Electrochemical Energy Storage
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Module - 04
Basic components in Li – ion batteries: Electrodes, Electrolytes, and collectors
Lecture - 16
Positive Electrodes: Lithiated Transition Metal Oxides, Lithiated Iron Oxyphosphates etc.

Welcome to my course Electrochemical Energy Storage and we are now in module number 4, where the basic components in lithium ion batteries that I will introduce and so far we have talked about the positive electrodes, we have talked about negative electrodes and apart from that we have separator, we have electrolyte, we have current collectors.

So, the details of those things that I will describe. So, in this particular lecture of this module, we will talk only about the positive electrode materials and mostly, as you know lithiated transition metal oxides, we will be talking about lithiated iron oxyphosphates and other relevant positive materials that we will describe in this course, in this particular lecture of the course.

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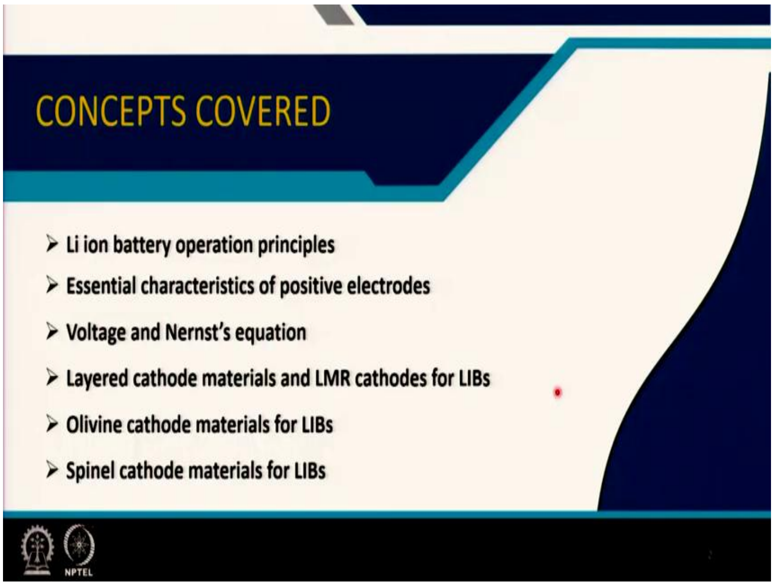

CONCEPTS COVERED

- Li ion battery operation principles
- Essential characteristics of positive electrodes
- Voltage and Nernst's equation
- Layered cathode materials and LMR cathodes for LIBs
- Olivine cathode materials for LIBs
- Spinel cathode materials for LIBs

Now, in this particular lecture, again, we will briefly talk about the lithium ion battery, their operation principles, then essential characteristics; particularly, the positive electrode materials and then we will talk about the relation of the derived Nernst's equation which I derived in earlier parts of the course. So, Nernst equation and how it affects the voltage.

So, far as you understand that we talked about the chemical potential of lithium and the free energy versus composition diagram and then, we try to understand the voltage profile.

So, Nernst equation also we will introduce that how it is related with the voltage in accordance to the operation of the lithium ion batteries. Then we will talk about the layered cathode materials and a special high voltage high capacity cathode material which is still under investigations and we have also done lot of work on this lithium manganese rich cathode materials for lithium ion batteries. Then, we will talk about the olivine cathode materials for lithium ion batteries and spinel cathode materials for lithium ion batteries.

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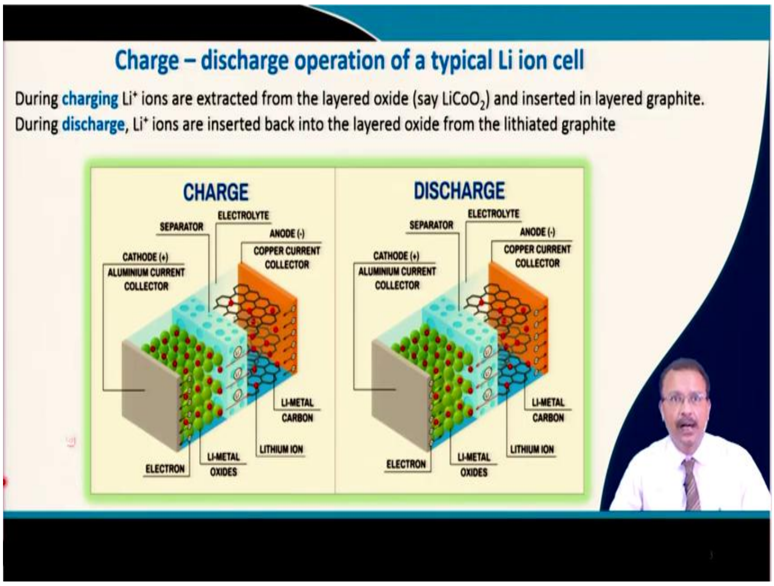

Charge – discharge operation of a typical Li ion cell

During **charging** Li^+ ions are extracted from the layered oxide (say $LiCoO_2$) and inserted in layered graphite.
During **discharge**, Li^+ ions are inserted back into the layered oxide from the lithiated graphite

So, the operation by this time is well understood. So, we have a charge operation and during charge lithium ions, they are extracted from your cathode material say layered cathode materials like lithium cobalt oxide and they pass through this porous separator and insert into the layered another layered graphite material. During discharge, lithium ions are inserted back into the layered oxide from lithiated graphite.

So, the components here you can see that we will be talking about throughout the module that the current collectors, they are different; in case of cathode, it is aluminium; in case of anode, it is copper current collector is used. Separators are basically polymer membranes porous polymer membranes and then, that is soaked in electrolyte which is organic electrolyte and some kind of solvent and lithium salts are dissolved in it.

So, that is used. So, we will be talking about the current collector, positive electrode, negative electrode, separator, current collectors as well as during construction you know the several other metals are attached to this current collector. So, those things will also be briefly introduced.

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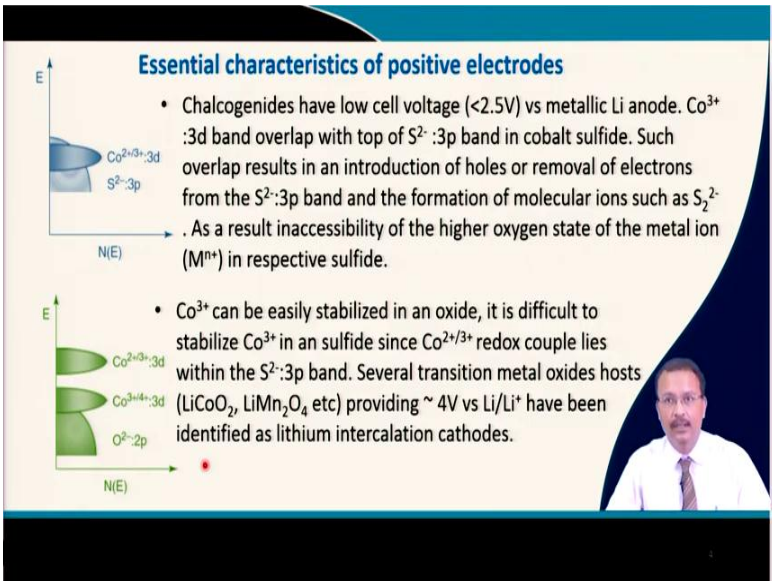

Essential characteristics of positive electrodes

- Chalcogenides have low cell voltage (<2.5V) vs metallic Li anode. Co^{3+} :3d band overlap with top of S^{2-} :3p band in cobalt sulfide. Such overlap results in an introduction of holes or removal of electrons from the S^{2-}:3p band and the formation of molecular ions such as S_2^{2-}. As a result inaccessibility of the higher oxygen state of the metal ion (M^{n+}) in respective sulfide.
- Co^{3+} can be easily stabilized in an oxide, it is difficult to stabilize Co^{3+} in an sulfide since $Co^{2+/3+}$ redox couple lies within the S^{2-}:3p band. Several transition metal oxides hosts ($LiCoO_2$, $LiMn_2O_4$ etc) providing ~ 4V vs Li/Li^+ have been identified as lithium intercalation cathodes.

Now, looking the problem at a slightly different perspective that why exactly we go for the oxide material. We can also try chalcogenides; but you know the chalcogenides, they have really slower voltage versus metallic lithium. So, in half cell configuration less than 2.5 Volt is achieved.

So, they are not comparable with the layered oxide material which yield you 4 Volt. So, if you look at a typical sulfide based chalcogenides, then you can see that this cobalt 3 plus that 3d band that overlap completely with the sulfur 3 p bands in cobalt sulfide if you use it as a suitable positive material.

And what happens? This overlap that results in an introduction of holes or removal of electron from the S 2 that S 2 3p band and also, it forms molecular ions such as S 2 2 minus and due to this, due to this overlap and this happening, there is an inaccessibility of higher oxidation state of the metal ion. So, it cannot go to the higher oxidation state from its virgin state. So, that basically reduce the voltage because you know the voltage from Nernst equation that depends on the redox potential.

Now, in case of the layered oxide; for example, cobalt 3 plus that can easily be stabilized in an oxide and it is difficult to stabilize cobalt 3 plus in a sulfide, since this redox potential cobalt 2 plus and 3 plus that actually lies within the this S 2 3p band that whatever I told. But, several transition metal oxides for example, lithium cobalt oxide, lithium manganese oxide, they provide 4 Volt versus metallic lithium that those kind of oxides in fact, they have been identified as an intercalation material, intercalation cathode for lithium ion batteries.

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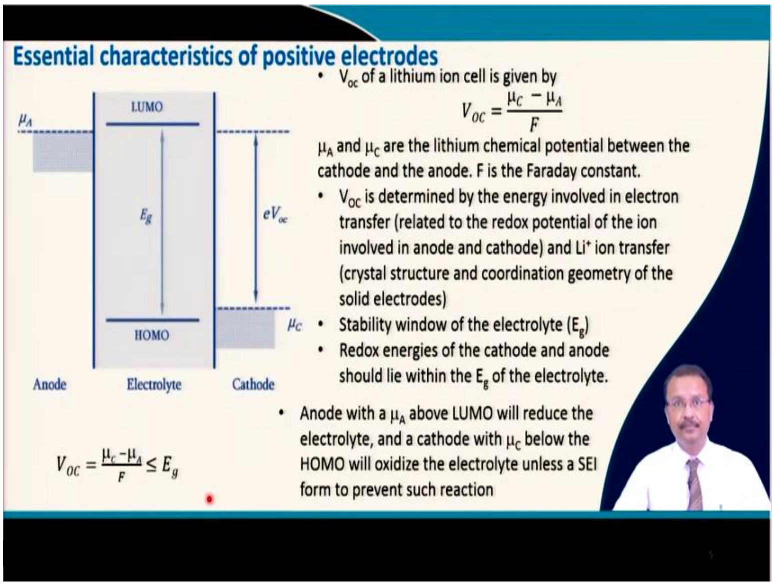

Essential characteristics of positive electrodes

- V_{oc} of a lithium ion cell is given by

$$V_{OC} = \frac{\mu_C - \mu_A}{F}$$

μ_A and μ_C are the lithium chemical potential between the cathode and the anode. F is the Faraday constant.

- V_{OC} is determined by the energy involved in electron transfer (related to the redox potential of the ion involved in anode and cathode) and Li^+ ion transfer (crystal structure and coordination geometry of the solid electrodes)
- Stability window of the electrolyte (E_g)
- Redox energies of the cathode and anode should lie within the E_g of the electrolyte.
- Anode with a μ_A above LUMO will reduce the electrolyte, and a cathode with μ_C below the HOMO will oxidize the electrolyte unless a SEI form to prevent such reaction

$$V_{OC} = \frac{\mu_C - \mu_A}{F} \leq E_g$$

So, again, the essential characteristics as you can now understand that the chemical potential of anode and chemical potential of cathode, they are important the in case of getting a higher open circuit voltage and here F is the Faraday constant. So, this relation between the open circuit potential and the chemical potential of lithium in cathode and anode that has been described earlier as well.

$$V_{OC} = \frac{\mu_C - \mu_A}{F}$$

So, this V oc that is determined basically the energy that is involved in electron transfer. So, that is in fact, related to the redox potential of the ions involved in anode and cathode and also, lithium ion transfer that depends on the crystal structure or the coordination geometry of the solid electrolyte, if you consider instead of liquid electrolyte.

Now, the stability window of the electrolyte which is given by this E g, the gap between the HOMO and LUMO, it also depends on that because your open circuit potential that should lie within this. So, anode with a chemical potential above this LUMO that will eventually reduce the electrolyte, that I have already explained earlier and a cathode which is having a chemical potential which is below the HOMO that will oxidize the electrolyte.

So, usually a stable SEI layer forms and that prevents this kind of reaction. But this relation that this gap E g must be larger than the V oc that is very important in selecting the electrolyte and the anode and cathode for lithium ion batteries.

$$V_{OC} = \frac{\mu_C - \mu_A}{F} \leq Eg$$

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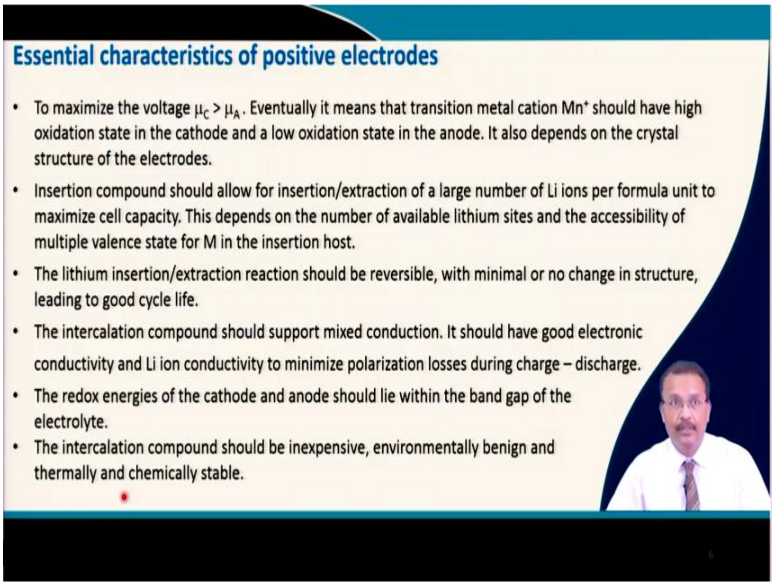

Essential characteristics of positive electrodes

- To maximize the voltage $\mu_C > \mu_A$. Eventually it means that transition metal cation Mn^+ should have high oxidation state in the cathode and a low oxidation state in the anode. It also depends on the crystal structure of the electrodes.
- Insertion compound should allow for insertion/extraction of a large number of Li ions per formula unit to maximize cell capacity. This depends on the number of available lithium sites and the accessibility of multiple valence state for M in the insertion host.
- The lithium insertion/extraction reaction should be reversible, with minimal or no change in structure, leading to good cycle life.
- The intercalation compound should support mixed conduction. It should have good electronic conductivity and Li ion conductivity to minimize polarization losses during charge – discharge.
- The redox energies of the cathode and anode should lie within the band gap of the electrolyte.
- The intercalation compound should be inexpensive, environmentally benign and thermally and chemically stable.

So, as you understand, if you want to maximize the voltage of course, the chemical potential of cathode must be higher than anode. So, that means, the transition metal cation for example, if you take Mn plus, it should have higher oxidation state in the cathode and if it is used in anode, it should have lower oxidation state. It also suddenly depends on the crystal structure.

Second, the insertion compound should allow for insertion or extraction of large number of lithium ions per formula unit that you have seen that in case of this metallic alloy say large number of lithium that is hosted, then you can calculate the theoretical capacity is much larger. So, that will increase the cell capacity.

So, that depends the number of available lithium sites and the accessibility of multiple valence state in the metal cation of the insertion host. Both are important; you should have available lithium site and at the same time, multiple valence state that is preferable if it is from nickel 3 plus to 4 plus and you have a situation, where it goes from say nickel 2 plus to nickel 4 plus.

So, one is 1 electron transfer, another one is 2 electron transfer. So, the capacity will be increased, if I go for 2 electron transfer. So, the transition metal cation should have the capability of doing it. Third is the lithium insertion and extraction reaction that should be reversible and there should not be any change in structure of the electrode material during cycling and that will lead good cycle life.

Fourth, the intercalation compound should support mixed conduction. That also I have illustrated, it should have both ionic conductivity as well as electronic conductivity. Most of this positive electrode material, they do not have sufficient electronic conductivity. Therefore, we need to add external conducting agent in the form of acetylene black or carbon black in order to increase its electronic conductivity and the redox energy of the cathode and anode should lie within the band gap as I have told.

Band gap of the electrode electrolyte and finally, the intercalation compound should be inexpensive. If it is very expensive, then environmentally, it should be benign and thermally and chemically stable. So, for example, if you have a option of lithium cobalt oxide and lithium manganese oxide; of course, cobalt is toxic, it is expensive, then we will go for lithium manganese oxide.

But, as you remember that we will have to take care of the crystal field stabilization energy, manganese has a tendency due to its lower oxidation state stabilization energy. It will migrate from transition metal site to lithium ion site and that will be detrimental for the electrochemical properties of the battery. So, even if they are much cheaper, it is difficult to use. So, lithium cobalt oxide was the first choice to make the commercial batteries.

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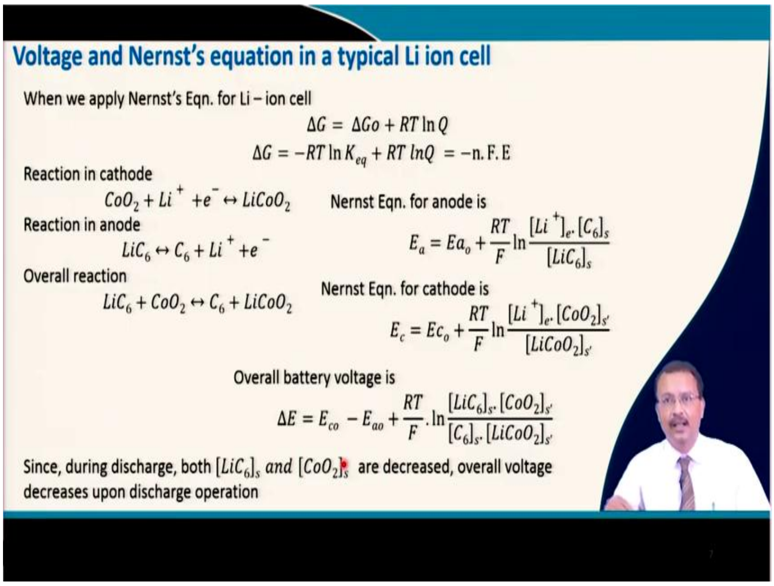

Voltage and Nernst's equation in a typical Li ion cell

When we apply Nernst's Eqn. for Li – ion cell

$$\Delta G = \Delta Go + RT \ln Q$$

$$\Delta G = -RT \ln K_{eq} + RT\, lnQ \ = -\text{n. F. E}$$

Reaction in cathode

$$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$$

Reaction in anode

$$LiC_6 \leftrightarrow C_6 + Li^+ + e^-$$

Overall reaction

$$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$$

Nernst Eqn. for anode is

$$E_a = Ea_o + \frac{RT}{F} \ln \frac{[Li^+]_{e'} [C_6]_s}{[LiC_6]_s}$$

Nernst Eqn. for cathode is

$$E_c = Ec_o + \frac{RT}{F} \ln \frac{[Li^+]_{e'} [CoO_2]_{s'}}{[LiCoO_2]_{s'}}$$

Overall battery voltage is

$$\Delta E = E_{co} - E_{ao} + \frac{RT}{F} . \ln \frac{[LiC_6]_{s'} [CoO_2]_{s'}}{[C_6]_{s'} [LiCoO_2]_{s'}}$$

Since, during discharge, both $[LiC_6]_s$ *and* $[CoO_2]_s$ are decreased, overall voltage decreases upon discharge operation

Now, it is quite straightforward to relate the voltage and Nernst equation in a typical lithium ion cell. So, when for example, we apply the Nernst equation in lithium ion cell, again we can write the free energy change that is equal to free energy change or standard condition and this term RT ln Q.

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G = -RT \ln K_{eq} + RT\, lnQ \ = -\text{n. F. E}$$

So, in equilibrium state, this is minus RT ln Q plus RT ln Q and this is actually number of electron that is being transferred faraday constant and the electric potential. So, this also, I have talked about as a part of my earlier lecture that you can replace this del G 0 term with minus RT ln Q because in the equilibrium state that free energy change is 0. So, this relation has been talked about.

Now, let us look at the reaction in the cathode. So, if it would have been possible to completely extract the lithium from lithium cobalt oxide, then during your discharge, this lithium will come back in the lithium cobalt oxide the host material and in the anode this is LiC 6 which forms after charging, it will again extract lithium.

So, during discharge, this lithium will come out and this eventually, will go and insert into the positive electrode material. So, the overall reaction is this one which I think you will be able to understand this relations.

Reaction in cathode

$$CoO_2 + Li^+ \ + e^- \ \leftrightarrow LiCoO_2$$

Reaction in anode

$$LiC_6 \leftrightarrow C_6 + Li^+ + e^-$$

Overall reaction

$$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$$

So, now, if you apply the Nernst equation; in case of anode, you have the potential in the standard state then RT by F will be there and this Q value will be the product whatever is there lithium ion and C 6 and the total concentration of this one. If you write the Nernst equation for the cathode, then this voltage will be the standard voltage again and RT F will be there.

Nernst Eqn. for anode is

$$E_a = E_a^0 + \frac{RT}{F} \ln \frac{[Li^+]e.\ [C_6]s}{[LiC_6]s}$$

Nernst Eqn. for cathode is

$$E_c = E_c^0 + \frac{RT}{F} \ln \frac{[Li^+]e.\ [CoO_2]s}{[LiCoO_2]s}$$

$$\Delta E = E_c^0 \ - E_a^0 + \frac{RT}{F} . \ln \frac{[LiC_6]s.[CoO_2]s'}{[C_6]s.[LiCoO_2]s'}$$

So, then, you will have to consider this relation. So, this product is lithium and sorry, lithium cobalt oxide and lithium ion with respect to lithium ion and cobalt oxide with respect to this one. So, we are considering the reverse reaction. So, this is the product and this is the reactant.

So, overall battery voltage that you can subtract between this and this and this will be RT by F ln of the concentration of this, concentration of this divided by concentration of carbon and concentration of lithium cobalt oxide. So, during discharge, in fact, this one and this one both are decreased right; these two concentration decreased.

So, overall, voltage will decrease upon discharge operation. So, if you actually know the concentration, then at each lithium ion insertion, you can estimate the voltage from this relation and you will see that once lithium is inserted during discharge in the positive material, indeed the voltage will drop down.

Now, the shape; if you want to understand the shape, then of course, you will have to know the composition del G mix versus composition that diagram and there the actual sigmoidal shape, which I earlier described that can be derived.

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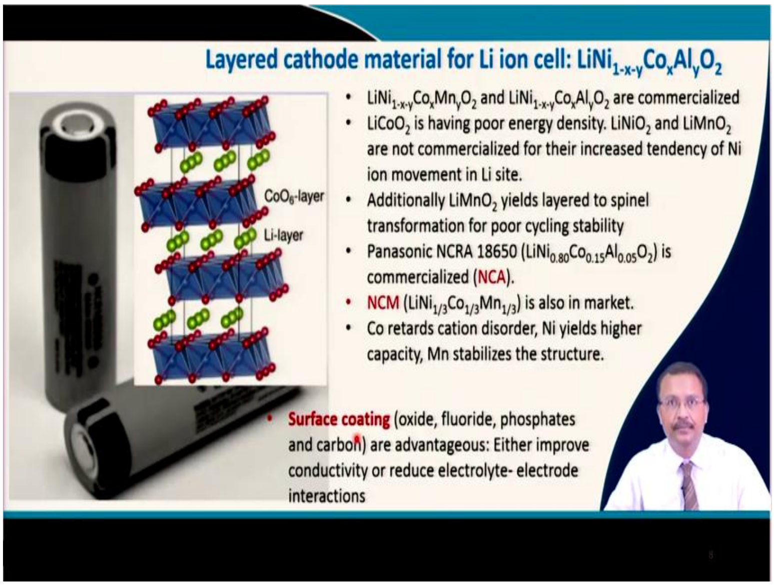

Layered cathode material for Li ion cell: $LiNi_{1-x-y}Co_xAl_yO_2$

- $LiNi_{1-x-y}Co_xMn_yO_2$ and $LiNi_{1-x-y}Co_xAl_yO_2$ are commercialized
- $LiCoO_2$ is having poor energy density. $LiNiO_2$ and $LiMnO_2$ are not commercialized for their increased tendency of Ni ion movement in Li site.
- Additionally $LiMnO_2$ yields layered to spinel transformation for poor cycling stability
- Panasonic NCRA 18650 ($LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$) is commercialized (NCA).
- NCM ($LiNi_{1/3}Co_{1/3}Mn_{1/3}$) is also in market.
- Co retards cation disorder, Ni yields higher capacity, Mn stabilizes the structure.
- **Surface coating** (oxide, fluoride, phosphates and carbon) are advantageous: Either improve conductivity or reduce electrolyte- electrode interactions

So, layered cathode material for lithium ion cell the which has been commercialized is part of cobalt has been replaced with nickel and not only that, little bit of aluminum is also introduced in the structure to form this composition. So, this particular composition, where both nickel, cobalt and manganese and also, the sighted composition that lithium, nickel, cobalt that is doped with aluminum, they are commercialized and why we have selected this particular composition that also I have illustrated earlier.

That it is good to have lithium cobalt oxide, but due to the cation mixing, nickel is coming, due to its relatively lower octahedral state stabilization energy, it comes into the path of lithium, where lithium stays in the layer structure.

But if you have the three component introduced, then you get certain advantage and from the tri-axial phase diagram, we have earlier understood that indeed this kind of composition is beneficial. So, lithium cobalt oxide is having poor energy density because you cannot take all the lithium out from lithium cobalt oxide. So, the voltage is not, its capacity is not that high.

So, your energy density will suffer and lithium nickel oxide and lithium manganese oxide, they are not commercialized for their increased tendency of nickel or magnesium movement in the lithium site and that we now understand, why it is so. Additionally, this lithium manganese oxide that yields layered to spinel transformation.

So, during cycling, there is a phase transformation that also you know that when we talked about lithium cobalt oxide, there are various phase transformation takes place O 3 to P 3, then O 1 because of the extraction of the lithium and that leads to the phase transformation.

So, this lithium manganese oxide, it undergoes a layer to spinel transformation and that actually yields poor cycling stability. Now, Panasonic is the company, who first commercialized this trade name is NCRA 18650 cell, we will talk about how the construction is done for 18650 cell.

So, it looks like this. It is a cylindrical cell. So, this composition they have commercialized nickel 0.8, cobalt 0.15. So, they have reduced the cobalt content and aluminum gives the stability of the structure and NCM which is abbreviated when nickel, cobalt, manganese all are there in one-third, one-third, one-third. So, that is also in the market and cobalt retards the cation disorder because it reverse travel to the lithium site.

Nickel actually yields higher capacity and manganese stabilizes this structure. So, NCM is a good alternative. So, this is the actual structure of this kind of layered cathode material. Sometimes, the cathode surface is coated with various oxides or fluoride or phosphate or carbon which are not electrochemically active.

So, this is the advantageous for you to coat it and that is done either to improve the conductivity because as I know the electronic conductivity is not that great or this kind of coating that reduce the electrode and electrolyte interaction. So, the ACI layer formation in positive electrode, as I have mentioned earlier that the ACI whatever ACI form unlike the anode material, they are not exactly deposited on the positive negative electrode substrate.

So, in positive electrode, they are most in most cases they are soluble. So, fresh surface is exposed again ACI layer forms. So, that is not that much good for the performance of the battery.

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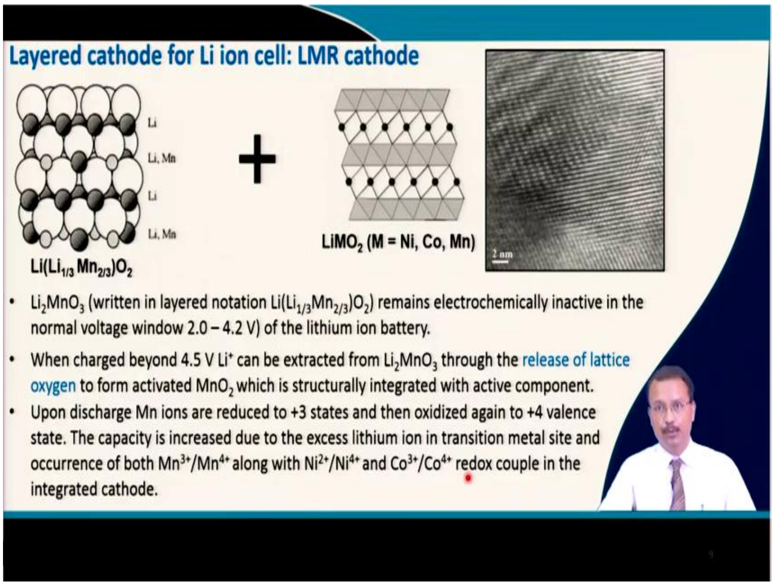

Layered cathode for Li ion cell: LMR cathode

$Li(Li_{1/3}Mn_{2/3})O_2$

$LiMO_2$ (M = Ni, Co, Mn)

- Li_2MnO_3 (written in layered notation $Li(Li_{1/3}Mn_{2/3})O_2$) remains electrochemically inactive in the normal voltage window 2.0 – 4.2 V) of the lithium ion battery.
- When charged beyond 4.5 V Li^+ can be extracted from Li_2MnO_3 through the release of lattice oxygen to form activated MnO_2 which is structurally integrated with active component.
- Upon discharge Mn ions are reduced to +3 states and then oxidized again to +4 valence state. The capacity is increased due to the excess lithium ion in transition metal site and occurrence of both Mn^{3+}/Mn^{4+} along with Ni^{2+}/Ni^{4+} and Co^{3+}/Co^{4+} redox couple in the integrated cathode.

So, this kind of surface coating, it has been proved quite good. Now, it was really a problem to get high voltage as well as high capacity to match the capacity of the positive negative electrode material. So, as you know if you take the example of graphite, it gives the capacity about 372 to 375 milli ampere hour per gram.

So, far there is no positive electrode material which can match this capacity. So, if you cannot match this capacity, then the total cell capacity that will be much lower; you cannot improve it. So, if you improve the voltage and if you improve the capacity simultaneously, then only the energy density of the battery will be high.

So, one intelligent aspect the procedure, they it was developed in Argonne National Laboratory and what they did? They took this compound Li 2 Mn O 3 and in layered location, it is having a monoclinic structure and in layered the notation, you can write it lithium in its lithium site and one-third of it, it goes to the manganese site, transition metal cation sites.

So, there is a ordering 1 is to 2 ordering of lithium and manganese and this kind of ordering, you can see in the transmission electron micrograph and this kind of domain, it forms it is a ordered structure inside the layered material. So, I will just explain it.

So, eventually, that is electrochemically inactive in the normal voltage window. So, that means, we operate the battery 2 to 4.2 Volt range. So, this lithium Li 2 Mn O3, they are electrochemically inactive. So, you cannot extract that easily lithium from it and manganese as you can see here, manganese is in plus 4 valence state, lithium is plus 2; so, that is getting balanced.

So, it is difficult to remove this. But, interestingly, when you charge it beyond 4.5 Volt, lithium can be extracted from Li 2 Mn O3 through the release of lattice oxygen. So, this lattice oxygen will be removed and then, you can extract the lithium and eventually, you will form a activated manganese dioxide.

So, activated manganese dioxide will substance is basically integrated with the active component. So, you use this material and you form a composite of the traditional layered oxide material and if you charge it up to 4.2 Volt, then the lithium from this cannot be extracted. But, if you increase the charge voltage beyond 4.5 Volt, then release of oxygen occurs from this part, from this part to form manganese dioxide which is structurally integrate with the layered component.

So, now when you discharge it, then this manganese which is in plus 4 valence state because Mn O 2, you can understand that oxidation state of manganese is plus 4. So, they are reduced in plus 3 valence state and then, again oxidize to plus 4 valence state.

So, the capacity is increased because in order to do that this manganese 4 to manganese 3 and this redox to take part in; you are introducing additional lithium. So, additional lithium in transition metal site that you are introducing.

So, eventually that will increase the capacity and this redox along with the traditional redox of nickel 2 plus to nickel 4 plus and cobalt 3 plus to cobalt 4 plus, which was already there plus the manganese here and if the manganese in plus 3 state is there in NMC kind of component, additionally you have this manganese and excess lithium. So, therefore, this type of composite cathode which is prepared quite intelligently. So, that increases the capacity and therefore, it is termed as lithium manganese rich cathode material.

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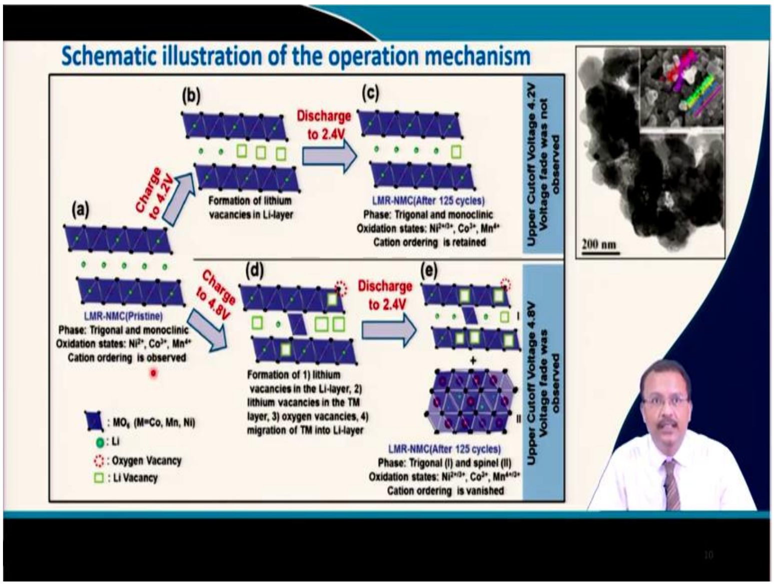

Schematic illustration of the operation mechanism

LMR-NMC(Pristine)
Phase: Trigonal and monoclinic
Oxidation states: Ni^{2+}, Co^{3+}, Mn^{4+}
Cation ordering is observed

Formation of lithium vacancies in Li-layer

LMR-NMC(After 125 cycles)
Phase: Trigonal and monoclinic
Oxidation states: $Ni^{2+/3+}$, Co^{3+}, Mn^{4+}
Cation ordering is retained

Formation of 1) lithium vacancies in the Li-layer, 2) lithium vacancies in the TM layer, 3) oxygen vacancies, 4) migration of TM into Li-layer

LMR-NMC(After 125 cycles)
Phase: Trigonal (I) and spinel (II)
Oxidation states: $Ni^{2+/3+}$, Co^{3+}, $Mn^{4+/3+}$
Cation ordering is vanished

Upper Cutoff Voltage 4.2V Voltage fade was not observed

Upper Cutoff Voltage 4.8V Voltage fade was observed

So, pictographically, if you see it that in this kind of layered material, if you charge to 4.2 Volt, then lithium will be extracted from these sites. So, the lithium vacancy will be there here. Then, you discharge it, then again lithium will come back and fill up these vacancies. So, after a number of charge discharge cycle, most of the lithium is coming back.

There is slight phase transition and oxidation state of course, the redox oxidation state will change; but this is the normal procedure which so far we have described. In this case, when you make a composite of this layer with your Li 2 Mn O3 type of otherwise inactive material and charged to for example, 4.8 Volt, then several other things happen here.

So, as you can see here it can form the lithium vacancy in the lithium layer, then number 2 is lithium vacancy is also formed in this layer because you can understand lithium is not only in the layered site; but it is also there in the transition metal site and oxygen vacancy that will form because oxygen will get released. So, several different phenomena is taking place and not only that this transition metal cation, they also migrate here.

So, during the charge several things happens which are very unlike than the traditional layered cathode materials. While you discharge it, then again the phase transition you cannot avoid; but this and this, these together, it gives you very large kind of capacity because of the inclusion of more lithium into the transition metal site and integration due to the integration of manganese oxide. So, the capacity is grossly increased.

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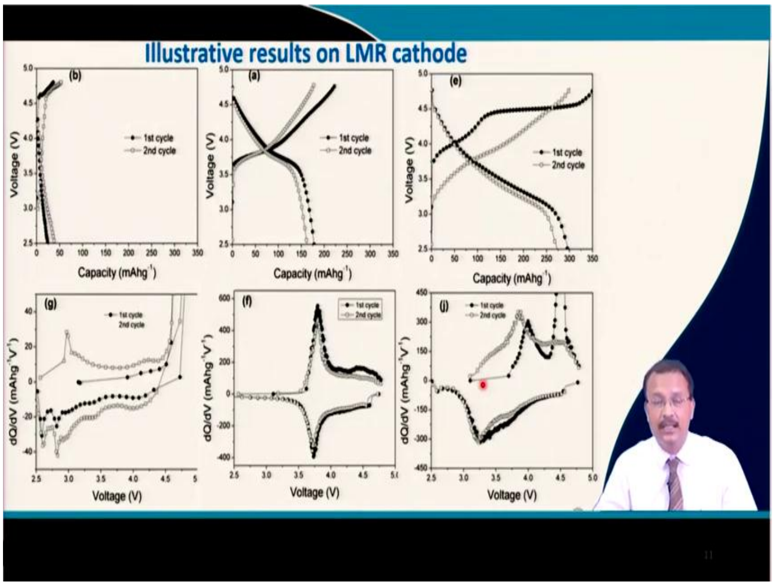

Illustrative results on LMR cathode

So, I am citing one example from our own work that as such your Li 2 Mn O3, they are having very low capacity. We did the differential capacity plot here. So, here as you can see that very very small capacity is achieved. Now, you have a layered material like lithium, nickel cobalt oxide, you get at the most of 180 milli ampere hour per gram. If I tell you the composition, it is point nickel is 0.8 and cobalt is 0.2. So, the capacity is in this range.

Now, you make a composite. You can see that this capacity has increased as high as; as high as 300 because of this integration and the oxygen, when it is coming out from the structure as you can see in the first cycle that if you do a differential capacity, you will see that is indicated by a very large positive anodic peak and which is otherwise absent in the second cycle. So, that means, in first cycle indeed there is some kind of structural change takes place, oxygen comes out from the lattice and the integration takes place and that increases the capacity.

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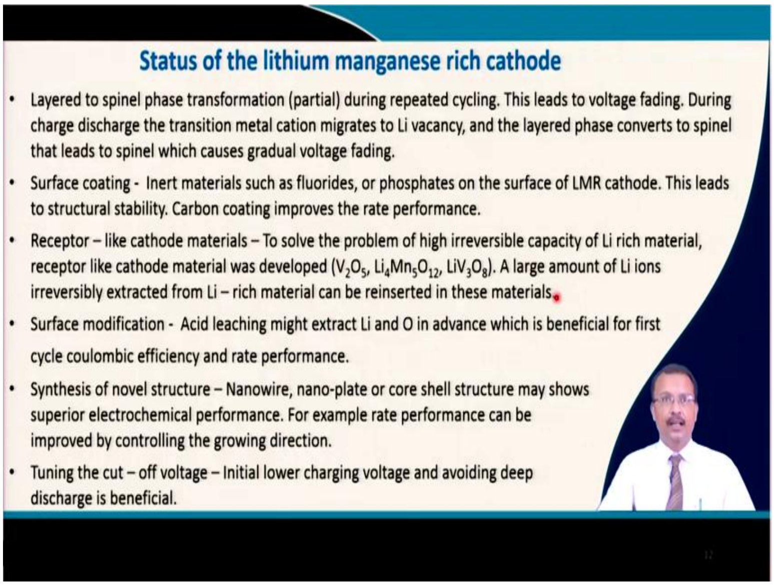

Status of the lithium manganese rich cathode

- Layered to spinel phase transformation (partial) during repeated cycling. This leads to voltage fading. During charge discharge the transition metal cation migrates to Li vacancy, and the layered phase converts to spinel that leads to spinel which causes gradual voltage fading.
- Surface coating - Inert materials such as fluorides, or phosphates on the surface of LMR cathode. This leads to structural stability. Carbon coating improves the rate performance.
- Receptor – like cathode materials – To solve the problem of high irreversible capacity of Li rich material, receptor like cathode material was developed (V_2O_5, $Li_4Mn_5O_{12}$, LiV_3O_8). A large amount of Li ions irreversibly extracted from Li – rich material can be reinserted in these materials.
- Surface modification - Acid leaching might extract Li and O in advance which is beneficial for first cycle coulombic efficiency and rate performance.
- Synthesis of novel structure – Nanowire, nano-plate or core shell structure may shows superior electrochemical performance. For example rate performance can be improved by controlling the growing direction.
- Tuning the cut – off voltage – Initial lower charging voltage and avoiding deep discharge is beneficial.

So, if you want to know about the status of this lithium manganese rich cathode, the first one is layered to spinel type of phase transformation. Although, it is a partial that with repeated cycling that leads the voltage fading.

So, completely, the fading characteristics cannot be avoided and during charge discharge, the transition metal cation migrates to lithium vacancy that already we have shown and the layered phase that converts into the spinel structure and this layered to spinel a structural change that basically causes a gradual voltage fading, not the capacity fading, but the voltage if the voltage itself that goes down.

So, it is not very apparent in second cycle, but if you keep on doing it, you will see that at this particular capacity which is given by the lithium ion concentration, a gradual fading of the voltage cannot be avoided. So, surface coating with the inert material like fluoride or phosphates on the surface of LMR that has been given that gives to structural stability.

Carbon coating they improve the electronic conductivity. So, eventually, enhance the rate performance. Now, one can use receptor like cathode material to the solve the problem of high irreversible capacity loss because this is also another problem that if you go for this type of first cycle and second cycle, if you see that there is a huge loss. So, the coulombic efficiency is not that great.

So, to solve that high reversible capacity of this LMR some cathode material was developed like V 2 O 5, this compound, this compound, this was developed. So, large amount of lithium ion that is irreversibly extracted from this lithium rich material can be reinserted into this material.

So, this material will become active and that will lead to the capacity. So, that is another improvement, some work is going on. Surface modification includes the acid leaching that might extract the lithium and oxygen in advance. Without electrochemical charging, you can do the acid leaching and that is beneficial for the first cycle coulombic efficiency to drop down significantly.

Novel structure you can make like nanowire or nano-plate or core shell type of structure that usually shows superior electrochemical performance. For example, the rate performance can be improved by controlling the growth direction, where the lithium ion transport is expedite. Cut off voltage is important. So, initially, lower charging voltage can and avoiding the deep discharge. So, if instead of going to 4.8 Volt, if you limit it to 4.7 Volt and do not deep discharge your battery that is also sometimes beneficial.

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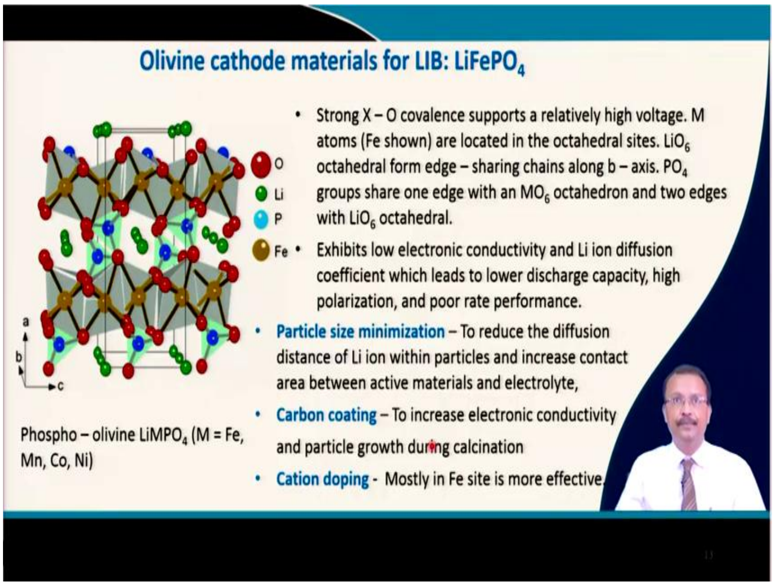

Olivine cathode materials for LIB: $LiFePO_4$

- Strong X – O covalence supports a relatively high voltage. M atoms (Fe shown) are located in the octahedral sites. LiO_6 octahedral form edge – sharing chains along b – axis. PO_4 groups share one edge with an MO_6 octahedron and two edges with LiO_6 octahedral.
- Exhibits low electronic conductivity and Li ion diffusion coefficient which leads to lower discharge capacity, high polarization, and poor rate performance.
- **Particle size minimization** – To reduce the diffusion distance of Li ion within particles and increase contact area between active materials and electrolyte,
- **Carbon coating** – To increase electronic conductivity and particle growth during calcination
- **Cation doping** - Mostly in Fe site is more effective.

Phospho – olivine $LiMPO_4$ (M = Fe, Mn, Co, Ni)

Olivine cathode material that is another category, this also I have explained. So, you can understand that there is a strong bond between this phosphate and phosphorus and oxygen, the covalence that supports a relatively high voltage. The M atom that is iron are located in the octahedral site as you can see here and LI O6 octahedral that form a edge sharing chains along the b axis. So, PO 4 group share one edge with a MO 6 that can clearly be shown here and two edges with Li O 6 kind of octahedral. So, this is a very stable structure.

But unfortunately, it exhibit very low electronic conductivity for lithium ion diffusion that basically leads to lower discharge capacity and higher polarization value and also, the rate performance is not that great. In order to overcome that, one can reduce the particle size.

So, if you reduce the particle size that reduce the diffusion distance and increase the contact area between the active material and electrolyte which sometimes is good; but sometimes, it creates problem because if ACI is formed and if it is dissolved, then that is not good for the cathode.

So, carbon coating is usually also done to increase the electronic conductivity almost all the commercial olivine based cathode material, they are coated with carbon. Sometimes this F e site, you can dope it with other element and that also. So, that is the bulk modification that also you can do to increase the electronic conductivity because of the

Li olivine dopant effect, it creates vacancy and eventually, it increases the electronic conductivity.

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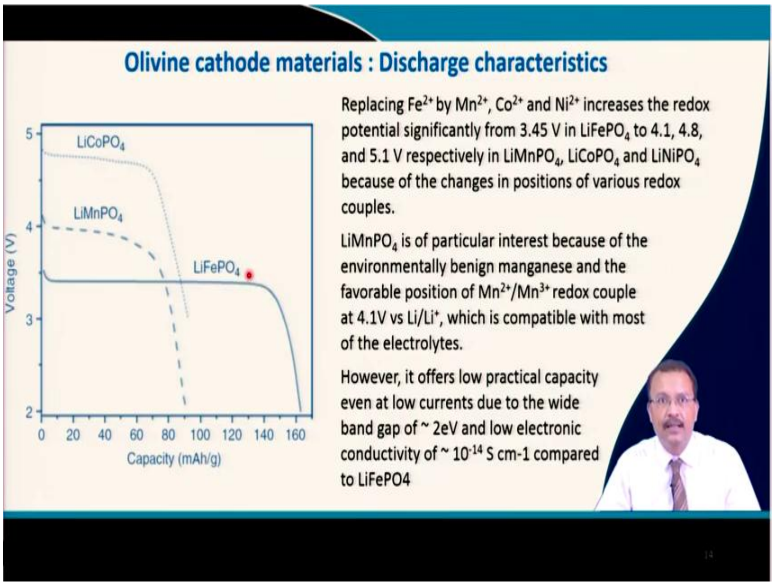

Olivine cathode materials : Discharge characteristics

Replacing Fe^{2+} by Mn^{2+}, Co^{2+} and Ni^{2+} increases the redox potential significantly from 3.45 V in $LiFePO_4$ to 4.1, 4.8, and 5.1 V respectively in $LiMnPO_4$, $LiCoPO_4$ and $LiNiPO_4$ because of the changes in positions of various redox couples.

$LiMnPO_4$ is of particular interest because of the environmentally benign manganese and the favorable position of Mn^{2+}/Mn^{3+} redox couple at 4.1V vs Li/Li^+, which is compatible with most of the electrolytes.

However, it offers low practical capacity even at low currents due to the wide band gap of ~ 2eV and low electronic conductivity of ~ 10^{-14} S cm-1 compared to LiFePO4

So, there are various types of olivine material. So, if you replace iron 2 plus by manganese 2 plus, cobalt 2 plus also can be replaced or nickel 2 plus that basically increases the redox potential. So, iron is somewhere here around 3.5. If it is here, then it is increased, it is increased further here, but the capacity also falls down. So, the energy density that is to be seen that how much energy density which is a product of the voltage and capacity that exactly you gain.

So, lithium manganese phosphate is of particular interest because this is environmentally benign; manganese is abundantly available particularly in India and the redox couple is around 4 Volt. So, which is higher than this. So, this material is of interest; but to my knowledge, this has not yet been commercialized.

But, low capacity of this practical capacity even at low current, this is not very good for the commercial adaptability and this is due to the wide band gap about 2 electron Volt and lower electronic conductivity which is about 10 to the power minus 14 Siemens per centimeter, this is much lower as compared to lithium iron phosphate.

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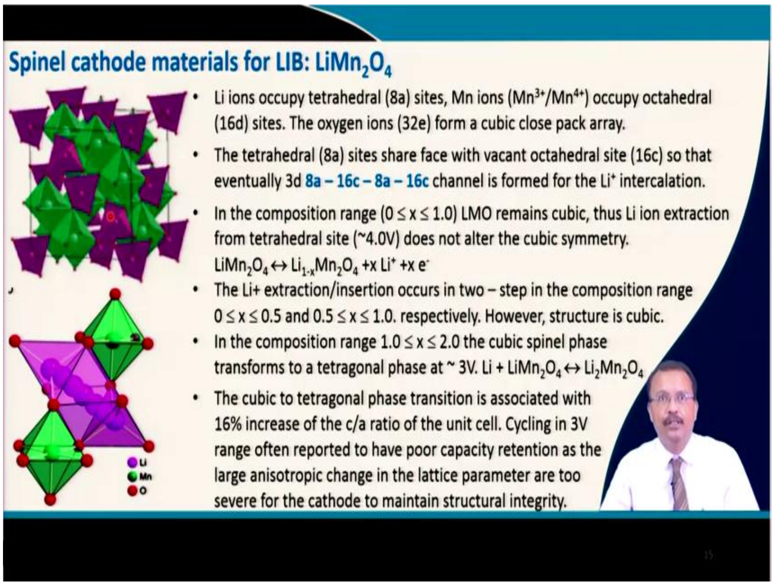

Spinel cathode materials for LIB: $LiMn_2O_4$

- Li ions occupy tetrahedral (8a) sites, Mn ions (Mn^{3+}/Mn^{4+}) occupy octahedral (16d) sites. The oxygen ions (32e) form a cubic close pack array.
- The tetrahedral (8a) sites share face with vacant octahedral site (16c) so that eventually 3d 8a – 16c – 8a – 16c channel is formed for the Li^+ intercalation.
- In the composition range ($0 \le x \le 1.0$) LMO remains cubic, thus Li ion extraction from tetrahedral site (~4.0V) does not alter the cubic symmetry.
  $LiMn_2O_4 \leftrightarrow Li_{1-x}Mn_2O_4 + x\,Li^+ + x\,e^-$
- The Li+ extraction/insertion occurs in two – step in the composition range $0 \le x \le 0.5$ and $0.5 \le x \le 1.0$. respectively. However, structure is cubic.
- In the composition range $1.0 \le x \le 2.0$ the cubic spinel phase transforms to a tetragonal phase at ~ 3V. $Li + LiMn_2O_4 \leftrightarrow Li_2Mn_2O_4$
- The cubic to tetragonal phase transition is associated with 16% increase of the c/a ratio of the unit cell. Cycling in 3V range often reported to have poor capacity retention as the large anisotropic change in the lattice parameter are too severe for the cathode to maintain structural integrity.

Spinel based cathode material. So, I have already explained it earlier. So, lithium ion they occupies 8a sites and manganese occupy the octahedral site and oxygen is 32e (Refer Time: 37:19) of notations that site and oxygen forms a close pack array. Tetrahedral sites are face shared with vacant octahedral site which I have denoted with 16c.

So, eventually this 8a, 16c, 8a, 16c that channel is available for lithium ion intercalation. So, in the composition range, where x is between 0 to 1, this lithium manganese oxide that remains cubic. So, lithium extraction from tetrahedral site does not alter the cubic symmetry; but the lithium extraction occurs in two step.

You remember when we talked about the charge profile, it has two plateau. So, one is in this composition range and other is in this composition range. So, it occurs in two step. Structure remains cubic, but in the composition range between 2 to 1, cubic spinel phase transformation takes place.

So, if you additionally put want to put lithium in this site to form Li 2 Mn 2 O4 which occurs typically at 3 Volt, then a cubic to tetragonal phase transition takes place and this is associated with 16 percent increase of c by a ratio of the unit cell. So, you can calculate the volume expansion, if you know the volume of the cubic cell and know the volume of the tetragonal cell by knowing the c by a ratio, then you can estimate that there will be substantial increase of the volume.

So, 3 Volt range if you do, the charge discharge, they will have a poor capacity retention because a continuous change of this lattice structure from cubic to tetragonal and back to cubic and structural integrity will not be maintained. So, you will have to restrict the deep discharge you cannot do, so you will have to restrict above 3 Volt region.

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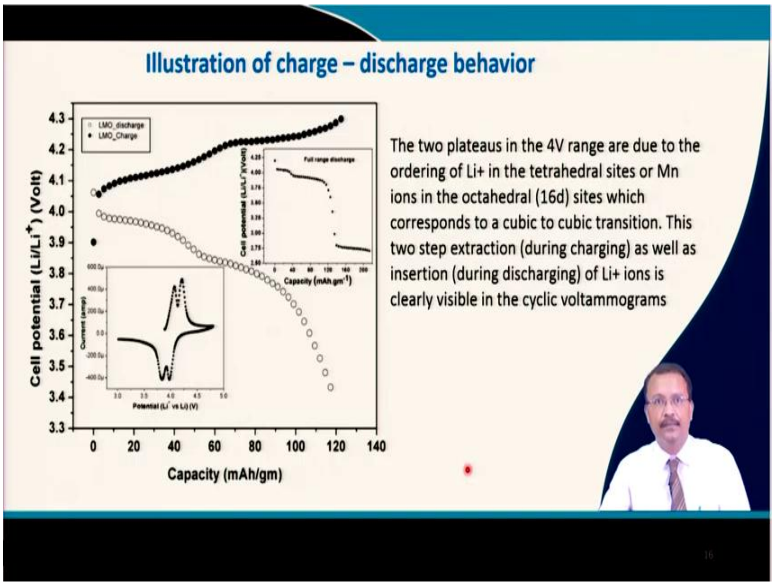

Illustration of charge – discharge behavior

The two plateaus in the 4V range are due to the ordering of Li+ in the tetrahedral sites or Mn ions in the octahedral (16d) sites which corresponds to a cubic to cubic transition. This two step extraction (during charging) as well as insertion (during discharging) of Li+ ions is clearly visible in the cyclic voltammograms

So, this is one of the examples. Again, from our own work that how it occurs. So, two plateau you can see at 4 Volt range that is due to the ordering of lithium and this is quite well-described in this cyclic volta voltammogram and then finally, there is a insertion around 3 Volt, around 3 Volt region, slightly lower than that. So, this increases the capacity because lot of lithium intake is there; but as I said that simultaneously, it will lead to the tetragonal phase transformation which is not good for the battery.

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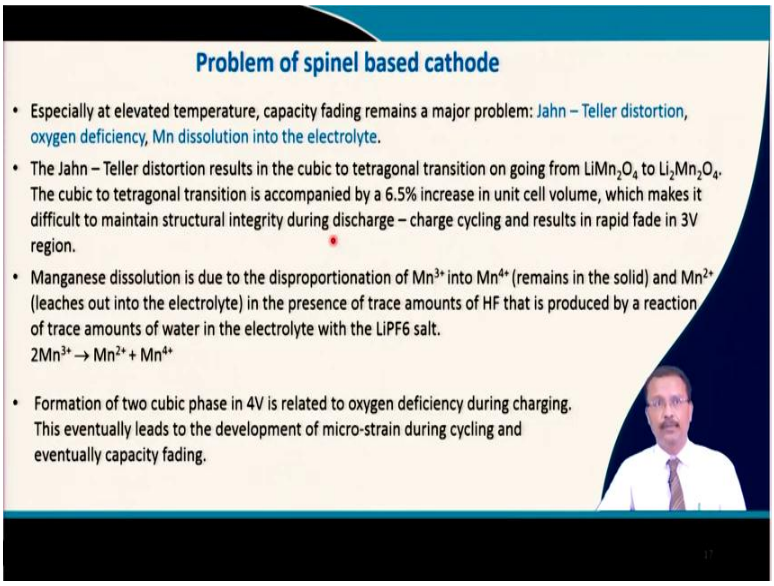

Problem of spinel based cathode

- Especially at elevated temperature, capacity fading remains a major problem: Jahn – Teller distortion, oxygen deficiency, Mn dissolution into the electrolyte.
- The Jahn – Teller distortion results in the cubic to tetragonal transition on going from $LiMn_2O_4$ to $Li_2Mn_2O_4$. The cubic to tetragonal transition is accompanied by a 6.5% increase in unit cell volume, which makes it difficult to maintain structural integrity during discharge – charge cycling and results in rapid fade in 3V region.
- Manganese dissolution is due to the disproportionation of Mn^{3+} into Mn^{4+} (remains in the solid) and Mn^{2+} (leaches out into the electrolyte) in the presence of trace amounts of HF that is produced by a reaction of trace amounts of water in the electrolyte with the LiPF6 salt.
  $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$
- Formation of two cubic phase in 4V is related to oxygen deficiency during charging. This eventually leads to the development of micro-strain during cycling and eventually capacity fading.

So, this is already explained earlier that what is the spinel based cathodes problem. So, at elevated temperature capacity fading that remains a major problem. Jahn-Teller distortion is also another, oxygen deficiency, manganese dissolution into the electrolyte.

So, these are the common problem and already I have explained the Jahn-Teller distortion results in the cubic to tetragonal transition from going to this to this phase and the cubic to tetragonal transition is accompanied by about 6.5 percent increase in unit cell volume which makes it difficult to maintain the structural integrity, during the charge discharge cycle and that results a rapid fade in 3 Volt region.

Manganese dissolution is due to a disproportionate reaction of manganese 3 plus to manganese 4 plus. So, this manganese 4 plus remains in the solid. But, once this actually transformed to manganese 2 plus, it leaches out to the electrolyte. So, in presence of the trace amount of water that is produced HF hydrofluoric acid because your salt is lithium fluoride based salt. So, trace amount of water that produces hydrofluoric acid, actually this disproportionate reaction takes place.

So, if you have affluent in manganese 3 plus cation. So, it will transform to manganese 2 plus and manganese 4 plus and as I said, manganese 4 plus will be there in the solid; that means, in the electrode itself. But, manganese 2 plus will get leached out from the electrode and it will go to the solutions, while losing your redox material and that will basically reduce the capacity.

Formation of the two cubic phases in 4 Volt range that gives these two plateau that is related to oxygen deficiency during charging. So, oxygen leaves from the structure. So, that is also another problem and that eventually, leads to the development of some kind of micro strain during the cycling and that also, leads to the capacity fading.

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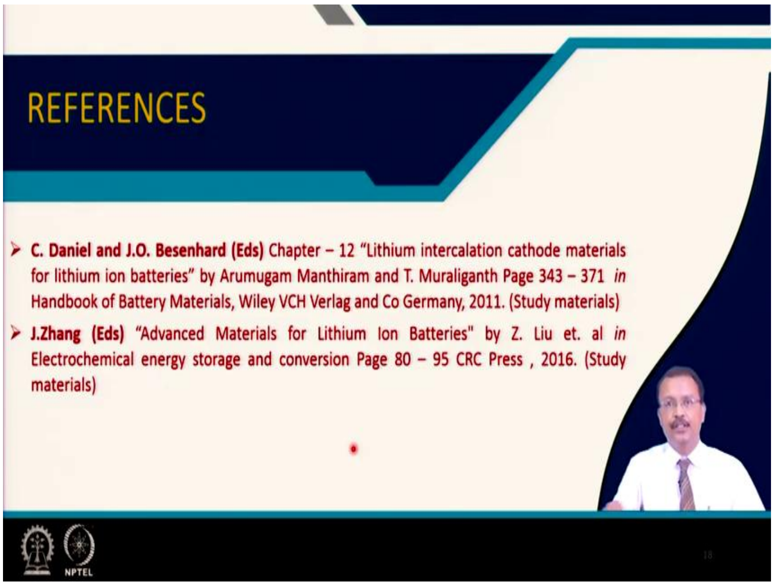

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- **J.Zhang (Eds)** "Advanced Materials for Lithium Ion Batteries" by Z. Liu et. al *in* Electrochemical energy storage and conversion Page 80 – 95 CRC Press , 2016. (Study materials)

So, the topic of this lecture that you can find in this book, particularly chapter 12 which is written by the student of good enough, who got the Nobel Prize, Professor Arumugam Manthiram. So, I had the opportunity to work with him, when I was in US for some time. So, that is a nice introduction of the positive electrode material and also, you can consult this book; particularly, page number 80 to 95 to study it more whatever I have covered in this lecture.

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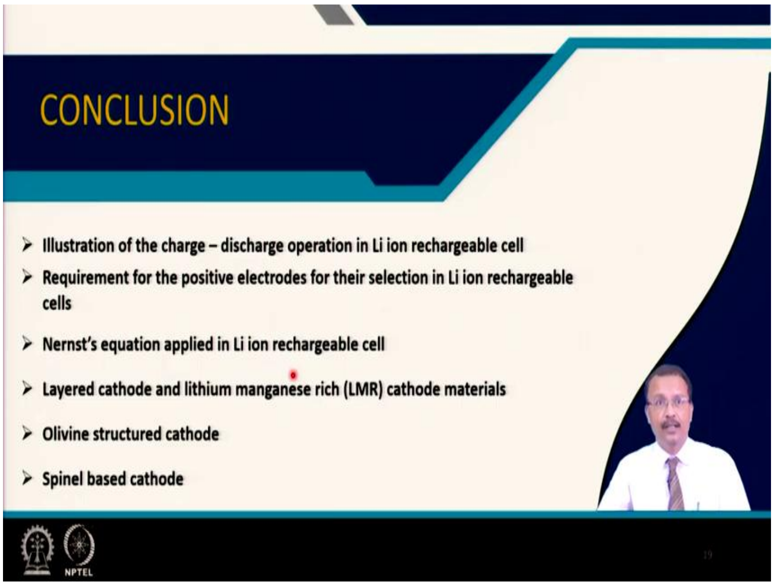

CONCLUSION

- Illustration of the charge – discharge operation in Li ion rechargeable cell
- Requirement for the positive electrodes for their selection in Li ion rechargeable cells
- Nernst's equation applied in Li ion rechargeable cell
- Layered cathode and lithium manganese rich (LMR) cathode materials
- Olivine structured cathode
- Spinel based cathode

So, I have illustrated the charge discharge operation in lithium ion rechargeable cell. Then, requirement of the positive electrodes for their selection in lithium ion rechargeable cells. Then, tried to show you that how Nernst equation is applied in lithium ion rechargeable cell to predict its voltage profile and layered cathode and particularly, in lithium manganese rich cathode material that is introduced.

So, this part is quite novel. So, lot of research is going on LMR based cathode material and olivine structured cathode that has been commercialized and spinel based cathode that also has been commercialized.

Thank you for your attention.