Electrochemical Energy Storage

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Module - 02
Definitions and measuring methods
Lecture - 07
Terminology Related to Secondary Battery: Half - Cell, Full - Cell, Redox Couple, Positive and Negative Electrodes, Active Materials, Module, Pack, Battery Management System

Welcome to my course Electrochemical Energy Storage and this is module number 2, where we are discussing the definitions and measuring method pertinent to rechargeable batteries. This is lecture number 7, where I will introduce various terminology that is Related to Secondary Batteries, including Half Cell, Full Cell, Redox Couple already I have introduced as a part of my earlier lecture.

Then Positive and Negative Electrode the concept of Positive and Negative Electrode we avoid calling the anode and cathode, then we will talk about the Active Materials and finally Module, Pack and Battery Management System.

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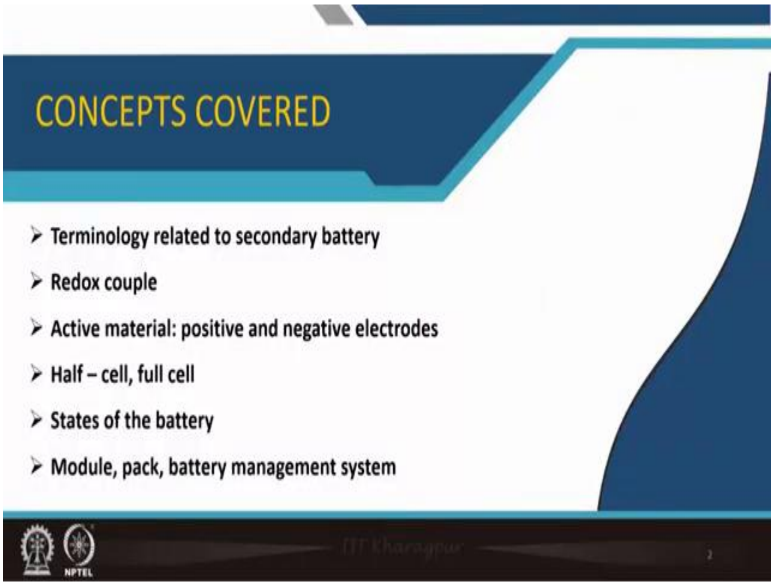

CONCEPTS COVERED

- Terminology related to secondary battery
- Redox couple
- Active material: positive and negative electrodes
- Half – cell, full cell
- States of the battery
- Module, pack, battery management system

So, in this particular lecture as I told, first we will talk about the terminology that is related to secondary battery, we talk about the redox couple in little bit more extent, then active material positive and negative electrodes, half cell and full cell concept, state of the battery we will introduce and finally the module, pack and battery management system.

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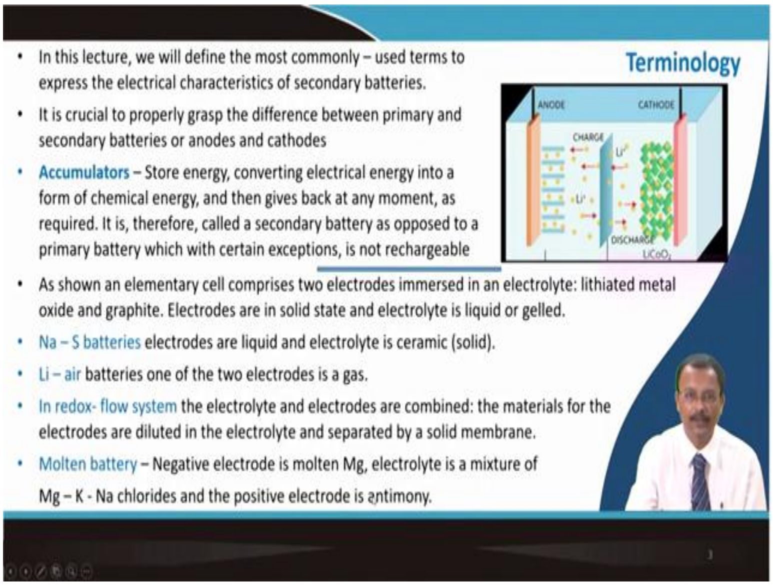

Terminology

- In this lecture, we will define the most commonly – used terms to express the electrical characteristics of secondary batteries.
- It is crucial to properly grasp the difference between primary and secondary batteries or anodes and cathodes
- **Accumulators** – Store energy, converting electrical energy into a form of chemical energy, and then gives back at any moment, as required. It is, therefore, called a secondary battery as opposed to a primary battery which with certain exceptions, is not rechargeable
- As shown an elementary cell comprises two electrodes immersed in an electrolyte: lithiated metal oxide and graphite. Electrodes are in solid state and electrolyte is liquid or gelled.
- Na – S batteries electrodes are liquid and electrolyte is ceramic (solid).
- Li – air batteries one of the two electrodes is a gas.
- In redox- flow system the electrolyte and electrodes are combined: the materials for the electrodes are diluted in the electrolyte and separated by a solid membrane.
- Molten battery – Negative electrode is molten Mg, electrolyte is a mixture of Mg – K - Na chlorides and the positive electrode is antimony.

So, this already you know by this time that it is actually very crucial to grasp the difference between a primary and secondary batteries and the term terminology which is anode and cathode. So, we will introduce a term which is accumulator, the accumulator stores the energy converting electrical energy into the form of a chemical energy.

So, in primary battery chemical energy gives you electrical energy, but the accumulator what it does you apply electrical energy and get back the chemical energy again for reuse. So, this energy can be given back at any moment. So, secondary battery as opposed to a primary battery with certain exception that primary battery is not rechargeable in most of the instances, but secondary battery you can reuse it.

So, the elementary cell that comprises of two electrode that is basically immersed in an electrolyte. So, lithiated metal oxide and graphite basically these are the two very common electrode and electrodes they are in solid state and electrolyte is either liquid or in a gel state. I have introduced different types of battery for example, if you remember sodium sulphur battery there the electrodes are liquid and electrolyte that was is solid ceramic.

In case of lithium air battery, one of the two electrodes is gaseous, in the redox flow battery the electrolyte and electrode they are combined the material for electrodes are basically diluted in the electrolyte and that is separated by a solid membrane. In molten battery negative electrode is basically molten magnesium, electrolyte is a mixture of magnesium, potassium and sodium chloride base mixture and positive electrode is antimony that is also under molten condition.

So, there are various types of possibilities that is there in the secondary electrode, but mostly we will confined our self to the solid electrodes and either gel or the liquid base electrolyte throughout the discussion of this particular course.

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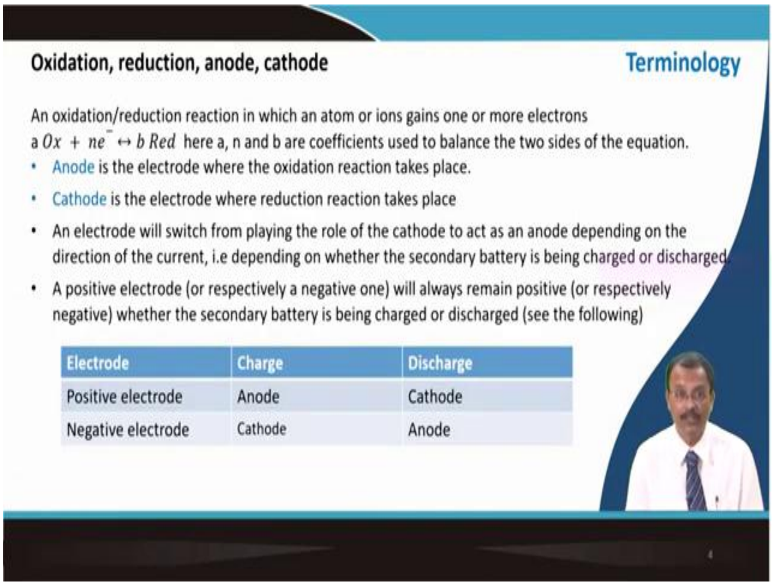

Oxidation, reduction, anode, cathode

Terminology

An oxidation/reduction reaction in which an atom or ions gains one or more electrons

$a\,Ox + ne^{-} \leftrightarrow b\,Red$ here a, n and b are coefficients used to balance the two sides of the equation.

- Anode is the electrode where the oxidation reaction takes place.
- Cathode is the electrode where reduction reaction takes place
- An electrode will switch from playing the role of the cathode to act as an anode depending on the direction of the current, i.e depending on whether the secondary battery is being charged or discharged.
- A positive electrode (or respectively a negative one) will always remain positive (or respectively negative) whether the secondary battery is being charged or discharged (see the following)

Electrode	Charge	Discharge
Positive electrode	Anode	Cathode
Negative electrode	Cathode	Anode

So, as I told that oxidation and reduction reaction where this atom or ions they gain one or more electron or vice versa. Whenever oxidation is taking place then from metal for example, electron is going out from this metal.

So, anode is the electrode where oxidation takes place that is for the primary battery, cathode is the electrode where reduction takes place. So, the electrode will switch from playing the role of cathode to act as anode depending on the direction of the current. So, you as you know from anode, the current goes to the cathode while the cells are discharged, the reverse occurs while the cell is charged.

So, a positive electrode or respectively a negative one will always remain positive or respectively negative, whether the secondary battery is being charged or discharged, see that is that one. So, I define as a positive electrode during charge, it acts as a anode and during discharge it is a cathode and the same thing applies for the negative electrode. So, during charge it acts as a cathode and discharge it acts as an anode.

So, in the rechargeable battery we will not use anymore the term cathode or anode instead we will always use this term as positive electrode or negative electrode in all our future description.

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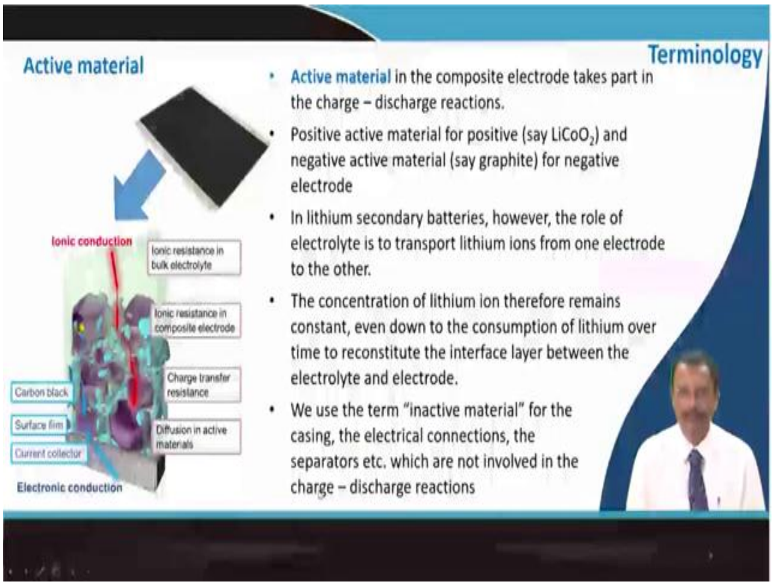

Terminology

Active material

- Active material in the composite electrode takes part in the charge – discharge reactions.
- Positive active material for positive (say $LiCoO_2$) and negative active material (say graphite) for negative electrode
- In lithium secondary batteries, however, the role of electrolyte is to transport lithium ions from one electrode to the other.
- The concentration of lithium ion therefore remains constant, even down to the consumption of lithium over time to reconstitute the interface layer between the electrolyte and electrode.
- We use the term "inactive material" for the casing, the electrical connections, the separators etc. which are not involved in the charge – discharge reactions

So, you know the active material which undergoes this redox reaction they takes part in this charge discharge reaction. So, say for example, lithium cobalt oxide and the negative active material is say graphite.

So, these are the material where the actual redox reaction takes place. So, lithium ion battery the role of electrolyte is just to transport lithium ions from one electrode to other. The concentration of lithium ion therefore, remains constant even down to the consumption of the lithium over time to reconstitute the interface layer between the electrolyte and electrode. This concept will be clarified when I will talk about a case study.

So, we will use the term inactive material which is added inside the electrode material for various purpose and also the casing of the battery, the electrical connections, the separator which is there in between two electrodes, which are not involved in the charge discharge reaction we call these are inactive material.

So, the active material is not all. So, usually a typical electrode if you see for a lithium ion or any rechargeable battery, it looks like that you have a current collector and then you have active material which is mixed with inactive material. In this case we use acetylene black which conduct the electrons and the binder which is PVDF which strongly adhered the whole mass into the current collector.

So, the total composite electrode looks like that. So, typically this is for the positive electrode. So, you have the ionic resistance in the bulk electrolyte that must overcome, then ionic resistance of the composite electrode that must be overcome, then there is a charge transfer resistance involved when the alkali ion is going inside the electrode material or going out from the electrode material.

And diffusion is also operative in the active material. So, a lot of phenomena that occurs inside this composite electrode during charge and discharge operation we will come back to it at the latter part of the course, in other lectures, but the active material is constitute only 80 percent of the total composite electrode and 20 percent is 10 is your acetylene black and 10 is the PVDF. So, that constitute the actual electrode material.

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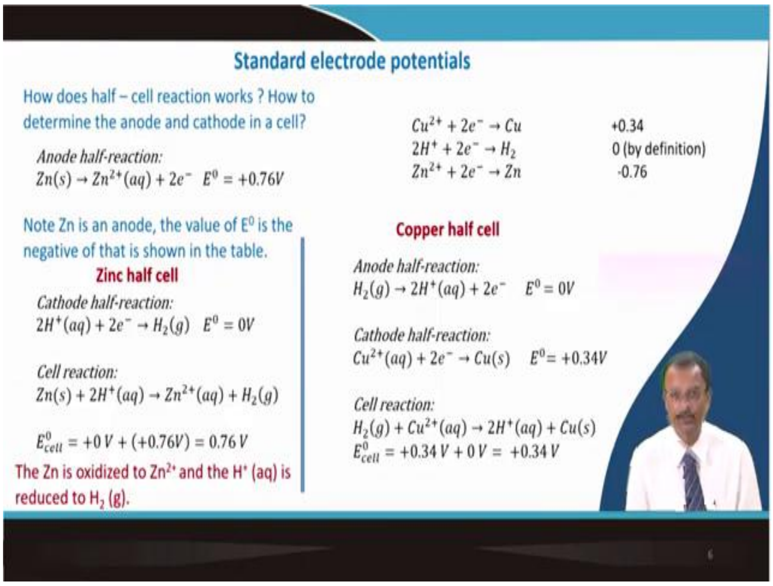

Standard electrode potentials

How does half – cell reaction works ? How to determine the anode and cathode in a cell?

$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H^+ + 2e^- \rightarrow H_2$	0 (by definition)
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

Anode half-reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^0 = +0.76V$

Note Zn is an anode, the value of E^0 is the negative of that is shown in the table.

Zinc half cell

Cathode half-reaction:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^0 = 0V$

Cell reaction:

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$E^0_{cell} = +0\,V + (+0.76V) = 0.76\,V$

The Zn is oxidized to Zn^{2+} and the H^+ (aq) is reduced to H_2 (g).

Copper half cell

Anode half-reaction:

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $E^0 = 0V$

Cathode half-reaction:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^0 = +0.34V$

Cell reaction:

$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$

$E^0_{cell} = +0.34\,V + 0\,V = +0.34\,V$

So, again if I come back to our old Daniell cell you can see that this half cell reaction when you talk about it. So, zinc is basically oxidized and the standard reduction potential as I told this is positive and it is measured with respect to a hydrogen standard NHE standard hydrogen electrode is about plus 0.76.

Anode half-reaction:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \quad E^{0} = +0.76V$$

Cathode half-reaction:

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \quad E^{0} = 0V$$

Cell reaction:

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

$$E^{0}_{cell} = +0\,V + (+0.76V) = 0.76\,V$$

And in the cathodic region copper ion is getting reduced to electroplate copper and this voltage is measured as plus 0.34 and by convention this voltage is taken as negative because basically it is not the standard reduction potential it is electro positive material.

Anode half-reaction:

$$H_2(g) \rightarrow 2H^{+}(aq) + 2e^{-} \quad E^{0} = 0V$$

Cathode half-reaction:

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^{0} = +0.34V$

Cell reaction:

$$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^{+}(aq) + Cu(s)$$

$$E^{0}_{cell} = +0.34\,V + 0\,V = \ +0.34\,V$$

So, the half cell reaction already I have described with respect to hydrogen it is measured for the zinc and copper half cell the reaction in my earlier part of the lecture already we covered that. So, this is given a voltage about 0.34 under standard condition.

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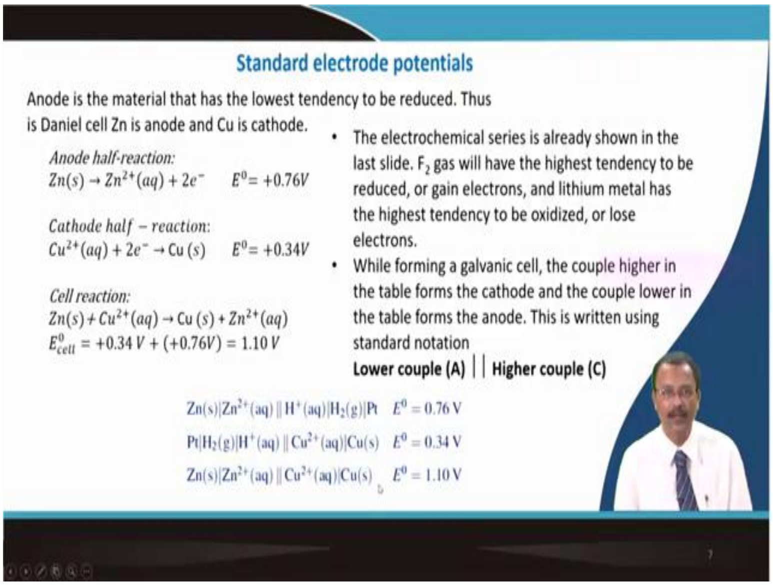

Standard electrode potentials

Anode is the material that has the lowest tendency to be reduced. Thus is Daniel cell Zn is anode and Cu is cathode.

Anode half-reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \quad E^0 = +0.76V$

Cathode half − reaction:

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^0 = +0.34V$

Cell reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

$E^0_{cell} = +0.34\,V + (+0.76V) = 1.10\,V$

- The electrochemical series is already shown in the last slide. F_2 gas will have the highest tendency to be reduced, or gain electrons, and lithium metal has the highest tendency to be oxidized, or lose electrons.
- While forming a galvanic cell, the couple higher in the table forms the cathode and the couple lower in the table forms the anode. This is written using standard notation

Lower couple (A) || Higher couple (C)

$Zn(s)|Zn^{2+}(aq)\,||\,H^{+}(aq)|H_2(g)|Pt \quad E^0 = 0.76\,V$

$Pt|H_2(g)|H^{+}(aq)\,||\,Cu^{2+}(aq)|Cu(s) \quad E^0 = 0.34\,V$

$Zn(s)|Zn^{2+}(aq)\,||\,Cu^{2+}(aq)|Cu(s) \quad E^0 = 1.10\,V$

So, this anode half cell reaction is plus 0.76 and cathode is 0.34. So, the electrochemical series which I described in my earlier lecture. So, if you consider that the fluorine gas will have the highest tendency to be reduced or gain electrons and lithium metal has a highest tendency to get oxidized or lose electron. So, if you want to make a high voltage battery you should take those these two material, but it is extremely difficult to construct this kind of material.

So, while forming a galvanic cell the couple higher in the table form the cathode usually and couple lower in the table that forms the anode. So, this is written in this kind of notation, that lower couple A this is separated by a separator and this is the higher couple higher redox couple which is cathode. So, for zinc the standard potential is 0.76 six for copper it is 0.34 and for the full cell you get therefore, 1.10 volt.

Anode half-reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad E^0 = +0.76V$

$$Cathode\ half-reaction:$$

$Cu^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}\ (s)$ $\quad E^0 = +0.34V$

Cell reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow \mathrm{Cu}\ (s) + Zn^{2+}(aq)$

$$E^0_{cell} = +0.34\ V + (+0.76V) = 1.10\ V$$

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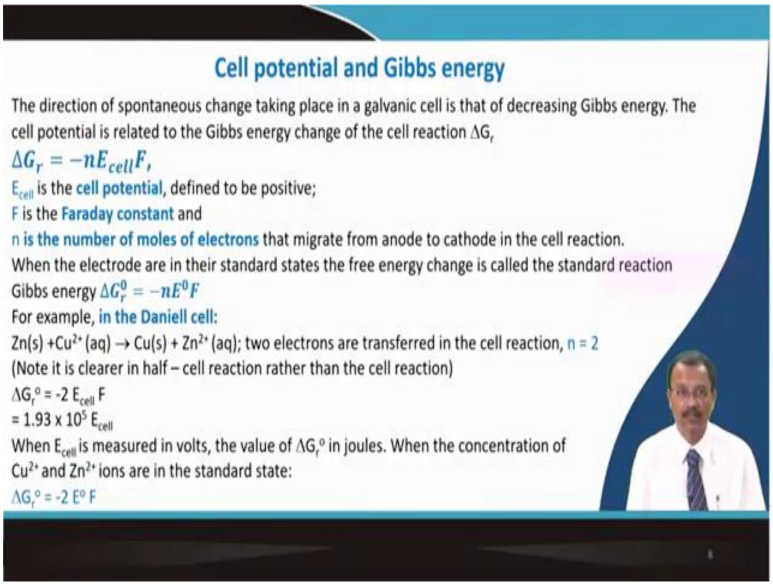

Cell potential and Gibbs energy

The direction of spontaneous change taking place in a galvanic cell is that of decreasing Gibbs energy. The cell potential is related to the Gibbs energy change of the cell reaction ΔG_r

$\Delta G_r = -nE_{cell}F,$

E_{cell} is the **cell potential**, defined to be positive;

F is the **Faraday constant** and

n **is the number of moles of electrons** that migrate from anode to cathode in the cell reaction.

When the electrode are in their standard states the free energy change is called the standard reaction Gibbs energy $\Delta G^0_r = -nE^0F$

For example, **in the Daniell cell:**

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$; two electrons are transferred in the cell reaction, n = 2

(Note it is clearer in half – cell reaction rather than the cell reaction)

$\Delta G_r^o = -2\ E_{cell}\ F$

$= 1.93 \times 10^5\ E_{cell}$

When E_{cell} is measured in volts, the value of ΔG_r^o in joules. When the concentration of Cu^{2+} and Zn^{2+} ions are in the standard state:

$\Delta G_r^o = -2\ E^o\ F$

So, the direction of the spontaneous change that takes place in a galvanic cell is the decreasing of the Gibbs free energy. So, the cell potential is related to the Gibb energy and this is defined as already I talked about, it is minus nE cell into F where this is the cell potential and this is defined to be positive F is faraday constant and n is the number of moles of electron that migrate from anode to cathode in the cell reaction.

So, when the electrode are in their standard state the free energy change is called the standard reaction standard reaction Gibbs energy. So, this is defined at del G 0 term. So, in the Daniell cell if you consider two electrons are transferred in the cell reaction. So, n is equal to 2, that half cell reaction it is very clear than the full cell reaction because when you talk about the full cell then the electron which is exchanged it is no longer appear there.

So, the value of del G r in the standard cell is minus 2 E cell into F and you can multiply with the faraday constant, so this value you will be getting. So, you can calculate the standard free energy and when E cell is measured in volt the value of del G r is usually in joule and the concentration of copper and zinc ions are in the standard state. So, this equation is valid only for the standard condition.

$$\boldsymbol{\Delta G_r = -nE_{cell}F}$$

in the Daniell cell:

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$; two electrons are transferred in the cell reaction, n = 2

(Note it is clearer in half – cell reaction rather than the cell reaction)

$\Delta G_r^o = -2\ E_{cell}\ F$

$= 1.93 \times 10^5\ E_{cell}$

$\Delta G_r^o = -2\ E_o\ F$

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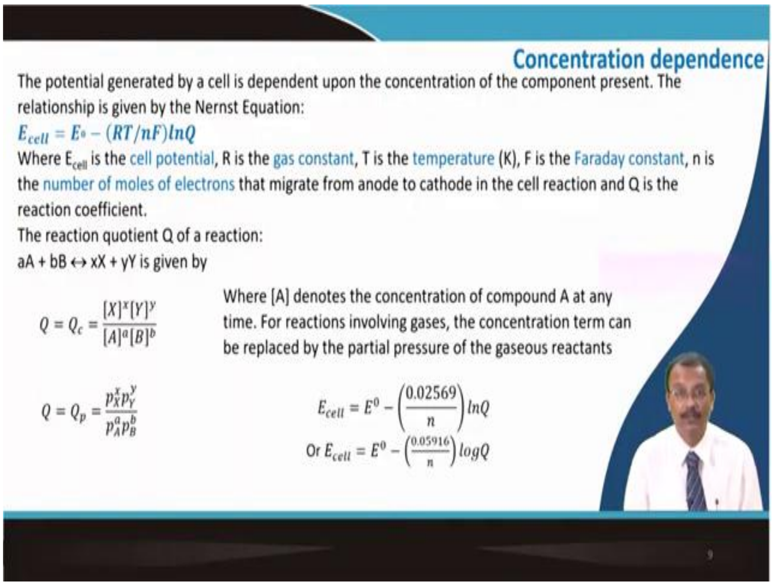

Concentration dependence

The potential generated by a cell is dependent upon the concentration of the component present. The relationship is given by the Nernst Equation:

$E_{cell} = E_0 - (RT/nF)lnQ$

Where E_{cell} is the cell potential, R is the gas constant, T is the temperature (K), F is the Faraday constant, n is the number of moles of electrons that migrate from anode to cathode in the cell reaction and Q is the reaction coefficient.

The reaction quotient Q of a reaction:

aA + bB ↔ xX + yY is given by

$$Q = Q_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Where [A] denotes the concentration of compound A at any time. For reactions involving gases, the concentration term can be replaced by the partial pressure of the gaseous reactants

$$Q = Q_p = \frac{p_X^x p_Y^y}{p_A^a p_B^b}$$

$$E_{cell} = E^0 - \left(\frac{0.02569}{n}\right) lnQ$$

$$\text{Or } E_{cell} = E^0 - \left(\frac{0.05916}{n}\right) logQ$$

Now, I already talked about the Nernst equation E cell is equal to E 0 minus RT by nF into l n of Q. So, that is the cell potential and R is the gas constant, T is the temperature, F is the faraday constant and n is the number of mole that is exchanged, that is migrated. Now as I told that earlier I talked about one particular redox couple.

$$\boldsymbol{E_{cell} = E_0 - (RT/nF)lnQ}$$

The reaction quotient Q of a reaction:

aA + bB ↔ xX + yY is given by

$$Q = Q_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Where [A] denotes the concentration of compound A at any time.

$$Q = Q_p = \frac{p_X^x p_Y^y}{p_A^a p_B^b}$$

For reactions involving gases, the concentration term can be replaced by the partial pressure of the gaseous reactants

So, we can always estimate the cell potential using the Nernst equation.

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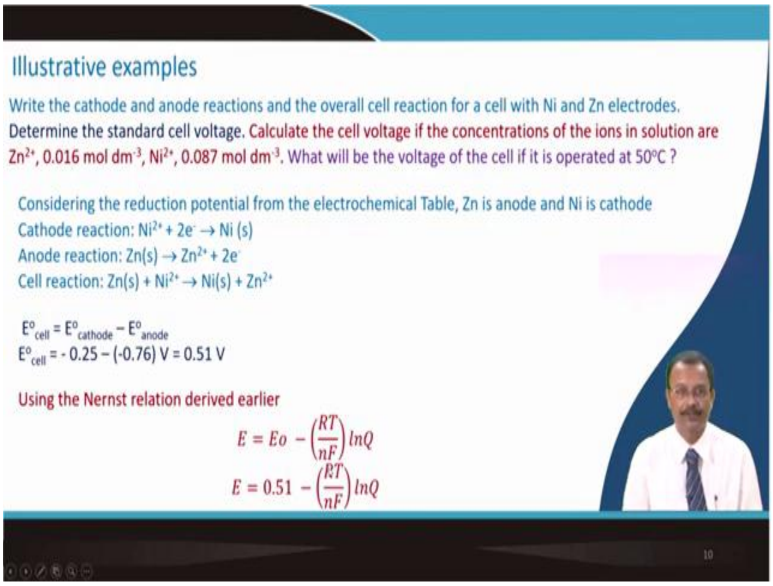

Illustrative examples

Write the cathode and anode reactions and the overall cell reaction for a cell with Ni and Zn electrodes. Determine the standard cell voltage. Calculate the cell voltage if the concentrations of the ions in solution are Zn^{2+}, 0.016 mol dm^{-3}, Ni^{2+}, 0.087 mol dm^{-3}. What will be the voltage of the cell if it is operated at 50°C ?

Considering the reduction potential from the electrochemical Table, Zn is anode and Ni is cathode

Cathode reaction: $Ni^{2+} + 2e^- \rightarrow Ni(s)$

Anode reaction: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cell reaction: $Zn(s) + Ni^{2+} \rightarrow Ni(s) + Zn^{2+}$

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$E^o_{cell} = -0.25 - (-0.76)\ V = 0.51\ V$

Using the Nernst relation derived earlier

$$E = Eo - \left(\frac{RT}{nF}\right) lnQ$$

$$E = 0.51 - \left(\frac{RT}{nF}\right) lnQ$$

Now, let us see how it works. So, I can write the cathode and anode reaction an overall cell reaction. Say for a couple of nickel and zinc electrodes. So, one can determine the standard cell voltage one can calculate the cell voltage if the concentration of the ions are not in standard state 1 mole per liter, but something else. And then finally, if the temperature is not in the standard state, then what will be the cell potential? So, this can be estimated from the Nernst equation and this is one of the examples.

So, for example, that you consider the reduction potential from the electrochemical table and zinc is acting as anode and nickel is acting as cathode. So, the cathode reaction is it is getting reduced and anode reaction this is getting oxidized. So, this is the total cell reaction for Daniell cell also I have described it earlier. So, for the total cell potential this is under standard condition is cathode minus anode.

So, the cathode value from the table we have gotten 0.25 and anode is minus 0.76 for zinc. So, the total cell potential under standard condition will be 0.51 volt. So, now we will apply the Nernst relation which already derived in my last lecture. So, value of E is E0 minus RT by nF into lnQ. So, I put the value of E0 here which is derived. So, RT by nF into lnQ.

Cathode reaction: $Ni^{2+} + 2e^- \rightarrow Ni\ (s)$

Anode reaction: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cell reaction: $Zn(s) + Ni^{2+} \rightarrow Ni(s) + Zn^{2+}$

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$E^o_{cell} = -0.25 - (-0.76)\ V = 0.51\ V$

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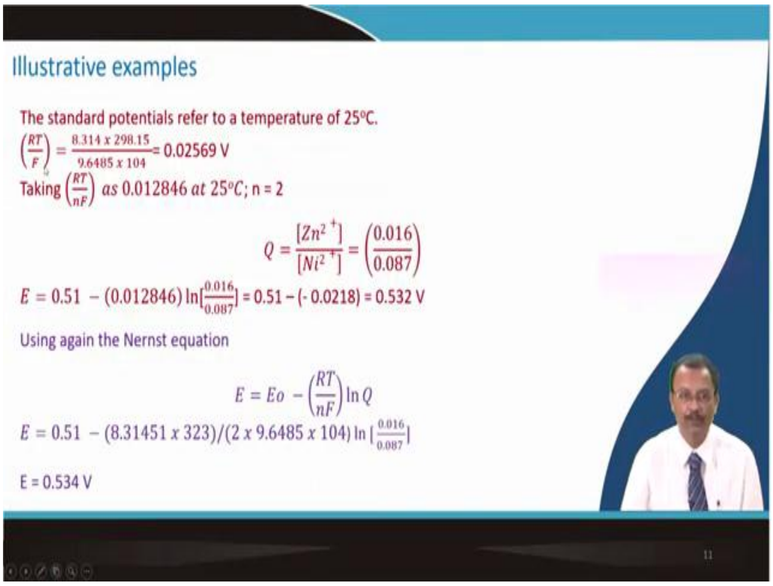

Illustrative examples

The standard potentials refer to a temperature of 25°C.

$\left(\frac{RT}{F}\right) = \frac{8.314 \ x\ 298.15}{9.6485\ x\ 104} = 0.02569\ V$

Taking $\left(\frac{RT}{nF}\right)$ *as 0.012846 at 25°C*; n = 2

$$Q = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \left(\frac{0.016}{0.087}\right)$$

$E = 0.51 - (0.012846) \ln[\frac{0.016}{0.087}] = 0.51 - (-0.0218) = 0.532\ V$

Using again the Nernst equation

$$E = Eo - \left(\frac{RT}{nF}\right) \ln Q$$

$E = 0.51 - (8.31451\ x\ 323)/(2\ x\ 9.6485\ x\ 104) \ln [\frac{0.016}{0.087}]$

E = 0.534 V

Now, this RT by F value I can calculate by putting the value of RT and F and which is coming about 0.02569 volt. This is if you take number of electron it is coming because number of electron is 2. So, this value is coming as this one and the Q can be estimated here not the activity, but the concentration in case of a dilute solution I told activity can be replaced by concentration.

So, this value the concentration of the product from the full cell reaction and the reactant. So, this value can estimate you can put this into the Nernst equation. And you see under the this condition the standard electrode potential was 0.51 it is increased to 0.532. Again you can use the Nernst equation and instead of T the value 298 you can put 323 Kelvin because at 50 degree Celsius it is asked that how much voltage that you will get.

And then you can estimate the value of E is 0.534 volt. So, you can see that it is not only standard electrode potential, but the temperature and concentration of the electrolyte in a cell that also affect the voltage.

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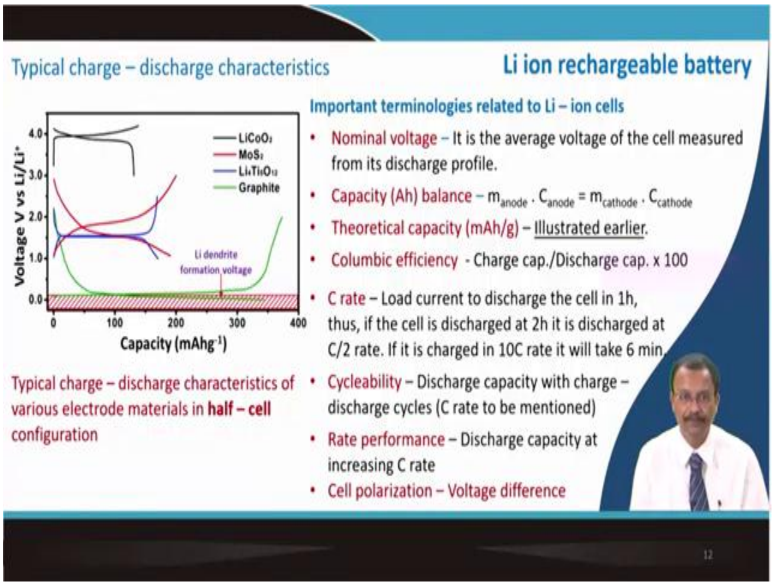

Typical charge – discharge characteristics

Li ion rechargeable battery

Typical charge – discharge characteristics of various electrode materials in **half – cell** configuration

Important terminologies related to Li – ion cells

- Nominal voltage – It is the average voltage of the cell measured from its discharge profile.
- Capacity (Ah) balance – $m_{anode} . C_{anode} = m_{cathode} . C_{cathode}$
- Theoretical capacity (mAh/g) – Illustrated earlier.
- Columbic efficiency - Charge cap./Discharge cap. x 100
- C rate – Load current to discharge the cell in 1h, thus, if the cell is discharged at 2h it is discharged at C/2 rate. If it is charged in 10C rate it will take 6 min.
- Cycleability – Discharge capacity with charge – discharge cycles (C rate to be mentioned)
- Rate performance – Discharge capacity at increasing C rate
- Cell polarization – Voltage difference

So, I have already introduced the thermodynamic concept to estimate this voltage this lecture also I will recapitulate that. So, you have seen that for different types of electrode materials, starting from lithium cobalt oxide or molybdenum disulfide or lithium titanium oxide LTO, what are the typical charge and discharge potential? So, the voltage is not always constant particularly for this material you see the voltage is continuously changing upon discharge and also upon charge of the cell.

So, the nominal voltage is the average voltage of the cell that is measured from the discharge profile we have already talked about the capacity of the cathode and anode and the capacity you see if you consider the graphite the voltage is pretty low here. So, it can act as your negative electrode and you can take any one of this as positive electrode.

So, the capacity will be very large here right. So, the charge must be balance in the positive and negative electrode. So, the charge balance can be done by this relation and then since the capacity of the negative electrode is pretty large for most of this battery material. Then you will see that it should have a very small amount of relatively smaller amount of mass in the negative electrode as compared to the positive electrode for the full chemical reaction to take place.

Capacity (Ah) balance : $m_{anode} . C_{anode} = m_{cathode} . C_{cathode}$

So, the theoretical capacity you can calculate from the Faraday law and that already I have explained in my earlier lecture, columbic efficiency is given by the charge capacity and discharge capacity ratio. So, usually this is multiply by 100. So, that gives you the columbic efficiency, that tells that the lithium which is transporting rocking between these two electrode, whether they are lost somewhere or the amount which is coming out from one electrode is exactly the amount is going back.

So, you can define a C rate that is the load current to discharge the cell in 1 hour. So, if the cell is discharged at 2 hour then it is discharged as C by 2 rate and if it is charged say for example, at 10 C rate that means, it will take only 6 minute for the cell to be charged. Then we can define the cycleability is the discharge capacity this discharge capacity value with charge discharge cycle.

And in during this cycleability it is customary to mention the C rate the C rate that you are using for this charge and discharge to operation. Rate performance is also important if you discharge or charge the battery at relatively higher constant current then you will see the capacity will be progressively reduced as you increase the current you will see the capacity is progressively reduced.

So, that is something related to its rate performance and why it happens, that we will come back to it when we will talk about the case study of particular cell chemistry. Cell polarization is basically the voltage difference between the charge and discharge. So, these are the important terminology which is pertinent to the lithium ion cell.

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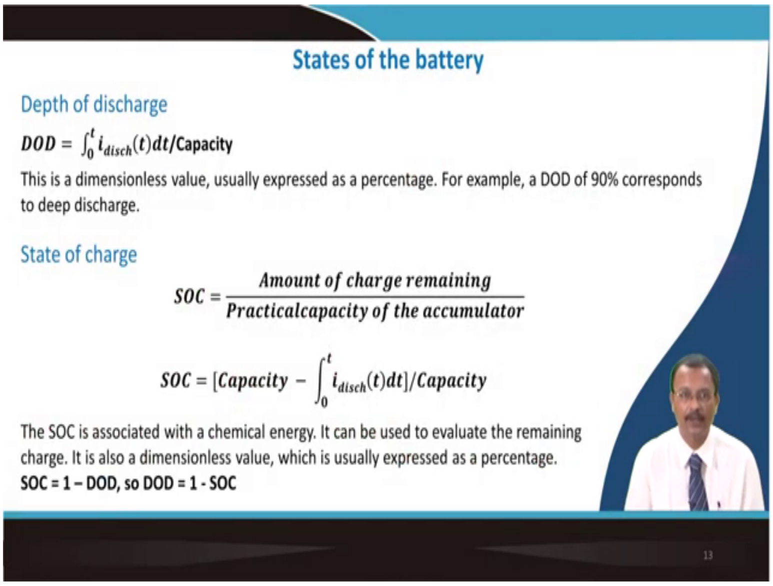

States of the battery

Depth of discharge

$DOD = \int_0^t i_{disch}(t)dt/\text{Capacity}$

This is a dimensionless value, usually expressed as a percentage. For example, a DOD of 90% corresponds to deep discharge.

State of charge

$$SOC = \frac{Amount\ of\ charge\ remaining}{Practicalcapacity\ of\ the\ accumulator}$$

$$SOC = [Capacity - \int_0^t i_{disch}(t)dt]/Capacity$$

The SOC is associated with a chemical energy. It can be used to evaluate the remaining charge. It is also a dimensionless value, which is usually expressed as a percentage.

SOC = 1 – DOD, so DOD = 1 - SOC

Now, the state states of the battery is important and there the depth of discharge is important. So, depth of discharge is how much discharge till what voltage you can discharge this battery. So, you can basically estimate the current and integrate it with the time of discharge with respect to its nominal capacity.

$$\boldsymbol{DOD = \int_0^t i_{disch}(t)dt/\textbf{Capacity}}$$

So, that will give you the depth of discharge. So, this is of course, a dimensionless value and this is actually expressed as a percentage. So, we define the term depth of discharge is 90 percent. That means, it is a deep discharge out of 100 percent nominal capacity we have discharged 90 percent of it.

State of charge is important that is the amount of the charge that is remaining with respect to the practical capacity of the rechargeable battery the accumulator. So, state of charge is the capacity minus the capacity that you are getting during the charging state with respect to the nominal capacity.

So, the SOC abbreviated form of State Of Charge is associated with chemical energy it can be used to evaluate the remaining charge in the battery, it is also a dimensionless value and which is actually expressed as a percentage. So, state of charge is 1 minus depth of discharge. So, vice versa depth of discharge is 1 minus state of charge.

$$\boldsymbol{SOC = \frac{Amount\ of\ charge\ remaining}{Practicalcapacity\ of\ the\ accumulator}}$$

$$\boldsymbol{SOC = [Capacity\ -\ \int_0^t i_{disch}(t)dt]/Capacity}$$

SOC = 1 – DOD, so DOD = 1 - SOC

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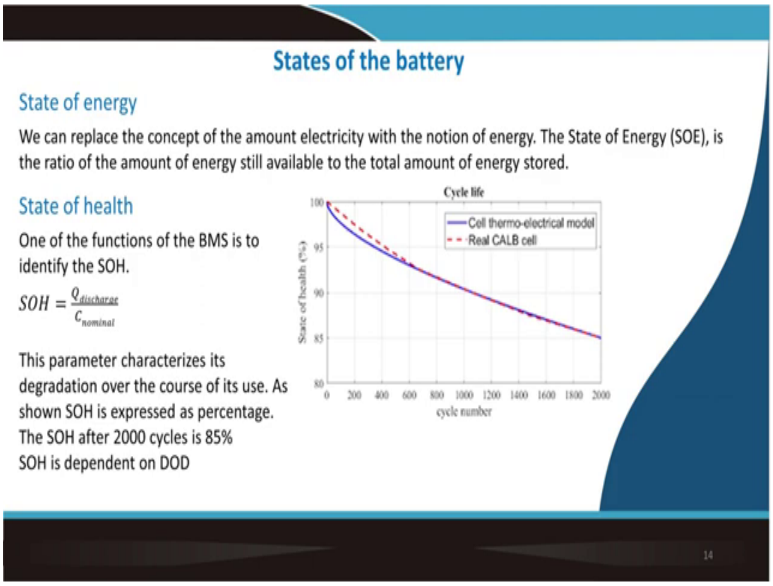

States of the battery

State of energy

We can replace the concept of the amount electricity with the notion of energy. The State of Energy (SOE), is the ratio of the amount of energy still available to the total amount of energy stored.

State of health

One of the functions of the BMS is to identify the SOH.

$$SOH = \frac{Q_{discharge}}{C_{nominal}}$$

This parameter characterizes its degradation over the course of its use. As shown SOH is expressed as percentage.
The SOH after 2000 cycles is 85%
SOH is dependent on DOD

State of energy is sometimes important we can replace the concept of the amount of electricity with the notion of energy. The State of Energy is the ratio of amount of energy still available within the cell with respect to the total amount of the energy which is stored therein.

Another thing which is very important is state of health that the battery management system actually measure in each of the cell what is the state of health. So, that is defined as the charge in discharge state with and the ratio with the nominal capacity of the battery.

$$SOH = \frac{Q_{discharge}}{C_{nominal}}$$

So, as you can see that if you cycle the battery for number of times. So, this is the cycle number, then progressively the nominal charge which I consider 100 percent, this is progressively going down and up to 2000 cycle typically it drops down to 85 percent.

So, that is quite typical for a good cell. So, the state of health that is depending on the depth of discharge. So, depth of discharge whatever I talked about. So, if you deep discharge it not necessarily you will be getting this kind of behaviour. So, it depends of the depth of discharge as well and lot of modeling work is going on, how to predict this kind of state of health. So, the dotted line is basically a fit with the experimental value which usually we get.

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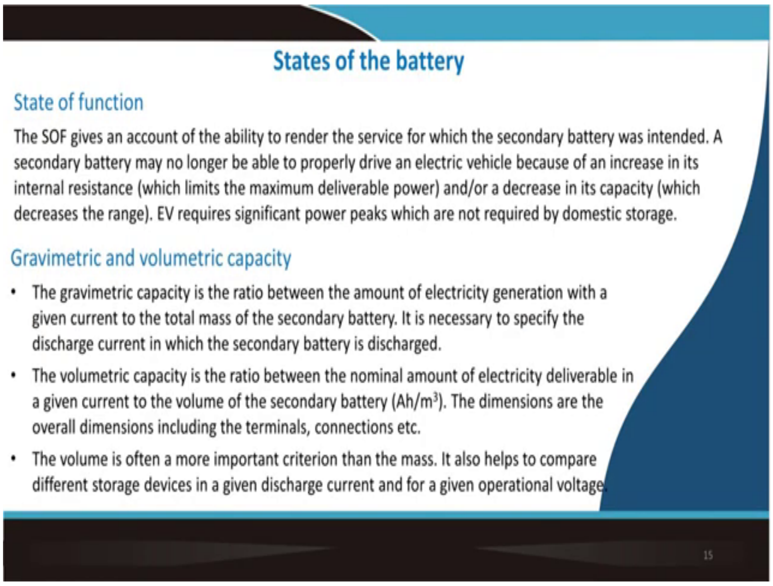

States of the battery

State of function

The SOF gives an account of the ability to render the service for which the secondary battery was intended. A secondary battery may no longer be able to properly drive an electric vehicle because of an increase in its internal resistance (which limits the maximum deliverable power) and/or a decrease in its capacity (which decreases the range). EV requires significant power peaks which are not required by domestic storage.

Gravimetric and volumetric capacity

- The gravimetric capacity is the ratio between the amount of electricity generation with a given current to the total mass of the secondary battery. It is necessary to specify the discharge current in which the secondary battery is discharged.
- The volumetric capacity is the ratio between the nominal amount of electricity deliverable in a given current to the volume of the secondary battery (Ah/m^3). The dimensions are the overall dimensions including the terminals, connections etc.
- The volume is often a more important criterion than the mass. It also helps to compare different storage devices in a given discharge current and for a given operational voltage.

Now, another thing which is important is state of function. The state of function is the ability to render the service for a practical application for example, the battery that you are using for consumer electronic application the current that you are draining from the battery that is relatively low and this battery may not be useful for your electric vehicle application, where the current profile is not always uniform.

So, sometimes while you accelerate the car you need to drain more current, while when you go for constant speed you are driving a constant current. So, when this profile is changed then you see that the battery does not perform well and eventually it depends on the chemistry of the battery. So, one must be careful not all the battery is useful for all the purpose. And therefore, newer chemistry is always needs to be worked out to serve a particular application.

Gravimetric and volumetric capacity is important. The gravimetric capacity is the ratio between the amount of the electricity generation with a given current to the total mass of the secondary battery. It is necessary to specify the discharge current at each stage because you know the rate capability that depends capacity depends on the drainage current.

So, that must be mentioned and volumetric capacity that is the ratio of the nominal amount of electricity delivered in a given current to the volume of the secondary battery usually this is charge per meter cube it is mentioned that, this dimension are the overall dimension of the battery module.

So, volume is more important criterion than the mass because you know particularly for the mobile application you need to fit the battery in a fixed space. So, volumetric energy density that is a very important criteria to cater the need of a particular application.

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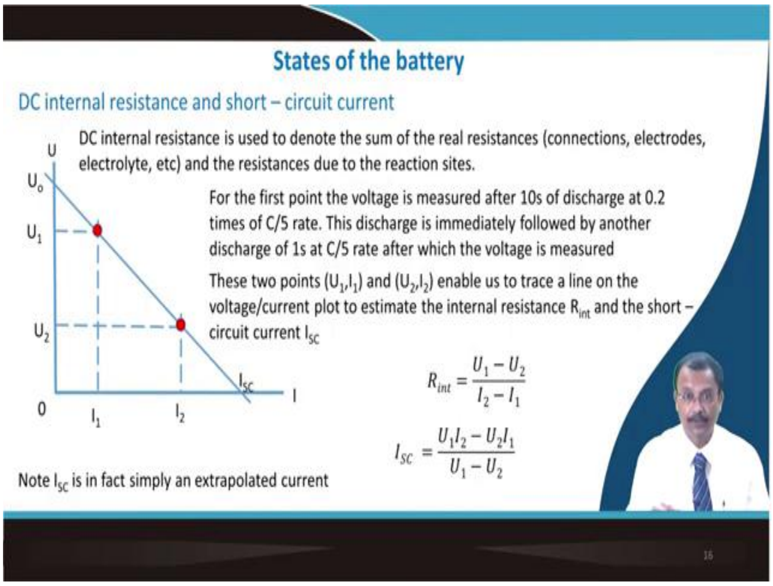

States of the battery

DC internal resistance and short – circuit current

DC internal resistance is used to denote the sum of the real resistances (connections, electrodes, electrolyte, etc) and the resistances due to the reaction sites.

For the first point the voltage is measured after 10s of discharge at 0.2 times of C/5 rate. This discharge is immediately followed by another discharge of 1s at C/5 rate after which the voltage is measured

These two points (U_1,I_1) and (U_2,I_2) enable us to trace a line on the voltage/current plot to estimate the internal resistance R_{int} and the short – circuit current I_{SC}

$$R_{int} = \frac{U_1 - U_2}{I_2 - I_1}$$

$$I_{SC} = \frac{U_1 I_2 - U_2 I_1}{U_1 - U_2}$$

Note I_{SC} is in fact simply an extrapolated current

Then we talk about the DC internal resistance that is used to denote the sum of the real resistance, which comes from the connection, the connectors, the electrodes, the electrolyte and also the resistance of the lithium flow inside the battery material.

So, this is a standard technique is used to estimate the DC internal resistance. The first point as you can see this voltage is measured after 10 second of a discharge at a specific current 0.2 times of C by 5 rate. So, that is relatively lower current and then the discharge is immediately followed by another 1 second at C by 5 rate. So, this is the second point. So, you get these two points, the two points have coordinates U1, I1 and U2, I2.

And we can trace this particular straight line between these two points. And, we can estimate the internal resistance as U1 minus U2 by I2 minus I1. And you extend this line and then it cuts this is the extrapolated line and it cuts this current axis and this current is known as short circuit current where the voltage turns out to be 0.

So, this short circuit current is given by this relation U1, I2 minus U2, I1 by U1 minus U2. As a part of an assignment problem I have asked you to estimate that how exactly these relations are coming from simple first principle calculation.

$$R_{int} = \frac{U_1 - U_2}{I_2 - I_1}$$

$$I_{SC} = \frac{U_1 I_2 - U_2 I_1}{U_1 - U_2}$$

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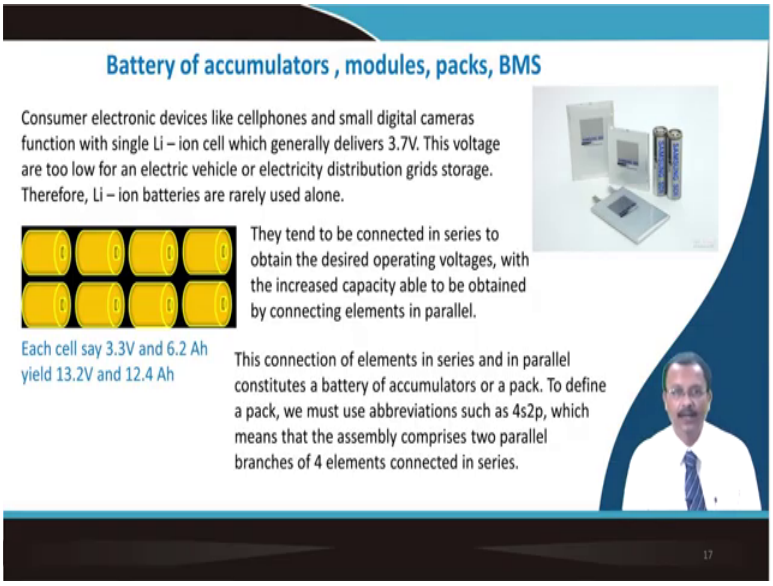

Battery of accumulators , modules, packs, BMS

Consumer electronic devices like cellphones and small digital cameras function with single Li – ion cell which generally delivers 3.7V. This voltage are too low for an electric vehicle or electricity distribution grids storage. Therefore, Li – ion batteries are rarely used alone.

They tend to be connected in series to obtain the desired operating voltages, with the increased capacity able to be obtained by connecting elements in parallel.

Each cell say 3.3V and 6.2 Ah yield 13.2V and 12.4 Ah

This connection of elements in series and in parallel constitutes a battery of accumulators or a pack. To define a pack, we must use abbreviations such as 4s2p, which means that the assembly comprises two parallel branches of 4 elements connected in series.

Then, consumer electronic devices like cell phone or small digital camera function with a single lithium ion cell, which generally delivers about 3.7 Volt with variable capacity starting from 1000 milli ampere hour to 2600 milli ampere hour depending on the chemistry that is used.

So, this is the typical shapes of the battery we call this is a pouch cell or prismatic cell and this is cylindrical cell. So, this typical voltage is too low for an electrical vehicle or if you are talking about the storage battery this voltage is too low. So, rarely lithium ion battery is used in alone means as a single piece. So, for the heavy duty application they tend to be connected in series to increase the voltage and connected in parallel to increase the capacity.

So, each of this cell as you can see and there are various ways to connect the battery the positive and negative terminal. So, each of this cell if I assume that depending on the chemistry it gives you a nominal voltage of 3.3 volt and capacity is 6.2 ampere hour for this particular shape.

Then this will have to be connected in series to get voltage about 13.2 volt and the capacity we will get 12.4 ampere hour 6.2 plus 6.2. So, that will give you 12.4 ampere hour.

So, this connections of elements in series and parallel that constitutes a battery of accumulators or we call this is a pack in a very loose sense, to define a pack we must use abbreviation like 4s2p. That means, 4 cells are in series and 2 in parallel and you can just increase it depending on your need, but the more important fact is it all depends on the chemistry.

So, I will come back to this at a later part of my course that how to improve the energy, how to improve the voltage, what are the fundamentals behind it that is more important for you to get the quality cells. So, that you can basically in a small space you can have lot of energy. So, that is the idea and also it should be light weight. So, volumetric energy density and gravimetric energy density both needs to be equally optimized.

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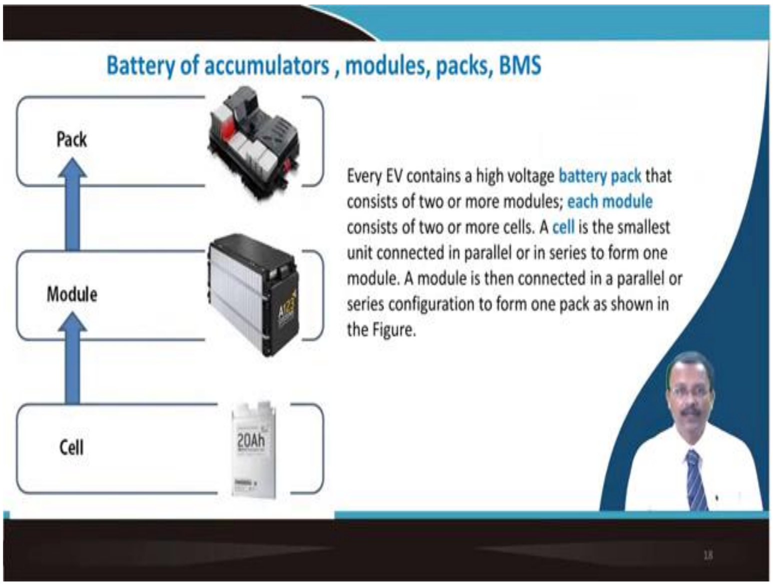

Battery of accumulators , modules, packs, BMS

Every EV contains a high voltage battery pack that consists of two or more modules; each module consists of two or more cells. A cell is the smallest unit connected in parallel or in series to form one module. A module is then connected in a parallel or series configuration to form one pack as shown in the Figure.

So, you have a single cell something like this and then you connect it series and parallel and you get this kind of combination and there are various way to connect it. So, I will talk about it while we will talk it in more details in the later part of the course. And then finally, this modules they are also connected in series and parallel to get what we call a battery pack.

So, battery pack is basically the minimum, the smallest unit is the cell. Then cells are connected in series and parallel to get the module. And then finally, the modules are connected in series and parallel to get the pack. So, that is the concept that is followed for larger battery which is having higher energy density.

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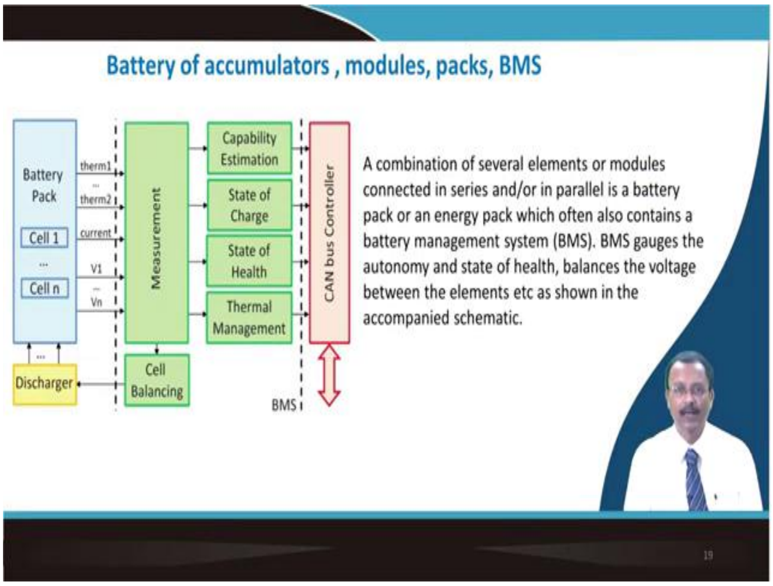

Battery of accumulators , modules, packs, BMS

A combination of several elements or modules connected in series and/or in parallel is a battery pack or an energy pack which often also contains a battery management system (BMS). BMS gauges the autonomy and state of health, balances the voltage between the elements etc as shown in the accompanied schematic.

So, now you need to have a battery management system and this is required because you are connecting the cells in series and also in parallel. So, one of the cell can malfunction. So, that is one way, second if it malfunction, then the whole battery should not be dead another problem is that the discharge capacity for each of the cell although they are from the same chemistry it need not to be same. So, some cell has higher capacity.

So, depth of discharge is maintained say 60 percent, but for some cell due to some reason the depth of discharge is far more say 90 percent. So, you need to have cell balance. So, capacity balance from one cell to another it can be done as a active way or passive way. We will talk about it when I will talk in details about the battery management system.

So, the battery management system basically that is a electronic module that control the cell. So, it estimate the capacity, it can estimate the state of the charge, it can estimate the state of the health and not only that if the cell is overrated.

If there is a possibility of thermal runaway because you know that you are using electrolyte which is organic electrolyte which are flammable. So, it can easily reach the flash point and the whole battery can explode. So, it needs to also properly manage the temperature within the cell the thermal management is equally important.

So, BMS actually they takes care of the battery. So, the combination of several elements or modules they are connected in series and parallel in a battery pack or an energy pack.

Which is often contained this kind of battery management for larger battery it is mass for smaller cells this is not required.

But for battery which is required for renewable energy storage or required for your electric vehicles the battery management system is the unit that must be developed. And you can actually log this data in a data logger or in a small car to see that how the battery exactly performed during charge and discharge in the practical application. So, this is one of the most important integral part to make a total battery pack.

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REFERENCES

- **Richard J. D. Tilley,** Understanding Solids, The Science of Materials, 2nd Edition, Wiley Chapter – 9 (Study material)
- **C. Glaize and S. Genies,** Lithium batteries and other electrochemical storage systems, Wiley Chapter - 2, Hoboken, 2013 (Study material)
- **C.A. Vincent and B. Scrosati,** Modern Batteries, 2nd Edition Elsevier, Amsterdam (1997)

So, this part of the talk is mostly these two books you can consider as a study material particularly the book by Glaize and Genies and also for some initial concept the book by Richard Tilley Chapter number 9 is useful. And this book you can use as a reference book for Modern Batteries this is a quite good book to clarify the concepts.

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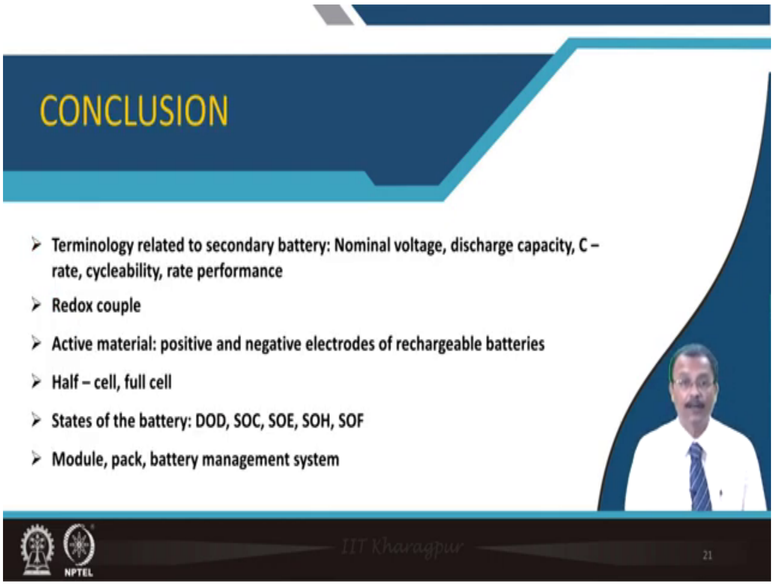

CONCLUSION

- Terminology related to secondary battery: Nominal voltage, discharge capacity, C – rate, cycleability, rate performance
- Redox couple
- Active material: positive and negative electrodes of rechargeable batteries
- Half – cell, full cell
- States of the battery: DOD, SOC, SOE, SOH, SOF
- Module, pack, battery management system

So, in this particular lecture we talked about terminology related to secondary battery, we talked about nominal voltage, then discharge capacity, C rate, cycleability, rate performance.

Then, again we reintroduce the redox couple for several components which is involved in the electrochemical cell. Then we talked about the active material, we clarify the concept of positive and negative electrodes.

Then we talked about half cell and full cell, then define the state of the battery in terms of depth of discharge, state of charge, state of energy, state of health and state of function for which purpose the battery is useful. Finally, we introduce the concept of module, battery pack and battery management system.

Thank you for your attention.