Physics of Renewable Energy Systems
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Lecture 25
Characteristics and Parameters of Li-ion Batteries

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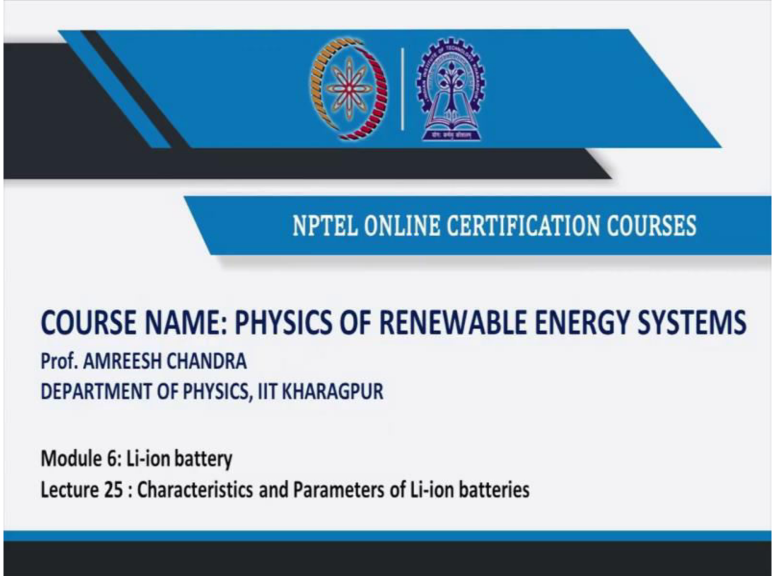

NPTEL ONLINE CERTIFICATION COURSES

COURSE NAME: PHYSICS OF RENEWABLE ENERGY SYSTEMS
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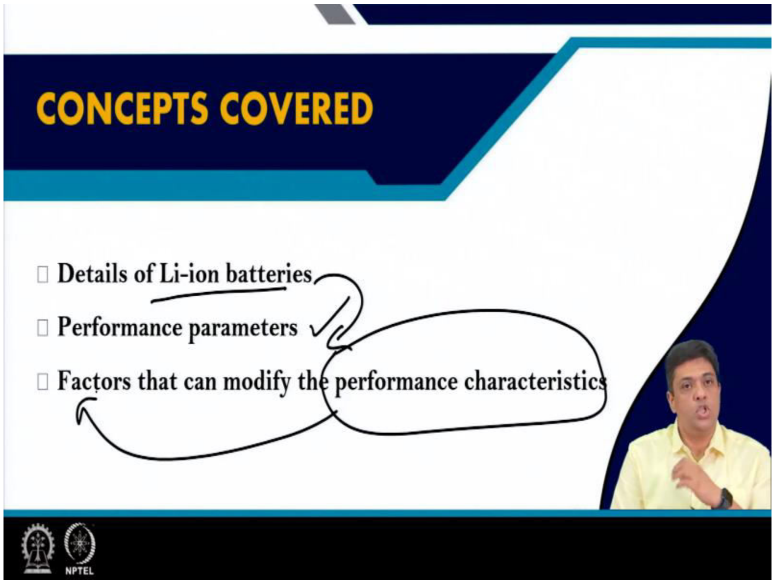
Module 6: Li-ion battery
Lecture 25 : Characteristics and Parameters of Li-ion batteries



CONCEPTS COVERED

- ☐ Details of Li-ion batteries
- ☐ Performance parameters
- ☐ Factors that can modify the performance characteristics

Hello. In this second lecture of week 6 of the course on Physics of Renewable Energy Systems I will be talking to you about the characteristics and the various parameters which are used to explain or understand the lithium ion batteries which were introduced to you in the previous lecture. There are large number of performance parameters which are used to define a lithium ion battery.

So, you will see that there are various types of parameters and it is not only a single factor which affects the performance but there are large number of factors both intrinsic and extrinsic which can modify the output or the performance of a lithium ion battery. So lithium ion battery characterized with various associated parameters and these parameters can actually get modulated due to various kind of factors.

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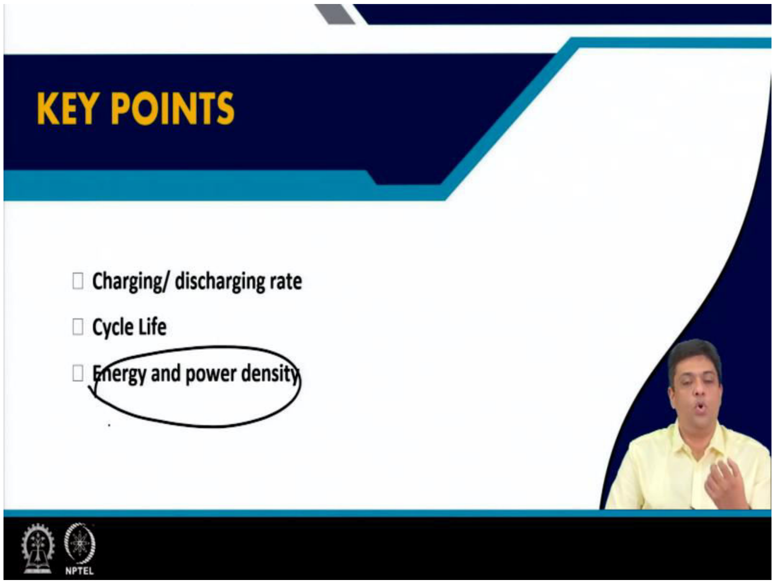

KEY POINTS

☐ Charging/ discharging rate

☐ Cycle Life

☐ Energy and power density

So, this is what we are going to understand in today’s lecture and you will be able to then explain the concepts of charging rates, the discharging rate what is actually a cycle life of a lithium ion battery. If you talk about your mobile phones for example you find that the battery of the phone can be used for a year or couple of years or if they are managed well maybe for three years and in this three year period the cycling which you have performed on the battery can vary from 500 cycles to 1000 cycles.

And please note charging and discharging cycle is that if you have a battery which is fully discharged and then you plug in and the battery charges to the maximum voltage that is one charging cycle and then you allow the battery to discharge not fully but let us say up to 20 percent of the maximum then that is the discharge cycle and one full charging cycle, charging discharging cycle makes one cycle.

So, these concepts would be explained to you and the importance of understanding the terms energy and power densities in such electrical energy storage technologies would also be clear after today's lecture.

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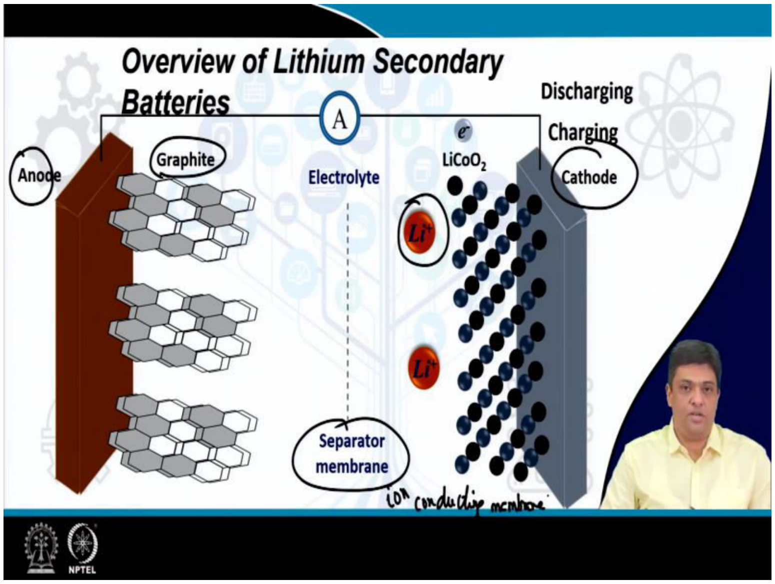

Overview of Lithium Secondary Batteries

As I showed in the previous lecture how does a lithium ion battery work it has an anode which is made up of the graphatic structure. Graphatic structures you have layered structures made up of carbon, you have a cathode which is made up of what it is made up of lithium based oxide or phosphates and what is the purpose, this lithium based cathode will be delivering the lithium ion. This lithium ion is going to move across the structure which also has a separator membrane, what type of separator membrane and ion conducting membrane.

Why an ion conducting membrane because it has two purpose it prevents the short circuiting between the two electrodes and also allows the ions to go through them but does not allow the electrons to flow through and if the electrons cannot flow through then you will have the flow from the external circuit so that the condition of charge neutrality can be obtained and that is the importance of the separator membrane.

The electrolytes would flow through the separator membrane and they will be flowing in an electrolyte. The separator membrane can be either made up of polymer or even ceramics and you have various types of ion conducting electrolytes. So this is the charging cycle you have the lithium moving from cathode to anode electron from the outer circuit and during discharging the reverse happens and when you if you have a load then electron will be flowing through an external load and that would be the electrical current that will drive the electrical load which if you say is your mobile battery which is driving the mobile phone circuit.

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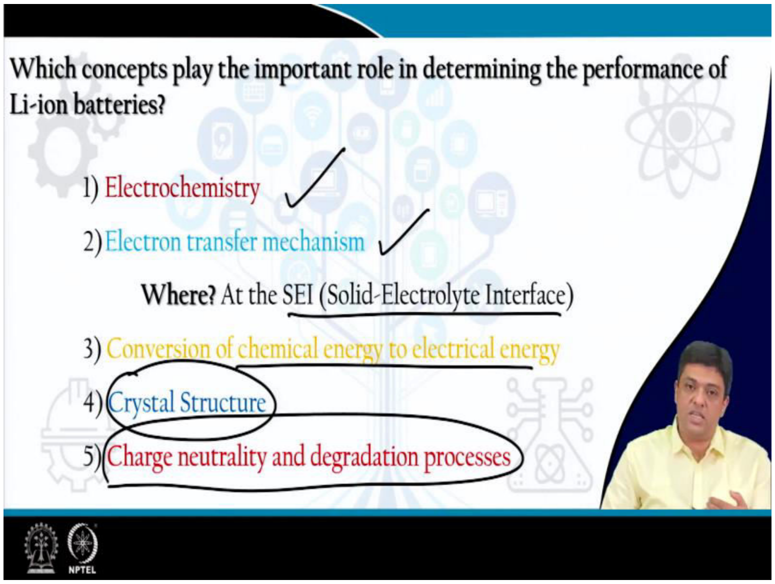

Which concepts play the important role in determining the performance of Li-ion batteries?

1) Electrochemistry ✓
2) Electron transfer mechanism ✓

Where? At the SEI (Solid-Electrolyte Interface)

3) Conversion of chemical energy to electrical energy
4) Crystal Structure
5) Charge neutrality and degradation processes

Immediately you would see you have ions moving, electrons moving, recombining at one place you have reduction other place you have oxidation, so what is happening it immediately means that the concept of electrochemistry becomes very critical. Then you have the electron transfer mechanism, so that is important but this is happening where it is happening at the SEI, what is SEI it is the solid electrolyte interface, so either you have the flow at the solid electrolyte interface.

Then the next concept which one should understand clearly and is very critical is the conversion processes of converting electrical energy to chemical energy and vice versa. So we are talking more so here the conversion of chemical energy to electrical energy then we are extracting the energy out of batteries. The whole concept or the whole device is driven by the performance of the materials, materials of various shapes, size, dimensions and crystal structure.

So, all the discussions we had about the free electron model, the semiconductors, the ion conductivity, the conductivity, resistance everything becomes important in this device and finally the necessity of having a charge neutrality condition and the associated degradation processes if you have the ions leaving a lattice and then coming back to occupy the vacant sites. So these concepts are very important and most of them have been discussed in the previous modules and the ones which have not been discussed would be discussed today.

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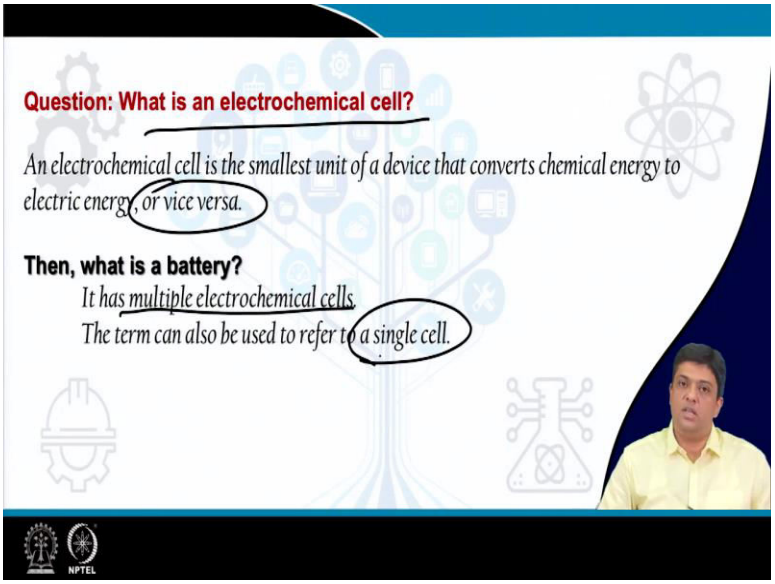

Question: What is an electrochemical cell?

An electrochemical cell is the smallest unit of a device that converts chemical energy to electric energy, or vice versa.

Then, what is a battery?

It has multiple electrochemical cells.

The term can also be used to refer to a single cell.

The first thing which I discussed was the electrochemical reactions and the cell where this kind of reaction or these kind of reactions are taking place will be called what, would be called as an electrochemical cell. So, what is an electrochemical cell? An electrochemical cell is the smallest unit that converts chemical energy to electric energy or vice versa.

Then what is battery? A battery has multiple electrochemical cells. The term can also be used to refer to a single cell. So you can also talk in terms of a single cell and then you can say it is a battery. But when you are talking about a real battery which is used then you are talking about multiple electrochemical cells.

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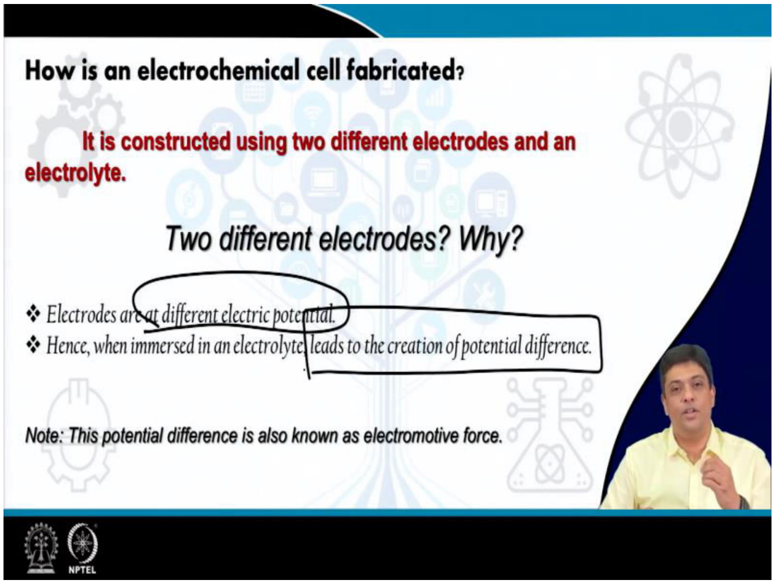

How is an electrochemical cell fabricated?

It is constructed using two different electrodes and an electrolyte.

Two different electrodes? Why?

- *Electrodes are at different electric potential.*
- *Hence, when immersed in an electrolyte, leads to the creation of potential difference.*

Note: This potential difference is also known as electromotive force.

How are they constructed? We have explained to you many times so how are they constructed they have various components the anode the cathode the electrolyte and the separator. Electrodes what are they doing? They are the ones which are actually at different electric potential. So you have two electrodes at different electric potential and hence what happens if you immerse these two electrodes in an electrolyte that leads to a creation of the potential difference and that is what is the origin of the battery.

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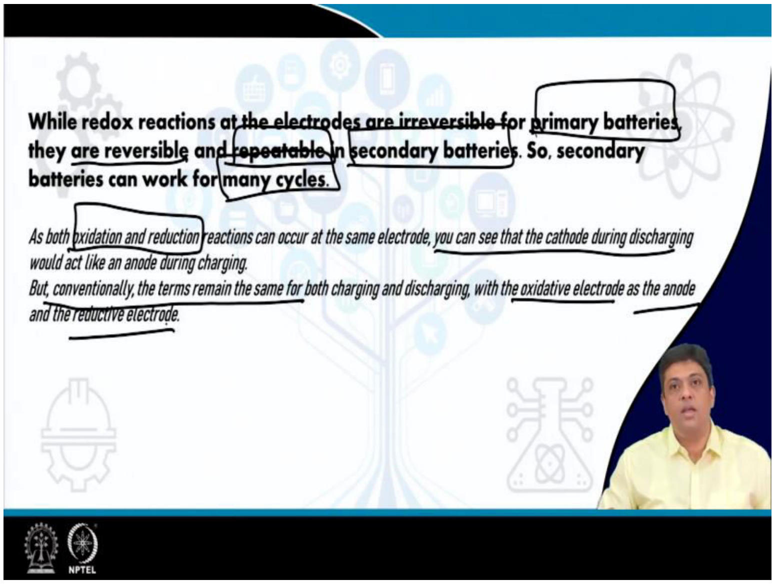

While redox reactions at the electrodes are irreversible for primary batteries, they are reversible and repeatable in secondary batteries. So, secondary batteries can work for many cycles.

As both oxidation and reduction reactions can occur at the same electrode, you can see that the cathode during discharging would act like an anode during charging.
But, conventionally, the terms remain the same for both charging and discharging, with the oxidative electrode as the anode and the reductive electrode.

If you compare the two types of batteries, what are those two types of batteries which we have discussed we have discussed the primary batteries and the secondary batteries. So in the case of primary batteries, the redox reactions are irreversible, so you do not have the capacity to reverse the reactions once they have actually taken place so they are irreversible and immediately you can explain what would be the nature of redox reactions in a secondary battery, the nature would be such that they would be reversible and repeatable.

If they are reversible and repeatable, what would be the consequence? The immediate consequence would be that you can use, reuse and you can use the battery for many cycles. Now electrochemical reactions, what are we talking about, release of electron or accepting electron or release of ions and acceptance of ions.

So, both oxidation and reduction reactions occur at the same electrode at that one time you can have the acceptance of the electron or the release of the electron by the same electrode, hence you can see that the cathode during discharging would act like anode during the charging cycle. But conventionally the terms remain same for both charging and discharging cycle. With the oxidative electrode as the anode and the electrode which is reductive is the cathode, okay.

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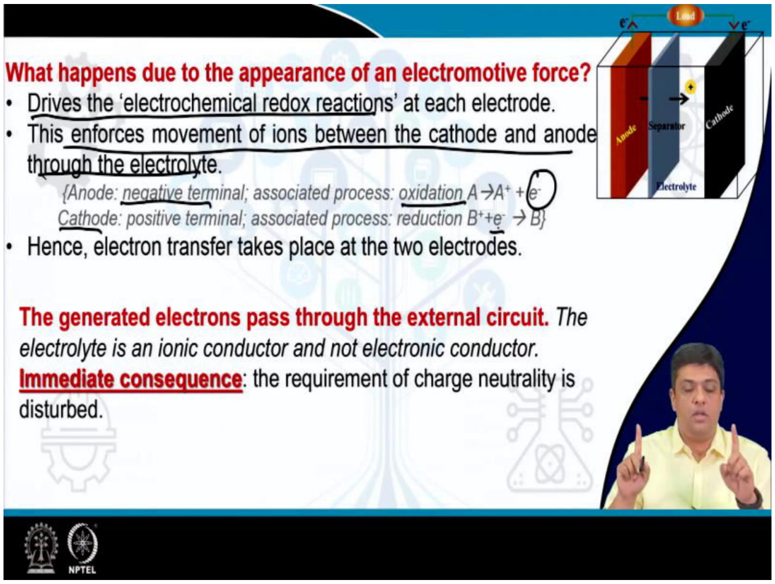

What happens due to the appearance of an electromotive force?

- Drives the 'electrochemical redox reactions' at each electrode.
- This enforces movement of ions between the cathode and anode through the electrolyte.

  {Anode: negative terminal; associated process: oxidation $A \rightarrow A^+ + e^-$
  Cathode: positive terminal; associated process: reduction $B^+ + e^- \rightarrow B$}
- Hence, electron transfer takes place at the two electrodes.

The generated electrons pass through the external circuit. *The electrolyte is an ionic conductor and not electronic conductor.*
Immediate consequence: the requirement of charge neutrality is disturbed.

So, now what we have done, we have seen a cathode and anode, we have the appearance of the electromotive force and what is this electromotive force actually doing? It is driving the redox reactions, redox reaction then because these electrodes are at different potential if they are immersed in electrolyte, you have the appearance of the potential and this enforces movement of ions between cathode and electrode that is anode through an electrolyte. Anode, what is anode? It is a negative terminal associated with oxidation that means you are having a release of electron whereas cathode you are accepting the electron.

Hence electron transfers take place at two electrodes and it actually occurs in the cycle where are charging as well as discharging it is only the way you are looking at the two systems. The general electrons pass through external circuit while the separator is ensuring the separation of the two electrodes, no short circuit and the flow of iron through it that is ionic conductivity.

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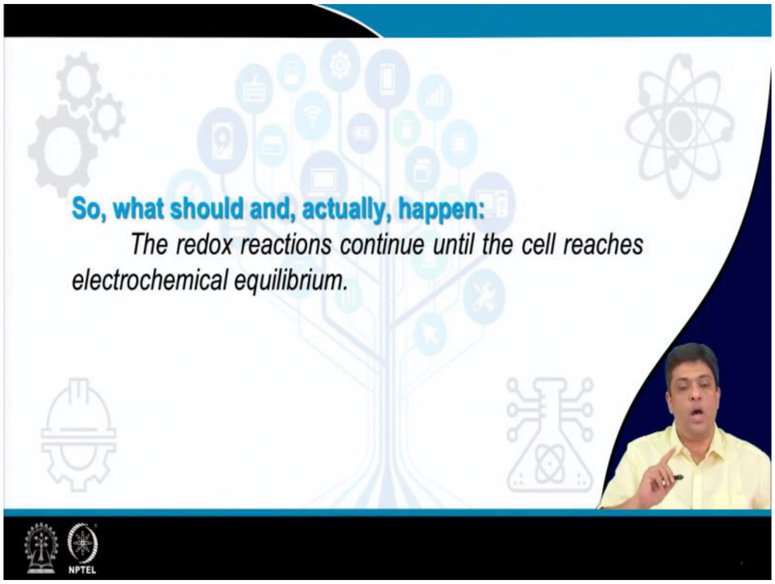

So, what should and, actually, happen:

The redox reactions continue until the cell reaches electrochemical equilibrium.

Hence, what would be the immediate consequence of the requirement of charged neutrality condition? The immediate consequence would be that the redox reactions would continue until the cell reaches the electrochemical equilibrium. So I hope now it is clear what is an electrochemical cell, what are the reactions taking place and based on those reactions how do you define the cathode, the anode and how the electron is flowing through the external circuit. So this is clear.

Another concept which is clear by now I hope is that the performance of the electrodes that is the materials used to fabricate the cathode or the anode are the critical features that will define the use of the batteries or the performance of the batteries. Hence, we should understand how to determine the performance of these electrodes. For that there are two terms which are used to explain the way you are determining the performance of the electrode materials.

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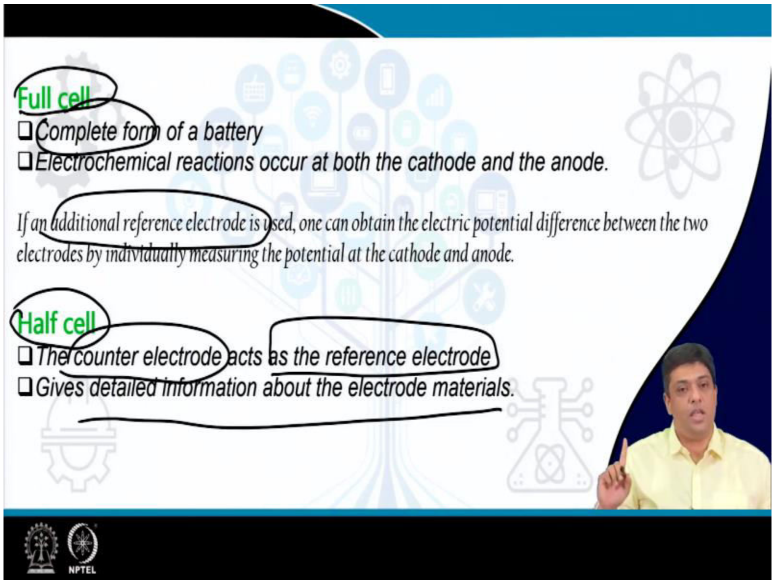
The concepts of

Full and Half Cells



Full cell

☐ Complete form of a battery

☐ Electrochemical reactions occur at both the cathode and the anode.

If an additional reference electrode is used, one can obtain the electric potential difference between the two electrodes by individually measuring the potential at the cathode and anode.

Half cell

☐ The counter electrode acts as the reference electrode

☐ Gives detailed information about the electrode materials.

These concepts are full or half cells. The full cell is actually the complete form of a battery. As the name suggests full cell complete form, full cell complete form and you are taking into consideration the electrochemical reactions occurring at both anode and at the cathode.

And if an additional reference electrode is used one can probably obtain the electric potential difference between the two electrons by individually measuring the potential at the cathode and anode. So what do we mean? You have cathode, anode full cell and you are also having the electrolyte and the separator.

Now, if you also insert a reference potential and with respect to this reference potential you measure the potential difference let us say for the cathode and then for the anode, then immediately with these two values you can find out the potential difference between the two electrodes that is getting stabilized in the cell, that is the full cell performance.

But how do we actually determine the performance of an individual electrode material, that is either the material used to fabricate a cathode or a material used to fabricate the anode materials or the anode. And for that we have the half cells which are constructed and then characterized. What are these half cells?

Here the counter electrode, the counter electrode acts as the reference electrode, so the reference electrode is your counter electrode and the you know the potential of the reference electrode and therefore the potential difference between these two electrodes that would be observed is coming in from the potential that is being obtained by the material that was used to fabricate either the cathode or the anode.

Only one material is used that is either the cathode side or the anode side and the second electrode is what reference electrode. One material if I have the information, you are getting what you are getting detailed information of the electrode material that was used for that measurement. Hence using the half cells, you can get information about the electrode material that is either used to fabricate the cathode or the electrode material that is used to fabricate the anode.

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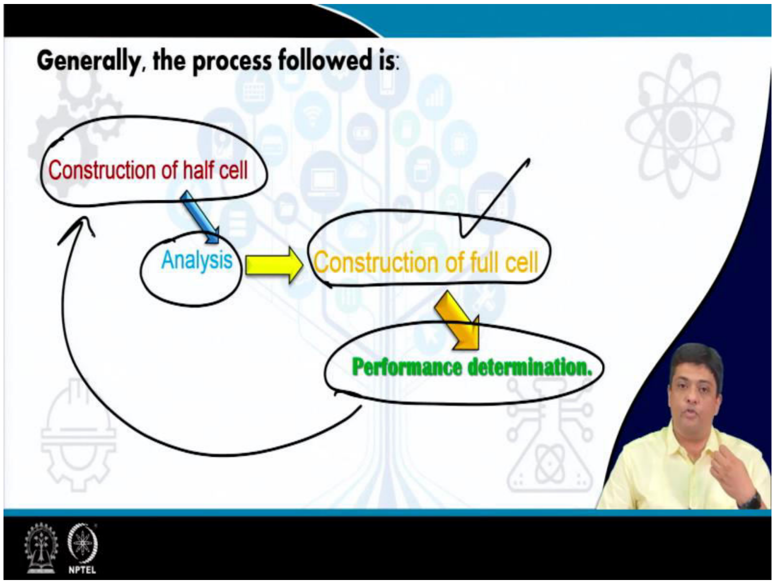

Generally, the process followed is:

Construction of half cell

Analysis

Construction of full cell

Performance determination.

This is generally the way one proceeds before recommending the lithium ion battery material or rejecting the material. What do you do? Once you have fabricated the material you construct the half cell, collect the data of the electro chemical performance, analyze it, if the analysis indicates that the material is giving the output required for a lithium ion battery like material then you construct the full cell using the material which is going to go either towards the anode side or the cathode side.

So, suppose I have chosen the anode material characterized it in the half cell then I must also characterize the cathode material using half cell and then only combine both of them because if I choose one material which is performing well the other is not responding as per the desired parameters from a battery material then the whole cell will not give you the desired output.

Hence both types of materials are first characterized using the half cell and then only the full cell is constructed and after the full cell is constructed then again you perform the electrochemical measurements and see the performance of the cell, that is the full cell. If the performance is reasonably good or you have seen improvement over the existing technologies then you recommend it for further use if not then you go back to the initial cycle where you make new materials, characterize them again then make a combination and see what is the output.

And that is the reason why different people are working at the same time because different teams are focusing on different types of materials and then seeing the performance of the full cell.

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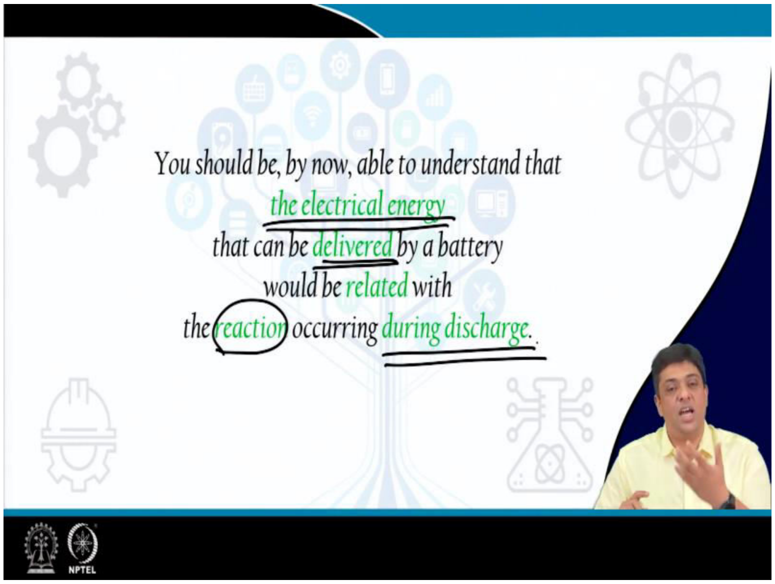

You should be, by now, able to understand that the electrical energy that can be delivered by a battery would be related with the reaction occurring during discharge.

So, you should be by now understanding well, the electrical energy that is delivered by a battery, how is it delivered by a battery and the electrical energy delivered by the battery is actually directly related to the reactions which are taking place during the discharge cycle if I am talking about a battery technology, because battery is used for storage. Storage that means it has to deliver the output when I need it and when it is delivering it is giving the energy that is it is the performance during the discharge cycle which is more relevant to us.

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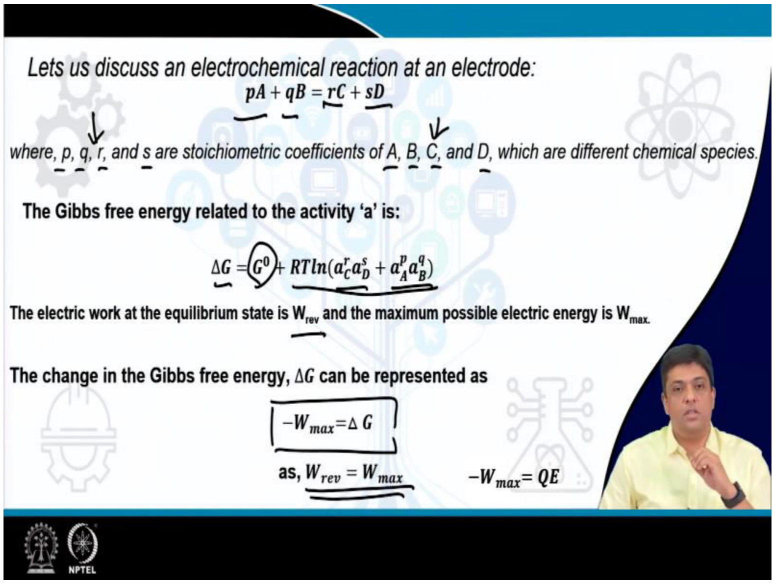

Lets us discuss an electrochemical reaction at an electrode:

$$pA + qB = rC + sD$$

where, p, q, r, and s are stoichiometric coefficients of A, B, C, and D, which are different chemical species.

The Gibbs free energy related to the activity 'a' is:

$$\Delta G = G^0 + RT\ln(a_C^r a_D^s + a_A^p a_B^q)$$

The electric work at the equilibrium state is W_{rev} and the maximum possible electric energy is W_{max}.

The change in the Gibbs free energy, ΔG can be represented as

$$\boxed{-W_{max} = \Delta G}$$

as, $W_{rev} = W_{max}$ $\quad$ $-W_{max} = QE$

For example, if you want to understand the whole mathematics of this, let us discuss the electrochemical reactions which take place at the electrode. If you have chemical species let us say A, B, C and D, you have these are the chemical species which are taking part in the electrochemical reactions and the stoichiometric coefficients for these A B C and D species are p q r and s respectively. Then for the case when you are getting an equilibrium condition you are talking about the state where pA plus qB should be equal to rC plus sD if you are taking into the complete electrochemical reactions taking place first set cathode side second is the anode side.

Now, when there is movement that means there is a change in the Gibbs free energy. The Gibbs free energy for an activity let us say 'a' is given by delta G equals to G0 plus RT ln a then the stoichiometric coefficients associated by the two species either at the cathode or the anode side and then you have the two activities related to each other.

The electric work at the equilibrium state is Wrev and the maximum possible electric energy is W max. What is delta G? The change in Gibbs free energy is actually the maximum possible electric energy. Hence minus of W max is equal to delta G what we know that Wrev is equal to W max.

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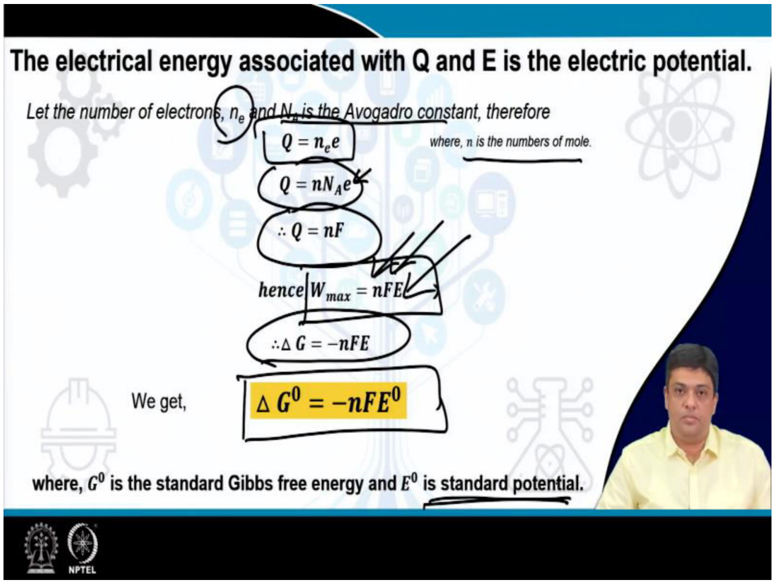

The electrical energy associated with Q and E is the electric potential.

Let the number of electrons, n_e and N_A is the Avogadro constant, therefore

$Q = n_e e$

where, n is the numbers of mole.

$Q = nN_Ae$

$\therefore Q = nF$

hence $W_{max} = nFE$

$\therefore \Delta G = -nFE$

We get, $\Delta G^0 = -nFE^0$

where, G^0 is the standard Gibbs free energy and E^0 is standard potential.

Hence, what will happen if you consider the condition where you are talking in terms of the change in Gibbs free energy, so the electrical energy associated with Q and E is the electric potential. Let us consider the electrons which are available to take part in the reaction or are getting released and they are in terms of moles and Na is the Avogadro's number then Q is equal to n e into e, that can be written as the number of moles into Avogadro's number into the charge that is n into Na into e, therefore what you get, you get Q is equal to n F.

What happens to the value of W max, you have W max is equal to n into F into E where F is the Faradays number or Faradays constant and delta G thus becomes equals to minus n F E. What would be the change in the G0 value, you have delta G0 is equal to minus n F E 0, where G0 is the standard Gibbs free energy and E0 is the standard potential you are talking.

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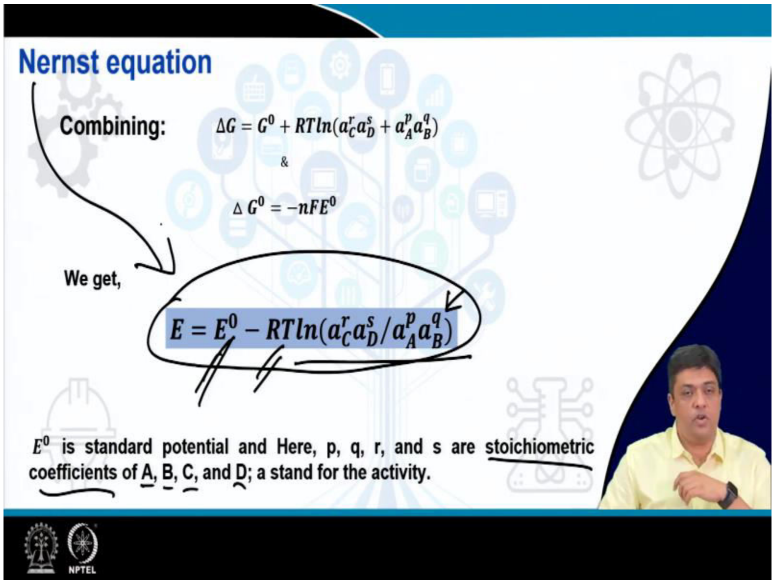

Nernst equation

Combining: $\Delta G = G^0 + RTln(a_C^r a_D^s + a_A^p a_B^q)$

&

$\Delta G^0 = -nFE^0$

We get,

$$E = E^0 - RTln(a_C^r a_D^s / a_A^p a_B^q)$$

E^0 is standard potential and Here, p, q, r, and s are stoichiometric coefficients of A, B, C, and D; a stand for the activity.

If you combine these two equations, what do you get you get the Nernst equation which is given by E is equal to the standard potential that is E0 minus RTln of a r c into a s d divided by a p by a, a b by q and remember what are p q r and s they are the stoichiometric coefficients of what of the chemical species A B C and D and a stands for the relevant activity which you are monitoring. So that is how the Nernst equation is written.

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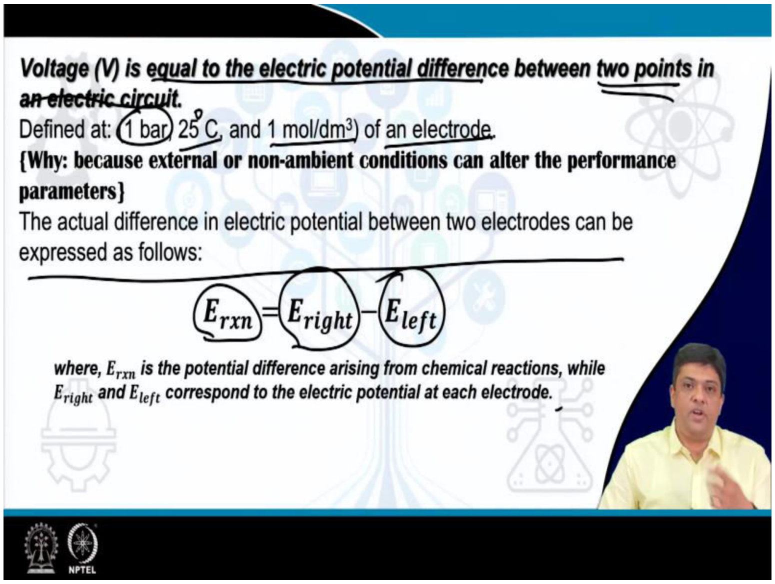
Voltage and Current of Batteries


Voltage (V) is equal to the electric potential difference between two points in an electric circuit.

Defined at: (1 bar, 25° C, and 1 mol/dm^3) of an electrode.

{Why: because external or non-ambient conditions can alter the performance parameters}

The actual difference in electric potential between two electrodes can be expressed as follows:

$$E_{rxn} = E_{right} - E_{left}$$

where, E_{rxn} is the potential difference arising from chemical reactions, while E_{right} and E_{left} correspond to the electric potential at each electrode.

After obtaining the Nernst equation, we can now talk about the Voltage and Current of the batteries. Voltage V is what is equal to the electric potential difference between two points in an electric circuit. Defined where, defined at 1 bar 25 degrees and 1 mole per decimeter cube standard condition for an electrode.

Why do we take this condition as the point where we will compare the performance? Why? Because external parameters and non-ambient conditions that means if you are analyzing the performance let us say at 65 degrees, 100 degrees, 25 degrees then the performance of the batteries are quite different and therefore if you need to compare the batteries and what is the voltage output from a particular batteries then the values obtained and these standard conditions are used.

And you will find that the actual difference so you can write the potential difference arising from chemical reactions as E r x n and that would become equal to the electric potential appearing where one electrode and the second electrode and the potential difference would be e let us say E right minus E left. So this is what the potential difference would be observed.

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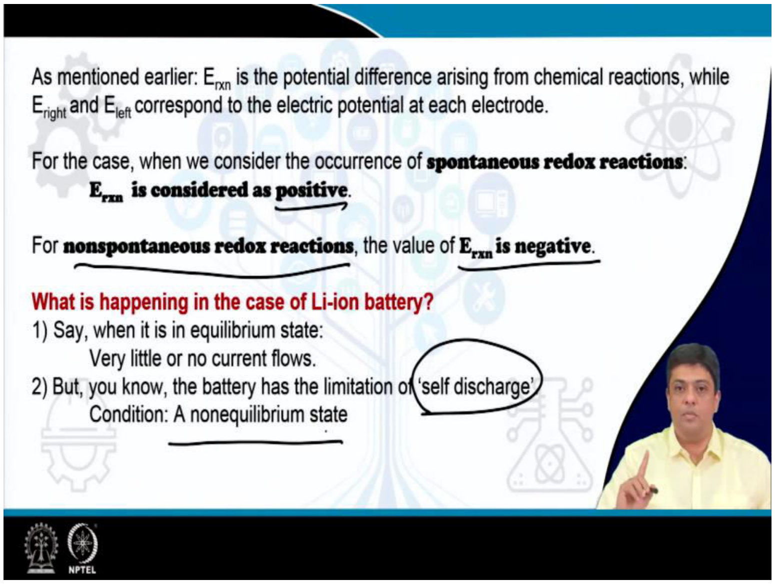

As mentioned earlier: E_{rxn} is the potential difference arising from chemical reactions, while E_{right} and E_{left} correspond to the electric potential at each electrode.

For the case, when we consider the occurrence of **spontaneous redox reactions**:

E_{rxn} is considered as positive.

For **nonspontaneous redox reactions**, the value of **E_{rxn} is negative**.

What is happening in the case of Li-ion battery?

1) Say, when it is in equilibrium state:
   Very little or no current flows.
2) But, you know, the battery has the limitation of 'self discharge'
   Condition: A nonequilibrium state

For the case when we consider the spontaneous redox reaction you consider that the potential difference arising from the chemical reactions is positive and for non-spontaneous redox reactions the values of E r x n is taken to be negative. But what is really happening in terms of lithium ion batteries? When it is in the equilibrium state you will find that very little or no current is flowing.

But if you charge for example, you can do this exercise or you can just think it over you have your mobile phone you charge your the battery of your mobile phone that is your mobile phone is having a battery which is fully charged 100 percent. You do not use the cell, you do not use the mobile phone for talking; for internet use; or for browsing and you just leave the phone switched on or even in a switched off mode.

You will find that after a certain time even when you have not used the phone if you monitor what is this percentage of charge remaining you will find that it is slowly reducing. You will think I have not used the phone then why is getting discharged? It is getting discharged because of an intrinsic phenomena that is associated with such kind of lithium-ion battery and that is called the self-discharge of a battery. And this leads to a condition that is a non-equilibrium condition and it is very much relevant for lithium-ion batteries.

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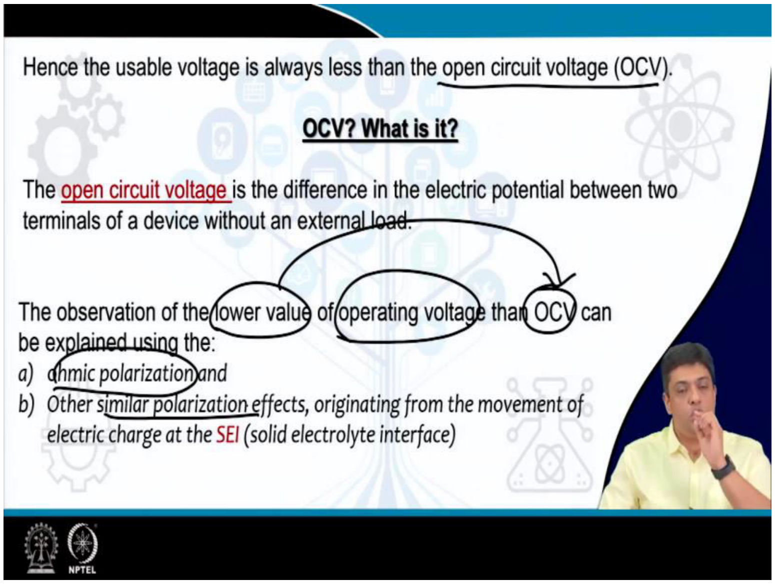

Hence the usable voltage is always less than the open circuit voltage (OCV).

OCV? What is it?

The open circuit voltage is the difference in the electric potential between two terminals of a device without an external load.

The observation of the lower value of operating voltage than OCV can be explained using the:

a) ohmic polarization and

b) Other similar polarization effects, originating from the movement of electric charge at the SEI (solid electrolyte interface)

So, what is the consequence? Even if you have a voltage which is called the open circuit voltage and this is the voltage which is the difference between the potentials that you have observed between the two electrodes even when there was no external load. So in absence of external load what is the voltage you obtain? That is the maximum voltage which you can get but when you actually observe the voltage which you are able to extract or the operating voltage then the values are mostly lower than the open circuit voltage; question is why?

Why I am not able to extract the full voltage? Or I am losing on the voltage which should have been there even when I was connecting the external node? This happens because of phenomena such as Ohmic polarization or similar polarization effects which originate due to the movement of electric charge at the solid electrolyte interface. Solid; the electrode, electrolyte: the aqueous media and where these two systems meet that there is an interface forming and that is called the solid electrolyte interface.

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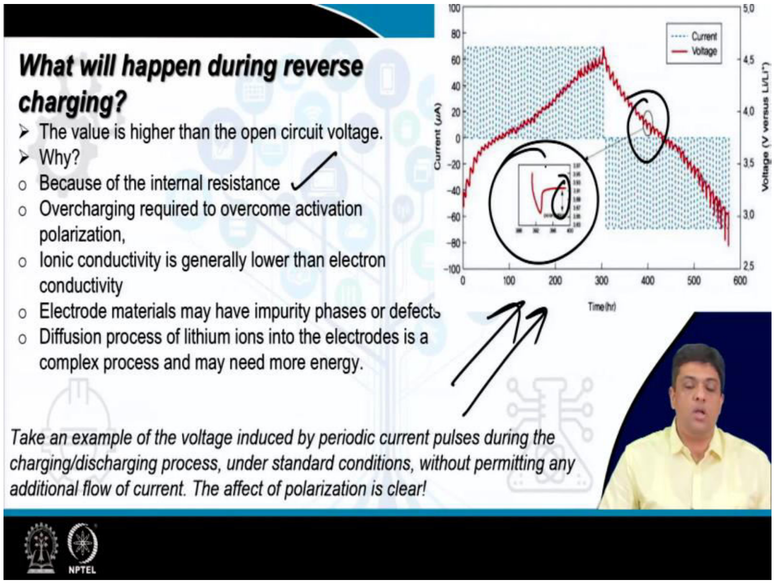

What will happen during reverse charging?

- ➢ The value is higher than the open circuit voltage.
- ➢ Why?
  - o Because of the internal resistance ✓
  - o Overcharging required to overcome activation polarization,
  - o Ionic conductivity is generally lower than electron conductivity
  - o Electrode materials may have impurity phases or defects
  - o Diffusion process of lithium ions into the electrodes is a complex process and may need more energy.

Take an example of the voltage induced by periodic current pulses during the charging/discharging process, under standard conditions, without permitting any additional flow of current. The affect of polarization is clear!

What happens? The value is higher than the open circuit voltage when you are seeing the reverse charging; why is it happening? Because of the internal resistance, because you have over charging required to overcome the activation polarization then along with that you have ionic conductivity which is generally lower than the electron conductivity.

Then you have to also take into consideration that the electron materials may have impurity phases or defects which have to be counter or you need to give more voltage to maintain the OCV. So you are actually losing some voltage during the charging process. What we are talking here is the reverse charging. And diffusion process of lithium ions into the electrodes is a complex process and may need more energy.

For example, in the graph here you can take an example of voltage induced by periodic current pulses. So you have current pulses which are giving the pulses during the charging and discharging process and there you will find that even under standard conditions without permitting any additional flow of current you find certain loss. So if you take the zoom picture of a particular region you find that you are losing some voltage or you are actually losing the current. So that is the reason why you talk about the effect of polarization.

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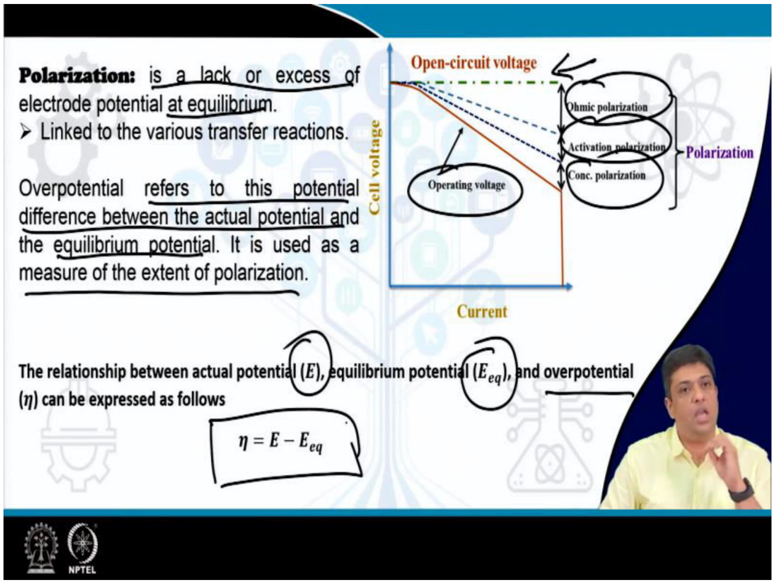

Polarization: is a lack or excess of electrode potential at equilibrium.

- Linked to the various transfer reactions.

Overpotential refers to this potential difference between the actual potential and the equilibrium potential. It is used as a measure of the extent of polarization.

The relationship between actual potential (E), equilibrium potential (E_{eq}), and overpotential (η) can be expressed as follows

$$\eta = E - E_{eq}$$

So, what is polarization? This is a lack or excess of electrode potential at equilibrium and that is directly linked to the various transfer reactions which are occurring at different places in the cell. Over-potential refers to the potential difference between the actual potential and the equilibrium potential and this is used as a measure of extent of polarization.

So, you can see what you are seeing; the green line shows the OCV. So what you are doing you have the electrodes immerse in electrolyte and without any external load you are measuring the voltage that is the maximum voltage you can extract. But what you see is actually a much lower voltage and this is appearing because of various phenomenas. The ohmic-polarization, the activation polarization and concentration polarization and you will see from this curve that the contribution from ohmic polarization is predominant in this case.

And the relationship between the actual potential E and the equilibrium potential with the over potential is given by E minus Eq. So your over potential is equal to the difference between the actual potential and the equilibrium potential.

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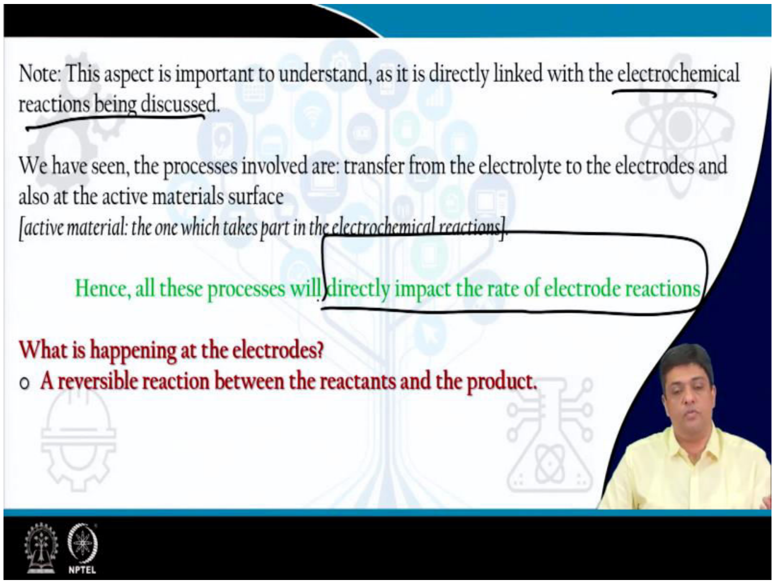

Note: This aspect is important to understand, as it is directly linked with the electrochemical reactions being discussed.

We have seen, the processes involved are: transfer from the electrolyte to the electrodes and also at the active materials surface

[active material: the one which takes part in the electrochemical reactions]

Hence, all these processes will directly impact the rate of electrode reactions

What is happening at the electrodes?

- **A reversible reaction between the reactants and the product.**

And this phenomena should be understood clearly because they are linked directly with the electrochemical reactions and if they are directly linked with the electrochemical reactions they will have a direct impact on the rate of electrode reactions which would then control the stability and other performance of the battery.

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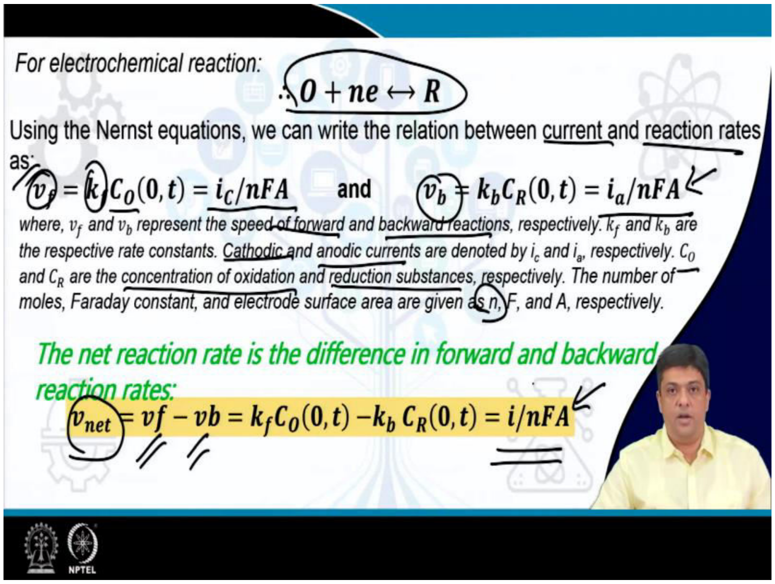

For electrochemical reaction:

$$O + ne \leftrightarrow R$$

Using the Nernst equations, we can write the relation between current and reaction rates as:

$$v_f = k_f C_O(0,t) = i_C/nFA \quad \text{and} \quad v_b = k_b C_R(0,t) = i_a/nFA$$

where, v_f and v_b represent the speed of forward and backward reactions, respectively. k_f and k_b are the respective rate constants. Cathodic and anodic currents are denoted by i_c and i_a, respectively. C_O and C_R are the concentration of oxidation and reduction substances, respectively. The number of moles, Faraday constant, and electrode surface area are given as n, F, and A, respectively.

The net reaction rate is the difference in forward and backward reaction rates:

$$v_{net} = vf - vb = k_f C_O(0,t) - k_b\, C_R(0,t) = i/nFA$$

Let us say for an electrochemical reaction what do you write? You have an oxidizing reactant then if you take O plus n e is equal to R using the Nernst relation, we can write the relation between the current and the reaction rates as Vf and Vb which represent the forward and the backward reactions. This can be written as Vf is equal to Kf into C0 o t is equal to i c by nFA and similarly you can write Vb is equal to i a by nFA; where i c and i a are the cathodic and anodic currents respectively.

Ic cathodic; Ia anodic. C0 and Cr, C0 concentration of oxidation and Cr concentration of reducing substances; F the faraday constant, A the surface area and the value of n represent the moles of the reactants. So the net reaction rate is the difference between what? What is the net reaction rate would be the difference in the forward and the back reaction rates. So v net is equal to Vf minus Vb that is equal to i by nFA this is what the relationship stands for the net reaction rate. So it depends quite a lot on the surface area and the current.

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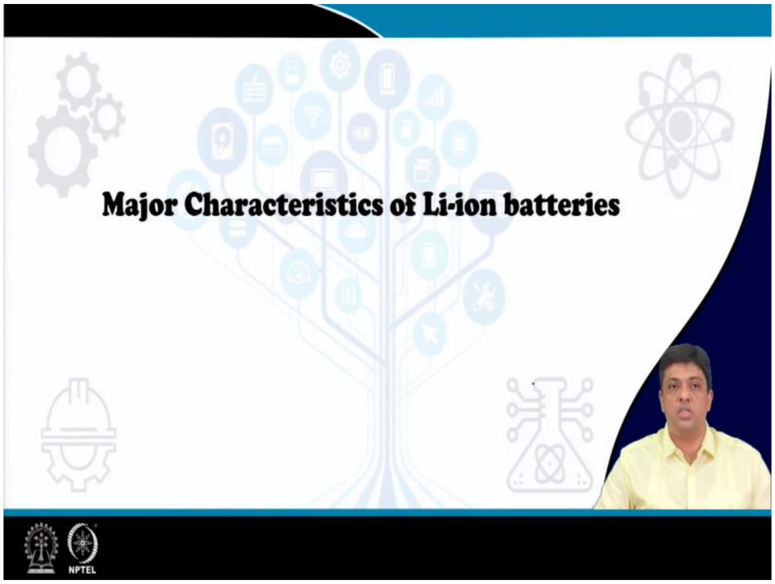
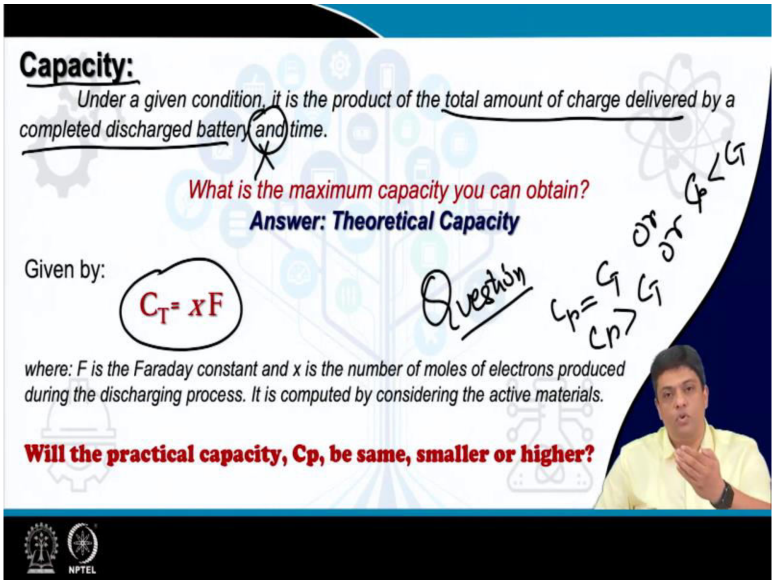


Major Characteristics of Li-ion batteries



Capacity:

Under a given condition, it is the product of the total amount of charge delivered by a completed discharged battery and time.

What is the maximum capacity you can obtain?

Answer: Theoretical Capacity

Given by: $C_T = xF$

where: F is the Faraday constant and x is the number of moles of electrons produced during the discharging process. It is computed by considering the active materials.

Will the practical capacity, Cp, be same, smaller or higher?

Question

$C_p = C_t$ or $C_p > C_t$ or $C_p < C_t$

Now, I have obtained the details about the electrochemical reactions, how do we measure those reactions, what are the parameters those impact these reactions then what would be the characteristics which would be defined using these informations? The first information which is used is the capacity. It is the product of total amount of charge delivered by a completely discharged battery and time. So you have the product of total amount of charge delivered by a battery and time.

If somebody ask what is the maximum capacity you can obtain? I can obtain the maximum capacity that is called the theoretical capacity that is given by Ct is equal to x into F this is what the answer would be. My next question would be in real terms, in a real battery will you get the value of the practical capacity that is same as Ct? So, if I ask a question will Cp be equal to Ct or Cp would be greater than Ct or Cp would be less than Ct? What do you think? Before I start discussing spend a time and then think it over before you go to the next slide which will give you a hint towards these questions. What do you think will be happening?

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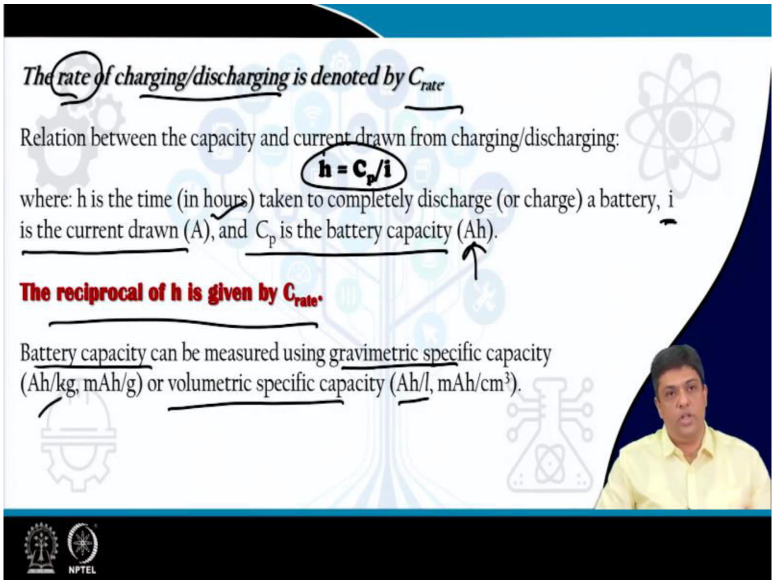

The rate of charging/discharging is denoted by C_{rate}

Relation between the capacity and current drawn from charging/discharging:

$$h = C_p/i$$

where: h is the time (in hours) taken to completely discharge (or charge) a battery, i is the current drawn (A), and C_p is the battery capacity (Ah).

The reciprocal of h is given by C_{rate}.

Battery capacity can be measured using gravimetric specific capacity (Ah/kg, mAh/g) or volumetric specific capacity (Ah/l, mAh/cm^3).

You will find that the rates would be mostly lower, why? We have already talked about the concepts of polarization and we have seen the zoom picture where you are seeing the losses due to polarization. And once I have obtained the value of Cp I can then define another term that is the charging or the discharging rate that is written as C rate and the relationship between the capacity and the current drawn from the charging discharging cycle is given as h is equal to Cp by i where h is in hours taken to completely discharge a battery or sometimes people also take the time taken to completely charge a battery.

i is the current drawn in amperes and Cp is a parameter that is linked to battery capacity and it is given in terms of ampere hours and the reciprocal of H gives the C rate. So if somebody says that I am charging the battery at 1C then what is the person indicating? If the person is now saying no I am charging the battery let us say I am charging up to 1 ampere then and then I am using 2C then what is it being indicated? Are you doubling the time or are you making time which was half the earlier case when you had 1C.

Think it over write it so that the concept becomes very clear. I am asking you to write the condition and understand what do you mean by 1C, 2C, 0.5C or any other similar values which you would like to write and then you will understand whether you are charging at a faster rate or a rate which is slower than the 1C condition. And the battery capacity can be measured as gravimetric specific capacity or volumetric specific capacities in different units.

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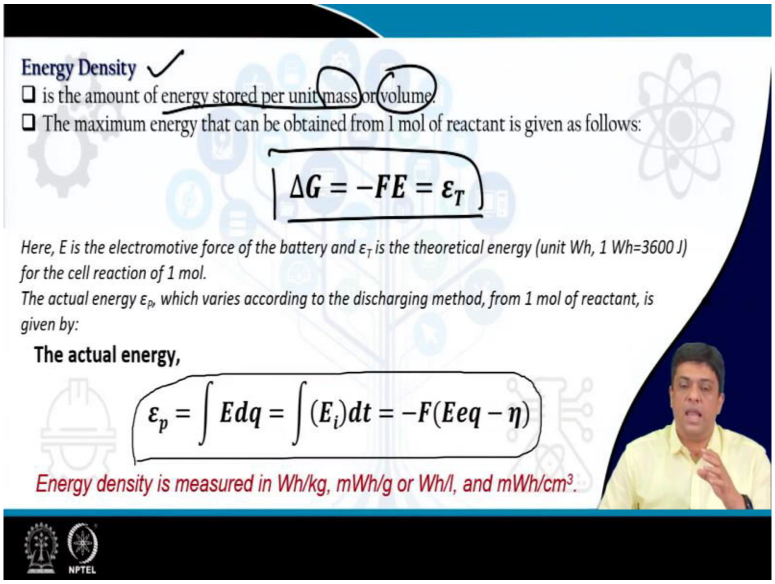

Energy Density ✓

- is the amount of energy stored per unit mass or volume.
- The maximum energy that can be obtained from 1 mol of reactant is given as follows:

$$\Delta G = -FE = \varepsilon_T$$

Here, E is the electromotive force of the battery and ε_T is the theoretical energy (unit Wh, 1 Wh=3600 J) for the cell reaction of 1 mol.

The actual energy ε_p, which varies according to the discharging method, from 1 mol of reactant, is given by:

The actual energy,

$$\varepsilon_p = \int Edq = \int (E_i)dt = -F(Eeq - \eta)$$

Energy density is measured in Wh/kg, mWh/g or Wh/l, and mWh/cm^3.

So, once I have obtained the value of capacity the next term which is used is the energy density. As mentioned earlier the maximum energy that can be obtained from one mole of reactant is given by delta G that is equal to minus FE here we write delta G is equal to epsilon t where E is the electromotive force of the battery, epsilon t is the theoretical energy in watt hour but if I have to simply define energy density then energy density is the energy stored per unit mass or energy stored per unit volume. And the actual energy is actually written as epsilon p that is equal to minus F into E equilibrium minus eta because you are losing some energy owing to phenomena like self-discharge.

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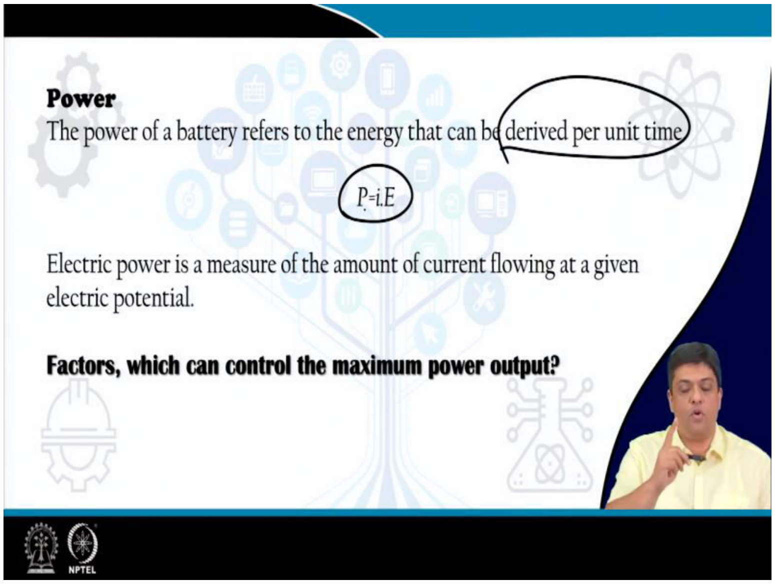

Power

The power of a battery refers to the energy that can be derived per unit time

$P = i.E$

Electric power is a measure of the amount of current flowing at a given electric potential.

Factors, which can control the maximum power output?

Next term which is relevant to energy is the power. What is the power? Power means how much energy I can extract in a given time. So the power of a battery refers to the energy that can be derived per unit time and is given by i into E. And this is a measure of the amount of current flowing at a given electric potential.

Can you please think which all parameters would be controlling the maximum power output based on the discussions we have had till now and lot of answers have already been given to this question in the previous part of this lecture.

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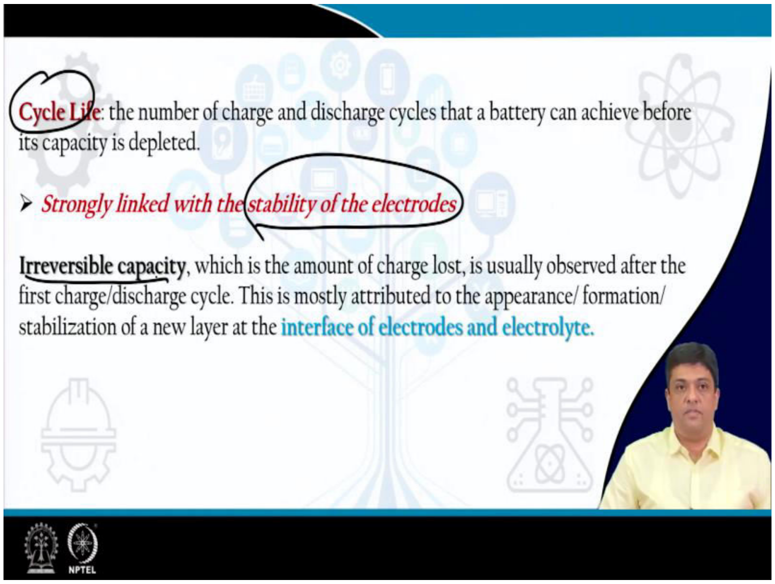

Cycle Life: the number of charge and discharge cycles that a battery can achieve before its capacity is depleted.

- *Strongly linked with the stability of the electrodes*

Irreversible capacity, which is the amount of charge lost, is usually observed after the first charge/discharge cycle. This is mostly attributed to the appearance/ formation/ stabilization of a new layer at the **interface of electrodes and electrolyte.**

We are talking about lithium-ion batteries which are rechargeable that means you will reuse them rechargeable for how many times? 1, 2, 3, 4, 10, 100, 1000 the number of cycles which the battery can achieve before its capacity is totally depleted defines its cycle life. And the cycling stability is directly linked with the stability of the electrode materials. Mostly the electrodes materials degrade as a function of cycling and that leads to the loss in performance.

There is also an additional term which should be understood that is the irreversible capacity which is the amount of charge lost usually observed after the first charge or discharge cycle. So if I fabricate a battery you will find that the first cycle may give you a value which is quite high or let us say is a value given by a parameter x when you go to the next cycle you may find that the value for that parameter has actually reduced to y where y is mostly less than x if I am talking in terms of energy or power densities.

This is mostly attributed to the appearance or formation or stabilization of new layers at the electrode electrolyte interfaces or you may have certain appearance of inactive sites within the electrodes itself.

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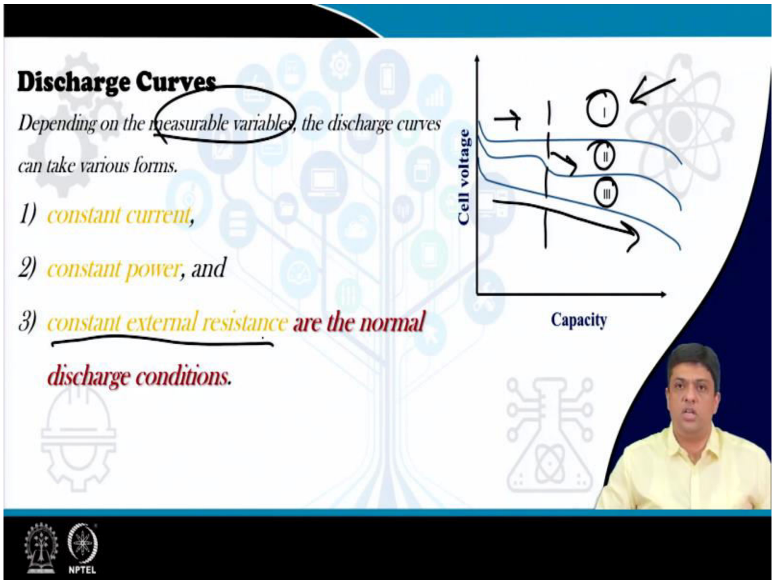

Discharge Curves

Depending on the measurable variables, the discharge curves can take various forms.

1) *constant current,*

2) *constant power, and*

3) *constant external resistance* **are the normal discharge conditions.**

Along with the irreversible capacity you will also see that depending upon the measurable variables the discharge curves can take various forms. Let us say here we are given 1, 2 and 3 types of forms.

In the first you can see that if you have discharge curve similar to the one showing by curve 1 there you are talking about a near constant current discharge curve. In the case of second you see two regions but two stable regions, so you move from one region to the next region. And here in these two regions at least you are talking about a constant power like discharge curves.

But in the third case you see a continuously decreasing trend that means that electrochemical reactions are such that you are continuously finding it changing its characteristic or if the reactions are there then the reactions are changing their characteristics. In addition, you can have other factors which can lead to such kind of continuously varying discharge curve and they are called as constant external resistance curves and are the normal discharge conditions which you observe.

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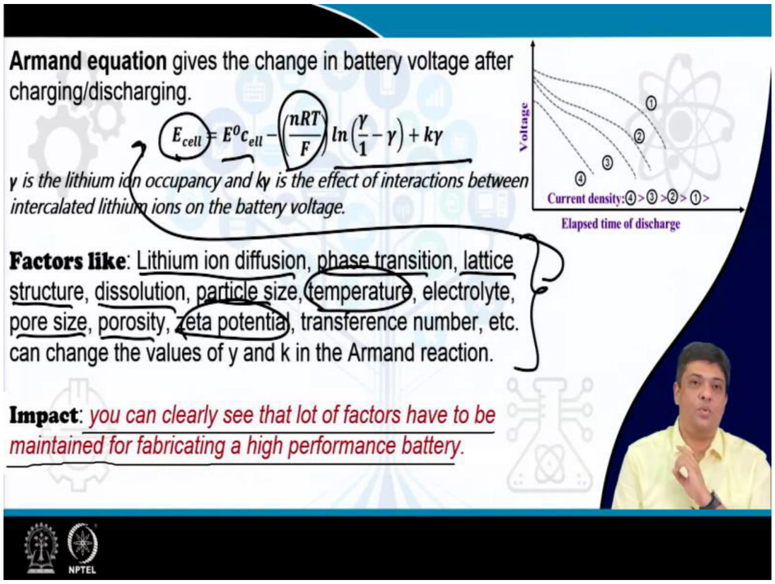

Armand equation gives the change in battery voltage after charging/discharging.

$$\boxed{E_{cell}} = E^0c_{ell} - \left(\frac{nRT}{F}\right) ln\left(\frac{\gamma}{1} - \gamma\right) + k\gamma$$

γ is the lithium ion occupancy and kγ is the effect of interactions between intercalated lithium ions on the battery voltage.

Factors like: Lithium ion diffusion, phase transition, lattice structure, dissolution, particle size, temperature, electrolyte, pore size, porosity, zeta potential, transference number, etc. can change the values of y and k in the Armand reaction.

Impact: *you can clearly see that lot of factors have to be maintained for fabricating a high performance battery.*

We have seen that the discharge curves can be of different shapes and forms. Armand equation which is given by professor Michel Armand from France who now has a research group in Spain gives the change in battery voltage after charging discharging. So, the cell voltage is the initial cell voltage minus nRT by f ln gamma by 1 minus gamma plus k gamma where gamma is the lithium ion occupancy and k gamma is the effect of interaction between intercalated lithium ions on the battery voltage.

These factors can change significantly as a function of let us say lithium ion diffusion, phase transitions. Phase transitions in the electrode; why? You will say I am not changing the temperature but yes what you are doing you are actually changing the phase of the material, how, let us say you are talking about lithium cobalt oxide $LiCoO_2$ but when I take lithium out I have Li 1 minus x Co O_2.

In this case what are we doing? We are actually changing the phase of the material and if in a process where the lithium is taken back into the lattice if all of lithium does not go back and occupy the same Wyckoff position they go and sit as an impurity or in at an interstitial site then your phase has changed. So because of this cycling you can see various changes in the phase of the material itself and that is what we are talking about not maybe a temperature dependent phase transition but because of this cycling you are seeing continuous change in the phase of the material.

You can see the change in the associated lattice structure, the dissolution; factors like particle size, extrinsic factors may be temperature, pressure, magnetic field, electric field those can change and then comes the factors associated with nanostructures, the pore size, the porosity, the surface to volume ratio and if you have the surface to volume ratio changing that means the size is changing. The zeta potential changes and all these factors can lead to the change in the battery voltage as a function of charging discharging.

So, why am I writing this equation? The reason is that you can clearly see that there are lot of factors which have to be maintained for fabrication of a high-performance battery that is the reason why I am indicating this formula.

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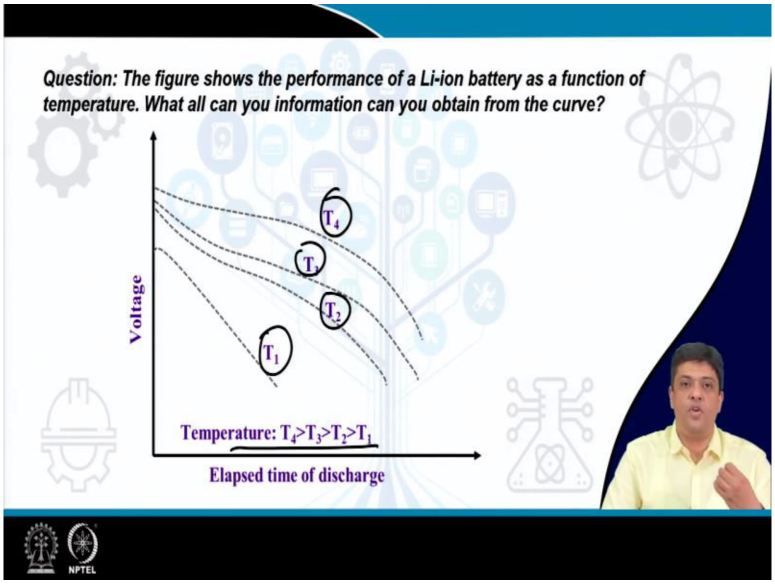

Question: The figure shows the performance of a Li-ion battery as a function of temperature. What all can you information can you obtain from the curve?

In the previous slide I mentioned that extrinsic factors can impact the performance of the battery. In this curve I have given you a question which says that please examine the voltage versus time curve in a lithium ion battery. But this battery is being operated at different temperatures. Let us say T1, T2, T3 and T4 such that T4 is greater than T3 which is greater than T2 and T1 is the lowest voltage.

You can clearly see that the performance is changing; can you list the change in the performance which you are seeing from this curve and find out the temperature where the battery is actually performing the best?

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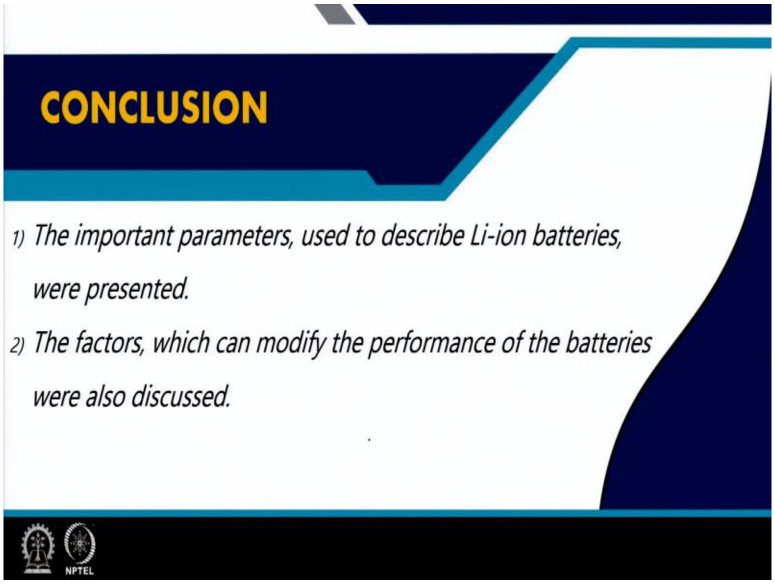

CONCLUSION

1) The important parameters, used to describe Li-ion batteries, were presented.
2) The factors, which can modify the performance of the batteries were also discussed.

If you are able to answer that question then it means you have clearly understood the parameters which are used to describe the lithium-ion batteries and how these parameters get modified both as a function of intrinsic factors as well as extrinsic factors.

If you have not been able to answer that question just listen to the points mentioned while the discussion was being presented in the earlier slides and you will be able to answer this question quite easily.

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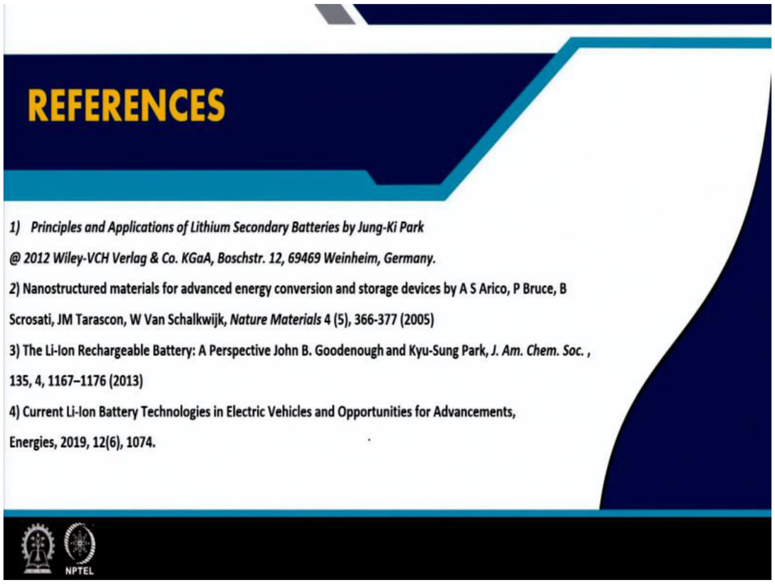

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These are the reference books or the materials which were used for preparing the lecture notes that were presented today and I thank you for attending the second lecture on lithium-ion batteries. Thank you.