Electrochemical Energy Storage
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Module - 01
Introduction to electrochemical energy storage and conversion
Lecture - 05
Kinetics of Electrochemical Cells and Structural Characteristics of Electrodes

Welcome to the course Electrochemical Energy Storage and we are in module 1 at the last lecture, lecture number 5, where I will be still continuing the thermodynamic aspect Kinetics of Electrochemical Cells. Then, I will introduce briefly the Structural Characteristics of the Electrode materials.

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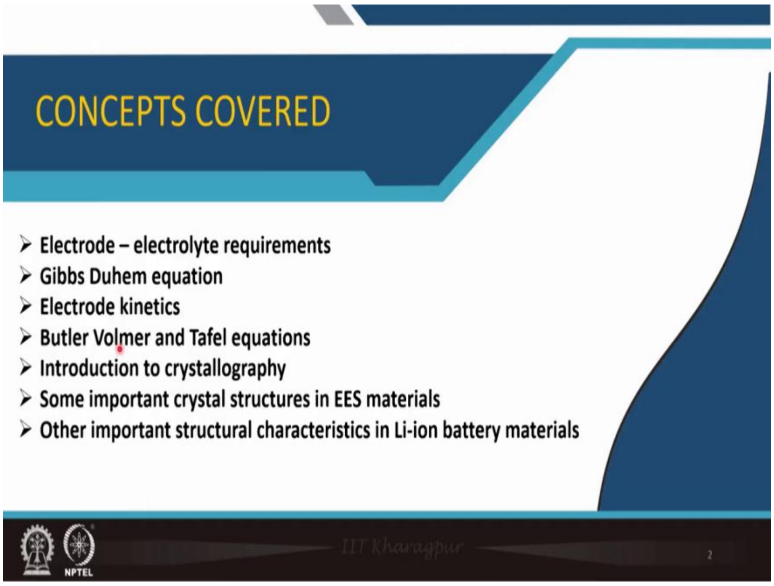

CONCEPTS COVERED

- Electrode – electrolyte requirements
- Gibbs Duhem equation
- Electrode kinetics
- Butler Volmer and Tafel equations
- Introduction to crystallography
- Some important crystal structures in EES materials
- Other important structural characteristics in Li-ion battery materials

Now, you know that in this particular lecture, we will consider electrode and electrolyte requirements to construct a cell. Then, we will introduce Gibbs-Duhem equation which is important to understand the other concepts I will teach.

Then, we will talk about electrode kinetics and its origin. And in order to do that, I will talk about Butler-Volmer and Tafel equations which are very important to understand a certain basics of electrochemical energy storage.

Then, I will briefly introduce the elementary crystallography and some important crystal structure pertinent to electrochemical energy storage and then, other important structural characteristics of lithium-ion battery materials.

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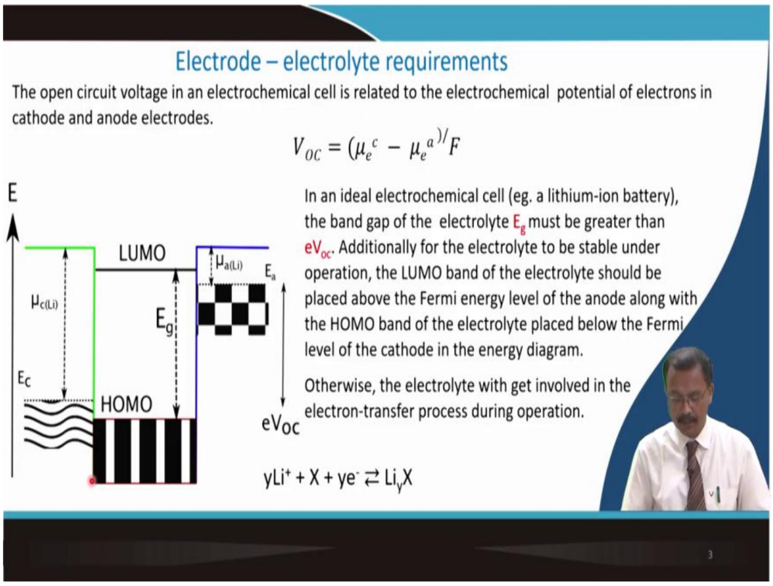

Electrode – electrolyte requirements

The open circuit voltage in an electrochemical cell is related to the electrochemical potential of electrons in cathode and anode electrodes.

$$V_{OC} = (\mu_e{}^c - \mu_e{}^a)/F$$

In an ideal electrochemical cell (eg. a lithium-ion battery), the band gap of the electrolyte E_g must be greater than eV_{oc}. Additionally for the electrolyte to be stable under operation, the LUMO band of the electrolyte should be placed above the Fermi energy level of the anode along with the HOMO band of the electrolyte placed below the Fermi level of the cathode in the energy diagram.

Otherwise, the electrolyte with get involved in the electron-transfer process during operation.

$$yLi^+ + X + ye^- \rightleftarrows Li_yX$$

So, you know that we already have this term defined and as you can see that there is open circuit voltage that I was talking about, this is the difference of the chemical potential of electron in cathode and anode.

$$V_{OC} = (\mu_e{}^c - \mu_e{}^a)/F$$

So, it is shown here the cathode which is given in the left-hand side and anode in the right-hand side. So, in an ideal electrochemical cell the band gap of the electrolyte, which is E_g, must be greater than this voltage eV_{OC}.

In addition to that, electrolyte to be stable under operation, it should not dissociate.

So, the LUMO band of the electrolyte should be placed above the Fermi energy level of the anode.

And on the other hand, the HOMO band this should be placed below the Fermi level of the cathode. This is required otherwise the electrolyte will get involved in the electron transfer process during operation.

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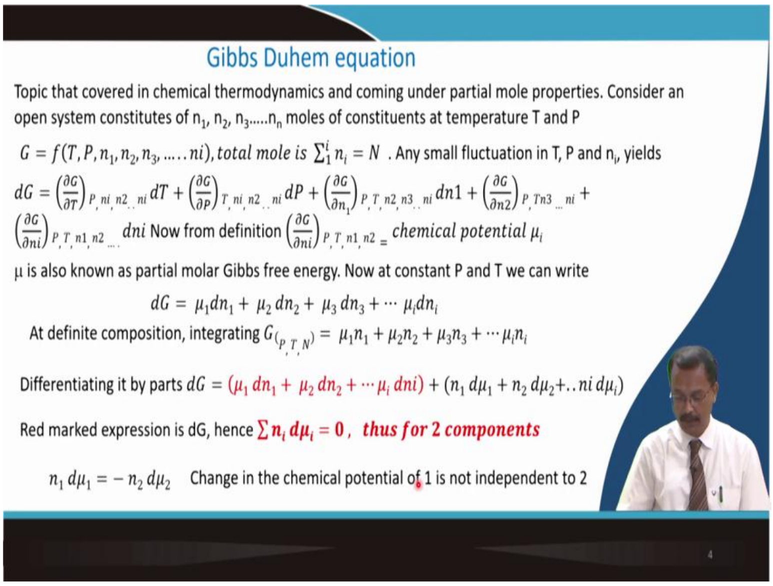

Gibbs Duhem equation

Topic that covered in chemical thermodynamics and coming under partial mole properties. Consider an open system constitutes of n_1, n_2, n_3.....n_n moles of constituents at temperature T and P

$G = f(T, P, n_1, n_2, n_3, \ldots..ni), total\ mole\ is\ \sum_1^i n_i = N$. Any small fluctuation in T, P and n_i, yields

$dG = \left(\frac{\partial G}{\partial T}\right)_{P,ni,n2..ni} dT + \left(\frac{\partial G}{\partial P}\right)_{T,ni,n2..ni} dP + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n2,n3..ni} dn1 + \left(\frac{\partial G}{\partial n2}\right)_{P,Tn3...ni} +$ $\left(\frac{\partial G}{\partial ni}\right)_{P,T,n1,n2....} dni$ Now from definition $\left(\frac{\partial G}{\partial ni}\right)_{P,T,n1,n2} =$ $chemical\ potential\ \mu_i$

μ is also known as partial molar Gibbs free energy. Now at constant P and T we can write

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \cdots \mu_i dn_i$$

At definite composition, integrating $G_{(P,T,N)} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \cdots \mu_i n_i$

Differentiating it by parts $dG = (\mu_1 dn_1 + \mu_2 dn_2 + \cdots \mu_i dni) + (n_1 d\mu_1 + n_2 d\mu_2 + .. ni\, d\mu_i)$

Red marked expression is dG, hence $\sum n_i d\mu_i = 0$, ***thus for 2 components***

$n_1 d\mu_1 = -n_2 d\mu_2$ Change in the chemical potential of 1 is not independent to 2

Now, in chemical thermodynamics, Gibbs-Duhem equation is a concept which comes under partial molar properties. Consider an open system with n_1, n_2, n_3…..n_n moles of constituents at temperature T and P. So, you can write the free energy that is a function of temperature, pressure and moles.

$$G = f(T, P,\ n_1,\ n_2,\ n_3,\ \ldots..n_i),\ total\ mole\ is\ \sum_1^i n_i = N$$

So, any small fluctuation either in temperature or in pressure or in this mole fraction n_i actually yields the following result.

$$dG = \left(\frac{\partial G}{\partial T}\right) P, ni,\ n2..ni\ dT + \left(\frac{\partial G}{\partial P}\right) T, ni,\ n2\ ..ni\ dP + \left(\frac{\partial G}{\partial n_1}\right) P, T,\ n2,\ n3..ni\ dn1 + \left(\frac{\partial G}{\partial n_2}\right) P, Tn3 \ldots ni + \ldots\ + \left(\frac{\partial G}{\partial n_i}\right) P, T,\ n1, n2 \ldots.\ dni$$

So, now, from the definition,

$$\left(\frac{\partial G}{\partial n_i}\right) P, T,\ n1,\ n2 \ldots. = chemical\ potential\ \mu_i$$

μ is also known as partial molar Gibbs free energy.

Now at constant P and T we can write

$$dG = \mu_1 dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \ldots\ \mu_i dn_i$$

At definite composition, integrating $G_{(P,T,N)} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots \mu_i n_i$

Differentiating it by parts

$$dG = (\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots \mu_i\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots n_i\, d\mu_i)$$

Red marked expression is dG, hence

$$\sum n_i\, d\mu_i = 0$$

For two components

$$n_1\, d\mu_1 = -\, n_2\, d\mu_2$$

So, this is actually the Gibbs Duhem equation. From this, I can understand that any change in chemical potential of any one of this component which is there in the system is not independent with the other component. The other component will also change to maintain this relationship. So, if you change the chemical potential of one particular component, the other component will also get affected.

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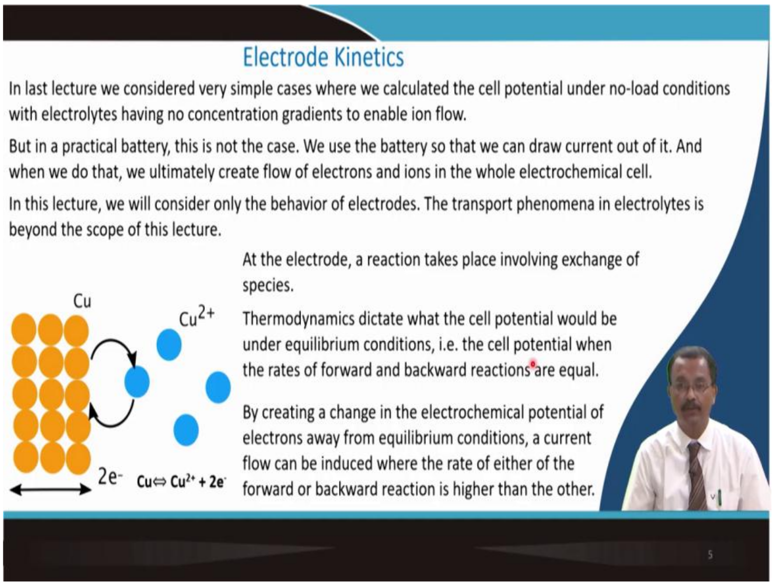

Electrode Kinetics

In last lecture we considered very simple cases where we calculated the cell potential under no-load conditions with electrolytes having no concentration gradients to enable ion flow.

But in a practical battery, this is not the case. We use the battery so that we can draw current out of it. And when we do that, we ultimately create flow of electrons and ions in the whole electrochemical cell.

In this lecture, we will consider only the behavior of electrodes. The transport phenomena in electrolytes is beyond the scope of this lecture.

At the electrode, a reaction takes place involving exchange of species.

Thermodynamics dictate what the cell potential would be under equilibrium conditions, i.e. the cell potential when the rates of forward and backward reactions are equal.

By creating a change in the electrochemical potential of electrons away from equilibrium conditions, a current flow can be induced where the rate of either of the forward or backward reaction is higher than the other.

So, now, we will talk about the electrode kinetics. In the last lecture, we considered a very simple case where we calculated the cell potential under no-load condition. But if you consider a practical battery, this is certainly not the case, we use the battery so that we can draw current out of it right.

So ultimately, we create a flow of electron and ions in the whole electrochemical cell. Consider a Daniel cell zinc and copper, you are connected with a wire so, zinc gets oxidized; electron flows from the wire and goes to the cathode; and from the electrolyte copper ions take this electron. And then, they get reduced. So, this part when a flow of electron is there, it is not under open circuit condition. So, we will consider only this behavior of electrode, the transport phenomena of the electrolyte is actually beyond the scope of this particular lecture.

So, at the electrode, a reaction takes place involving the exchange of the species. So, thermodynamics dictates that what is the cell potential would be under equilibrium condition when the rates of forward and backward reactions are equal.

So, by creating a change in the electrochemical potential of the electrons away from the equilibrium condition, a current flow can be induced, where the rate of either of the forward or backward reaction is higher than the other. So, that is the concept of the so-called electrode kinetics. So, we will elaborate it.

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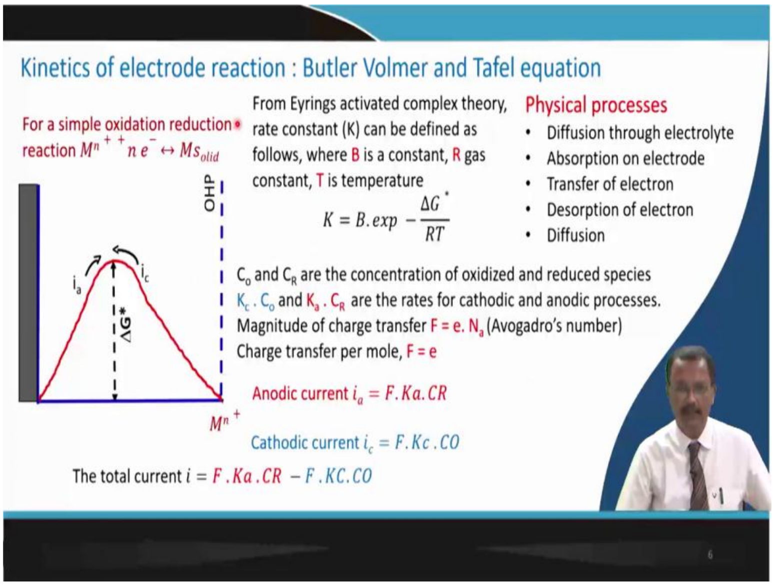

Kinetics of electrode reaction : Butler Volmer and Tafel equation

For a simple oxidation reduction reaction $M^{n+} + n e^- \leftrightarrow Ms_{olid}$

From Eyrings activated complex theory, rate constant (K) can be defined as follows, where B is a constant, R gas constant, T is temperature

$$K = B.exp - \frac{\Delta G^*}{RT}$$

Physical processes

- Diffusion through electrolyte
- Absorption on electrode
- Transfer of electron
- Desorption of electron
- Diffusion

C_o and C_R are the concentration of oxidized and reduced species

$K_c . C_o$ and $K_a . C_R$ are the rates for cathodic and anodic processes.

Magnitude of charge transfer F = e. N_a (Avogadro's number)

Charge transfer per mole, F = e

Anodic current $i_a = F.Ka.CR$

Cathodic current $i_c = F.Kc.CO$

The total current $i = F.Ka.CR - F.KC.CO$

From Eyring’s activated complex theory

Rate constant (K) can be defined as follows, where B is a constant, R gas constant, T is temperature

$$K = B.\ exp\ (-\frac{\Delta G *}{RT})$$

So, again, you consider the physical process what is going on, diffusion is prevailing through electrolyte. Lithium-ion is coming from anode or cathode and going to the respective other electrode. Then, absorption on the electrode is taking place. At this point, transfer of electron is possible. Electron is coming from the outer circuit and then, transfer of electron possible and then finally, desorption of electron is taking place at the interface. This lithium is finally diffusing inside the electrode. So, electrolyte diffusion is there, absorption of this charge species is there, transfer of electron is there, desorption of electron is there. And then finally, diffusion of the uncharged species inside the active material is occuring.

C_o and C_R are the concentration of oxidized and reduced species

$K_c . C_o$ and $K_a . C_R$ are the rates for cathodic and anodic processes.

Magnitude of charge transfer F = e. N_a (Avogadro’s number)

Charge transfer per mole, F = e

I can always write the anodic current as

Anodic current $i_a = F.\ K_a.C_R$

Cathodic current i_c=F. $K_c.C_O$

Total Current i = $F.\ K_a.C_R -$ F. $K_c.C_O$

So, under equilibrium process, probably this two anodic and cathodic current will be equal. So, this is your electrode surface. And here, there is a potential barrier, it must cross for this anodic and cathodic current to flow and this is the Helmholtz plane which I already defined so, that is due to this charged surface this double layer this plane that is there.

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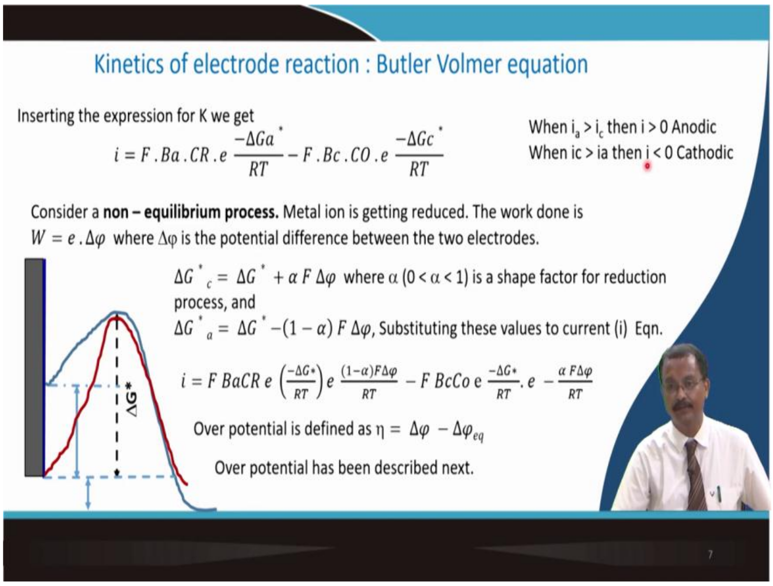

Kinetics of electrode reaction : Butler Volmer equation

Inserting the expression for K we get

$$i = F\,.Ba\,.CR\,.e\,\frac{-\Delta Ga^*}{RT} - F\,.Bc\,.CO\,.e\,\frac{-\Delta Gc^*}{RT}$$

When $i_a > i_c$ then i > 0 Anodic

When ic > ia then i < 0 Cathodic

Consider a **non – equilibrium process.** Metal ion is getting reduced. The work done is $W = e\,.\Delta\varphi$ where Δφ is the potential difference between the two electrodes.

$\Delta G^*_c = \Delta G^* + \alpha F \Delta\varphi$ where α (0 < α < 1) is a shape factor for reduction process, and

$\Delta G^*_a = \Delta G^* -(1-\alpha) F \Delta\varphi$, Substituting these values to current (i) Eqn.

$$i = F\,BaCR\,e\left(\frac{-\Delta G*}{RT}\right)e\,\frac{(1-\alpha)F\Delta\varphi}{RT} - F\,BcCo\,e\,\frac{-\Delta G*}{RT}.\,e\,-\frac{\alpha F\Delta\varphi}{RT}$$

Over potential is defined as $\eta = \Delta\varphi - \Delta\varphi_{eq}$

Over potential has been described next.

Inserting the expression for K we get

$$i = F.\ B_a.C_R\ .\ e\ \frac{-\Delta G_a^*}{RT} - F\ .B_c.C_O\ .\ e\ \frac{-\Delta G_a^*}{RT}$$

So, clearly when this anodic current is more than the cathodic current, then total current is positive. When cathodic current is more than anodic current, then the total current is negative. So, we call it is a cathodic process.

So, now, you consider an equilibrium process. So, in the non-equilibrium process so, metal ion is getting reduced, the work done is we can define this electron and the potential difference because now, it is not any more equilibrium process, but one is favorable with respect to others.

So, this was the red one was the so-called equilibrium process, but the blue one is a non-equilibrium process. You can see that if this if it if I consider this is cathodic, if it wants to go, you will have to cross an extra barrier here and then, pass this barrier and move here and on the other hand, in case of anodic process, you are gaining this so, you will have to go from only here to here. So, this is the difference.

So, in the cathodic process as I have said that del G star plus this alpha F and potential difference where this alpha term is a shape factor, it defines that where exactly is this electron, what is their position so, either it could be at 0 at 1 time one end and 1 is an other end so, the value will be in between 0 to 1.

So, you will have to cross this barrier and in case of anode, basically this one is gaining so, del G minus 1 minus alpha and F and del phi so, I can substitute the value for current i equation which I derive here.

$\Delta G^*_c = \Delta G^* + \alpha F \Delta\varphi$ where α ($0 < \alpha < 1$) is a shape factor for reduction process, and

$$\Delta G^*_a = \Delta G^* - (1-\alpha) F \Delta\varphi$$

$$i = F.\ B_a.C_R\ e \left(\frac{-\Delta G^*}{RT}\right) e\ \frac{(1-\alpha)F\Delta\varphi}{RT} - F\ .B_c.C_O\ e\ \frac{-\Delta G^*}{RT}.\ e - \frac{\alpha\ F\Delta\varphi}{RT}$$

So, I can define the over potential which is

$$\eta = \Delta\varphi - \Delta\varphi_{eq}$$

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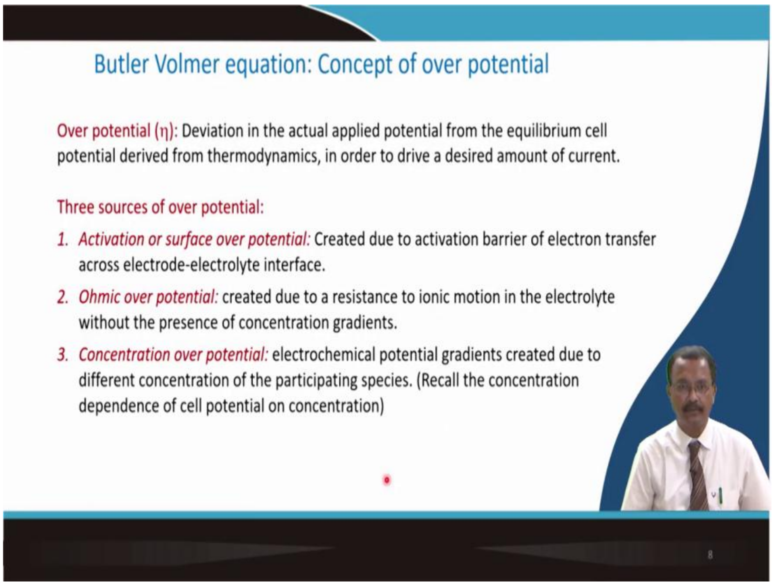

Butler Volmer equation: Concept of over potential

Over potential (η): Deviation in the actual applied potential from the equilibrium cell potential derived from thermodynamics, in order to drive a desired amount of current.

Three sources of over potential:

1. *Activation or surface over potential:* Created due to activation barrier of electron transfer across electrode-electrolyte interface.
2. *Ohmic over potential:* created due to a resistance to ionic motion in the electrolyte without the presence of concentration gradients.
3. *Concentration over potential:* electrochemical potential gradients created due to different concentration of the participating species. (Recall the concentration dependence of cell potential on concentration)

So, over potential is defined as eta and this is a deviation from actual applied potential from equilibrium cell potential derived from thermodynamics, in order to drive a desired amount of current. So, there are three possible sources of this over potential. The 1st one is we call activation or surface potential that is basically created due to the activation barrier of electron transfer across the electrode-electrolyte interface.

2nd one is the ohmic over potential that is created due a resistance to ionic motion in the electrolyte, because ions are moving through the electrolyte in presence of a concentration gradient which otherwise was not there when we were talking about the equilibrium kind of situation. 3rd one is the concentration over potential.

So, electrochemical potential gradient is created due to the different concentration of the participating species. So, remember when we estimate the cell potential, it varies with the concentration.

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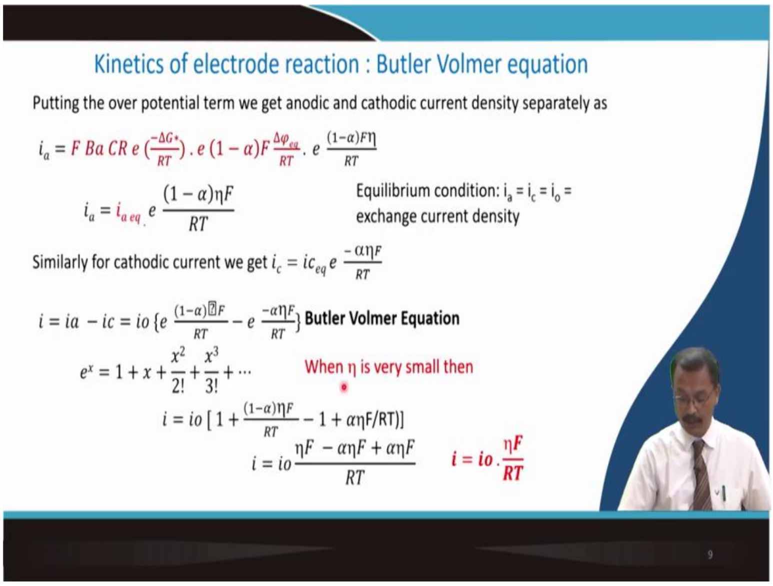

Kinetics of electrode reaction : Butler Volmer equation

Putting the over potential term we get anodic and cathodic current density separately as

$$i_a = F\ Ba\ CR\ e\ (\frac{-\Delta G*}{RT})\ .\ e\ (1-\alpha)F\frac{\Delta\varphi_{eq}}{RT}.\ e\ \frac{(1-\alpha)F\eta}{RT}$$

$$i_a = i_{a\ eq}\ e\ \frac{(1-\alpha)\eta F}{RT}$$

Equilibrium condition: $i_a = i_c = i_o =$ exchange current density

Similarly for cathodic current we get $i_c = ic_{eq}\ e\ \frac{-\alpha\eta F}{RT}$

$$i = ia - ic = io\ \{e\ \frac{(1-\alpha)\square F}{RT} - e\ \frac{-\alpha\eta F}{RT}\}$$ **Butler Volmer Equation**

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

When η is very small then

$$i = io\ [1 + \frac{(1-\alpha)\eta F}{RT} - 1 + \alpha\eta F/RT)]$$

$$i = io\frac{\eta F - \alpha\eta F + \alpha\eta F}{RT}$$

$$i = io\ .\frac{\eta F}{RT}$$

So, this over potential term I will now introduce in anodic current

$$i_a = F.\ B_a.C_R\ e\ (\frac{-\Delta G*}{RT})\ .\ \mathrm{e}\ \frac{(1\text{-}\alpha)\mathrm{F}\Delta\varphi_{eq}}{\mathrm{RT}}.\ \ e\ \frac{(1-\alpha)F\eta}{RT} = i_a{}^{eq}\ .\ e\ \frac{(1-\alpha)\eta F}{RT}$$

Similarly for cathodic current we get $i_c = i_c{}^{eq}\ e\ \frac{-\alpha\eta F}{RT}$

Equilibrium condition: $i_a = i_c = i_o$ = exchange current density

$i = i_a - i_c = i_0\ \{e\ \frac{(1-\alpha)\eta F}{RT} - e\ \frac{-\alpha\eta F}{RT}\}$ [Butler Volmer Equation]

Now, when this over potential is very small, then you can put this exponential series and take the first two term.

$$\mathrm{e}^{\mathrm{x}} = 1 + x + \frac{x2}{2!} + \frac{x3}{3!} + \cdots$$

$\mathrm{i}=i_0\ [\ 1+\frac{(1\text{-}\alpha)\eta\mathrm{F}}{\mathrm{RT}}\text{-}1+\ \alpha\eta\mathrm{F}/\mathrm{RT})]$

$$\mathrm{i}=i_0\frac{\eta\mathrm{F}\ \text{-}\alpha\eta\mathrm{F}+\alpha\eta\mathrm{F}}{\mathrm{RT}} = i_0\ .\frac{\eta F}{RT}$$

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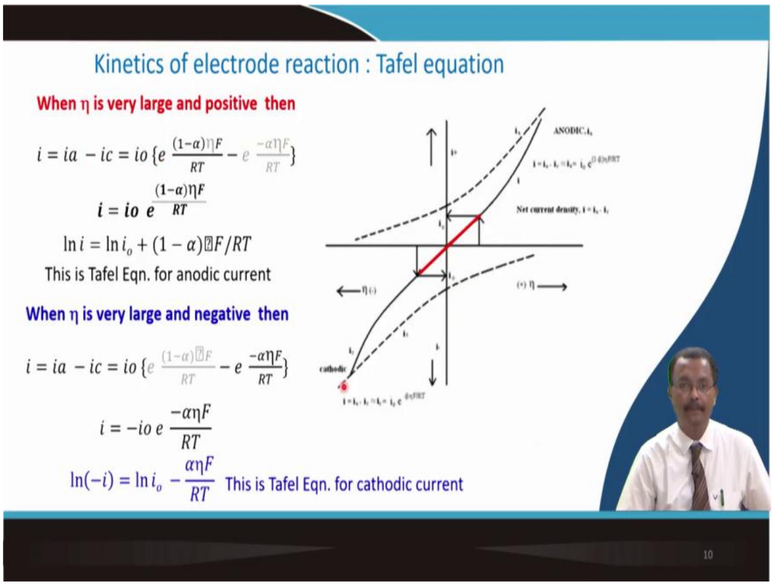

Kinetics of electrode reaction : Tafel equation

When η is very large and positive then

$$i = ia - ic = io\left\{e^{\frac{(1-\alpha)\eta F}{RT}} - e^{\frac{-\alpha\eta F}{RT}}\right\}$$

$$i = io\ e^{\frac{(1-\alpha)\eta F}{RT}}$$

$$\ln i = \ln i_o + (1-\alpha)\square F/RT$$

This is Tafel Eqn. for anodic current

When η is very large and negative then

$$i = ia - ic = io\left\{e^{\frac{(1-\alpha)\square F}{RT}} - e^{\frac{-\alpha\eta F}{RT}}\right\}$$

$$i = -io\ e\ \frac{-\alpha\eta F}{RT}$$

$$\ln(-i) = \ln i_o - \frac{\alpha\eta F}{RT}$$ This is Tafel Eqn. for cathodic current

Now, there are two other possibility, another one is this over potential is very large and it is positive.

$$i = i_0\ e^{\frac{(1-\alpha)\eta F}{RT}}$$

$$\ln i = \ln i_o + (1-\alpha)\eta F/RT$$

The third possibility is over potential is very large and negative

$$i = -i_0\ e\ \frac{-\alpha\eta F}{RT}$$

$$\ln(-i) = \ln i_0\ - \frac{\alpha\eta F}{RT}$$

So, this is the total summation of this two particular current right and you can see a part of it is linear so, that linear part is almost the case where your over potential is very small. So, from the Butler Volmer equation, we can actually derive the Tafel equation and it will be very important for us to see later how it works.

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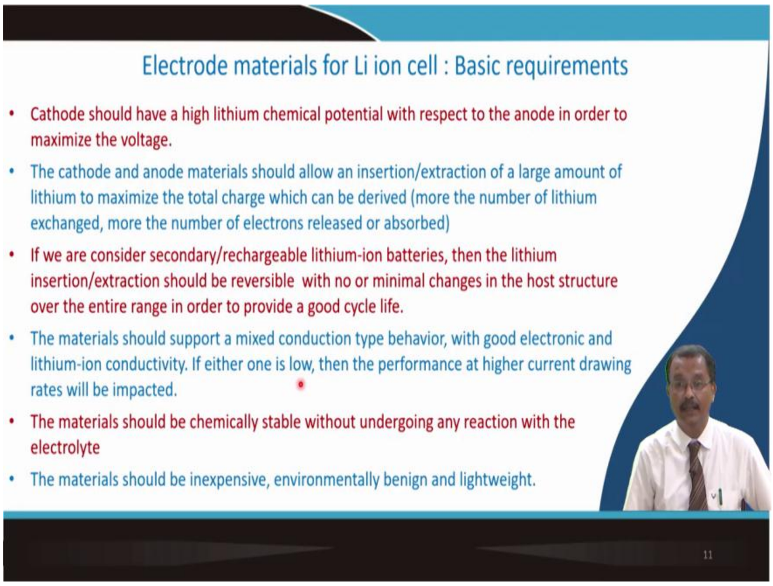

Electrode materials for Li ion cell : Basic requirements

- Cathode should have a high lithium chemical potential with respect to the anode in order to maximize the voltage.
- The cathode and anode materials should allow an insertion/extraction of a large amount of lithium to maximize the total charge which can be derived (more the number of lithium exchanged, more the number of electrons released or absorbed)
- If we are consider secondary/rechargeable lithium-ion batteries, then the lithium insertion/extraction should be reversible with no or minimal changes in the host structure over the entire range in order to provide a good cycle life.
- The materials should support a mixed conduction type behavior, with good electronic and lithium-ion conductivity. If either one is low, then the performance at higher current drawing rates will be impacted.
- The materials should be chemically stable without undergoing any reaction with the electrolyte
- The materials should be inexpensive, environmentally benign and lightweight.

So, now, the structure of the cathode or anode material is important. So, few basic requirements are there. The cathode should have a very high lithium chemical potential with respect to anode in order to maximize the voltage. So, voltage is high means your energy is also high.

Cathode and anode material should allow the insertion and exertion of large amount of lithium to maximize the total charge. So, we will have to search for that kind of electrode material.

If you consider the secondary or rechargeable lithium battery, then lithium insertion exertion should be reversible. Once it is coming out during charging, during discharging it must go back by an equal amount. There should not be any loss of lithium anywhere. So, that will give a good cycle life. Material should support a mixed conduction type of behavior with good electronic and lithium-ion conductivity. The performance at high current rates will get affected if either one is low. The material should be chemically stable without undergoing any reaction with the electrolyte. And finally, the material should be inexpensive and environmentally benign and lightweight in order to increase the gravimetric energy density.

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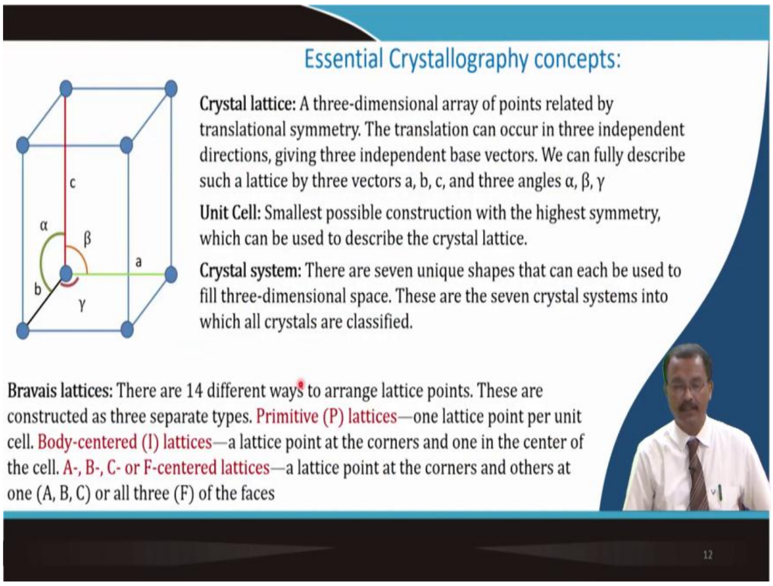

Essential Crystallography concepts:

Crystal lattice: A three-dimensional array of points related by translational symmetry. The translation can occur in three independent directions, giving three independent base vectors. We can fully describe such a lattice by three vectors a, b, c, and three angles α, β, γ

Unit Cell: Smallest possible construction with the highest symmetry, which can be used to describe the crystal lattice.

Crystal system: There are seven unique shapes that can each be used to fill three-dimensional space. These are the seven crystal systems into which all crystals are classified.

Bravais lattices: There are 14 different ways to arrange lattice points. These are constructed as three separate types. Primitive (P) lattices—one lattice point per unit cell. Body-centered (I) lattices—a lattice point at the corners and one in the center of the cell. A-, B-, C- or F-centered lattices—a lattice point at the corners and others at one (A, B, C) or all three (F) of the faces

So, now, I will just brush you with certain known crystallographic concepts which you might have read in your second year course. If not, then I have cited two important references. You please read this chapter on crystal structure.

So, the crystal lattice is a three-dimensional array of points, and this is related by translation symmetry. So, translation you can occur at three independent directions. Depending on that, you have the lattice parameter and the angle between the respective lattice parameter that constitute the crystal lattice.

Unit cell is the smallest possible construction which is having highest symmetry. Crystal system: there are seven unique shapes that can be used to fill the three-dimensional space. These are seven crystal systems into which all crystals are classified.

Bravais lattice, there are 14 Bravais lattice, this constructed by three separate type: one is primitive with one lattice point per unit cell, then body centered lattice, one lattice point at the corners and one at the center or A, B, C or F centered lattice, a lattice point at the corners and others at either A, B or three F of the faces.

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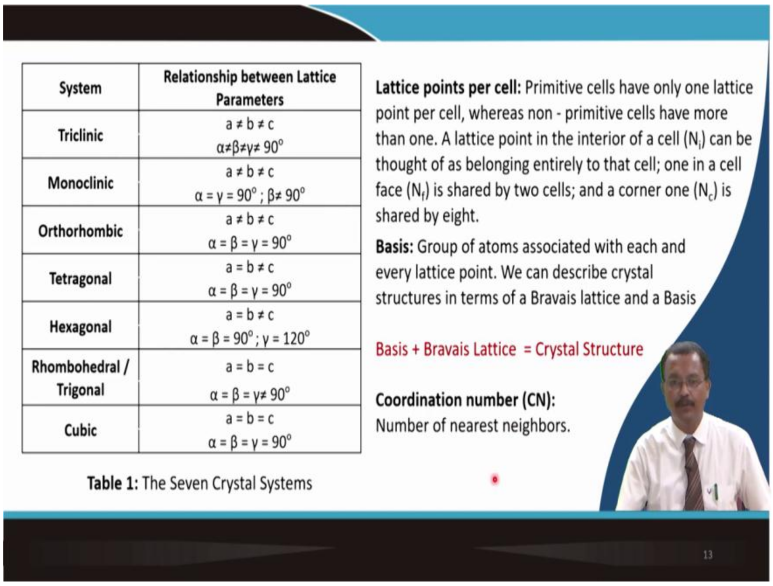

System	Relationship between Lattice Parameters
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$; $\beta \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$
Rhombohedral / Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$

Table 1: The Seven Crystal Systems

Lattice points per cell: Primitive cells have only one lattice point per cell, whereas non - primitive cells have more than one. A lattice point in the interior of a cell (N_i) can be thought of as belonging entirely to that cell; one in a cell face (N_f) is shared by two cells; and a corner one (N_c) is shared by eight.

Basis: Group of atoms associated with each and every lattice point. We can describe crystal structures in terms of a Bravais lattice and a Basis

Basis + Bravais Lattice = Crystal Structure

Coordination number (CN):
Number of nearest neighbors.

Then, this is the relation between the lattice constant and the angle between them that define the different types of the crystal system and the highest symmetry is cubic, lowest symmetry is triclinic right.

And lattice point per cell, you can estimate for example, if you have a primitive lattice one lattice point at the interior of the cell can be thought belonging to entirely to that particular cell, if it is face, then it is half shared; if it is at the corner, it is shared by eight. So, we call basis which is group of atoms associated with each and every lattice point.

We can describe the crystal structure in terms of a Bravais lattice and a basis. So, basis and Bravais lattice constitute the crystal structure and the coordination number is important; number of nearest neighbor that we have.

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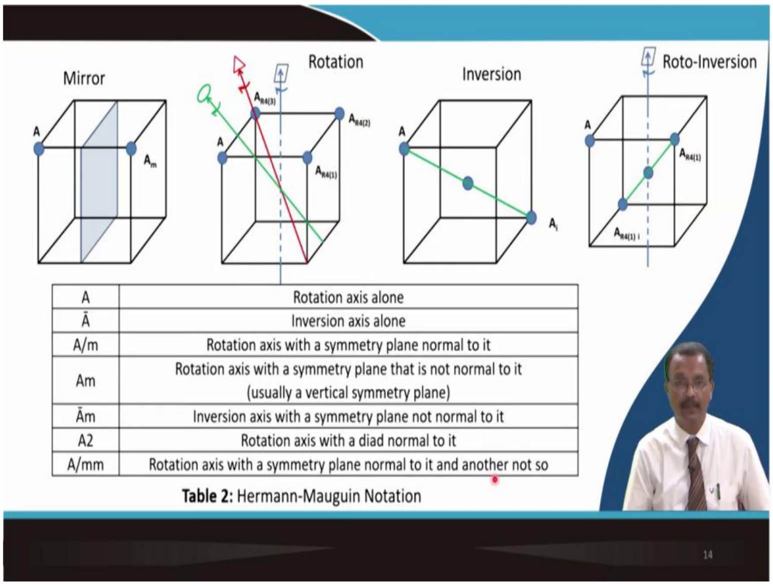

A	Rotation axis alone
$\bar{A}$	Inversion axis alone
A/m	Rotation axis with a symmetry plane normal to it
Am	Rotation axis with a symmetry plane that is not normal to it (usually a vertical symmetry plane)
$\bar{A}$m	Inversion axis with a symmetry plane not normal to it
A2	Rotation axis with a diad normal to it
A/mm	Rotation axis with a symmetry plane normal to it and another not so

Table 2: Hermann-Mauguin Notation

So, there are various types of symmetry and depending on the symmetry, we have 32 types of point group. This is a mirror plane, this one is first one is a 2-fold axis, 3-fold axis and 4-fold axis and it has shown that in case of 4-fold axis, if you 90 degree rotate it, you will get back the same points.

There could be an inversion. So, across this line, it is just inverted. There could be roto inversion, if it is a 4-fold axis, you go 90 degree and then, it will go to the other side, invert it. So, these are different types of symmetry operation.

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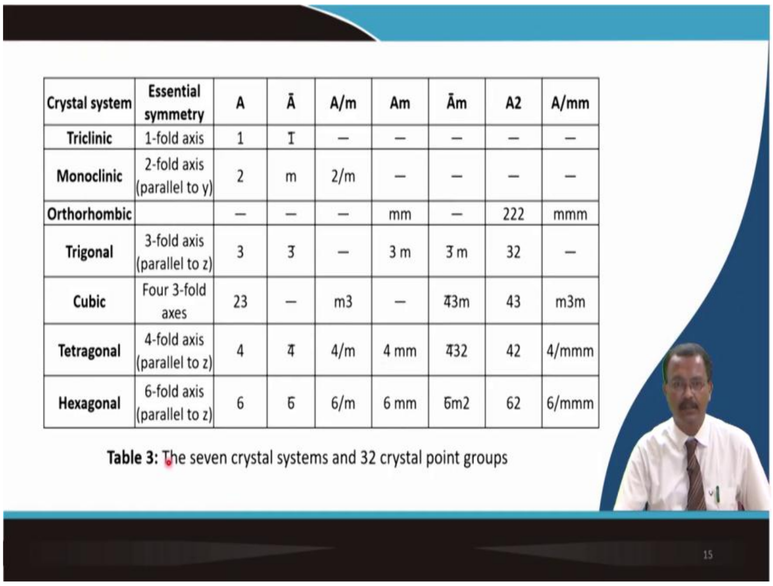

Crystal system	Essential symmetry	A	$\bar{A}$	A/m	Am	$\bar{A}$m	A2	A/mm
Triclinic	1-fold axis	1	$\bar{1}$	–	–	–	–	–
Monoclinic	2-fold axis (parallel to y)	2	m	2/m	–	–	–	–
Orthorhombic		–	–	–	mm	–	222	mmm
Trigonal	3-fold axis (parallel to z)	3	$\bar{3}$	–	3 m	$\bar{3}$ m	32	–
Cubic	Four 3-fold axes	23	–	m3	–	$\bar{4}$3m	43	m3m
Tetragonal	4-fold axis (parallel to z)	4	$\bar{4}$	4/m	4 mm	$\bar{4}$32	42	4/mmm
Hexagonal	6-fold axis (parallel to z)	6	$\bar{6}$	6/m	6 mm	$\bar{6}$m2	62	6/mmm

Table 3: The seven crystal systems and 32 crystal point groups

If you have this symmetry operation across the all crystal system, then in total you have 32 point groups and then, this point groups are arranged to give you the space group which is beyond the scope for this particular course, but indeed, we will be using the space group in defining certain things.

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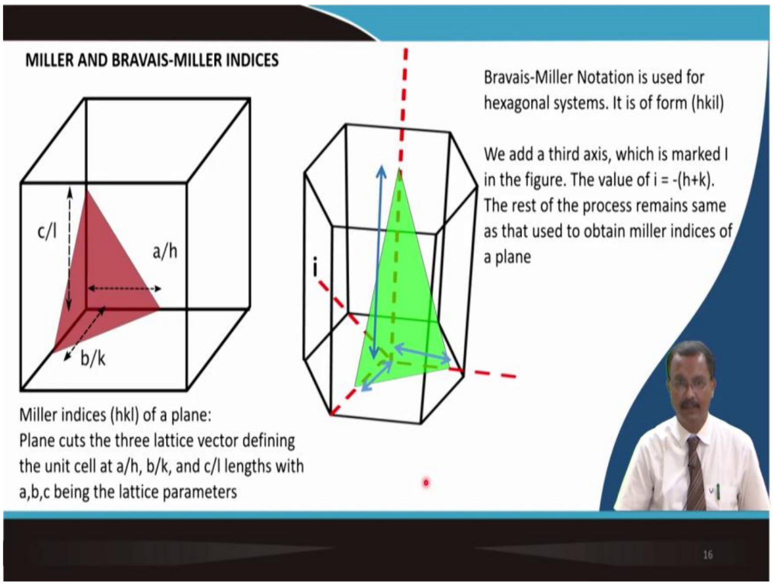

MILLER AND BRAVAIS-MILLER INDICES

Bravais-Miller Notation is used for hexagonal systems. It is of form (hkil)

We add a third axis, which is marked I in the figure. The value of i = -(h+k). The rest of the process remains same as that used to obtain miller indices of a plane

Miller indices (hkl) of a plane:
Plane cuts the three lattice vector defining the unit cell at a/h, b/k, and c/l lengths with a,b,c being the lattice parameters

So, sometimes a 3 axis system is not enough particularly, for the rhombohedral and hexagonal system so, there is a Miller indices hkl plane. In case of the hexagonal system, we have a Bravais-Miller notation which is having 4 index system and this three index system can be converted into four index system both for plane and direction and vice-versa. So, there are certain algebraic way to do that, please go through the literature that I will suggest to clarify this idea

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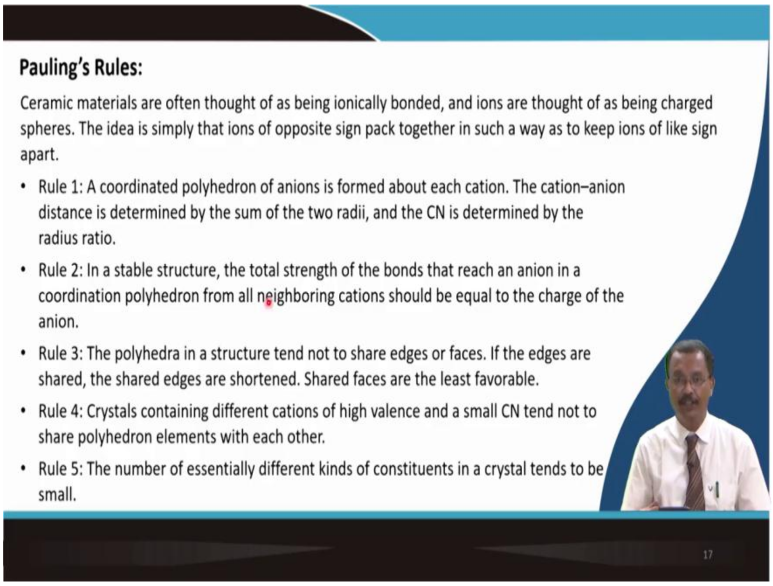

Pauling's Rules:

Ceramic materials are often thought of as being ionically bonded, and ions are thought of as being charged spheres. The idea is simply that ions of opposite sign pack together in such a way as to keep ions of like sign apart.

- Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio.
- Rule 2: In a stable structure, the total strength of the bonds that reach an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.
- Rule 3: The polyhedra in a structure tend not to share edges or faces. If the edges are shared, the shared edges are shortened. Shared faces are the least favorable.
- Rule 4: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other.
- Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small.

And then, we have this Pauling rule which is important. The rule 1 is the coordinated polyhedron anion is formed about each cation and cation-anion distance is determined by the sum of these two radii and coordination number is determined by the radius ratio. Again, I am telling that this is the gist of the crystal structure, and you will have to read the chapter whatever I will give in the study material very thoroughly.

2nd rule is the stable structure, the total strength of bond that reach an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion. 3rd one, the polyhedra in a structure tend not to share edges or faces. If the edge are shared, the shared edges are shortened.

Shared faces are the least favorable. Then, the 4th rule is crystal containing different cations of high valance, and a small coordination number tends not to share polyhedron element with each other so, they will remain separated and final rule is the number of essential different kinds of constituents in the crystal tends to be small.

So, this Pauling rule defined particularly for the ionically bonded solid that how they are packed together. It is not an individual unit cell, but we are now considering the polyhedra which are connected.

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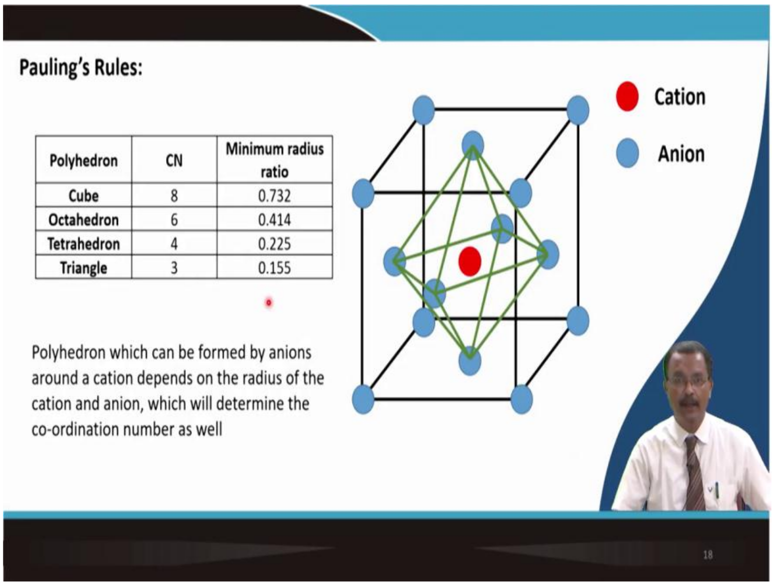

Pauling's Rules:

Polyhedron	CN	Minimum radius ratio
Cube	8	0.732
Octahedron	6	0.414
Tetrahedron	4	0.225
Triangle	3	0.155

Polyhedron which can be formed by anions around a cation depends on the radius of the cation and anion, which will determine the co-ordination number as well

So, here is one example for the cube coordination number is 8 and R_c by R_a ratio, anion to cation, cation to anion ratio is 0.732 and you change that thing, your coordination number will change and the polyhedra will also change. Therefore, the triangle for example, it is lowest 0.155, for cube it is highest 0.732.

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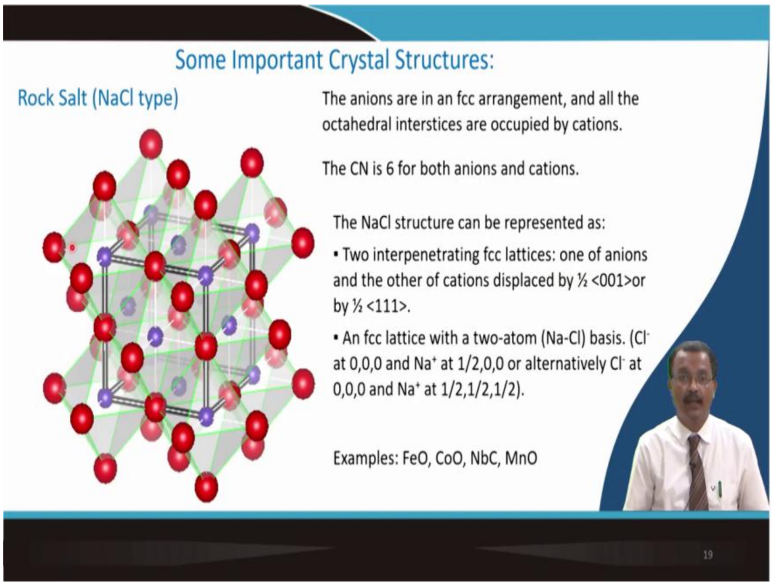

Some Important Crystal Structures:

Rock Salt (NaCl type)

The anions are in an fcc arrangement, and all the octahedral interstices are occupied by cations.

The CN is 6 for both anions and cations.

The NaCl structure can be represented as:

- Two interpenetrating fcc lattices: one of anions and the other of cations displaced by ½ <001>or by ½ <111>.
- An fcc lattice with a two-atom (Na-Cl) basis. (Cl^- at 0,0,0 and Na^+ at 1/2,0,0 or alternatively Cl^- at 0,0,0 and Na^+ at 1/2,1/2,1/2).

Examples: FeO, CoO, NbC, MnO

Now, rock salt structure is one of them. Here, you can see that two interpenetrating fcc lattice that is there and example of this type of crystal lattice is FeO, cobalt oxide and manganese oxide etcetera.

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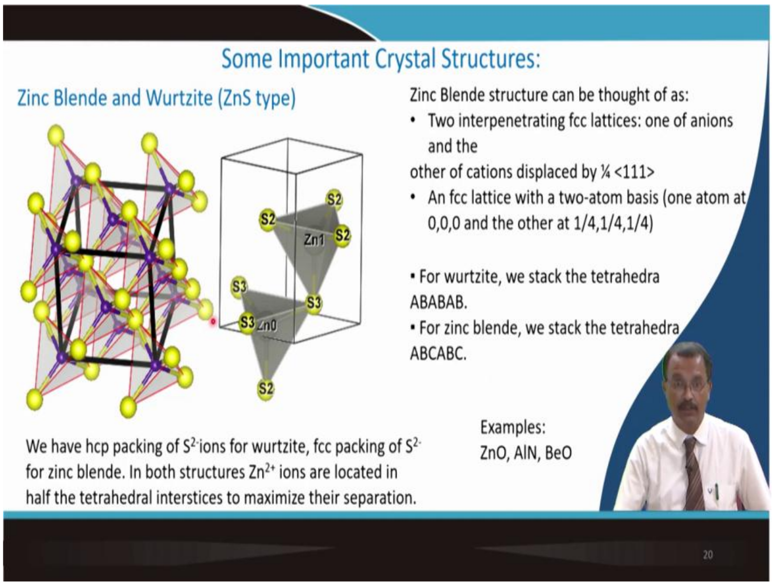

Some Important Crystal Structures:

Zinc Blende and Wurtzite (ZnS type)

Zinc Blende structure can be thought of as:

- Two interpenetrating fcc lattices: one of anions and the

other of cations displaced by ¼ <111>

- An fcc lattice with a two-atom basis (one atom at 0,0,0 and the other at 1/4,1/4,1/4)

- For wurtzite, we stack the tetrahedra ABABAB.
- For zinc blende, we stack the tetrahedra ABCABC.

We have hcp packing of S^{2-} ions for wurtzite, fcc packing of S^{2-} for zinc blende. In both structures Zn^{2+} ions are located in half the tetrahedral interstices to maximize their separation.

Examples:
ZnO, AlN, BeO

And then, we have another important crystal lattice is zinc blende and this is interpenetrating fcc lattice; one of anions and another one of cation which you can see it here. So, for wurtzite type of structure, we stack the tetrahedra as ABAB. For zinc blende, we stack the tetrahedra as ABCABC. So, this is also another important crystal structure. Examples are zinc oxide, aluminum nitrate and beryllium oxide.

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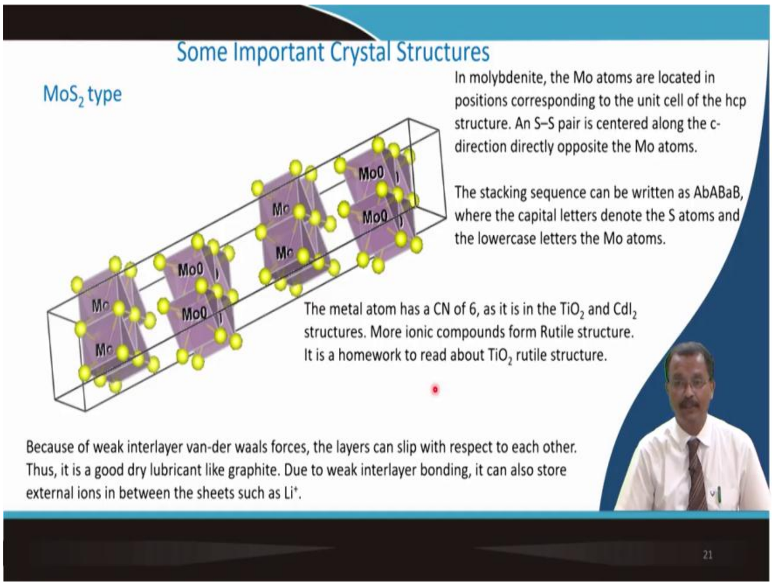

Some Important Crystal Structures

MoS_2 type

In molybdenite, the Mo atoms are located in positions corresponding to the unit cell of the hcp structure. An S–S pair is centered along the c-direction directly opposite the Mo atoms.

The stacking sequence can be written as AbABaB, where the capital letters denote the S atoms and the lowercase letters the Mo atoms.

The metal atom has a CN of 6, as it is in the TiO_2 and CdI_2 structures. More ionic compounds form Rutile structure. It is a homework to read about TiO_2 rutile structure.

Because of weak interlayer van-der waals forces, the layers can slip with respect to each other. Thus, it is a good dry lubricant like graphite. Due to weak interlayer bonding, it can also store external ions in between the sheets such as Li^+.

The other one is molybdenum disulfide. In molybdenite, the Mo atoms are located in the position which correspond to the unit cell of the fcc structure and sulphur-sulphur pair is centered along the c-direction here and the stacking sequence can be written as A and small b and then again, capital A capital B small a capital B. The capital letter that denotes the S atom and lower-case letter as Mo atoms.

The metal atom has coordination number 6 as it is in the TiO 2 and cadmium iodide structure. More ionic compound form rutile structure which I have not defined in this particular lecture, and it is a homework to read about the rutile structure for you.

Because of the weak interlayer van-der waals forces, the layer can slip with respect to each other. This is a good dry lubricant like graphite. Graphite is also having a layer structure. Due to weak inter layer bonding, it can also store external ions between the sheets. So, for lithium-ion also, this kind of structure for lithium-ion battery will be important.

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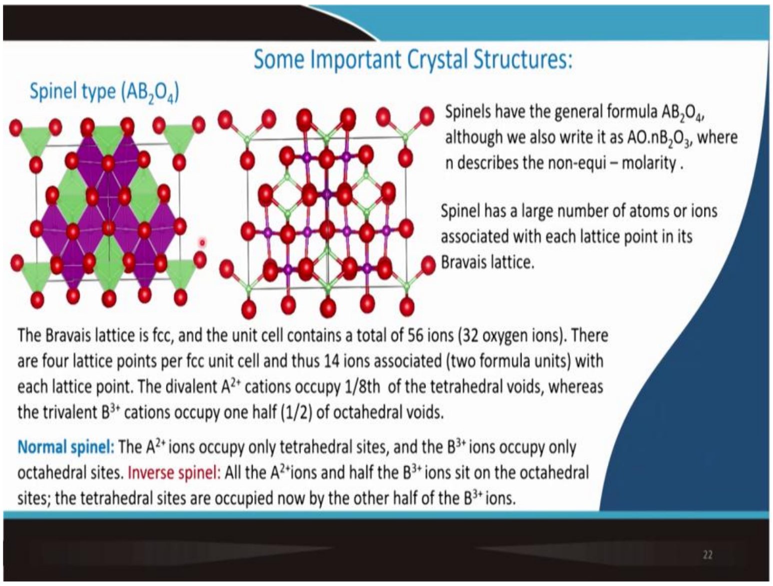

Some Important Crystal Structures:

Spinel type (AB_2O_4)

Spinels have the general formula AB_2O_4, although we also write it as $AO.nB_2O_3$, where n describes the non-equi – molarity .

Spinel has a large number of atoms or ions associated with each lattice point in its Bravais lattice.

The Bravais lattice is fcc, and the unit cell contains a total of 56 ions (32 oxygen ions). There are four lattice points per fcc unit cell and thus 14 ions associated (two formula units) with each lattice point. The divalent A^{2+} cations occupy 1/8th of the tetrahedral voids, whereas the trivalent B^{3+} cations occupy one half (1/2) of octahedral voids.

Normal spinel: The A^{2+} ions occupy only tetrahedral sites, and the B^{3+} ions occupy only octahedral sites. **Inverse spinel:** All the A^{2+}ions and half the B^{3+} ions sit on the octahedral sites; the tetrahedral sites are occupied now by the other half of the B^{3+} ions.

Spinel structure, I will be talking in details. It is basically a cubic closed pack structure and inside the oxygen packing, there are two types of void, tetrahedral type and octahedral type. Tetrahedral type voids are assumed by double valent cations and octahedral are usually trivalent cation.

The normal spinel is having a structure AB 2 O 4 and there are possibility for inverse spinal structure where the formula is BAB O 4, all the octahedral void content comes to the tetrahedral void and sorry half of this octahedral bond octahedral void content comes to the tetrahedral and whole tetrahedral goes to the octahedral. So, that is the inverse spinel structure and we will come back to this type of structure while I will be talking more about the lithium-ion battery operation.

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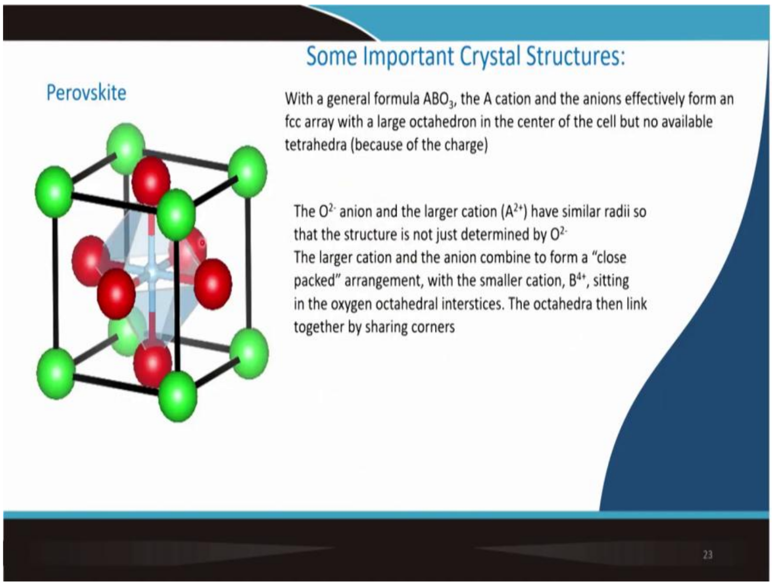

Some Important Crystal Structures:

Perovskite

With a general formula ABO_3, the A cation and the anions effectively form an fcc array with a large octahedron in the center of the cell but no available tetrahedra (because of the charge)

The O^{2-} anion and the larger cation (A^{2+}) have similar radii so that the structure is not just determined by O^{2-}
The larger cation and the anion combine to form a "close packed" arrangement, with the smaller cation, B^{4+}, sitting in the oxygen octahedral interstices. The octahedra then link together by sharing corners

Finally, perovskite structure is as you can see there are three different types of cation, the central octahedral position usually titanium sits here, oxygen shows sits in the face centered and corners resumed by larger cation like barium and this type of material also we have used to make the electrode material although not very common.

But as a part of a short case study, I will introduce it more whenever we talk about the use of perovskite and spinel structure for lithium-ion battery.

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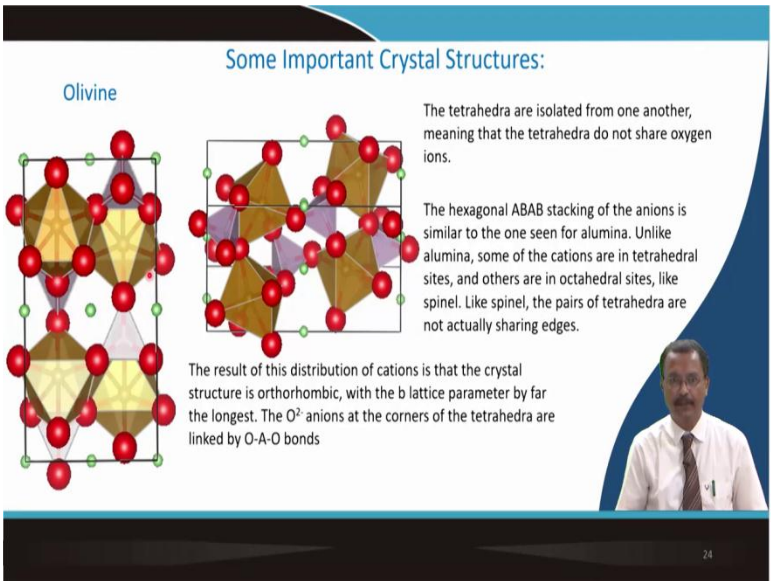

Some Important Crystal Structures:

Olivine

The tetrahedra are isolated from one another, meaning that the tetrahedra do not share oxygen ions.

The hexagonal ABAB stacking of the anions is similar to the one seen for alumina. Unlike alumina, some of the cations are in tetrahedral sites, and others are in octahedral sites, like spinel. Like spinel, the pairs of tetrahedra are not actually sharing edges.

The result of this distribution of cations is that the crystal structure is orthorhombic, with the b lattice parameter by far the longest. The O^{2-} anions at the corners of the tetrahedra are linked by O-A-O bonds

And finally, these are the olivine structure the tetrahedra is associated from one another that means, the tetrahedra do not share any oxygen ions. Usually, hexagonal ABAB kind of stacking of anions is similar to one seen in alumina. Unlike alumina, some of the cations are also in the tetrahedral sites and others are in the octahedral sites like spinel. Like spinel the pairs of tetrahedra are not actually sharing edge. So, this is the complicacy of this type of structure.

The result of this kind of distribution of cations is that the crystal structure is orthorhombic, with a b lattice parameter by far the longest one and O 2 minus ions, they are at the corner of the tetrahedra, they are linked by O-A and O bonds. This is also another type of structure which is heavily used in case of lithium as well as sodium ion batteries.

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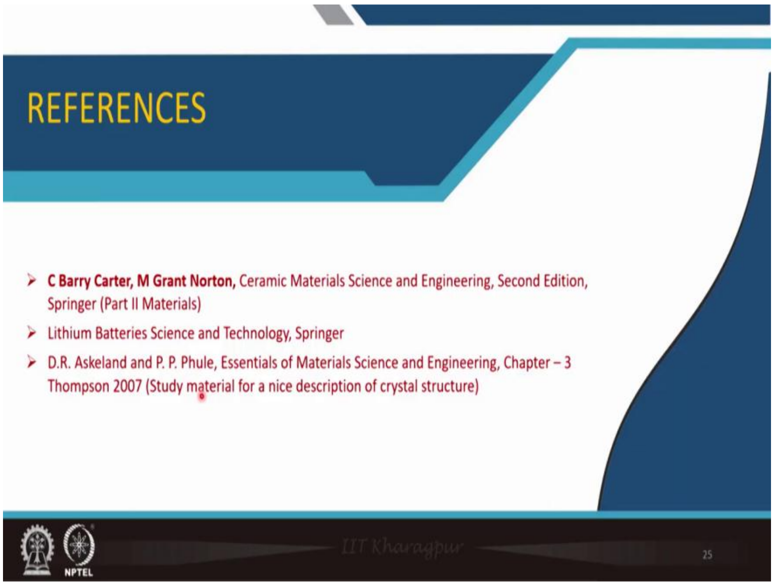

REFERENCES

- **C Barry Carter, M Grant Norton,** Ceramic Materials Science and Engineering, Second Edition, Springer (Part II Materials)
- Lithium Batteries Science and Technology, Springer
- D.R. Askeland and P. P. Phule, Essentials of Materials Science and Engineering, Chapter – 3 Thompson 2007 (Study material for a nice description of crystal structure)

So, for a this particular lecture, the Barry Carter book is a good one and for the other part, the thermodynamic part along with the other reference, you should consider this book as well and especially, the basics of crystal structure Askeland and Phule, this book is quite good and the whole chapter 3 should be read very seriously.

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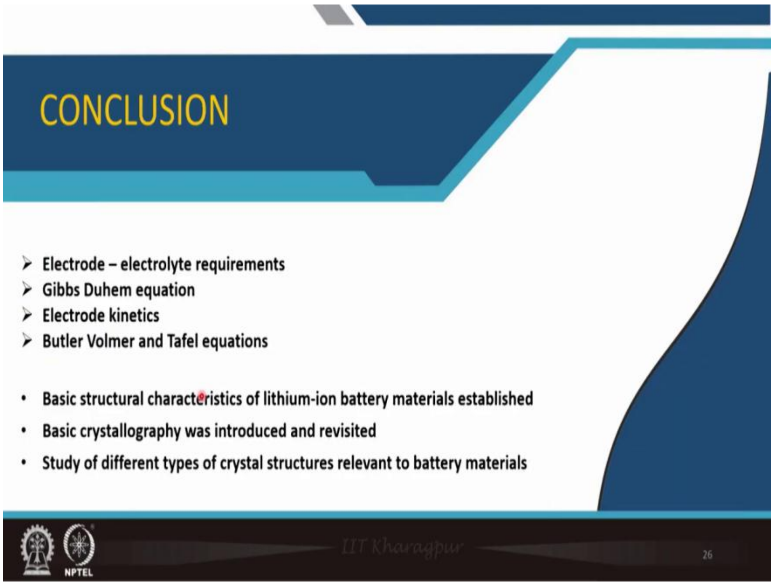

CONCLUSION

- Electrode – electrolyte requirements
- Gibbs Duhem equation
- Electrode kinetics
- Butler Volmer and Tafel equations

- Basic structural characteristics of lithium-ion battery materials established
- Basic crystallography was introduced and revisited
- Study of different types of crystal structures relevant to battery materials

So, in this particular lecture, initially I talked about electrode-electrolyte requirement, then Gibbs Duhem equation, then electrode kinetics and then, Butler Volmer and Tafel equations. Then, basic structure characteristics of lithium-ion battery materials are established, crystallography was introduced and revisited.

Although, it is not a exhaustive treatment and I just touch certain points and you will have to read if you are not familiar with this, whoever is familiar with this structure, it is ok and study of different types of crystal structure relevant to battery materials are introduced.

Thank you for your attention.