; that means, once again a the self life shelf life is long self discharge is not very high. So, that is a and all these properties all these properties, depend on both on the cathode material and the anode material but, this when you use lithium cobaltite as cathode, these are some the property is met, because you consider in this. Because, in the later stage, we are discussing about the alternative cathode material, also not be unique material. Certainly, it is almost a used material, and most common materials over used but, developments are taking place for replacing it and will see, how it compares, how they compare with this particular cathode material.

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This is a typical curve discharge curve, where the capacity is in micro amps micro amps hour per centimetre square, here centimetres square of the cathode and current density is of the order of milliamps per centimetre square. So, depending on the area electrodes, one can get a this values, and this is the kind of energy in Joules can will, this is just typical one, will not go into details of this.

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A few Disadvantages of LiCoO_2 as the cathode material

- Transformation of rhombohedral to monoclinic structure after repeated charge-discharge cycles.
- Only 50% of theoretical capacity is realized due to structural instability.
- High Cost of Cobalt and insufficient availability
- Thermodynamic incompatibility with the organic electrolyte



However, as I have earlier mentioned, lithium cobalt although it is very well, accepted cathode material and it is being used extensively for the commercial purpose, it is not absolutely trouble-free, it has certain disadvantages also. Transformational of rhombohedral to monoclinic structure, after repeated charge, discharge cycles. So, as we intercalate lithium and deintercalate large number of times slowly, the structure gets distorted, and there is a change from the layered structure of the rhombohedral structure to a monoclinic symmetry; that becomes less one of the less symmetric, and that reduces as that reduces the intercalation capacity.

The capacity to intercalate more and more lithium reduced, which means ultimately the charging, discharging characteristics of the capacity to discharge and charge, same amount of energy rate capacity gets decreased, but, even then it is much better much better, than the other variety of a rechargeable atoms only 50 percent of the theoretical capacity realised, due to structural instability, will we have seen that. x value is about 0.5, he cannot go more than that, and that is also a some kind of disadvantages.

Although, this value is far better than other rechargeable batteries are even then, maybe they are maybe one can find out a much better material much better material, where more amount of lithium can be intercalated. So, it is only about 50 percent can be realised. In fact, high cost of cobalt, insufficient ability, these is one of the very critical issues. So, far is the commercial applications is concerned currently, that is one of the

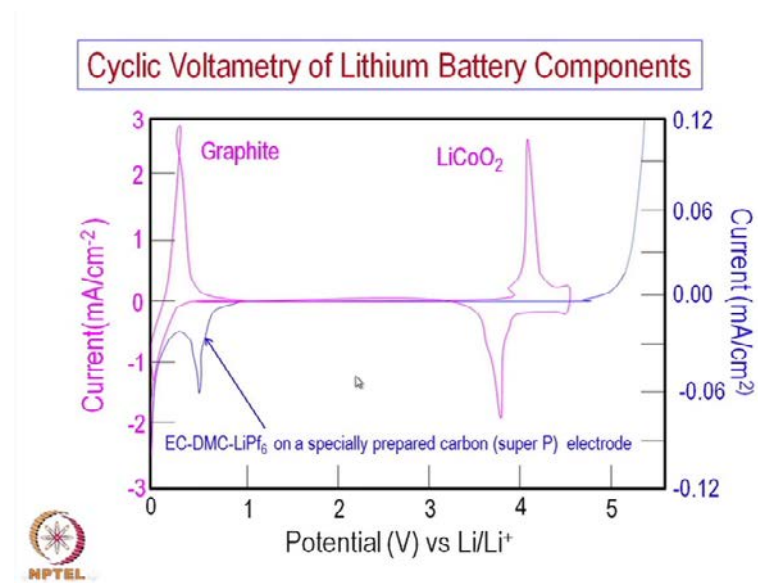
biggest limitations. So, far as the technological applications is concerned, it is being used extensively.

Because, there is no other material. So, far and compared to other rechargeable batteries, and they have a much better capability and much better property is and therefore, even in spite of the some on the difficulties is being used, it simply no doubt but, there is a scope; that the scope for improvement tremendous scope of improvement, and one of the problems of course, is the cobalt; cobalt is a highly costly material, much much costlier than nickel manganese and so on.

The other alternative materials, and insufficient availability the world deposit of cobalt is not very high. So, it is like a hydrogen copper and aluminium in the cobalt, available in the metal cobalt, available in this country in the whole world is much less. So, there is always that poses a problem of, how it can expand? What kind of a cost or economic will quickly? So, that is another problem and thermodynamic in compatibility with the organic electrolyte. Although it is a very good material. So, far very good different system, that seen, that the electrolyte is a liquid electrolyte and its organic solvent, in which a L i P F 6 is resolved, that is the best a electrolyte, which is compatible with the system.

So, far but, there is a certain amount of incompatibility, thermal dynamic incompetent, although it is working at the time the but, once again, it will look at the thermodynamics and they are not that stable and the electrolytes are not that stable, either with the anode material, the graphite cathode material, the cobaltite lithium cobaltite. So, I will discuss that, what exactly this kind of incompatibility is and if there is a look out people are looking out for replacing lithium cobaltite and also all graphite, it possible and at the same time in the electrolyte. So, these are the different areas were more and more research is being carried out, and then scope of improvement consider scope of improvement.

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Well, this gives you are, what is the problem exactly? what is the incompatibility? as just I have told you, this is a cyclic voltametric curve, in which apply a voltage and the current and then find out, what is the intercalation of charging and discharging kind of phenomenon, which is taking place another two curves; one is this blue-color, this is for the electrolyte, the organic electrolyte; and there is a one pink here are and then, there is no other phenomena and it goes a kind of get decomposes at higher voltage.

So, when we apply a very high-voltage 5 volts; it gets decomposed, so that is the current more more; and more current passes through, and there is a some kind of electric chemical phenomena takes place at a very low voltage, otherwise it is a fairly good stable as such at different voltages.

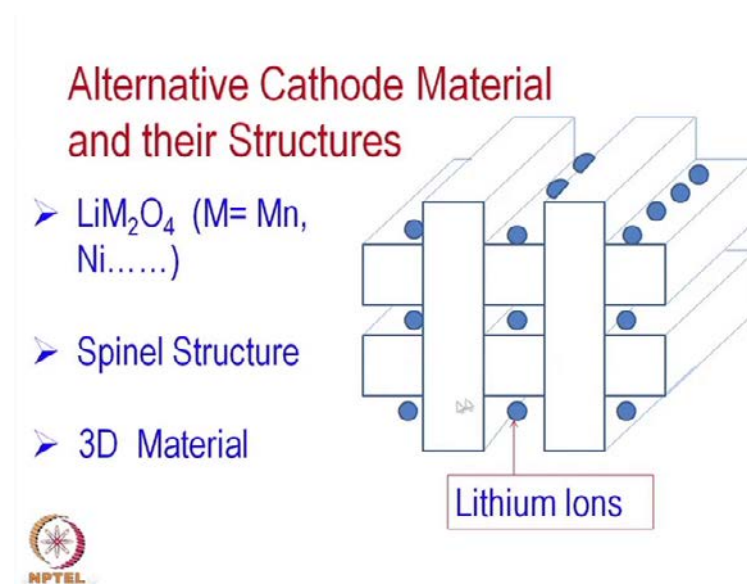
However, in connection with the cathode and anode and this is these are the two peaks; that here it is for the lithium cobalt oxide and this is for the graphite of course, this does not crossover like that, there is a problem of drawing in the curve, this is not a loop, it so this is just a picth is for the graphite, so it is the intercalation, deintercalation and this is of course, reversible lithium carbon cobalt. Again should one takes place is much higher voltage, this takes place in a much high-voltage and this takes place in a much low voltage graphite intercalation and one can see, that in the voltage range in the 4 volt.

There is some kind of a decomposition reaction takes place, in fact lithium cobaltite and graphite both of them are not fully stable, are not fully stable in this kind of voltage and

it is fortunately fortunately, what happens it is stable in the kinetic point of view. From the kinetic point, although thermodynamic point of view, are they are not that stable but, in kinetic point view, there is no problem, because some both on the lithium cobaltite as well as graphite are some products, gets the product of decomposition gives deposited and further decomposition does not takes place, there is one more mistake here that f should be capital let me change that right.

So, what happens from this point, it indicates that there is some kind of decomposition takes place but, fortunately or fortunate for everybody, that are that decomposition products gets deposited on this surface, and further decomposition is not allowed, or is the abstract for the decomposition of the electrolyte therefore, and this is another problem, with this to system on the graphite and lithium cobaltite system, that otherwise quite good there is some research going on, whether we can replace both graphite and lithium and it can enhance and the properties are both the capacity, as well as the recyclability and so on.

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So, this is the information about, be alternative cathode and anode materials. There are large number of anode and cathode materials are being tried out. So, I will give indication of few of them. Alternative cathode material and the structures are of course, as per requirement, there has to be intercalation; the property of intercalation, the

materials must be able to interconnect lithium ions, true that are structurally, there must be up sides, where lithium carbon can go and sit there.

And, should this is another type of oxides structures. This is a LiM_2O_4 , our aim is again manganese and nickel. So, this is not a purely layered structure, is not exactly a layered structure but, it is a more compact structure. However, there are some sites, where lithium can go and place itself, this is what called 3D, 3D material, because there is not fully layer, can see this is layer but, there are cross layer also can. So, these are also a M_2O_4 structure, say a these are the channels, in which are the lithium can go and move.

So instead of, if you compare the cobalt oxide structure, and here M_2O_4 structure are quite different, and these are called 3D materials, because the particular structure, where the way the lithium ions can go in and the sites it can occupy. So, this is one kind of spinal structure, and in which are which has also be intercalation property.

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Alternative Cathode Material and their Structures

- LiFePO_4 (LFP)
- Olivine Structure
- 1D Material

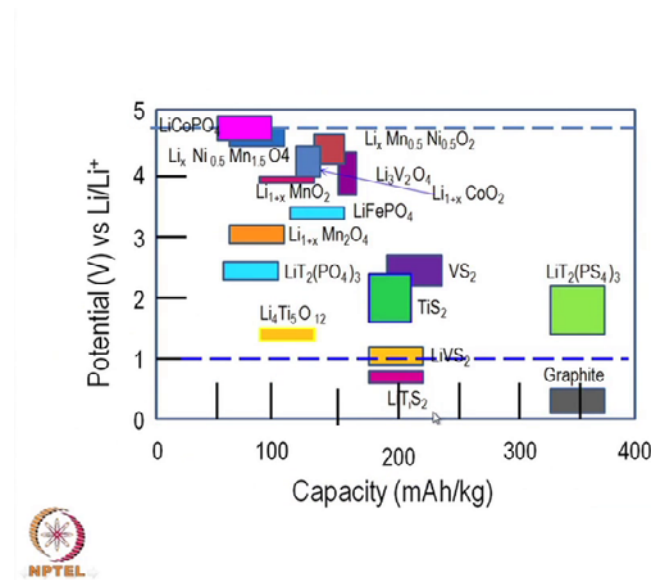


Lithium ions



Another important, compound is in this series is actually a lithium iron phosphate a LiFePO_4 , which is not spinal structure but, is olivine structure, these are once again kind of very close to silicate structures; and these are 1D structures 1D, because they are holes are more or less like a zeolite structure through, which the Lithium ion can pass through or it can position itself. So, this is another compound, an alternative compound to CO_2 .

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Well, these are there are large number, these are only at, I have given you two alternative structures, two compounds, which is tried out to replace lithium cobaltite. However depending on the potential, these are the different kind of compounds, which is been tried out, which is been synthesised and experiments of been carried out, and their respective electrochemical potential also. The capacity will, how much energy one can store in the material?

So, the this at capacity has been plotted against potential, once again up to 5 V on can have, here is our lithium cobaltite. So, this is C O 2 structure and one can have about 100 to 200 these are again not very precise but, this kind of schematic relative a values are given. So, this is the area, where lithium cobaltite stands but, there are many others. I will tell you, another two compounds, which were are just discuss. This is a L i Fe PO 4, one of the very promising material L i Fe PO 4, that is also comparable. So, far the capacity is concerned you, also comparable to cobalt oxide.

And, another spinal structure discussed just now; is M n 2 O 4 structure M n 2 O 4 structure, and that is slightly lower. So, the voltage is a slightly lower compared to the cobalt oxide, here and also compared to lithium phosphate, lithium iron phosphate but, a in the capacity also slightly low. But, it is a suddenly a alternative material, a these are lithium, titanium, phosphorus, sulphate and titanium sulphide and vanadium sulphide,

lithium vanadium sulphide, lithium titanium sulphide, many many compounds, lithium titanium oxide is also. There, then they have titanium phosphate is also there and so on.

So, forth here is another compound, which is M site M site in the MO_2 structure of the cobalt cobalt has been replaced partly by manganese partly ionic. So, instructs cobalt, you have the half manganese and nickel here Mn_2O_4 structure; this Mn_2O_4 is here, and in that MnO_2 is very close to cobalt oxide. But this Mn_2O_4 structure, again the part of be a Mn is been replaced by nickel about 1 by 4 of manganese is replaced by nickel.

So, this also is a possibility and you can see is voltage is very high, and although the capacity slightly low, and lithium cobalt phosphate is also another compound, so there are many many possibilities come, alternative to cobalt and some of them have useful properties and some of them are not so useful. We will find out, what are the different possibilities for the future battery? and what are the replacements of graphite and cobaltite oxide or lithium cobaltite? The time is up, so we will continue discussion in the next class.

Thank you.