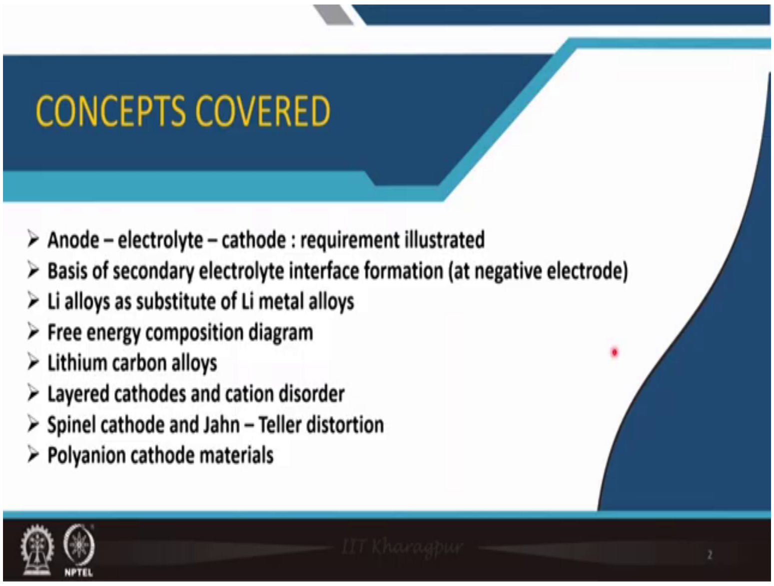
Electrochemical Energy Storage
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 03
Lithium batteries
Lecture - 12
Operational Mechanisms for Lithium Batteries: Intercalation Materials, Alloys, Direct Conversion Materials, Electrolyte

Welcome to my course Electrochemical Energy Storage. And, this is module number 3 where, we are talking about lithium batteries this is lecture number 12, where I will introduce certain Operational Mechanism for Lithium ion Batteries, including the Intercalation Materials, Alloys, Direct Conversion Material and also Electrolyte.

(Refer Slide Time: 00:53)



CONCEPTS COVERED

- Anode – electrolyte – cathode : requirement illustrated
- Basis of secondary electrolyte interface formation (at negative electrode)
- Li alloys as substitute of Li metal alloys
- Free energy composition diagram
- Lithium carbon alloys
- Layered cathodes and cation disorder
- Spinel cathode and Jahn – Teller distortion
- Polyanion cathode materials

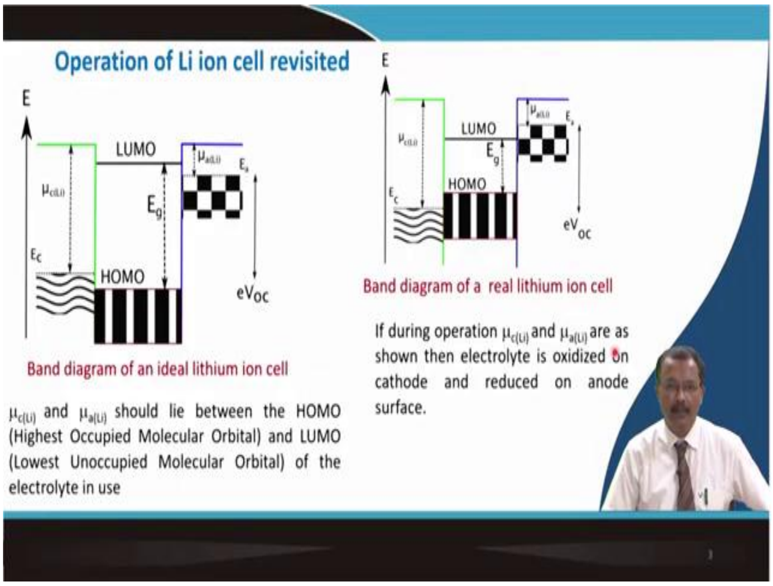
So, we will concept first the anode electrolyte cathode; the requirement this is a recap already we have described it so, just to remind you once again. And, then there are certain phenomena, which I am talking about. I was talking about the SEI layer formation particularly at the negative electrode material.

So, what is the genesis of this kind of secondary electrolyte interface layer? So, that I will explain, lithium alloys as substitute of lithium metal alloys, that we have talked about, then we also talked about the free energy composition diagram, and from free energy composition diagram, we extracted the voltage profile.

Lithium carbon alloys we will talk about, then we will also talk about the intercalation material, and why certain intercalation material is easy to make, and certain intercalation material is very difficult to make, in case of lithium manganese oxide for example.

So, we will introduce the crystal field theory. The basic component which is which will help you to understand this phenomena better. Then, we will talk about in Spinel cathode material the Jahn Teller distortion, which is detrimental for the Cyclability of this material. And, finally, Polyanion type of cathode material will be described.

(Refer Slide Time: 02:41)



Operation of Li ion cell revisited

Band diagram of an ideal lithium ion cell

$\mu_{c(Li)}$ and $\mu_{a(Li)}$ should lie between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of the electrolyte in use

Band diagram of a real lithium ion cell

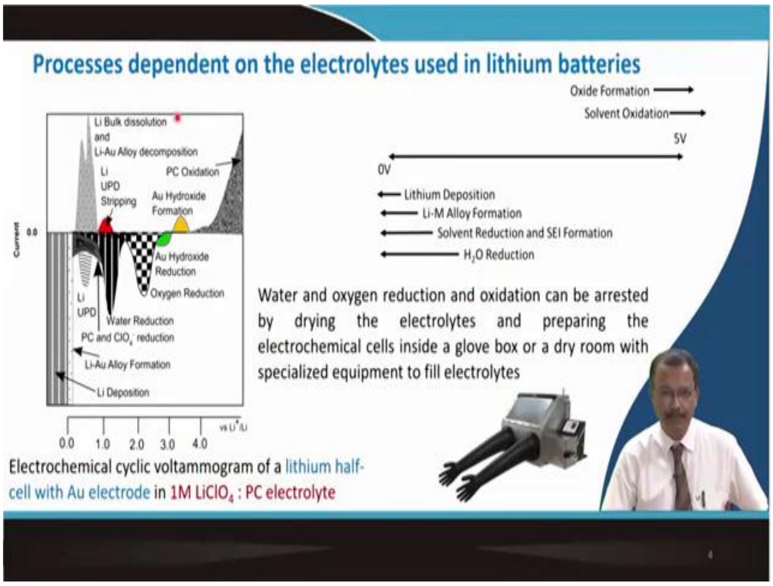
If during operation $\mu_{c(Li)}$ and $\mu_{a(Li)}$ are as shown then electrolyte is oxidized on cathode and reduced on anode surface.

So, again you are familiar now with this diagram. So, the chemical potential of cathode and chemical potential of anode, that should lie in between the highest occupied molecular orbital, which is homo and the lowest unoccupied molecular orbital, which is LUMO.

So, this band gap, this band gap these two should be in between these two. So, in real cell as you can see that instead of this, that the Fermi energy for the cathode, it should always lie a little bit above from the HOMO. And, the Fermi energy for anode it should lie little bit below of the LUMO, it is slightly different as you can see that this is lower than HOMO and this Fermi level is slightly upper than LUMO.

So, during operation if this chemical potential of lithium in cathode and lithium in anode are like this, then the electrolyte is oxidized on cathode. So, electrolyte will get oxidized here. So, it will leave electron and it will reduce on the anode surface. Because of this kind of positioning of the Fermi energy level and relative positioning of Fermi energy level in HOMO and with respect to HOMO and LUMO bond

(Refer Slide Time: 04:37)



Processes dependent on the electrolytes used in lithium batteries

Oxide Formation →
Solvent Oxidation →
0V ↔ 5V
← Lithium Deposition
← Li-M Alloy Formation
← Solvent Reduction and SEI Formation
← H_2O Reduction

Water and oxygen reduction and oxidation can be arrested by drying the electrolytes and preparing the electrochemical cells inside a glove box or a dry room with specialized equipment to fill electrolytes

Electrochemical cyclic voltammogram of a lithium half-cell with Au electrode in 1M $LiClO_4$: PC electrolyte

So, if I take a simple example of a half cell, lithium half cell, with gold electrode and it is having an electrolyte, 1 molar of lithium chlorate in polycarbonate. So, this electrolyte if we consider, then you can see at different level of lithium voltage. If you go lower than 0 volt, then there is a possibility of lithium deposition.

Then, slightly above that again at lower potential limit if you go to really low in half cell configuration. Then lithium and gold alloy will form, then slightly above voltage here, the lithium UPD, this is this will form and then water reduction will also take place.

Then, gold hydroxide reduction will take place along with this type of voltage and this is due to oxygen reduction. So, several reaction will take place for this simple cell. And, in the anodic reaction also we will have lithium bulk dissolution whatever was deposited, that will get dissolved into the electrolyte back. Lithium gold alloy decomposition reaction will take place.

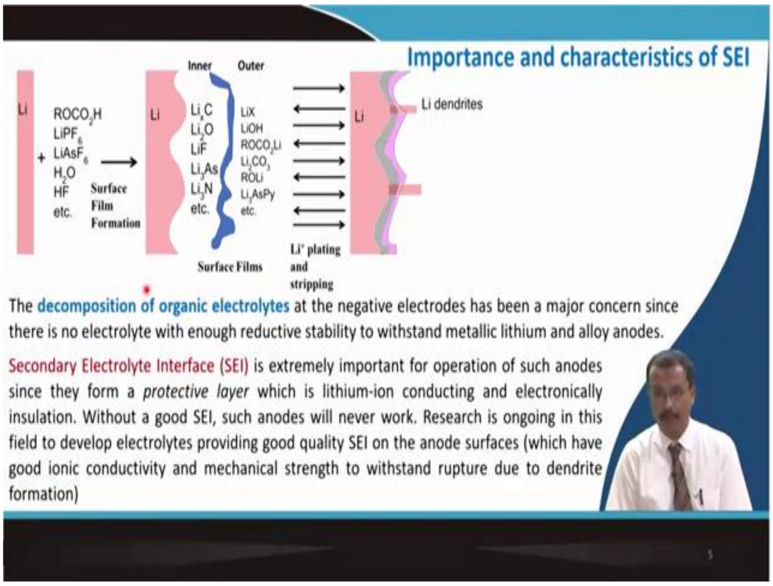
Then, lithium this under potential deposition, that stripping will occur at slightly higher voltage than this. Then, gold hydroxide reduction was here so, it will form and finally, at relatively higher voltage the polycarbonate oxidation will take place. So, lot of electrochemical phenomena will take place in general.

And, when we are talking about the a voltage range of 0 to 5 volt, then the oxide formation or solvent oxidation, that is usually in the higher voltage regime, higher voltage window. And, lithium deposition, lithium metal alloy formation, solvent reduction, and secondary electrolyte inter phase layer formation, and also in case of aqueous electrolyte the water decomposition all will take place near 0 volt regime.

So, while you select the voltage in window, one should be quite cautious about particularly the presence of water and oxygen reduction and oxidation. So, that should be avoided, and that can be arrested by drawing the electrolyte. So, electrolyte particularly which are used for lithium ion battery the organic type electrolyte, they should be dry, there should not be any moisture present.

So, usually all this experiment it is better to do in a dry room with a very low level of relative humidity, or in laboratory experiment usually we use a glove box. So, that the detrimental effect of water and oxygen reduction and oxidation, that can be arrested, so, that one should keep it in mind.

(Refer Slide Time: 08:32)



Importance and characteristics of SEI

The decomposition of organic electrolytes at the negative electrodes has been a major concern since there is no electrolyte with enough reductive stability to withstand metallic lithium and alloy anodes.

Secondary Electrolyte Interface (SEI) is extremely important for operation of such anodes since they form a *protective layer* which is lithium-ion conducting and electronically insulation. Without a good SEI, such anodes will never work. Research is ongoing in this field to develop electrolytes providing good quality SEI on the anode surfaces (which have good ionic conductivity and mechanical strength to withstand rupture due to dendrite formation)

Now, the SEI layer we are talking about. So, what is this importance and what are the characteristics of this SEI? So, let us take the example of lithium. So, the decomposition of organic electrolyte at the negative electrode, this is a major concern.

And, there is something to do with the relative position of the Fermi level of the anode and the homo band for the electrolyte, as I have explained. And, it is having a major concern and there is, in fact, no electrolyte with enough reductive stability to withstand the metallic lithium and alloy anodes.

So, if you go to lower voltage this problem is always there. So, secondary electrolyte interface is basically extremely important for the operation of such anode, particularly lithium metal and metal alloy. And, they eventually first produce a protective layer. As you can see the first there are lot of material that is generating inside the electrolyte and lithium is exposed to that.

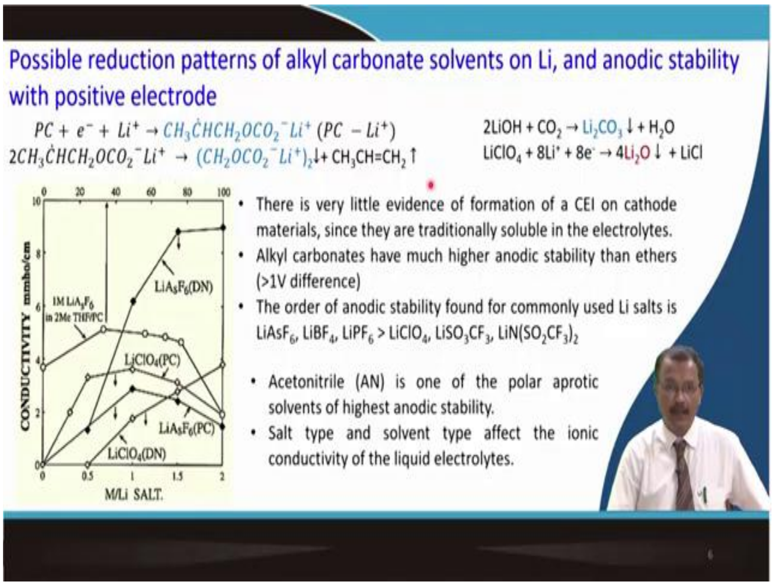
So, initially it forms a surface film like this. And, also the metallic lithium this is undulated, that you can see. So, a protective layer forms on top of that and it is fortunately this is also lithium conducting, but electrically insulating. So, lithium intercalation, I should not say intercalation, lithium electroplating should not be actually a problem, because of the formation of the surface film.

So, without a good SEI, this anode will never work, because somehow you will have to stop this, otherwise your lithium will all get exhausted. So, this lithium this surface layer formation in one way it is good, otherwise this lithium anode will never work.

So, research is ongoing in this field to develop the electrolytes providing a good quality of this surface electrolyte interface on the anode surface, which eventually is having a good ionic conductivity and also having a good better mechanical strength. Because, if it is punctured somewhere, then again it will expose the lithium and again this kind of surface layer will form. So, more surface layer will form.

So, that is why their mechanical strength should also be high. And, it should have good mechanical along with mechanical strength good ionic conductivity to just withstand the rupture, due to the formation of the dendrite. So, eventually what will happen this lithium formation on top of this surface layer, it will form a dendrite. So, if the mechanical stability of the film is not that great, then it will puncture it and it will start to grow and it will lead to internal short circuiting.

(Refer Slide Time: 12:00)



Possible reduction patterns of alkyl carbonate solvents on Li, and anodic stability with positive electrode

$$PC + e^- + Li^+ \rightarrow CH_3\dot{C}HCH_2OCO_2^-Li^+ \ (PC - Li^+)$$

$$2CH_3\dot{C}HCH_2OCO_2^-Li^+ \rightarrow (CH_2OCO_2^-Li^+)_2\downarrow + CH_3CH{=}CH_2\uparrow$$

$$2LiOH + CO_2 \rightarrow Li_2CO_3\downarrow + H_2O$$

$$LiClO_4 + 8Li^+ + 8e^- \rightarrow 4Li_2O\downarrow + LiCl$$

- There is very little evidence of formation of a CEI on cathode materials, since they are traditionally soluble in the electrolytes.
- Alkyl carbonates have much higher anodic stability than ethers (>1V difference)
- The order of anodic stability found for commonly used Li salts is $LiAsF_6$, $LiBF_4$, $LiPF_6$ > $LiClO_4$, $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$

- Acetonitrile (AN) is one of the polar aprotic solvents of highest anodic stability.
- Salt type and solvent type affect the ionic conductivity of the liquid electrolytes.

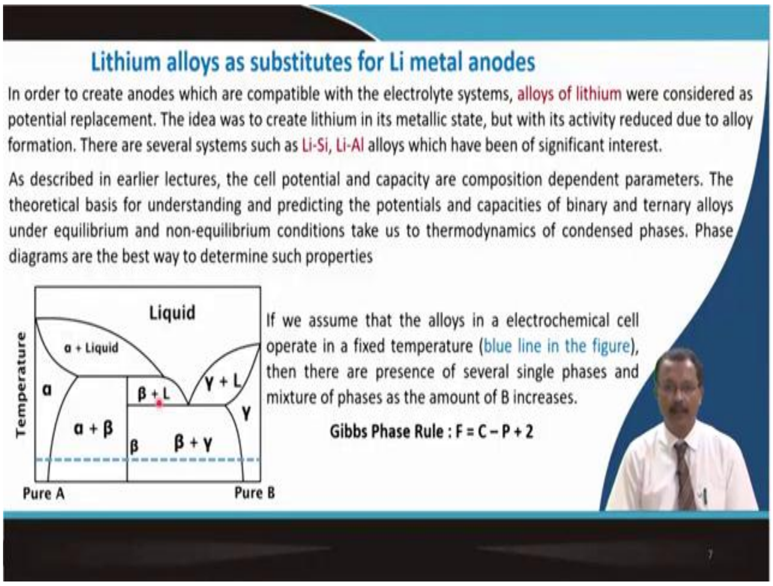
Now, here is some example of the formation of various types of this alkali carbonate solvent if you using on lithium. So, this type of polycarbonate they reacts with lithium to form this PC Li this kind of compound. And, also this is basically get deposited.

So, this type of organic compound can form as a part of your SEI layer. From the lithium salt it forms carbonate, which is also precipitate on top of the electrode material and the chloride salt this also lithium oxide is precipitate. So, there is very little evidence of the formation of a cathode interface layer, since they are traditionally soluble.

So, they do not deposit on top of the surface, but they are soluble in the electrolyte. Usually, alkali carbonates they have much higher anodic stability, than ethers that also we will describe later. The order of anodic stability in common salts is arsenic then LiBF 4, then LiPF 6 they are all larger as compared to the chlorate and these salts. So, usually commercial battery they use this type of salt.

And, acetonitrile is one of the polar aprotic solvent of highest anodic stability. So, the salts are dissolved in it. And, salt type and solvent type affect the ionic conductivity as you can see here there are several examples we have shown. And, the ionic conductivity they depend on the salt and solvent combination, so, that you should keep it in mind, while selecting the particular organic electrolyte.

(Refer Slide Time: 14:18)



Lithium alloys as substitutes for Li metal anodes

In order to create anodes which are compatible with the electrolyte systems, alloys of lithium were considered as potential replacement. The idea was to create lithium in its metallic state, but with its activity reduced due to alloy formation. There are several systems such as Li-Si, Li-Al alloys which have been of significant interest.

As described in earlier lectures, the cell potential and capacity are composition dependent parameters. The theoretical basis for understanding and predicting the potentials and capacities of binary and ternary alloys under equilibrium and non-equilibrium conditions take us to thermodynamics of condensed phases. Phase diagrams are the best way to determine such properties

If we assume that the alloys in a electrochemical cell operate in a fixed temperature (blue line in the figure), then there are presence of several single phases and mixture of phases as the amount of B increases.

Gibbs Phase Rule : $F = C - P + 2$

Now, you know that lithium alloys, that I have explained that it can be a substitute for lithium metal anodes, because lithium metal has a problem of formation of this dendrite structure. So, in order to create the anode, which are compatible to the electrolyte system, alloys of lithium they are considered as a potential replacement.

So, the idea was to create lithium in it is metallic state, but it is activity is reduced due to the formation of the alloy. So, there are several system lithium silicon, lithium aluminium alloy they are significantly they are being studied and of interest. So, in the earlier lecture we described that the cell potential and capacity are composition dependent parameters.

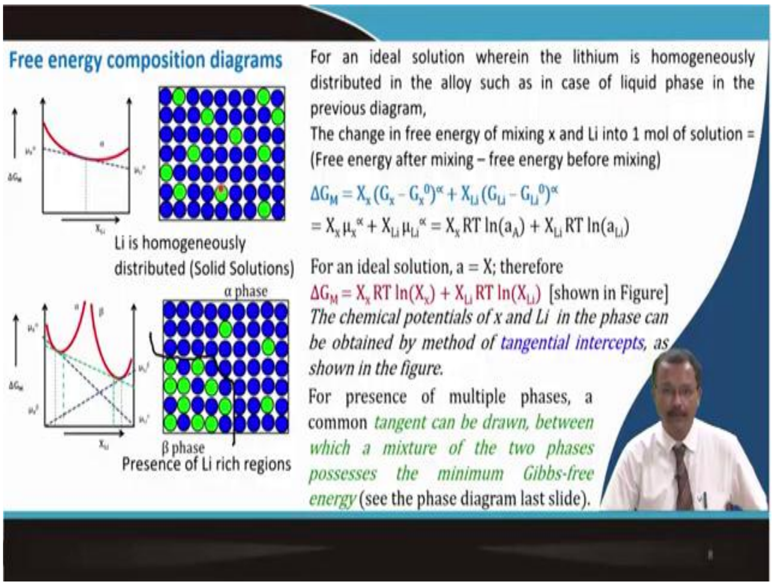
So, the theoretical basis for understanding and predicting the potential and capacity of binary as well as ternary alloys, under equilibrium as well as nonequilibrium conditions. Take us to the thermodynamics of condensed phase. So, phase diagram is the best thing to determine such property. And, this is the generic phase diagram.

If, you are not familiar with the phase diagram, then you will have to study it separately from standard textbook. So, in short you can see that pure metal A and metal B. They can form various types of phases. So, they can form a solid solution alpha, where A content is more as compared to B, because B is increasing in this direction.

Then, apart from that you have the formation of a gamma phase, formation of liquid phase. So, the composition of each of this phase the liquid composition and the solid solution composition you can apply the lever rule to know the composition. So, the knowledge basic knowledge of phase diagram is absolutely important to understand this concept. So, if we assume that the alloys in a electrochemical cell operates in a fixed temperature, I have shown the fixed temperature is in the blue line.

Then, there are presence of several single phase as well as mixture of phase. For example, alpha is there, alpha plus beta is there, then a line compound beta is there, then beta plus gamma then gamma solid solution so, they are there. So, you know the Gibbs phase rule tells us the degree of freedom that depends on the component, number of component; number of phase and these 2 terms, this plus 2 is coming because of temperature and pressure.

(Refer Slide Time: 17:24)



Free energy composition diagrams

Li is homogeneously distributed (Solid Solutions)

Presence of Li rich regions

For an ideal solution wherein the lithium is homogeneously distributed in the alloy such as in case of liquid phase in the previous diagram,

The change in free energy of mixing x and Li into 1 mol of solution = (Free energy after mixing – free energy before mixing)

$$\Delta G_M = X_x(G_x - G_x^0)^\alpha + X_{Li}(G_{Li} - G_{Li}^0)^\alpha$$

$$= X_x\mu_x^\alpha + X_{Li}\mu_{Li}^\alpha = X_x RT\ln(a_A) + X_{Li} RT\ln(a_{Li})$$

For an ideal solution, a = X; therefore

$\Delta G_M = X_x RT\ln(X_x) + X_{Li} RT\ln(X_{Li})$ [shown in Figure]

The chemical potentials of x and Li in the phase can be obtained by method of tangential intercepts, as shown in the figure.

For presence of multiple phases, a common *tangent can be drawn, between which a mixture of the two phases possesses the minimum Gibbs-free energy* (see the phase diagram last slide).

Now, this is a familiar diagram, already I talked about it, if you consider a ideal solution of lithium, that is homogeneously dispersed in the alloy distributed in the alloy just like this. So, this is just somewhere here a single phase solid solution, then I can write the free energy of mixing x and lithium into 1 mole of this solution.

So, that is equal to free energy after mixing minus free energy before mixing. So, that is the difference in free energy of mixing. So, that is given by X X the molar fraction, then the free energy of X and free energy of X at standard condition for alpha phase and this is for the lithium the other one.

$$\Delta G_M = X_x (G_x - G_x^0)^{\propto} + X_{Li} (G_{Li} - G_{Li}^0)^{\propto}$$

$$= X_x \mu_x^{\propto} + X_{Li} \mu_{Li}^{\propto} = X_x RT \ln(a_A) + X_{Li} RT \ln(a_{Li})$$

For an ideal solution, a = X; therefore

$$\Delta G_M = X_x RT \ln(X_x) + X_{Li} RT \ln(X_{Li})$$

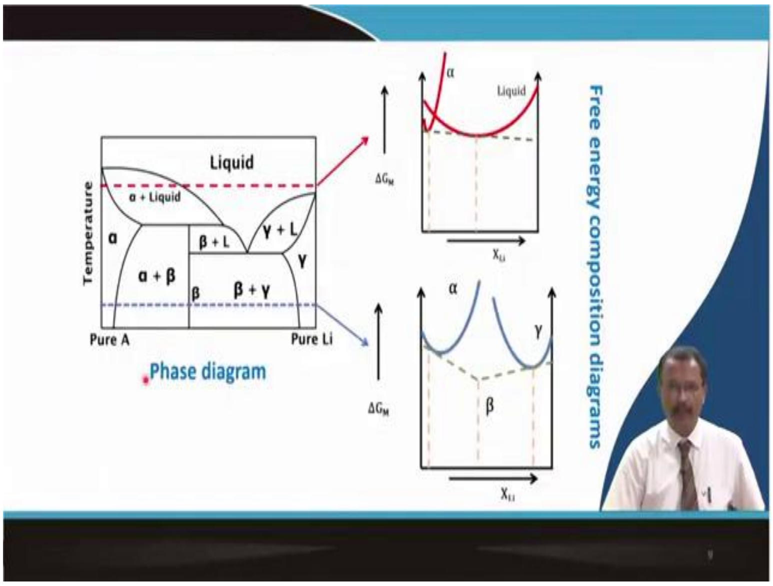
So, this is lithium and lithium standard case for the alpha phase right. So, this I can replace it with the chemical potential and then put the value of the chemical potential which is RT ln a Li. So, you can derive this relation. So, the concentration part for an ideal solution the activity is nothing, but X the molar fraction. So, this already I have described while I was talking about the chemical potential.

So, you can understand it better I am not repeating it elaborately. So, your free energy of mixing is given by this relation, which is shown in the figure. So, which is related with the mole fraction of the X component and the mole fraction of lithium component, that is in the mixture. So, the chemical potential of x and lithium in phase can be obtained by the method of tangential intercepts.

So, for this particular composition, if you want to know the chemical potential of lithium, then you just draw a tangent here and you get the chemical potential of lithium here and chemical potential of X component here. Similarly, for other compositions also you can have, you can have this measured. So, here you see the lithium potential is increasing here and for this composition this will be decreasing for x. So, this is for the single phase solid solution.

For multiphase like this, a common tangent you can draw here. So, this common tangent between which the mixture of two phase possesses the minimum Gibbs free energy. So, in the last slide you see that this is a phase mixture and here the free energy minimum is same along with the tangent. So, here also you can identify the chemical potentials.

(Refer Slide Time: 20:51)



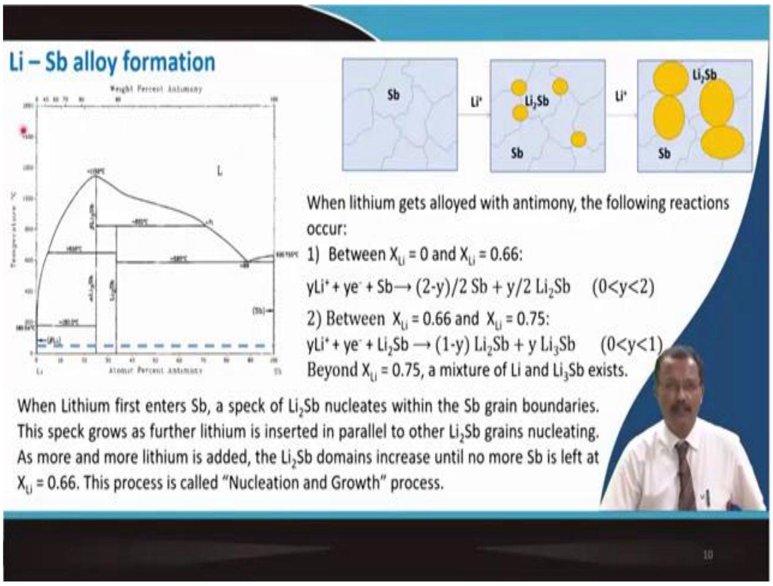
Free energy composition diagrams

Phase diagram

So, I have elaborated it for this hypothetical phase diagram. If you can take this temperature, which is the high temperature regime, you have the alpha phase, then a mixture of alpha phase and the liquid and then you have pure liquid phase. So, corresponding composition versus composition diagram, here in this case it is lithium increasing in this side.

This can be given by this type of relation, because it is a two phase mixture. When you come down to the lower temperature, then again there is a phase mixture and there are several phase. So, you can have alpha phase, you can have beta phase, and you can have the gamma phase. So, likewise you can also draw the free energy change versus lithium ion composition diagram the way it is shown here.

(Refer Slide Time: 21:58)



Li – Sb alloy formation

When lithium gets alloyed with antimony, the following reactions occur:

1) Between $X_{Li} = 0$ and $X_{Li} = 0.66$:

$yLi^+ + ye^- + Sb \longrightarrow (2-y)/2\ Sb + y/2\ Li_2Sb \quad (0<y<2)$

2) Between $X_{Li} = 0.66$ and $X_{Li} = 0.75$:

$yLi^+ + ye^- + Li_2Sb \longrightarrow (1-y)\ Li_2Sb + y\ Li_3Sb \quad (0<y<1)$

Beyond $X_{Li} = 0.75$, a mixture of Li and Li_3Sb exists.

When Lithium first enters Sb, a speck of Li_2Sb nucleates within the Sb grain boundaries. This speck grows as further lithium is inserted in parallel to other Li_2Sb grains nucleating. As more and more lithium is added, the Li_2Sb domains increase until no more Sb is left at $X_{Li} = 0.66$. This process is called “Nucleation and Growth” process.

So, if you consider the lithium and antimony alloy formation. So, I will go by this phase diagram of lithium and antimony. And, there are several phase that is formed when lithium is forming an alloy with antimony. So, if you take the example between lithium 0, which is somewhere here pure antimony and lithium where it is 0.66.

1) Between $X_{Li} = 0$ and $X_{Li} = 0.66$:

$yLi^+ + ye^- + Sb \longrightarrow (2-y)/2\ Sb + y/2\ Li_2Sb \quad (0<y<2)$

Then the phase that is forming is Li 2 Sb and again in this composition of lithium 0.66 to 0.75 you have this phase, that is forming this Li 2 Sb as well as Li 3 Sb in this composition range. And, when lithium is beyond 0.75, then you have a mixture of pure lithium and Li 3 Sb. So, in pure antimony when you allow it with lithium there is a nucleation of this speck of Li 2 Sb that nucleates with the antimony grain boundaries.

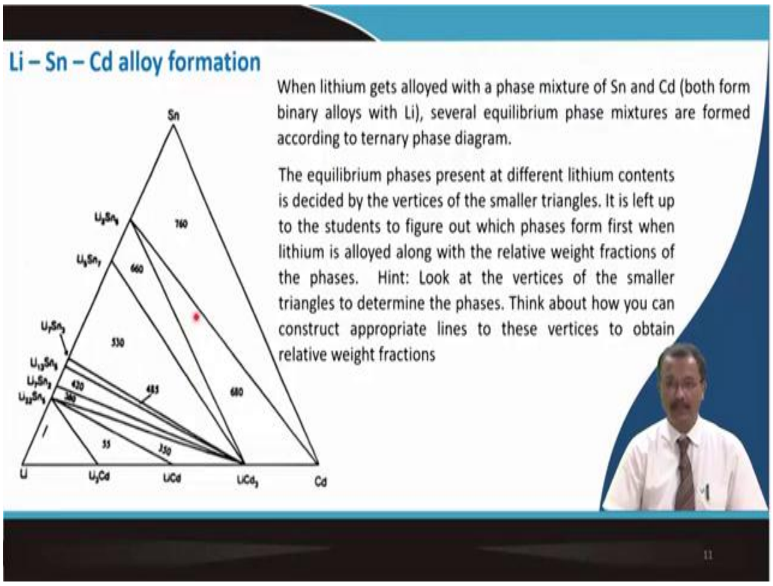
And, this actually the speck grows as further lithium is inserted in parallel to Li 2 Sb, grains they start to nucleate as more and more lithium is added then Li 2 Sb, that domains increases until there is no more antimony left at X equal to 0.66. And, this process is known as nucleation and growth process for this alloy formation. So, you can choose any of this alloy composition and start using it for your anode material.

Between $X_{Li} = 0.66$ and $X_{Li} = 0.75$:

$yLi^+ + ye^- + Li_2Sb \longrightarrow (1-y)\ Li_2Sb + y\ Li_3Sb \quad (0<y<1)$

Beyond $X_{Li} = 0.75$, a mixture of Li and Li_3Sb exists.

(Refer Slide Time: 23:45)



Li – Sn – Cd alloy formation

When lithium gets alloyed with a phase mixture of Sn and Cd (both form binary alloys with Li), several equilibrium phase mixtures are formed according to ternary phase diagram.

The equilibrium phases present at different lithium contents is decided by the vertices of the smaller triangles. It is left up to the students to figure out which phases form first when lithium is alloyed along with the relative weight fractions of the phases. Hint: Look at the vertices of the smaller triangles to determine the phases. Think about how you can construct appropriate lines to these vertices to obtain relative weight fractions

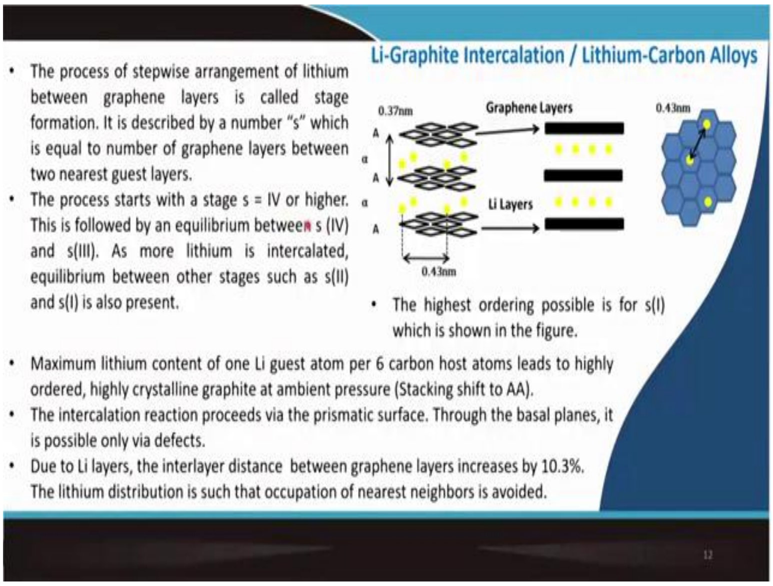
Similarly, a triaxial phase diagram can be constructed, explicitly I will not be able to talk on this triaxial phase diagram, but in my non metallic material course, the phase diagram I have elaborated lectures. So, I will recommend all of you to go through those lecture to understand the triaxial phase diagram.

And, as you can see there are many many phase that basically can form. And, when lithium gets alloyed with a phase of mixture of tin and cadmium, both forms binary alloy with lithium, several equilibrium phase mixture are formed according to this triaxial phase diagram.

So, the equilibrium phase present at different lithium contents that is decided by the vertices of the respective smaller triangle. So, you can actually you are welcome to figure out, which phases will form first, when lithium is alloyed along with the relative weight fraction of the other phases. So, you can look at the vertices of this triangle and you can construct appropriate line and apply lever rule to get the relative weight fraction.

This may look like little bit complicated at this stage, but I sincerely hope that you will try to read the triaxial phase diagram from the book by Tilley. And, my earlier lectures where it has been very well described including certain illustrative example to know the relative phase fraction for a triaxial phase diagram.

(Refer Slide Time: 25:53)



Li-Graphite Intercalation / Lithium-Carbon Alloys

- The process of stepwise arrangement of lithium between graphene layers is called stage formation. It is described by a number "s" which is equal to number of graphene layers between two nearest guest layers.
- The process starts with a stage s = IV or higher. This is followed by an equilibrium between s (IV) and s(III). As more lithium is intercalated, equilibrium between other stages such as s(II) and s(I) is also present.

- The highest ordering possible is for s(I) which is shown in the figure.
- Maximum lithium content of one Li guest atom per 6 carbon host atoms leads to highly ordered, highly crystalline graphite at ambient pressure (Stacking shift to AA).
- The intercalation reaction proceeds via the prismatic surface. Through the basal planes, it is possible only via defects.
- Due to Li layers, the interlayer distance between graphene layers increases by 10.3%. The lithium distribution is such that occupation of nearest neighbors is avoided.

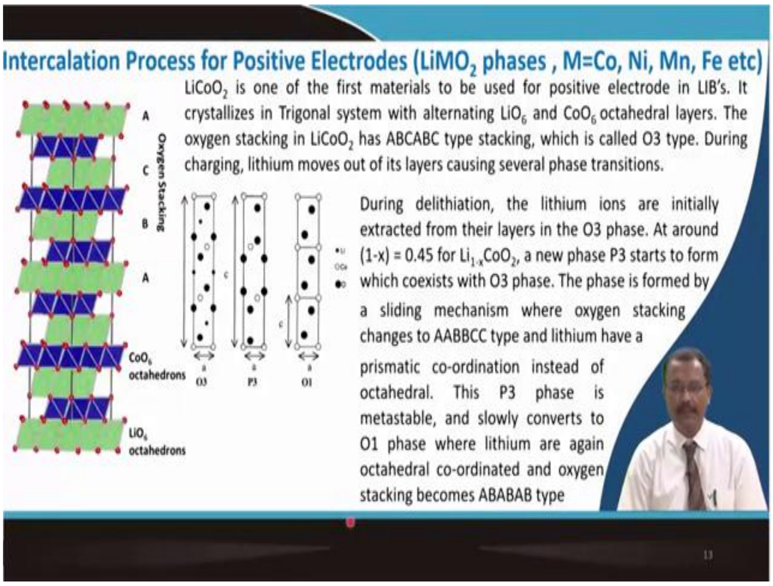
Now, in case of graphite there is another type of carbonaceous material that we are using. Basically, there is a stepwise arrangement of lithium between the so, called graphene layer. So, each of single layer of graphite is grapheme. And, this is formed by this number s which is equal to the number of graphene layers between two nearest guest layer here the guest layer is lithium.

So, the process starts with a stage of s equal to IV or higher. And, this is followed by an equilibrium between s equal to 4, and then s equal to 3 s 3, as more and more lithium intercalated, then finally, other stage like s 2 and s 1, that is also present. So, lithium basically intercalates like this.

So, maximum lithium content of 1 lithium guest is per 6 carbon atom as a host. And, it is a highly ordered highly crystalline graphite ambient graphite under ambient pressure. So, the stacking is shifted to a kind of arrangement. The intercalation reaction proceeds via the prismatic surface through the basal plane; it is possible only via defect.

So, the basal plane this thing is only via defect lithium can intercalate. Due to lithium layers the interlayer distance between graphene layer increases, because lithium is going inside this layer as high as 10.3 percent and the lithium distribution is such that the occupation of the nearest neighbour is avoided.

(Refer Slide Time: 27:57)



Intercalation Process for Positive Electrodes ($LiMO_2$ phases , M=Co, Ni, Mn, Fe etc)

$LiCoO_2$ is one of the first materials to be used for positive electrode in LIB's. It crystallizes in Trigonal system with alternating LiO_6 and CoO_6 octahedral layers. The oxygen stacking in $LiCoO_2$ has ABCABC type stacking, which is called O3 type. During charging, lithium moves out of its layers causing several phase transitions.

During delithiation, the lithium ions are initially extracted from their layers in the O3 phase. At around (1-x) = 0.45 for $Li_{1-x}CoO_2$, a new phase P3 starts to form which coexists with O3 phase. The phase is formed by a sliding mechanism where oxygen stacking changes to AABBCC type and lithium have a prismatic co-ordination instead of octahedral. This P3 phase is metastable, and slowly converts to O1 phase where lithium are again octahedral co-ordinated and oxygen stacking becomes ABABAB type

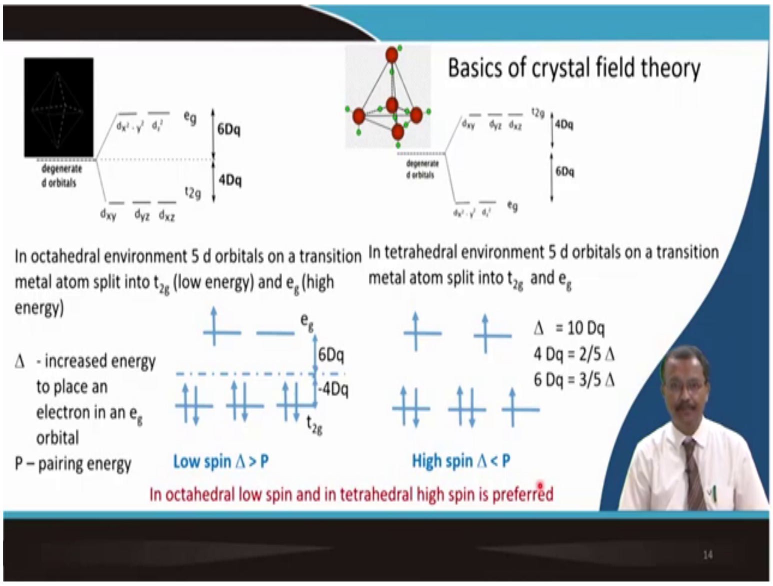
So, in case of positive electrode material LiMO 2, M is cobalt, nickel, manganese, iron etcetera. So, lithium cobalt oxide is one of the first material to be used for positive electrode in lithium ion batteries. So, initially it crystallizes into a trigonal system with alternate LiO 6 and cobalt O 6 octahedral layer. The oxygen stacking in lithium cobalt oxide, this is having a ABC ABC kind of cubic structure and which is actually called this O 3 type of structure.

During charging lithium moves out of this layer, causing several other types of phase transition, because of this cobalt coming out. So, during delithiation the lithium ions are initially extracted from their layers in the O 3 phase. At around typically 0.45, 1 minus x is 0.45 1 is the full lithium content. Then, a new phase a P 3, which is shown here that starts to form which basically coexists with O 3 phase.

So, this phase is formed by a sliding mechanism, where oxygen stacking changes from this cubic structure ABC ABC to AABBCC type. So, that is shown here in this diagram. So, it has a prismatic coordination instead of a octahedral coordination. Now, this P 3 phase is metastable. So, it slowly converts to a O 1 phase.

So, in O 1 phase lithium is again octahedrally coordinated as in this case and this is actually the O 1 phase is having a stacking of hexagonal AB AB type. So, once lithium is coming out from the structure of lithium cobalt oxide, then there are several type of phase transition that takes place. Some of them is having volumetric expansion or sometimes the crystal structure is slightly rotated to form a different types of phase.

(Refer Slide Time: 30:26)



Basics of crystal field theory

In octahedral environment 5 d orbitals on a transition metal atom split into t_{2g} (low energy) and e_g (high energy)

In tetrahedral environment 5 d orbitals on a transition metal atom split into t_{2g} and e_g

Δ - increased energy to place an electron in an e_g orbital

P – pairing energy

Δ = 10 Dq

4 Dq = 2/5 Δ

6 Dq = 3/5 Δ

Low spin Δ > P

High spin Δ < P

In octahedral low spin and in tetrahedral high spin is preferred

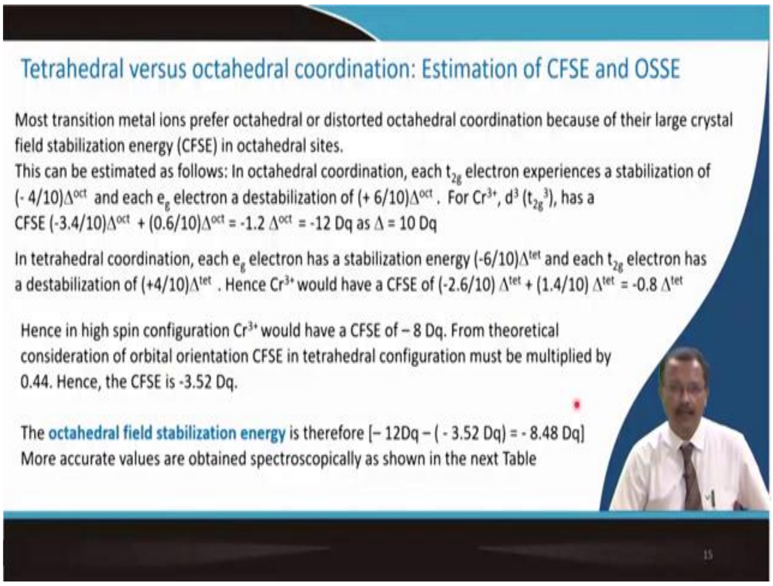
Now, I will talk a little bit about the basic crystal field theory. In tetrahedral and octahedral environment the 5 d orbital’s on a transition metal atom. They basically split into a t 2 g level having lower energy and e g level that is of higher energy. In tetrahedral this is just the reverse 5 d orbital’s in a transition metal atom, which is sitting inside this tetrahedral arrangement, this splits into t 2 g and e g.

So, this is shown here. Now, this energy is total is 10 D q in both the cases. Now, I can define two parameter; one is this delta it is the increased energy to place an electron in an e g orbital, and P is the pairing energy. So, I will call this d cation, it is in low spin state when this delta term is more than pairing. So, pairing will not be done, but it will actually go to the increased energy.

So, if you consider here there are 7 electron spin, this is D 7 kind of configuration. So, here since this energy is more than pairing energy. So, it will prefer to pair. So, it will first try to pair and then it will go to the higher energy state. And, in case of high spin this pairing energy is more as compared to this delta.

So, here what will happen this will actually first fill this orbital and then it will start to have the pairing. So, in octahedral the low spin and tetrahedral the high spin that is preferred. And, as I said the total delta value is 10 D q from the from this. So, 4 D q is equivalent to 2 by 5 delta and 6 D q is equivalent to 3 by 5 delta. So, this is a basic crystal field theory.

(Refer Slide Time: 33:00)



Tetrahedral versus octahedral coordination: Estimation of CFSE and OSSE

Most transition metal ions prefer octahedral or distorted octahedral coordination because of their large crystal field stabilization energy (CFSE) in octahedral sites.
This can be estimated as follows: In octahedral coordination, each t_{2g} electron experiences a stabilization of $(-4/10)\Delta^{oct}$ and each e_g electron a destabilization of $(+6/10)\Delta^{oct}$. For Cr^{3+}, d^3 (t_{2g}^3), has a CFSE $(-3.4/10)\Delta^{oct} + (0.6/10)\Delta^{oct} = -1.2\ \Delta^{oct} = -12$ Dq as $\Delta = 10$ Dq

In tetrahedral coordination, each e_g electron has a stabilization energy $(-6/10)\Delta^{tet}$ and each t_{2g} electron has a destabilization of $(+4/10)\Delta^{tet}$. Hence Cr^{3+} would have a CFSE of $(-2.6/10)\ \Delta^{tet} + (1.4/10)\ \Delta^{tet} = -0.8\ \Delta^{tet}$

Hence in high spin configuration Cr^{3+} would have a CFSE of – 8 Dq. From theoretical consideration of orbital orientation CFSE in tetrahedral configuration must be multiplied by 0.44. Hence, the CFSE is -3.52 Dq.

The **octahedral field stabilization energy** is therefore [– 12Dq – (- 3.52 Dq) = - 8.48 Dq]
More accurate values are obtained spectroscopically as shown in the next Table

Now, let us consider the tetrahedral versus octahedral coordination, we can actually estimate the crystal field stabilization energy and listen it carefully. Most transition metal ions prefer octahedral or distorted octahedral coordination; because of their large crystal field stabilization energy, in the octahedral site this can be actually estimated.

So, in octahedral coordination, each of this t 2 g electron experiences a stabilization of minus 4 by 10 into delta octahedral. And, each e g it experiences a destabilization of plus 6 by 10 into delta octahedral, this is from the earlier picture whichever I have drawn right.

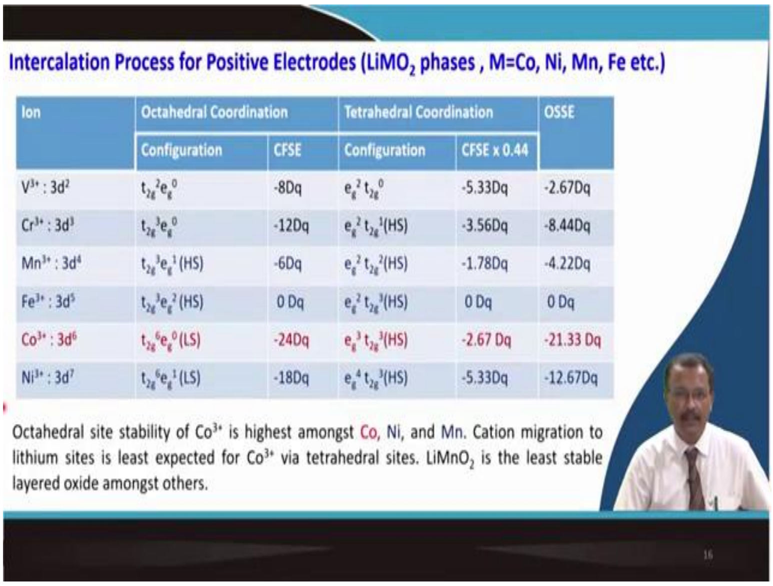
So, this is 4 Dq and this is 6 Dq. So, this one is total 10. So, accordingly one can do this calculation. So, if you now consider a chromium plus 3 3 D electron has a crystal field stabilization energy is 3. So, this will be minus into 3 point sorry 3 into 4 by 10 delta octahedral plus 0.0 into 6 this is not point 0.06, this is 0 into 6, because there is no electron here.

So, total energy is 1.2 delta octahedral and this is the value is 10. So, it is minus 12 Dq as delta is equal to 10 Dq. Now, if you do the same in tetrahedral coordination each e g electron, it has a stabilization energy of minus 6 by 10 into del tetra, and each t 2 g has a destabilization energy plus 4 by 10 into del t tetrahedra from this diagram for plus 3 d 3 plus.

So, in tetrahedral coordination this is having a high spin configuration. So, chromium 3 plus would have a crystal field stabilization energy of minus 8 D q. So, from theoretical consideration of orbital orientation of CFSE, this tetrahedral configuration must be multiplied by a factor of 0.44.

Hence, the crystal field stabilization energy is minus 3.52 Dq. So, the octahedral field stabilization energy is therefore, minus 12 Dq minus of minus 3.52 Dq so; that means, it is minus 8.48 Dq. So, more accurate value one can get by spectroscopically, as you can see in the next table.

(Refer Slide Time: 36:20)



Intercalation Process for Positive Electrodes ($LiMO_2$ phases , M=Co, Ni, Mn, Fe etc.)

Ion	Octahedral Coordination		Tetrahedral Coordination		OSSE
	Configuration	CFSE	Configuration	CFSE x 0.44	
V^{3+} : $3d^2$	$t_{2g}^2 e_g^0$	-8Dq	$e_g^2 t_{2g}^0$	-5.33Dq	-2.67Dq
Cr^{3+} : $3d^3$	$t_{2g}^3 e_g^0$	-12Dq	$e_g^2 t_{2g}^1$(HS)	-3.56Dq	-8.44Dq
Mn^{3+} : $3d^4$	$t_{2g}^3 e_g^1$ (HS)	-6Dq	$e_g^2 t_{2g}^2$(HS)	-1.78Dq	-4.22Dq
Fe^{3+} : $3d^5$	$t_{2g}^3 e_g^2$ (HS)	0 Dq	$e_g^2 t_{2g}^3$(HS)	0 Dq	0 Dq
Co^{3+} : $3d^6$	$t_{2g}^6 e_g^0$ (LS)	-24Dq	$e_g^3 t_{2g}^3$(HS)	-2.67 Dq	-21.33 Dq
Ni^{3+} : $3d^7$	$t_{2g}^6 e_g^1$ (LS)	-18Dq	$e_g^4 t_{2g}^3$(HS)	-5.33Dq	-12.67Dq

Octahedral site stability of Co^{3+} is highest amongst Co, Ni, and Mn. Cation migration to lithium sites is least expected for Co^{3+} via tetrahedral sites. $LiMnO_2$ is the least stable layered oxide amongst others.

So, I have done it for a variety of cations d 2, d 3, d 4, d 5, d 6, d 7. So, as you can see that for cobalt ion this octahedral field stabilization energy, I can calculate from the crystal field stabilization energy in octahedral coordination, and crystal field stabilization energy after multiplication with 0.44, in tetrahedral coordination.

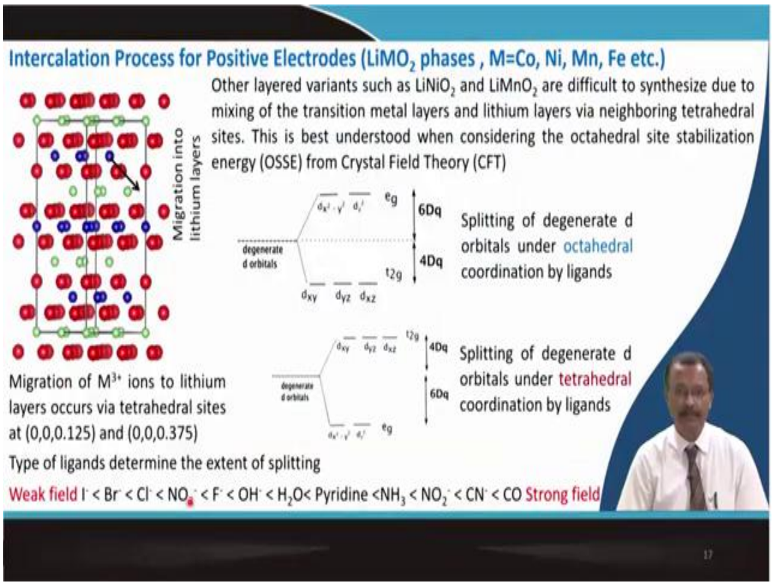
In the same way what I have been illustrated in the last slide. And, then finally, this minus this gives me, this value. Now, look at the values of manganese, which is much smaller iron is 0 in that respect which is D 5. And, chromium already I have calculated vanadium is minus 2.67 and nickel is minus 12.67.

So, that tells me that the octahedral site stability of cobalt 3 ion, cobalt plus 3 cation, which is that, which is there in lithium cobalt oxide. It is the highest among cobalt nickel and manganese. So, cation migration to lithium site is least expected for cobalt 3 plus by a tetrahedral site.

So, therefore, lithium cobalt oxide is the highest stable oxide, that cobalt from the transition metal site, it will never come to the lithium site to block it is passage, because lithium is coming out and going in. So, if the transition metal cation, due to this factor they comes in between that will return it is movement.

So, lithium manganese oxide it is least stable layered oxide amongst other. So, it is very difficult to make lithium Meta, lithium manganese oxide, to make a rechargeable battery. And, lithium nickel oxide is also equally difficult because of this cation mixing. And, therefore, the first material that good enough who got the Nobel Prize for this, considered is lithium cobalt oxide.

(Refer Slide Time: 38:42)



Intercalation Process for Positive Electrodes ($LiMO_2$ phases , M=Co, Ni, Mn, Fe etc.)

Other layered variants such as $LiNiO_2$ and $LiMnO_2$ are difficult to synthesize due to mixing of the transition metal layers and lithium layers via neighboring tetrahedral sites. This is best understood when considering the octahedral site stabilization energy (OSSE) from Crystal Field Theory (CFT)

Splitting of degenerate d orbitals under octahedral coordination by ligands

Splitting of degenerate d orbitals under tetrahedral coordination by ligands

Migration of M^{3+} ions to lithium layers occurs via tetrahedral sites at (0,0,0.125) and (0,0,0.375)

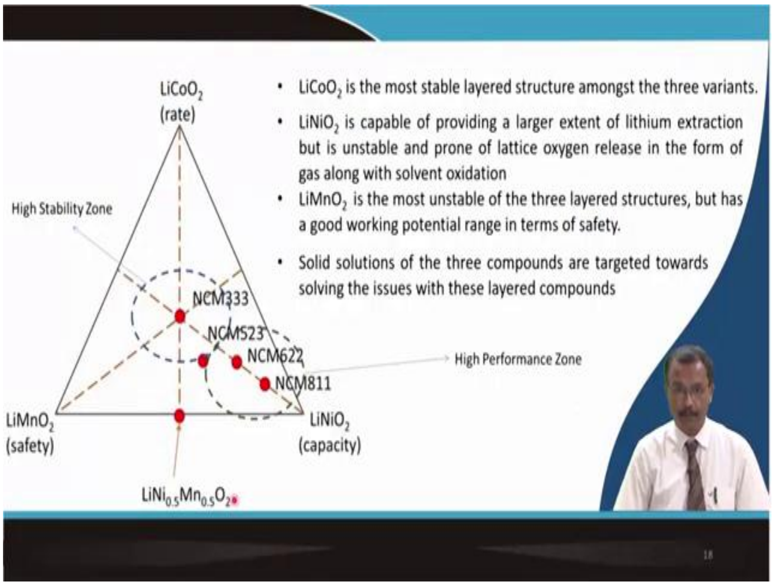
Type of ligands determine the extent of splitting

Weak field $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^- < CO$ Strong field

So, this is one thing which is quite important and lithium metal oxide phases, like metal is cobalt, nickel, manganese iron etcetera. So, as I told that other layered variant like nickel oxide and manganese oxide are difficult to synthesize due to the mixing of the transition metal cation.

This is best understood by the consideration of the octahedral state stabilization energy from Crystal Field Theory. And, this is again I have shown the same thing for this type of structure. And, we will also talk about the splitting of the ligand and in the weak field this anion, that they varies like this in case of the ligand following the similar kind of explanation.

(Refer Slide Time: 39:48)



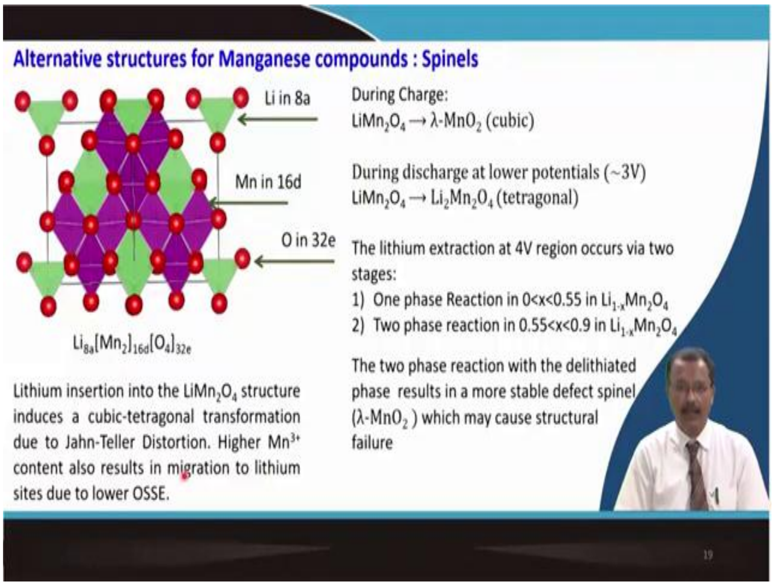
- $LiCoO_2$ is the most stable layered structure amongst the three variants.
- $LiNiO_2$ is capable of providing a larger extent of lithium extraction but is unstable and prone of lattice oxygen release in the form of gas along with solvent oxidation
- $LiMnO_2$ is the most unstable of the three layered structures, but has a good working potential range in terms of safety.
- Solid solutions of the three compounds are targeted towards solving the issues with these layered compounds

So, lithium cobalt oxide is most stable layered structured lithium nickel oxide is capable of providing a larger extent of lithium extraction, which cobalt oxide does not give. And, lithium manganese oxide is most unstable for the three layered structure, but it has a good working potential range in terms of safety.

So, each of this having their plus point and negative point. So, this three solution solid solution one can make a certain composition. So, you can see lithium cobalt oxide, you can see lithium manganese oxide, you can see lithium nickel oxide, and there are several in between composition and as you move here it is a high stability zone.

So, several composition like, nickel, cobalt manganese, one-third, one-third, one-third or this composition, or this composition, or this composition, they have been tried along with lithium nickel manganese oxide, lithium nickel cobalt oxide is also tried. So, in other words we try to mix it and form a solid solution, where the high rate or high capacity or safety, they are least compromised to have a reasonably good commercial cathode materials. So, this is very interesting field of study.

(Refer Slide Time: 41:17)



Alternative structures for Manganese compounds : Spinels

$Li_{8a}[Mn_2]_{16d}[O_4]_{32e}$

Lithium insertion into the $LiMn_2O_4$ structure induces a cubic-tetragonal transformation due to Jahn-Teller Distortion. Higher Mn^{3+} content also results in migration to lithium sites due to lower OSSE.

During Charge:
$LiMn_2O_4 \rightarrow \lambda\text{-}MnO_2$ (cubic)

During discharge at lower potentials (~3V)
$LiMn_2O_4 \rightarrow Li_2Mn_2O_4$ (tetragonal)

The lithium extraction at 4V region occurs via two stages:

1) One phase Reaction in $0<x<0.55$ in $Li_{1-x}Mn_2O_4$
2) Two phase reaction in $0.55<x<0.9$ in $Li_{1-x}Mn_2O_4$

The two phase reaction with the delithiated phase results in a more stable defect spinel ($\lambda\text{-}MnO_2$) which may cause structural failure

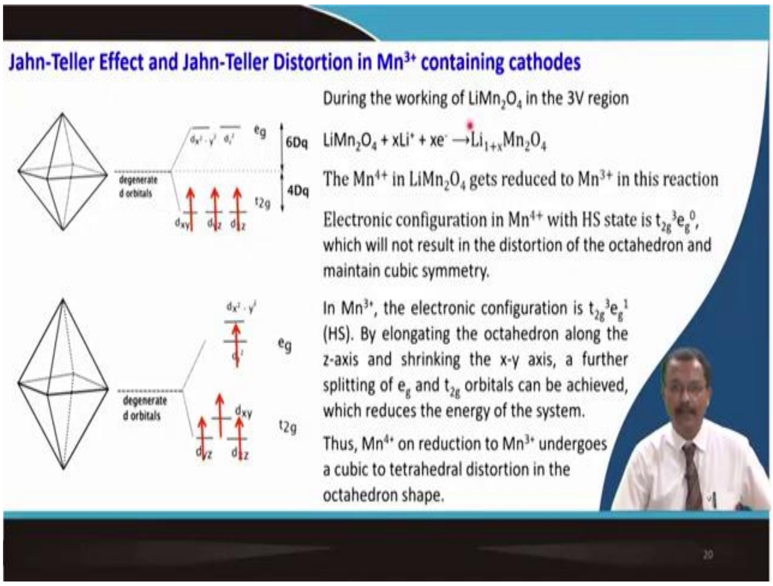
So, alternative structure for this manganese is the spinel compound, already I have described it. So, during charge you can see that all lithium you can take out it is unlike lithium cobalt oxide where only 0.5 mole you can take it out. Otherwise, this layer structure will collapse. For lithium nickel oxide and lithium manganese oxide it has a problem of cation mixing and which can be well established by the calculation of octahedral state stabilization energy.

So, the lithium extraction at 4 volt region for this type of material, they occur by a one phase reaction and two phase reaction. This I will come back again when we will talk about the case studies. So, during charging you have two plateau although there is no crystal structure change, but there is a slight modification in it.

So, this two phase reaction with delithiated phase results in a more stable defect spinel, which may cause a structural failure. Because, there is a change in the volume expansion, because of this slight crystal structure change. But, when once you go to lower voltage potential, then there is a problem of lithium insertion into this structure.

So, further lithium you can insert here. So, that will eventually increase it is capacity. So, that leads to a cubic to tetragonal transformation and that is due to the so, called Jahn-Teller Distortion. So, higher manganese 3 plus content that also results the migration of lithium site, due to it is lower octahedral state stabilization energy.

(Refer Slide Time: 43:16)



Jahn-Teller Effect and Jahn-Teller Distortion in Mn^{3+} containing cathodes

During the working of $LiMn_2O_4$ in the 3V region

$LiMn_2O_4 + xLi^+ + xe^- \rightarrow Li_{1+x}Mn_2O_4$

The Mn^{4+} in $LiMn_2O_4$ gets reduced to Mn^{3+} in this reaction

Electronic configuration in Mn^{4+} with HS state is $t_{2g}^3e_g^0$, which will not result in the distortion of the octahedron and maintain cubic symmetry.

In Mn^{3+}, the electronic configuration is $t_{2g}^3e_g^1$ (HS). By elongating the octahedron along the z-axis and shrinking the x-y axis, a further splitting of e_g and t_{2g} orbitals can be achieved, which reduces the energy of the system.

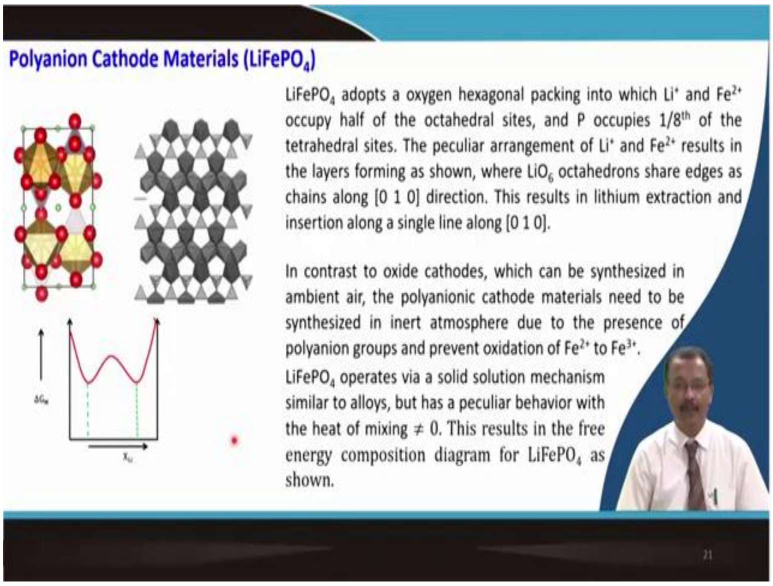
Thus, Mn^{4+} on reduction to Mn^{3+} undergoes a cubic to tetrahedral distortion in the octahedron shape.

So, during the working of lithium manganese oxide in the 3 volt region, which rarely one does, as I told that more lithium will be inserted. So, the manganese in lithium manganese oxide they gets reduced to Mn 3 plus in this reaction. So, again we will go back to the electronic configuration of Mn 4 plus with high spin state.

So, this is t g 3, t 2 g 3 and e g 0, which will not result any distortion of the octahedral and maintain the cubic stability. But, if it is transformed into Mn 3 plus because of this lithium insertion, then electronic configuration will change t 2 g 3 and e g 1 again high spin configuration.

So, that will elongate the octahedron along the z axis and shrink the x y axis. A further split occurs in the e g and t 2 g orbital, which eventually reduces the energy of the system. So, in a nutshell M n 4 plus on reduction to M n 3 plus that undergoes a cubic to tetragonal distortion in the octahedral shape and that is detrimental for the cyclability of this type of cathode.

(Refer Slide Time: 44:42)



Polyanion Cathode Materials ($LiFePO_4$)

$LiFePO_4$ adopts a oxygen hexagonal packing into which Li^+ and Fe^{2+} occupy half of the octahedral sites, and P occupies 1/8th of the tetrahedral sites. The peculiar arrangement of Li^+ and Fe^{2+} results in the layers forming as shown, where LiO_6 octahedrons share edges as chains along [0 1 0] direction. This results in lithium extraction and insertion along a single line along [0 1 0].

In contrast to oxide cathodes, which can be synthesized in ambient air, the polyanionic cathode materials need to be synthesized in inert atmosphere due to the presence of polyanion groups and prevent oxidation of Fe^{2+} to Fe^{3+}.

$LiFePO_4$ operates via a solid solution mechanism similar to alloys, but has a peculiar behavior with the heat of mixing $\neq 0$. This results in the free energy composition diagram for $LiFePO_4$ as shown.

In case of polyanion based cathode material like, lithium iron phosphate, it adopts a oxygen hexagonal packing into which lithium and iron occupies half of the octahedral site. And, this peak occupies 1 8th of the tetrahedral site. This is a peculiar arrangement of lithium and iron 2 plus that, results eventually as shown in this figure.

So, LiO 6 octahedron share edge as chain along this will be 0 1 0 direction. And, this results the lithium extraction and insertion along a single line, which is 0 1 0. So, in contrast to the oxide cathode which can be synthesized in ambient air, this polyanion material needs to be synthesized in argon atmosphere or inert atmosphere.

Due to the presence of this PO 4 group and prevent oxidation from Fe 2 plus to Fe 3 plus. So, this operates lithium iron phosphate operates via solid solution mechanism. Similar to alloys, but it has a peculiar behavior with the heat of mixing.

So, you can see that the result free energy composition diagram is not really the way I have shown it or I have asked you to derive like this, but it is showing 2 minima. The implication of it in the voltage profile that we will discuss later.

(Refer Slide Time: 46:32)

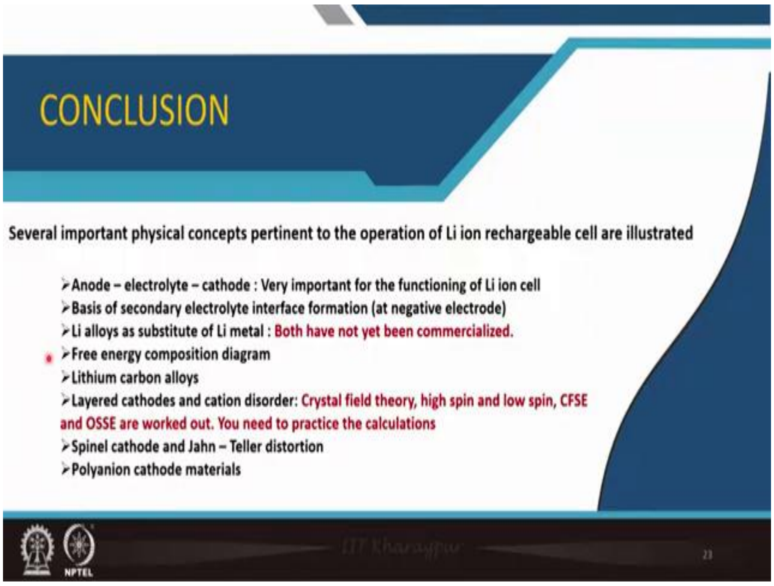
REFERENCES

- **Brief overview of electrochemical potential in lithium ion batteries** , J. Gao, S-Q Shi, and Hong Li, *Chin. Phys. B* **25**, 018210 (2016) DOI 10.1088/1674 – 1056/25/1/018210 (Study material)
- **Understanding electrochemical potentials of cathode materials in rechargeable batteri**es, C Liu, Z.G. Neale, and G. Cao, *Materials Today* **19**, 109 (2016) (Study material)
- **Solid state chemistry and its applications**, A.R. West, 2nd Edition, Wiley (2014), Chapter – 3 Bonding in solids page 153 – 161 (Reference material)

So, this is an important physical concepts which is pertinent to lithium ion battery you listen to this lecture repeatedly and try to follow my slides along with this literatures.

So, this two published paper they are very important and I ask you to read at a study material this one and this one. And, the book by A. R. West, that tells about this bonding behaviour this t 2 g and e g splitting, which also needs to be read from proper grasping the material taught in this class.

(Refer Slide Time: 47:14)



CONCLUSION

Several important physical concepts pertinent to the operation of Li ion rechargeable cell are illustrated

- Anode – electrolyte – cathode : Very important for the functioning of Li ion cell
- Basis of secondary electrolyte interface formation (at negative electrode)
- Li alloys as substitute of Li metal : Both have not yet been commercialized.
- Free energy composition diagram
- Lithium carbon alloys
- Layered cathodes and cation disorder: Crystal field theory, high spin and low spin, CFSE and OSSE are worked out. You need to practice the calculations
- Spinel cathode and Jahn – Teller distortion
- Polyanion cathode materials

So, several important physical concepts pertinent to the operation of lithium ion rechargeable cells I have illustrated. Anode electrolyte cathode very important for functioning of lithium ion cell, basis of secondary electrolyte interface formation as a negative electrode we have illustrated.

Lithium alloys and their substitute of lithium metal, both they have not commercialized yet free energy and composition diagram in fact, you can work out and you can prepare this kind of diagram, layered cathode and cation disorder that has been explained in terms of crystal field theory high spin and low spin criteria.

And crystal field stabilization energy and octahedral state stabilization energy they are worked out and you need to practice these calculations. Spinal cathode and it is relation with Jahn-Teller distortion has been explained. And, finally, polyanion based cathode material we have illustrated

Thank you for your attention.