Electrochemical Energy Storage

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Module - 03
Lithium batteries
Lecture - 13
Differences of Voltage Profiles between Intercalation Materials, Alloys, and Conversion Materials

Welcome to my course, Electrochemical Storage. And, this is module number 3 on Lithium Batteries and this is lecture 13. So, here I will show, what is the genesis of various types of voltage profile between different types of electrode material? So, far we have talked about intercalation material, alloy conversion materials. So, do you get similar type of pattern voltage versus lithium composition or you get different types of pattern and what are the genesis of that?

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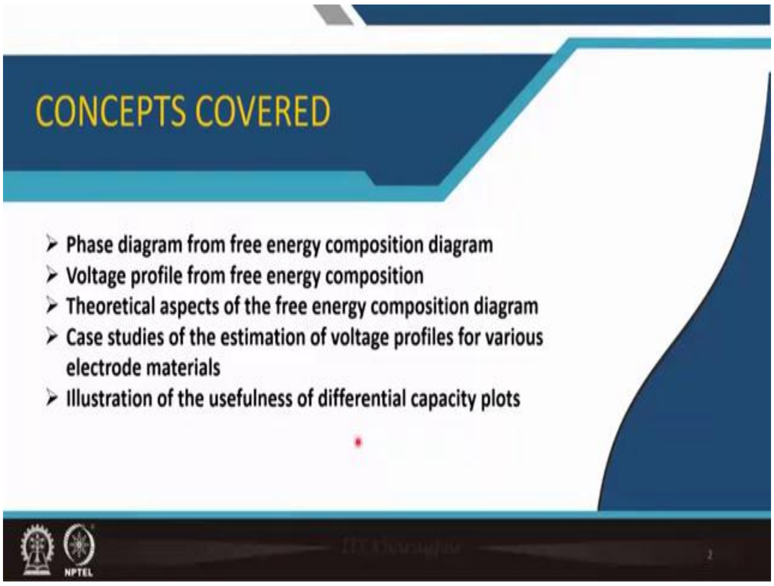

CONCEPTS COVERED

- Phase diagram from free energy composition diagram
- Voltage profile from free energy composition
- Theoretical aspects of the free energy composition diagram
- Case studies of the estimation of voltage profiles for various electrode materials
- Illustration of the usefulness of differential capacity plots

So, we will again talk about the phase diagram from the free energy composition how they are related. Then, we will estimate the voltage profile from free energy composition diagram, then we will explain the theoretical aspects of the free energy composition diagram, then we will have certain case studies for the estimation of voltage profile for various electrode materials.

And, finally, the differential capacity plot, which I showed in one of the my earlier lectures differential capacity plot the illustration of their usefulness, that I will cover.

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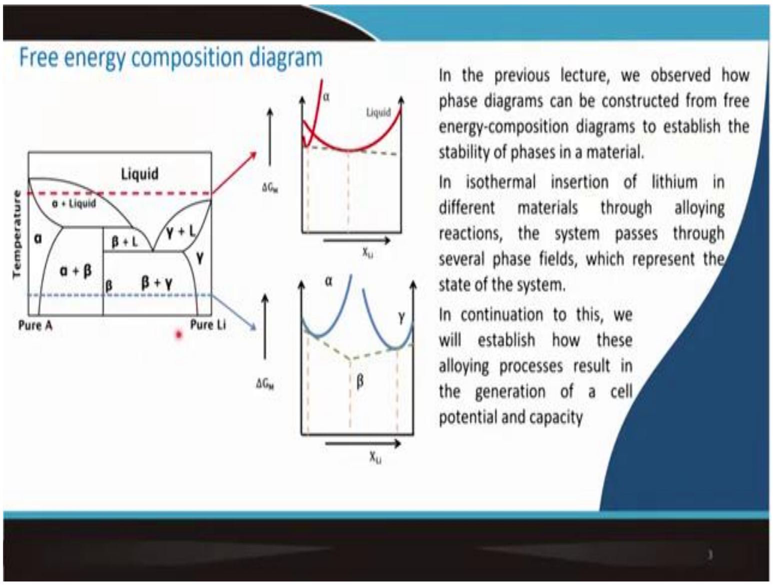

Free energy composition diagram

In the previous lecture, we observed how phase diagrams can be constructed from free energy-composition diagrams to establish the stability of phases in a material.

In isothermal insertion of lithium in different materials through alloying reactions, the system passes through several phase fields, which represent the state of the system.

In continuation to this, we will establish how these alloying processes result in the generation of a cell potential and capacity

So, we will start with again the free energy composition diagram and the phase diagram of a binary component system, one is a pure component which is defined as A, and another side is pure lithium. So, sometimes in some of my slide instead of A I put X and the right hand side is always lithium. So, lithium content increases here and it forms various types of solid solution and mixture of solid solution.

So, if you go by this particular red line, then you end up with the free energy versus lithium diagram like this, which already I explained. And, if you go by this blue line then this kind of free energy versus composition diagram one can easily identify. So, in the previous lecture we observed how this phase diagram can be constructed from this free energy composition diagrams, we explained the genesis of this.

In isothermal in intersection of lithium in different materials through alloying reactions, the system passes through several phase field as you can see which represent the state of the system. So, in continuation to this we will now establish, how this alloying process, result in the generation of cell potential and capacity?

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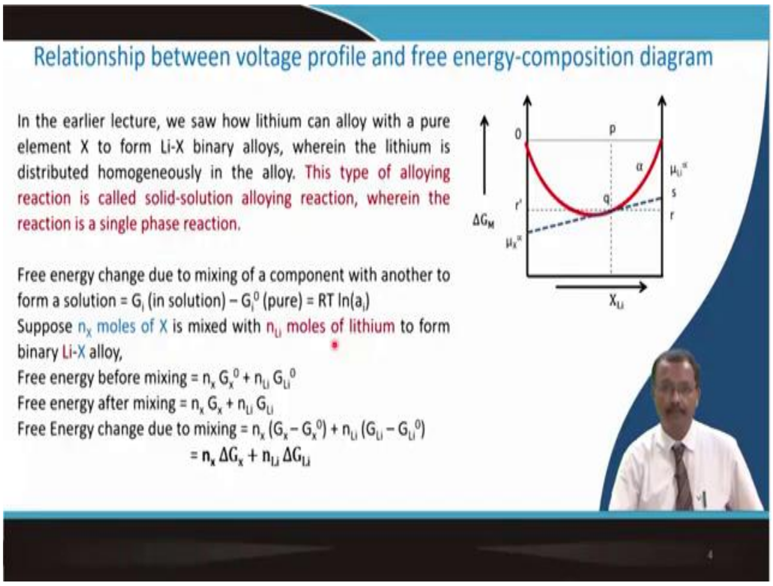

Relationship between voltage profile and free energy-composition diagram

In the earlier lecture, we saw how lithium can alloy with a pure element X to form Li-X binary alloys, wherein the lithium is distributed homogeneously in the alloy. This type of alloying reaction is called solid-solution alloying reaction, wherein the reaction is a single phase reaction.

Free energy change due to mixing of a component with another to form a solution = G_i (in solution) – G_i^0 (pure) = RT ln(a_i)
Suppose n_x moles of X is mixed with n_{Li} moles of lithium to form binary Li-X alloy,
Free energy before mixing = $n_x G_x^0 + n_{Li} G_{Li}^0$
Free energy after mixing = $n_x G_x + n_{Li} G_{Li}$
Free Energy change due to mixing = $n_x (G_x – G_x^0) + n_{Li} (G_{Li} – G_{Li}^0)$
$= \mathbf{n_x \Delta G_x + n_{Li} \Delta G_{Li}}$

So, in earlier lecture, we saw how lithium can alloy with pure element X. So, as I told in here, I have defined the left part as X to form a lithium X binary alloys, wherein the lithium distributed homogeneously in the alloy. So, remember the diagram that I showed where lithium and this X component and sometimes I define as a. So, they are homogeneously distributed.

This type of alloying reaction is called a solid solution alloying reactions, wherein this reaction is a single phase reaction. So, the free energy change due to mixing of the component with another to form a solution. So, I can have this G 1 in solution minus this G i in pure case and that is equated with RT ln into the activity. So, you suppose that n x mole of this X component is mixed with n Li moles of lithium to form this binary alloy. So, I am defining this composition.

So, the free energy before mixing you can write with this equation, where n x and G x and n Li and G Li is already defined. And, after mixing this is n x G x plus n Li G Li, so, this is after mixing. So, free energy change due to mixing is just this minus this. So, we will work out with n x del G x plus n Li del G Li simple calculations.

Free energy before mixing = $n_x G_x^0 + n_{Li} G_{Li}^0$

Free energy after mixing = $n_x G_x + n_{Li} G_{Li}$

Free Energy change due to mixing = $n_x (G_x – G_x^0) + n_{Li} (G_{Li} – G_{Li}^0)$

$$= \mathbf{n_x \, \Delta G_x + n_{Li} \, \Delta G_{Li}}$$

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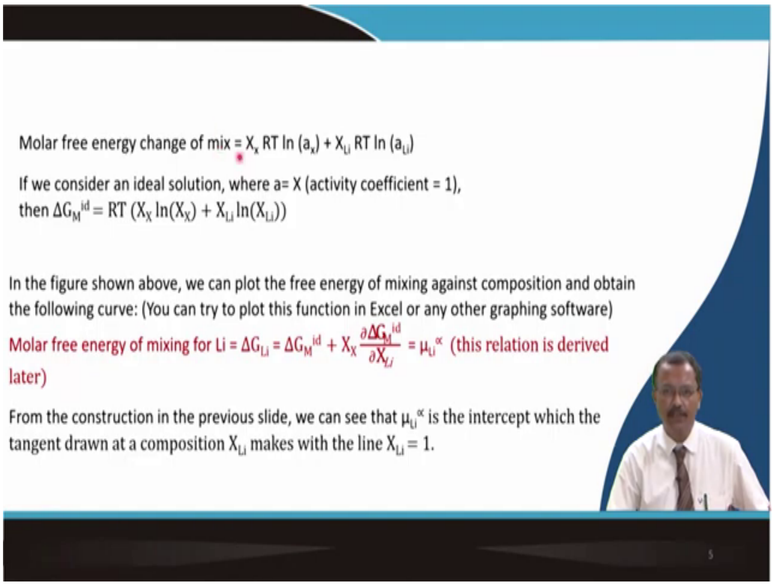

Molar free energy change of mix = X_x RT ln (a_x) + X_{Li} RT ln (a_{Li})

If we consider an ideal solution, where a= X (activity coefficient = 1),
then $\Delta G_M^{id} = RT\,(X_X \ln(X_X) + X_{Li} \ln(X_{Li}))$

In the figure shown above, we can plot the free energy of mixing against composition and obtain the following curve: (You can try to plot this function in Excel or any other graphing software)

Molar free energy of mixing for Li = $\Delta G_{Li} = \Delta G_M^{id} + X_X \frac{\partial \Delta G_M^{id}}{\partial X_{Li}} = \mu_{Li}^{\alpha}$ (this relation is derived later)

From the construction in the previous slide, we can see that μ_{Li}^{α} is the intercept which the tangent drawn at a composition X_{Li} makes with the line $X_{Li} = 1$.

Now, molar free energy change of the mix. So, that is n mole and divided by the total mole. So, that is the molar fraction. So, that RT ln a i sorry a x plus mole fraction of Li RT ln activity of Li. So, if you consider an ideal solution, where this activity coefficient is 1, then this free energy mixing is RT into X X ln, X X plus X L i ln X Li.

Molar free energy change of mix = X_x RT ln (a_x) + X_{Li} RT ln (a_{Li})

If we consider an ideal solution, where a= X (activity coefficient = 1),

then $\Delta G_M^{id} = RT\,(X_X \ln(X_X) + X_{Li} \ln(X_{Li}))$

So, the figure that is shown here, we can plot the free energy of mixing against the composition of lithium usually with the lithium composition it is shown. And, you can get the plot of the free energy of mixing against the composition.

So, I will ask you to try this plot try to plot this function in excel or origin or any other graphical software to actually see that you are getting this kind of shape. So, one can also estimate, that this molar free energy of mixing for lithium, this is the free energy change of the mixing in the ideal case plus X X, then del of this del G M ideal by del X lithium.

Molar free energy of mixing for Li = $\Delta G_{Li} = \Delta G_{M}^{id} + X_{X}\frac{\partial \Delta G_{M}^{id}}{\partial X_{Li}} = \mu_{Li}^{\propto}$

And, this is nothing, but the chemical potential of lithium. So, this relation I have derived it for you initially I thought that you can derive it yourself, but later I thought that let us derive it. So, this is shown as this tangent, you can see that at this particular composition if you take and you draw a tangent here, then this molar chemical potential of lithium and this X component you can easily identify.

So, for the construction in the previous slide, we can see that this is the intercept which is the tangent drawn at a composition makes with the line X Li equal to 1. So, with this if you draw the tangent, which is passing through this lithium composition you get the chemical potential for lithium.

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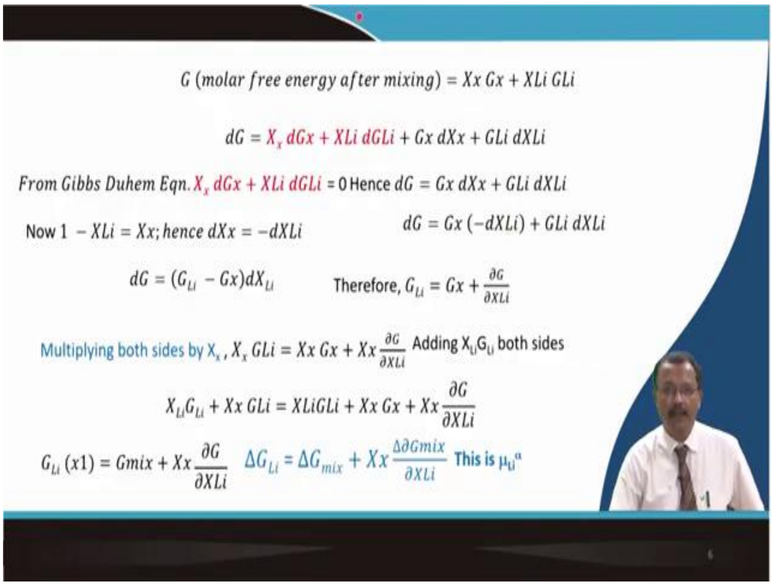

$G\ (molar\ free\ energy\ after\ mixing) = Xx\ Gx + XLi\ GLi$

$dG = X_x\ dGx + XLi\ dGLi + Gx\ dXx + GLi\ dXLi$

From Gibbs Duhem Eqn. $X_x\ dGx + XLi\ dGLi = 0$ Hence $dG = Gx\ dXx + GLi\ dXLi$

Now $1 - XLi = Xx; hence\ dXx = -dXLi$ $\quad$ $dG = Gx\,(-dXLi) + GLi\ dXLi$

$dG = (G_{Li} - Gx)dX_{Li}$ $\quad$ Therefore, $G_{Li} = Gx + \frac{\partial G}{\partial XLi}$

Multiplying both sides by X_x , $X_x\ GLi = Xx\ Gx + Xx\frac{\partial G}{\partial XLi}$ Adding $X_{Li}G_{Li}$ both sides

$X_{Li}G_{Li} + Xx\ GLi = XLiGLi + Xx\ Gx + Xx\frac{\partial G}{\partial XLi}$

$G_{Li}\,(x1) = Gmix + Xx\frac{\partial G}{\partial XLi}$ $\quad$ $\Delta G_{Li} = \Delta G_{mix} + Xx\frac{\Delta\partial Gmix}{\partial XLi}$ This is μ_{Li}^{α}

So, let us try to solve this. So, G is the molar free energy after mixing so, you can write this relation and again this will all be subscript, this will all be subscript, then differentiate this relation.

$$G\ (molar\ free\ energy\ after\ mixing) = X_x\ G_x + X_{Li}\ G_{Li}$$

$$dG = X_x\ dG_x + X_{Li}\ dG_{Li} + G_x\ dX_x + G_{Li}\ dX_{Li}$$

Now earlier I proved the Gibbs Duhem equation. So, this part the rate part is Gibbs Duhem equation and that is equal to 0. So, you have dG equal to this plus this.

$$X_x\ dG_x + X_{Li}\ dG_{Li} = 0$$

$$dG = G_x\ dX_x + G_{Li}\ dX_{Li}$$

Now, from the consideration that X mole of lithium and X mole of X, that is basically the total mixture. So, this relation is valid. So, I can always differentiate this and then you put the value of dXx here, replace it with minus dX Li. So, your dG is free energy of lithium minus free energy of x component into dX Li

$$dG = (G_{Li} - G_x)dX_{Li}$$

. $G_{Li} = G_x + \frac{\partial G}{\partial X_{Li}}$

So, therefore, your G Li is Gx plus the partial differentiation of del G with respect to del x lithium. So, in this equation if you multiply both side with X x, then we get X x of G Li and here also Xx of Gx and Xx of del G by del X Li. Then, you add this term X Li G Li in both side.

$$X_{Li}G_{Li} + X_x\ G_{Li} = X_{Li}G_{Li} + X_x\ G_x + X_x \frac{\partial G}{\partial X_{Li}}$$

So, you get this relation. So, that leads you to G Li of x is G mix plus Xx of del G by del X Li. So, differentiation of this will give you this relation, which is nothing, but the tangent and that gives the chemical potential for lithium in the solid solution phase.

$$G_{Li} = G_{mix} + X_x \frac{\partial G_{mix}}{\partial X_{Li}}$$

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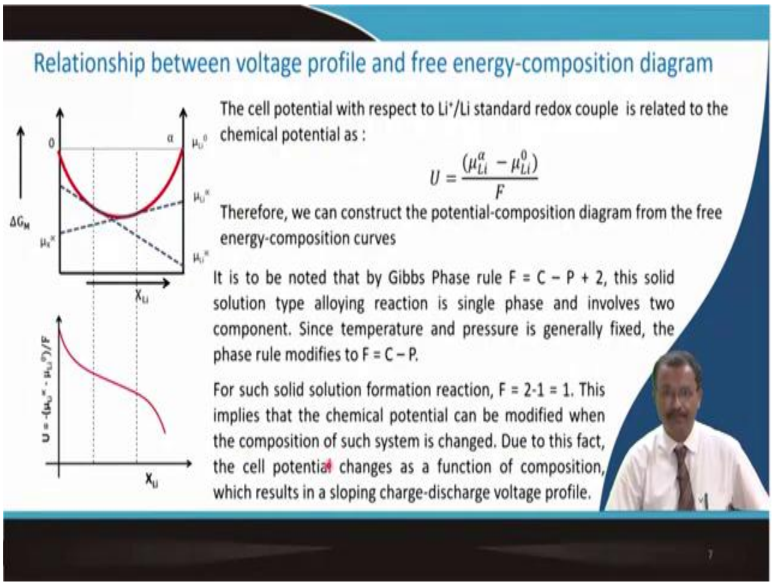

Relationship between voltage profile and free energy-composition diagram

The cell potential with respect to Li⁺/Li standard redox couple is related to the chemical potential as :

$$U = \frac{(\mu_{Li}^\alpha - \mu_{Li}^0)}{F}$$

Therefore, we can construct the potential-composition diagram from the free energy-composition curves

It is to be noted that by Gibbs Phase rule F = C − P + 2, this solid solution type alloying reaction is single phase and involves two component. Since temperature and pressure is generally fixed, the phase rule modifies to F = C − P.

For such solid solution formation reaction, F = 2-1 = 1. This implies that the chemical potential can be modified when the composition of such system is changed. Due to this fact, the cell potential changes as a function of composition, which results in a sloping charge-discharge voltage profile.

So, the cell potential with respect to lithium redox couple is standard redox couple is related to chemical potential and this already we have talked about several times this relation. So, your lithium is here for this particular composition if you take, then draw a tangent here. And, for pure lithium it is in this state, in this state.

$$U = \frac{(\mu_{Li}^\alpha - \mu_{Li}^0)}{F}$$

So, the difference you can get, this difference you can get. And, similarly if you take this composition, here your lithium potential is here and this one is here again. So, this value if you take the lithium potential value with respect to this two composition, then the voltage certainly will get affected.

So, we can see it diagrammatically here. So, here the difference is this and this. So, this difference is relatively small as compared to this difference, which is much larger. So, when lithium composition is low, then it is in this side the higher potential side, when it is relatively higher, then the potential drops down.

So, it get it gets a s type of curve. So, you can apply that Gibbs phase rule which says the degree of freedom is number of component minus phase plus 2. So, this is solid solution type alloying reaction in single phase and involves two component. Since the temperature and pressure is generally constant, then the phase rule modifies to degree of freedom is nothing, but C minus P.

So, here the component is 2 and phase is 1. So, only 1 degree of freedom is there so; that means, it implies that the chemical potential can be modified, when the composition of this system is changed. Due to this fact the cell potential change as a function of composition which results this sloping charge discharge profile. So, this is as simple as that.

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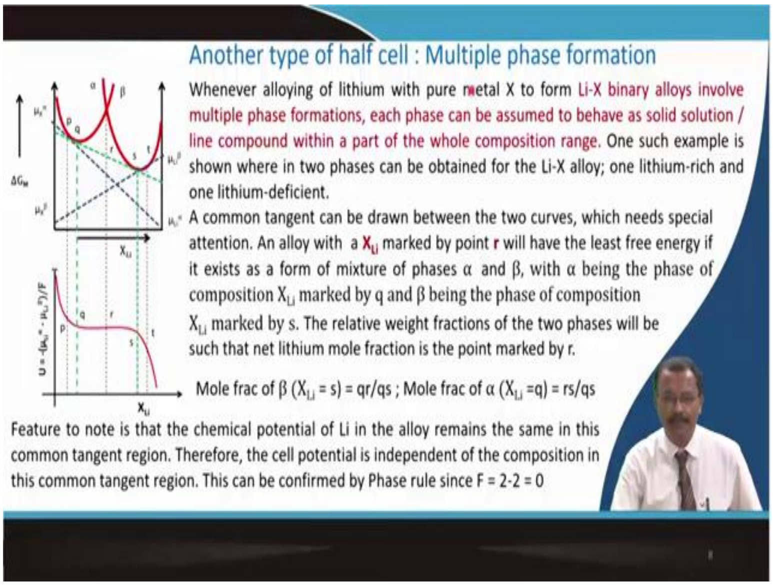

Another type of half cell : Multiple phase formation

Whenever alloying of lithium with pure metal X to form Li-X binary alloys involve multiple phase formations, each phase can be assumed to behave as solid solution / line compound within a part of the whole composition range. One such example is shown where in two phases can be obtained for the Li-X alloy; one lithium-rich and one lithium-deficient.

A common tangent can be drawn between the two curves, which needs special attention. An alloy with a **X_{Li}** marked by point **r** will have the least free energy if it exists as a form of mixture of phases α and β, with α being the phase of composition X_{Li} marked by q and β being the phase of composition X_{Li} marked by s. The relative weight fractions of the two phases will be such that net lithium mole fraction is the point marked by r.

Mole frac of β (X_{Li} = s) = qr/qs ; Mole frac of α (X_{Li} =q) = rs/qs

Feature to note is that the chemical potential of Li in the alloy remains the same in this common tangent region. Therefore, the cell potential is independent of the composition in this common tangent region. This can be confirmed by Phase rule since F = 2-2 = 0

Now, another type of half cell where you use lithium and in particular alloy, which is having multiphase formation. So, two different phase formation you can see. So, whenever alloying of lithium with pure metal X to form Li X type of binary alloy, that involved multiple phase formation, you remember the phase diagram you have alpha, then alpha plus beta and beta. So, there are several phases. So, each phase can assume to behave like a solid solution or a line compound within the part of the whole composition range, you remember the phase diagram which I showed earlier.

So, one such example is shown here in two phase can be obtained in lithium X alloy; one is lithium rich and another one is lithium deficient. Pictographically that also I have shown in one of my earlier slides, you remember with small circles colored in different one is red and another one was green. So, when you draw a common tangent between 2 curves which needs some kind of special attention.

So, an alloy with X Li marked by the point r. So, that is in between here. That will have the least free energy, if it exists as a form of mixture of two phases marked as alpha and beta from the phase diagram. With being alpha is the phase of composition X Li marked by q so, this part. And, beta is a phase of composition X Li marked by s so, this. So, the relative weight fraction of this two phase is such that, the lithium mole fraction is the point which is marked by r, that is from the standard phase diagram and applying the lever rule in it.

So, the mole fraction of beta is given by qr this divided by the whole qs. And, mole fraction of alpha which is in this side, that given by rs divided by the whole qs. Now, the feature that is worth noting is that the chemical potential of lithium in the alloys, remains the same in the common tangent right.

So, the chemical potential will remain same here along with the common tangent. Therefore, the cell potential will not be dramatically affected. So, the cell potential is independent of this composition. So, in the common tangent region you can see, that the cell potential will remain constant and if you apply phase rule here also.

So, component and phase this 2 minus 2 is equal to 0 so; that means, you cannot change anything. So, the with the composition of lithium your voltage will remain same, but when you have the single phase solid solution and as I showed earlier, you will have this kind of drop.

So, this is typical for multiphase for the alloy which forms a multiphase. And, therefore, you can correlate the free energy composition diagram with the voltage, that is resulting from it.

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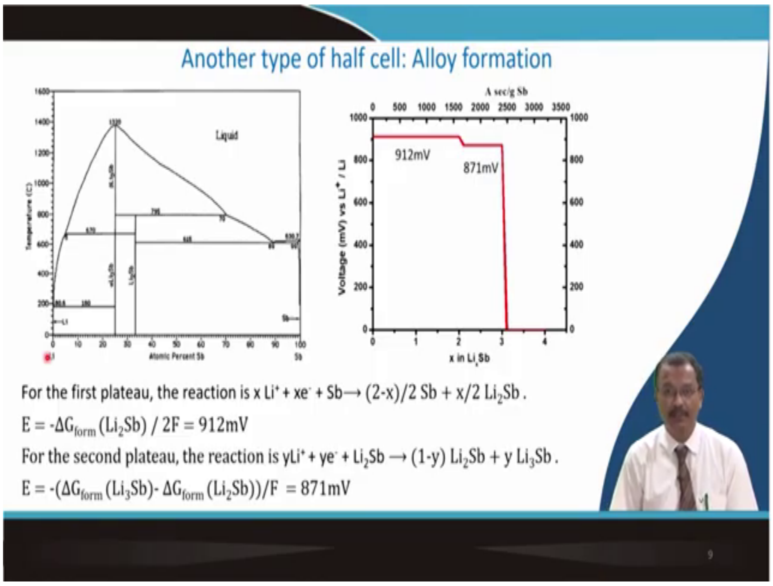

Another type of half cell: Alloy formation

For the first plateau, the reaction is $x\,Li^+ + xe^- + Sb \rightarrow (2-x)/2\ Sb + x/2\ Li_2Sb$.

$E = -\Delta G_{form}(Li_2Sb)\,/\,2F = 912mV$

For the second plateau, the reaction is $yLi^+ + ye^- + Li_2Sb \rightarrow (1-y)\ Li_2Sb + y\ Li_3Sb$.

$E = -(\Delta G_{form}(Li_3Sb) - \Delta G_{form}(Li_2Sb))/F = 871mV$

So, another type of half cell where this alloy formation take place, this also I have defined in antimony and lithium case. So, here the first plateau, the reaction is lithium reacts with antimony to form Li 2 Sb which is given by this line. And, the value of E that is minus del G formation of Li 2 Sb by 2F, because 2 electrons are involved. And, this is can be calculated I will show it, that it will be about 912 milli volt around that. And, for the second plateau whatever you are getting again it is a two phase mixture this is given by this relation.

So, the formation free energy is for Li 3 Sb minus formation of Li 2 S Sb. So, that is this 2 component Li 2 Sb and Li 3 Sb. So, the voltage is 871 milli volt and this kind of step profile you will get in this type of alloy.

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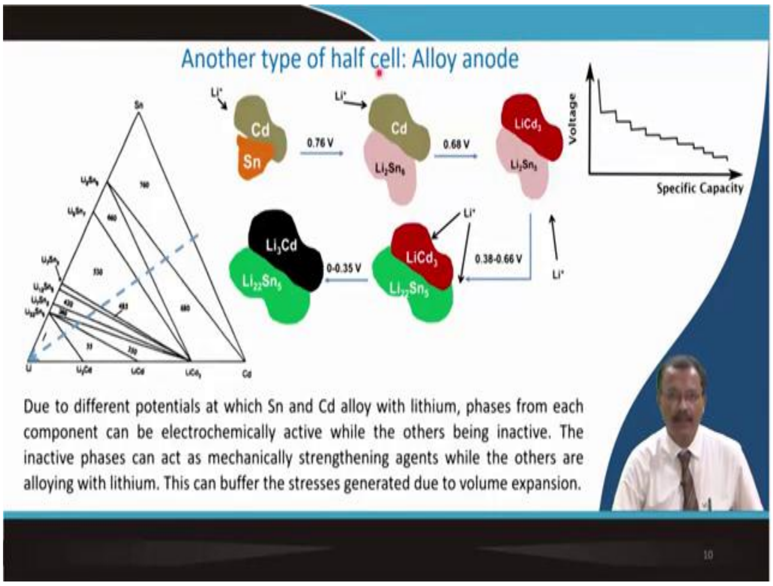

Another type of half cell: Alloy anode

Due to different potentials at which Sn and Cd alloy with lithium, phases from each component can be electrochemically active while the others being inactive. The inactive phases can act as mechanically strengthening agents while the others are alloying with lithium. This can buffer the stresses generated due to volume expansion.

Another example can be shown where it is a ternary kind of phase system. So, this is already I have explained how it forms. So, if you have lithium alloying across this line, then for tin cadmium this binary alloy lithium will progressively form various types of alloying initially it will start to form with this cadmium will remain like this. And, then another voltage which you can calculate back this two will form.

And, then this two phases will form which is apparent from this phase diagram and for this type of multiple alloying reaction for this solid solution this inter metallics, you will get this kind of step profile. So, due to different potential at which tin and cadmium alloy with lithium phase’s form from each component can be electrochemically active while others are being inactive.

The inactive phase can act as a mechanically strengthening agent as I have told that when lithium comes in, then the volume expansion can be buffered by this metallic element. While the other phase that alloy with lithium. So, the presence of this metal eventually at this stage at least, it can reduce the volume expansion and buffer the stress which is generated.

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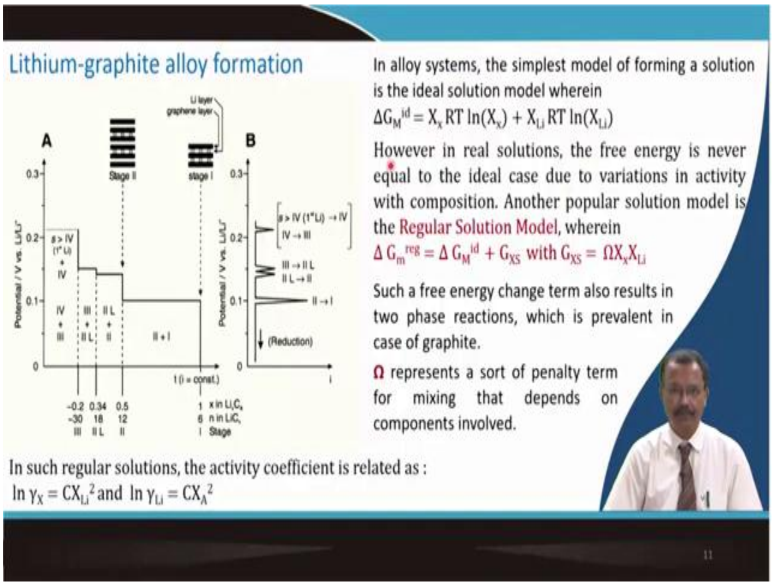

Lithium-graphite alloy formation

In alloy systems, the simplest model of forming a solution is the ideal solution model wherein

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

However in real solutions, the free energy is never equal to the ideal case due to variations in activity with composition. Another popular solution model is the Regular Solution Model, wherein

$\Delta G_m^{reg} = \Delta G_M^{id} + G_{XS}$ with $G_{XS} = \Omega X_x X_{Li}$

Such a free energy change term also results in two phase reactions, which is prevalent in case of graphite.

Ω represents a sort of penalty term for mixing that depends on components involved.

In such regular solutions, the activity coefficient is related as :

$\ln \gamma_X = CX_{Li}^2$ and $\ln \gamma_{Li} = CX_A^2$

In case of lithium graphite alloy formation the simplest model that forming a solution that is the ideal solution that I described this relation this is a bit modified. So, in real solution the free energy is never equal to the ideal case due to the variation in the activity with the composition.

So, when carbon and lithium they form this kind of alloy, then it is not considered as a ideal solution. So, one can use another popular solution model, which is termed as regular solution model, where along with this you have another term which is added. And, this is actually defined by omega into molar fraction of X and lithium X in this case is carbon.

$$\Delta G_m^{reg} = \Delta G_M^{id} + G_{XS} \text{ with } G_{XS} = \Omega X_x X_{Li}$$

So, such free energy change is also results a two phase reaction, which is prevalent in case of graphite as well. So, delta that eventually some kind of penalty term for mixing, that depends on the component which is involved. So, here also the step type of reaction that takes place and as I told the value of S in the last lecture starting from 432 and 1, and this alloying takes place. And, progressively the voltage step kind of voltage profile that you get, the lowest 1 is here.

So, in such regular solution the activity coefficient that can be defined by this relation, I will try to frame a assignment problem to better illustrate this. So, ln gamma X this is CX Li whole square and ln gamma Li is CX A whole square. So, this will be illustrated in the assignment problem set. So, the voltage correspond to this is actually you can see in this view graph as well.

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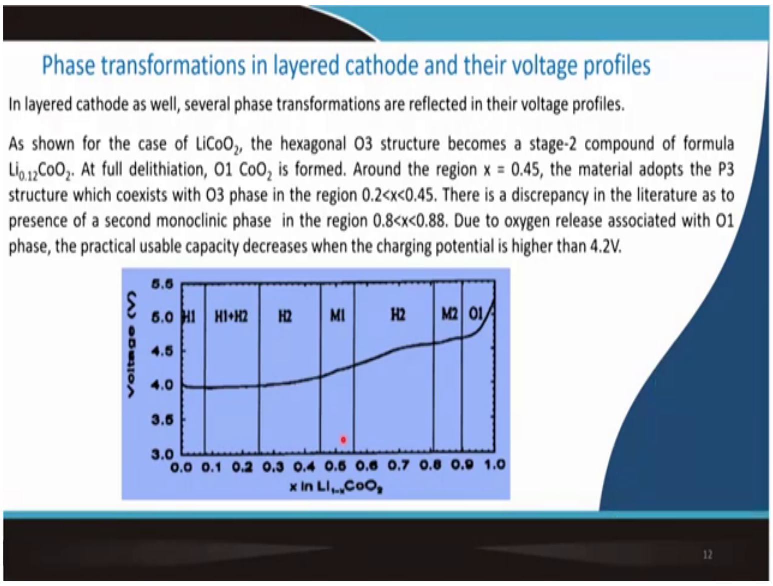

Phase transformations in layered cathode and their voltage profiles

In layered cathode as well, several phase transformations are reflected in their voltage profiles.

As shown for the case of $LiCoO_2$, the hexagonal O3 structure becomes a stage-2 compound of formula $Li_{0.12}CoO_2$. At full delithiation, O1 CoO_2 is formed. Around the region x = 0.45, the material adopts the P3 structure which coexists with O3 phase in the region 0.2<x<0.45. There is a discrepancy in the literature as to presence of a second monoclinic phase in the region 0.8<x<0.88. Due to oxygen release associated with O1 phase, the practical usable capacity decreases when the charging potential is higher than 4.2V.

So, phase transformation already I defined in case of lithium cobalt oxide several phase transformation that is possible. So, in case lithium cobalt oxide hexagonal O3 structure becomes a stage-2 compound with formula of typical formula of Li 0.12 Cobalt Oxide. At full delithiation, O1 type of cobalt oxide formed. Around the region x equal to 0.45 the material adopts a P3 structure.

All these I have explained in my last lecture, which coexist with O3 phase in this region when the lithium content is in between 0.45 to 0.2. Although there is a discrepancy in the literature, the presence of a second monoclinic phase in the region typically here. So, here oxygen start to release and that is associated with O1 phase, the practicable usable capacity when charging potential is higher than 4.2, then this oxygen evolution cannot be avoided.

So, we will limit the lithium extraction from lithium cobalt oxide, because of this structural complicacy up to 0.5 up to 5.5 lithium. So, according to the Faraday law, if you estimate the capacity we will find this estimated capacity of lithium cobalt oxide is pretty large, but actually it is halved because you are not able to extract the whole lithium out of it.

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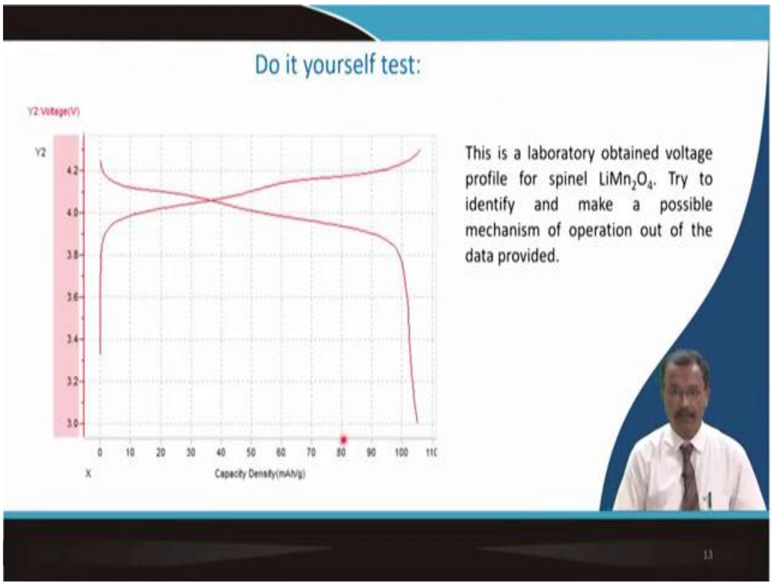

Do it yourself test:

This is a laboratory obtained voltage profile for spinel $LiMn_2O_4$. Try to identify and make a possible mechanism of operation out of the data provided.

So, I have given a typical charge discharge profile of lithium manganese oxide a well known spinel. So, you can try to identify based on the lecture that we had so, far we are discussing, you can try to identify and make a possible mechanism of operations. So, what is happening during charging up to this? What is happening in this plateau and during discharge what is happening here, and what is also happening here and what is happening here?

So, based on the discussion I leave it on you to provide an explanation and come up with your answer.

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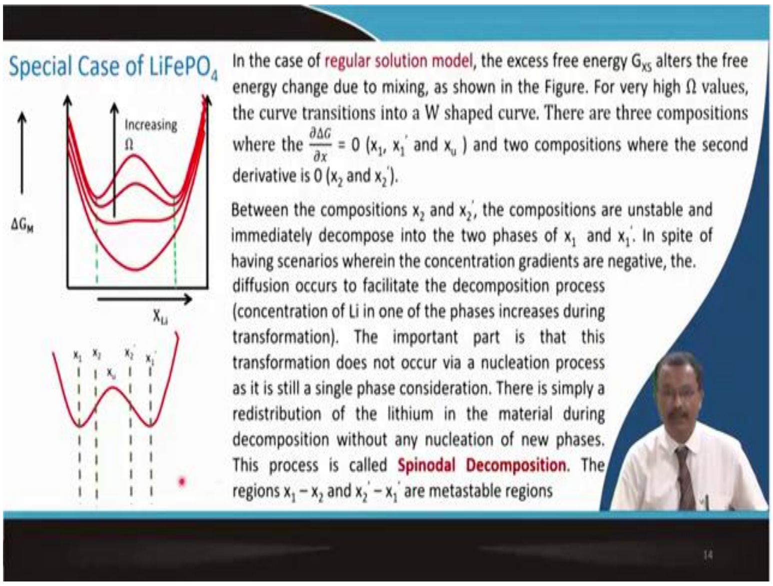

Special Case of $LiFePO_4$

In the case of regular solution model, the excess free energy G_{XS} alters the free energy change due to mixing, as shown in the Figure. For very high Ω values, the curve transitions into a W shaped curve. There are three compositions where the $\frac{\partial \Delta G}{\partial x} = 0$ (x_1, x_1' and x_u) and two compositions where the second derivative is 0 (x_2 and x_2').

Between the compositions x_2 and x_2', the compositions are unstable and immediately decompose into the two phases of x_1 and x_1'. In spite of having scenarios wherein the concentration gradients are negative, the. diffusion occurs to facilitate the decomposition process (concentration of Li in one of the phases increases during transformation). The important part is that this transformation does not occur via a nucleation process as it is still a single phase consideration. There is simply a redistribution of the lithium in the material during decomposition without any nucleation of new phases. This process is called **Spinodal Decomposition**. The regions $x_1 - x_2$ and $x_2' - x_1'$ are metastable regions

A special case is lithium iron phosphate where this regular solution model is prevalent then the ideal solution model. We talked about the excess free energy term this alters the free energy change due to mixing so, as shown in the figure. So, this term when this omega term increases, then from regular this type of bold type of free energy diagram as you increase this delta term, you see that slowly it goes to a 2 minima condition.

So, for very high omega value, the curve transition to a W type of curve. So, there are three composition where this partial derivative of free energy with x is 0; one is x 1 another one is x 1 dash and here another one is x 1 and the third one is x of lithium which is here. So, these three cases you have this partial derivative is 0, and, two compositions, where the second derivative is 0. So, this two composition this x 2 and this x 2 dash, which is in between this slope, it is 0.

So, between the composition of x 2 and x 2 dash this composition are unstable and immediately decomposes into x 1 and x 1 dash phase. So, in spite of having the scenario, where in the concentration gradient is negative, the diffusion occurs to facilitate, the decomposition process. So, the composition or rather concentration of lithium in one of the phase increase during this transformation.

The important part is that the transformation does not occur via a nucleation process. So, that is very important, as it is still a single phase consideration. So, there is a I remember in case of the alloy we talked about say antimony and tin. So, this nucleates and then grows, but this is not a two phase system. So, there is simply a redistribution of lithium in the material during the decomposition, without any nucleation of a new phase. So, this particular process that is known as spinodal decomposition, which some of the metallurgists may be familiar of.

And, the region x 1 to x 2 and x 2 dash x 2 dash to x 1, they are actually meta stable regions.

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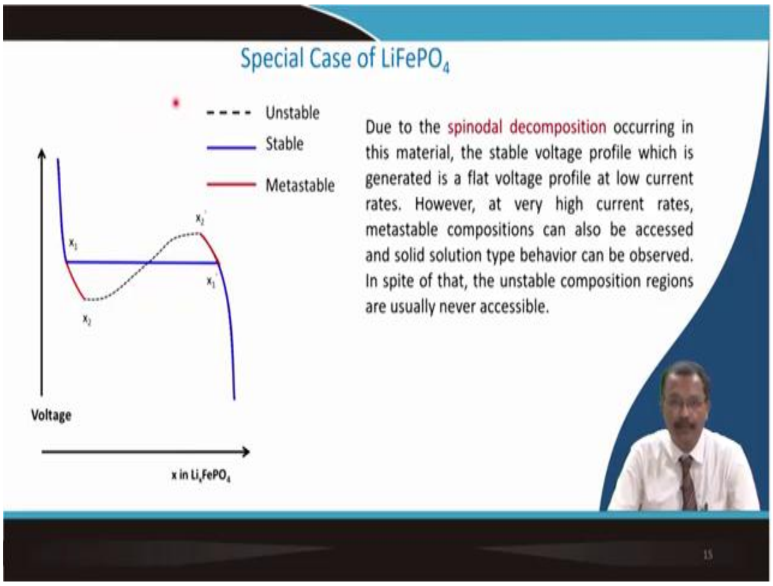

Special Case of $LiFePO_4$

Due to the spinodal decomposition occurring in this material, the stable voltage profile which is generated is a flat voltage profile at low current rates. However, at very high current rates, metastable compositions can also be accessed and solid solution type behavior can be observed. In spite of that, the unstable composition regions are usually never accessible.

So, now if you have the voltage profile due to this spinodal decomposition, the stable voltage profile is generated whatever is generated is this flat voltage profile. And, this is occurring at a relatively lower current of discharge. However, when a very high current rates are applied, then this metastable region, that can also be accessed and solid solution type behavior you can see where this sloping profile you can see here right. In spite of that the unstable composition regions; usually they are never accessed except for a very high current probably it will look like this.

But, like the two phase type of alloy always you get a flat profile like this one, not the one that has been shown here except for a very high current. So, the mechanism of the this two things are very different, but the profile is more or less similar in nature.

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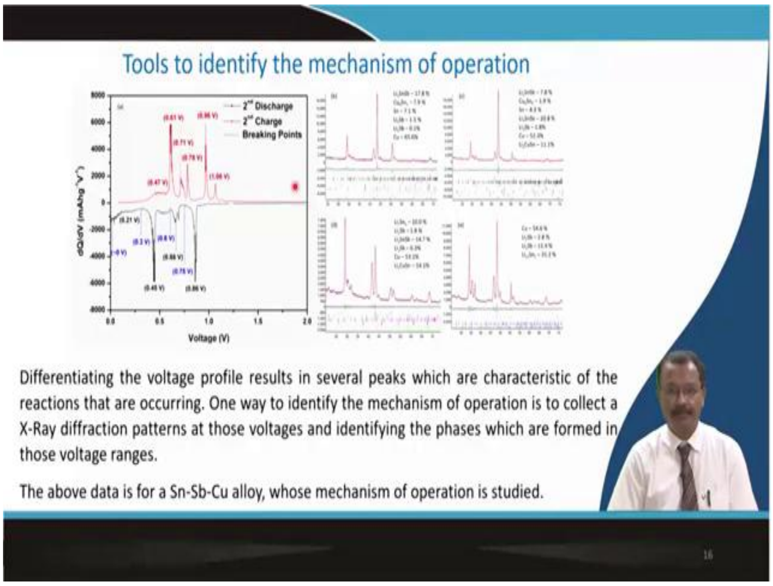

Tools to identify the mechanism of operation

Differentiating the voltage profile results in several peaks which are characteristic of the reactions that are occurring. One way to identify the mechanism of operation is to collect a X-Ray diffraction patterns at those voltages and identifying the phases which are formed in those voltage ranges.

The above data is for a Sn-Sb-Cu alloy, whose mechanism of operation is studied.

Now, once you get the discharge profile like, the 1 like this and this. In order to better understand this profile what we do, we do a differential capacity plot, where we plot the dQ Dv, where Q is the charge the capacity with respect to voltage. And, plot it with the respective voltage to get this kind of dQ Dv curve. So, particularly for the step reaction for alloy materials, we do this thing. And, wherever the oxidation and reduction takes place, this is this gives a very sharp because there is a change in slope.

So, there is a very sharp peak oxidation and reduction peak, that is observed. And, schematically it is shown for various compositions through the X-Ray diffraction studies. And each of this particular phase is identified, whether indeed during oxidation and reduction this kind of alloys are forming you can stop your measurement right at that point and then this electrode you can do the X-Ray diffraction to identify the phase. And, then indeed whether it is forming or not that can be identified and at which voltage it is forming that also can be identified.

So, this is a very useful technique of differentiating the voltage profile they result several peaks which are characteristics of the reaction that is occurring. So, one way to identify the mechanism of operation is to collect the X-Ray diffraction pattern at those voltages to identify this phase, which are formed in those voltage ranges.

So, this above data, this data is our own data on a system tin antimony copper. So, tin and antimony they indeed form alloy with lithium and copper acts as a buffered layer.

So, the stress basically is buffered through the dislocation movement along the slip plane. So, that is I have cited as one of the examples.

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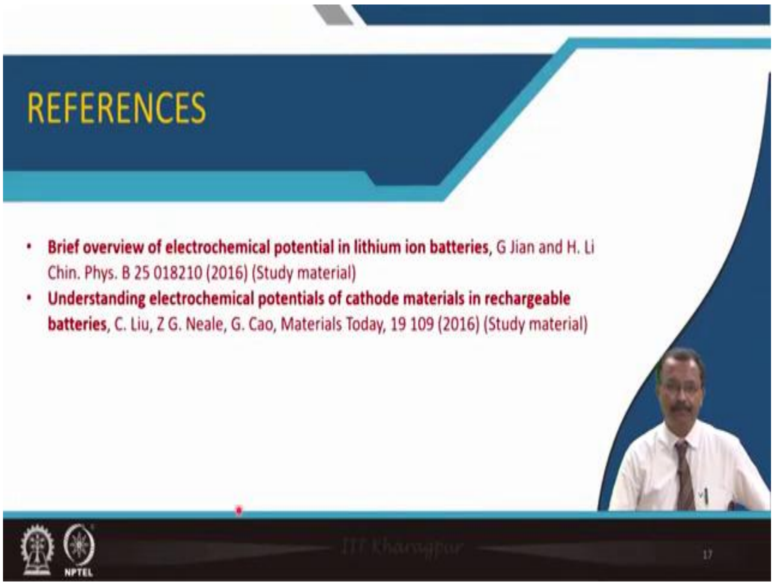

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- **Brief overview of electrochemical potential in lithium ion batteries**, G Jian and H. Li Chin. Phys. B 25 018210 (2016) (Study material)
- **Understanding electrochemical potentials of cathode materials in rechargeable batteries**, C. Liu, Z G. Neale, G. Cao, Materials Today, 19 109 (2016) (Study material)

So, again there are two important publications that is the study material for this part of the work. And, this these two papers will give you a more insight about the topic covered.

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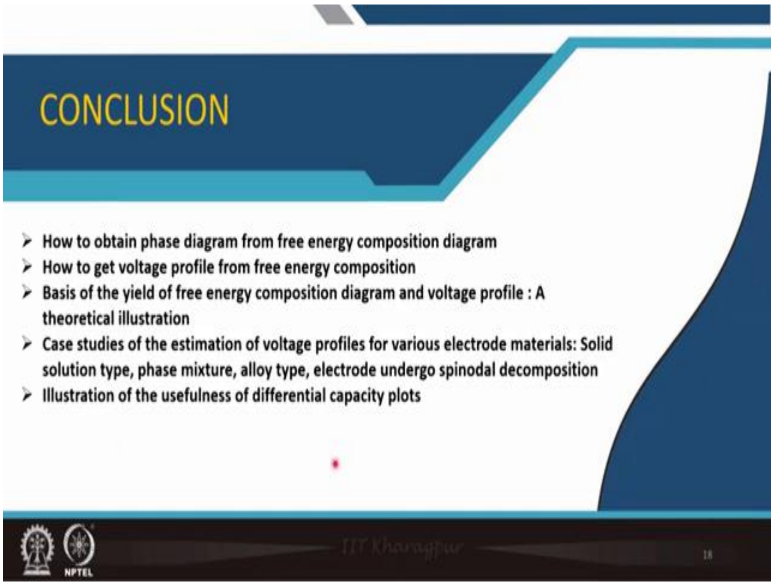

CONCLUSION

- How to obtain phase diagram from free energy composition diagram
- How to get voltage profile from free energy composition
- Basis of the yield of free energy composition diagram and voltage profile : A theoretical illustration
- Case studies of the estimation of voltage profiles for various electrode materials: Solid solution type, phase mixture, alloy type, electrode undergo spinodal decomposition
- Illustration of the usefulness of differential capacity plots

So, wherein this particular lecture I have demonstrated that how to obtain the phase diagram from free energy composition diagram, then how to get the voltage profile from free energy composition? Then basis of the yield of free energy composition diagram and voltage profile; a theoretical illustration has been done. And, I will suggest you to do a line by line calculation, to estimate the straight line, the tangential line that gives you, the estimation of mu of lithium.

And, then point by point analysis of the free energy; versus composition diagram to see the exact voltage profile in case of a single phase, or at least binary phase electrode material. And, then a case study of estimation of voltage profile of various electrode material, we will talk more on it during the case study the remaining 2 lectures, solid solution type, phase mixture type, alloy type, and the electrode which undergoes a spinodal decomposition.

And, finally, the illustration of the usefulness of differential capacity plot.

Thank you for your attention.