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

Module - 01
Introduction to energy storage and conversion
Lecture - 02
Primary Batteries and Secondary Batteries

Welcome to the course: Electrochemical Energy Storage. This is module number 1: Introduction to Energy Storage and Conversion. We are covering lecture number 2, where I will be talking about the Primary Batteries and Secondary Batteries.

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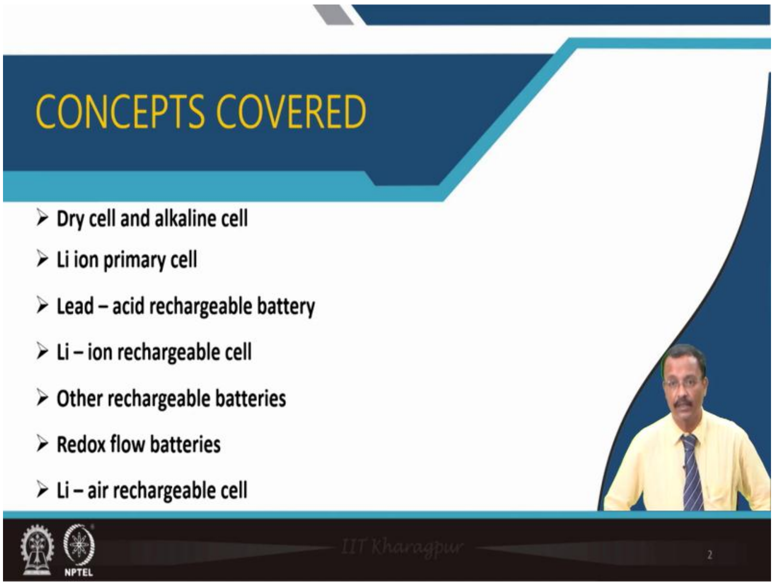

CONCEPTS COVERED

- Dry cell and alkaline cell
- Li ion primary cell
- Lead – acid rechargeable battery
- Li – ion rechargeable cell
- Other rechargeable batteries
- Redox flow batteries
- Li – air rechargeable cell

This lecture is an overview of various types of primary and secondary batteries which will be elaborated throughout the course. So we will cover an introduction of various types of primary and rechargeable batteries in this lecture, but will elaborate them as we proceed with the course.

In this particular lecture, we will start off with the description of dry cell and the alkaline cell. One must have purchased these types of cells at one point from the market and hence, are familiar with them. Next, we will cover lithium-ion primary cell, which is available in the market in the form of a small button cell. Then, we will describe lead-acid rechargeable batteries, which are used in scooters, toto or motorcycles (for ignition and lighting of headlights). We will also introduce lithium-ion rechargeable cell, which are gaining traction with the advent of electric vehicles. Certain other rechargeable batteries such as redox flow batteries will also be covered in the later parts of the course. Finally, a new concept of lithium-air rechargeable battery will be discussed, which I consider as the ultimate battery. We will describe its functioning in later parts of the course as well.

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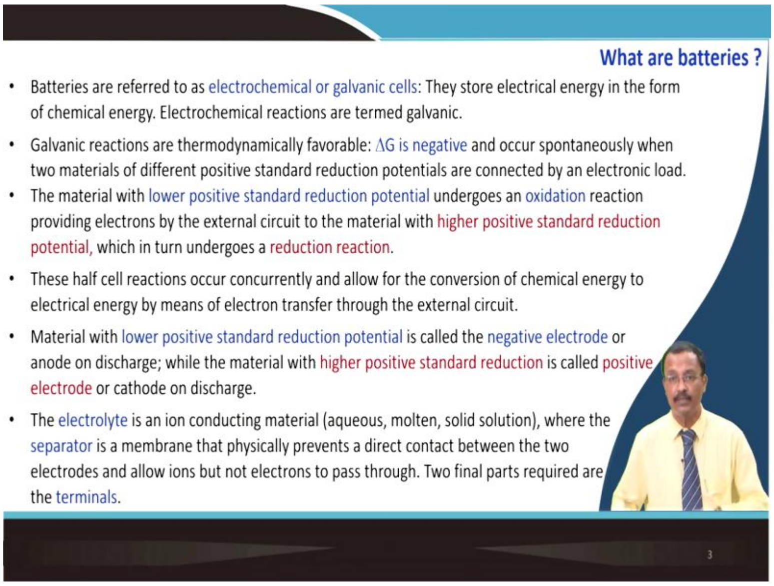

What are batteries ?

- Batteries are referred to as electrochemical or galvanic cells: They store electrical energy in the form of chemical energy. Electrochemical reactions are termed galvanic.
- Galvanic reactions are thermodynamically favorable: ΔG is negative and occur spontaneously when two materials of different positive standard reduction potentials are connected by an electronic load.
- The material with lower positive standard reduction potential undergoes an oxidation reaction providing electrons by the external circuit to the material with higher positive standard reduction potential, which in turn undergoes a reduction reaction.
- These half cell reactions occur concurrently and allow for the conversion of chemical energy to electrical energy by means of electron transfer through the external circuit.
- Material with lower positive standard reduction potential is called the negative electrode or anode on discharge; while the material with higher positive standard reduction is called positive electrode or cathode on discharge.
- The electrolyte is an ion conducting material (aqueous, molten, solid solution), where the separator is a membrane that physically prevents a direct contact between the two electrodes and allow ions but not electrons to pass through. Two final parts required are the terminals.

In the last lecture, we discussed about the electrolyzer and power source modes. The battery is eventually recharged in the electrolyzer mode, whereas it is operational in the power source mode. By adopting electrolyzer mode in the electrochemical cell, you can basically recharge the battery. Therefore, batteries can be referred as electrochemical cells. Galvanic reactions occur spontaneously in the battery during discharge, which are thermodynamically favourable. Here, the free energy change of the reaction is negative. When two different materials with different positive standard reduction potential are connected across an electric load, reactions may occur spontaneously. In a spontaneous reaction, the material with a lower positive standard reduction potential undergoes an oxidation reaction, while the other undergoes a reduction reaction. Recall, the copper-zinc case. Zinc undergoes oxidation and releases electrons in the external circuit. On the other hand, copper undergoes reduction reaction wherein the released electrons from zinc are used to reduce copper ions in the electrolyte solution.

So, these reactions allow for the conversion of chemical energy to electrical energy. Material with lower positive standard reduction potential is called the negative electrode or anode on discharge, while material with higher positive standard reduction is called positive electrode or cathode on discharge. I am stressing the term discharge because once you charge it, this is just reversed.

The electrolyte is an ion conducting material. It could be aqueous, it could be molten, it could be a solid solution. The separator is a membrane that physically prevents the direct contact between these two electrodes and allows ions; but not electron to pass through. Two final parts that are required for the formation of a battery are the two terminals. So, we will talk about this the construction in details.

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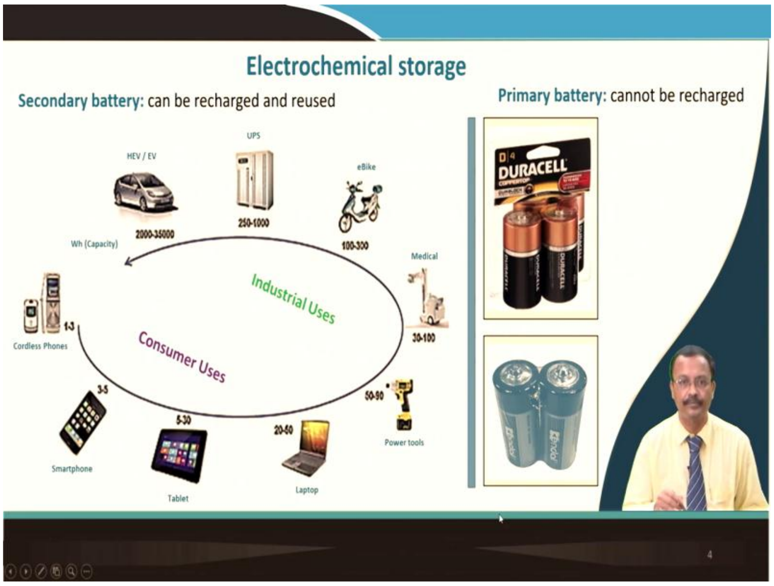

Electrochemical storage

Secondary battery: can be recharged and reused

Primary battery: cannot be recharged

You can easily identify a primary battery because you can purchase this from the market, and it cannot be recharged. Once you use it, you just throw it or dispose it (do not dispose it anywhere or everywhere).

Rechargeable batteries are used in smart phone, tablet, laptop, then power tool, then your medical facilities, then your small scooty and UPS and then finally, the hybrid electric vehicle or electric vehicle. So, all these applications and it started from the cordless phone of course.

Throughout the course, we will be talking about different types of battery which are not only useful for the consumer electronic applications; but they are also equally useful for industrial application in details.

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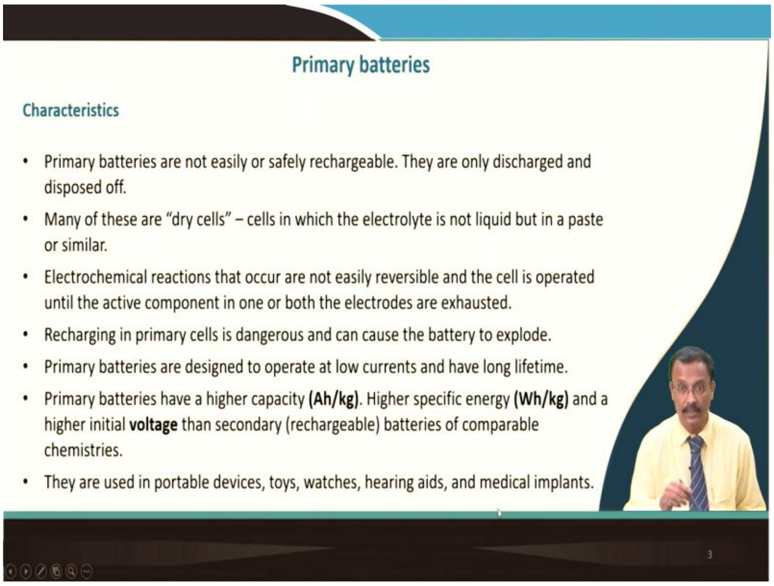

Primary batteries

Characteristics

- Primary batteries are not easily or safely rechargeable. They are only discharged and disposed off.
- Many of these are "dry cells" – cells in which the electrolyte is not liquid but in a paste or similar.
- Electrochemical reactions that occur are not easily reversible and the cell is operated until the active component in one or both the electrodes are exhausted.
- Recharging in primary cells is dangerous and can cause the battery to explode.
- Primary batteries are designed to operate at low currents and have long lifetime.
- Primary batteries have a higher capacity **(Ah/kg)**. Higher specific energy **(Wh/kg)** and a higher initial **voltage** than secondary (rechargeable) batteries of comparable chemistries.
- They are used in portable devices, toys, watches, hearing aids, and medical implants.

So, primary batteries have a set of characteristics. This primary battery are not easily rechargeable, they are only discharged and disposed off; many of this so called "dry cells" in which electrolyte is not liquid, but in the form of a paste or similar.

In the last lecture, we always talked about liquid electrolyte. But in dry cells, they have a paste like electrolyte. Electrochemical reactions that occur in these cells are not easily reversible, and the cell is operated until the active material in the cell in one or both the electrodes are completely exhausted. So, once they are exhausted, you just throw it up.

Recharging the primary cell is dangerous and can cause the battery to explode. So, never try to recharge a primary battery. The primary batteries are designed to operate at low currents and therefore, they have long lifetime. So, you cannot use primary battery for heavy duty applications. There are certain batteries which will give you little bit heavy duty; but it is not very common. Primary batteries have high capacity, and that is measured in terms of ampere hour. It means the amount of current that you can drain out of the battery in 1 hour. If you divide it by the weight of the battery, you get the specific capacity value.

Primary batteries also possess higher specific energy in terms of Watt hour per kilogram and a higher initial voltage than the secondary batteries of comparable chemistry. However, the chemistry has changed quite a bit and we will talk about all these parameters: capacity, specific energy, specific capacity in more details in my forthcoming lectures.

So, do not worry too much about this terminology at this point. They are usually used for portable device, toys, watches, hearing aids and medical implants; so the primary batteries are not used for heavy duty applications.

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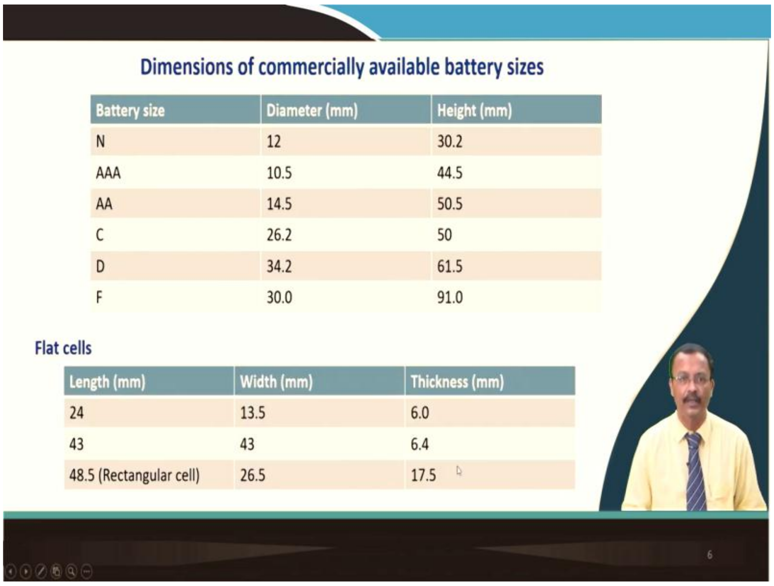

Dimensions of commercially available battery sizes

Battery size	Diameter (mm)	Height (mm)
N	12	30.2
AAA	10.5	44.5
AA	14.5	50.5
C	26.2	50
D	34.2	61.5
F	30.0	91.0

Flat cells

Length (mm)	Width (mm)	Thickness (mm)
24	13.5	6.0
43	43	6.4
48.5 (Rectangular cell)	26.5	17.5

So, there are various dimensions of the commercial available batteries. When you go to the market, you talk about mostly AA type of battery or triple A type of battery that actually denotes the diameter and the height of the battery.

So, as you can see triple A is little bit thinner in diameter as compared to double A, C battery is fatter. So, likewise you can have battery size depending on their diameter and height and they are presented in this table. They actually follow international standard. There are certain flat cells as well.

So, in the flat cell, you have length, width and thickness. Some of these flat cells are also called rectangular cells. So, as you can see these dimensions are very stringent because depending on the dimension of the battery, you make your electronic consumer electronic devices. So, therefore, they are very specific about the size, their dimension and their tolerance.

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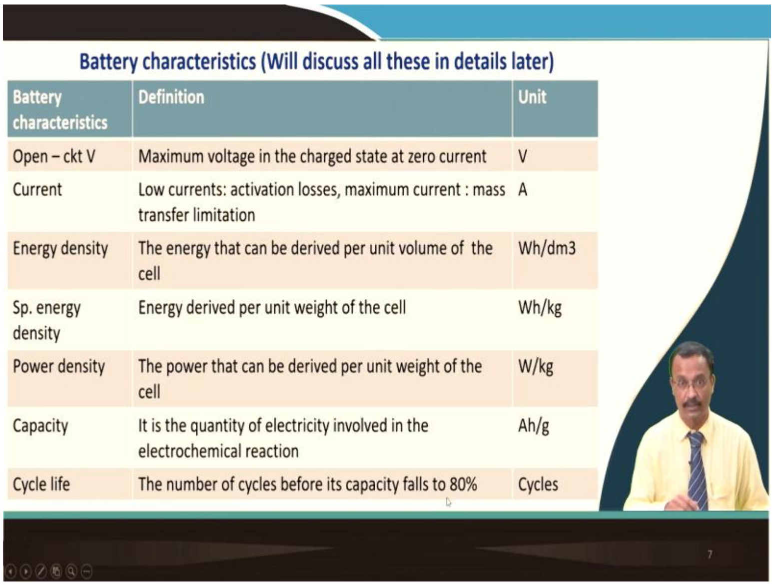

Battery characteristics (Will discuss all these in details later)

Battery characteristics	Definition	Unit
Open – ckt V	Maximum voltage in the charged state at zero current	V
Current	Low currents: activation losses, maximum current : mass transfer limitation	A
Energy density	The energy that can be derived per unit volume of the cell	Wh/dm3
Sp. energy density	Energy derived per unit weight of the cell	Wh/kg
Power density	The power that can be derived per unit weight of the cell	W/kg
Capacity	It is the quantity of electricity involved in the electrochemical reaction	Ah/g
Cycle life	The number of cycles before its capacity falls to 80%	Cycles

Now, I will introduce certain battery characteristics. So, open circuit voltage is the maximum voltage in the charged state when current is 0. Current is the amount of current drawn/supplied to the battery. Low current- activation losses predominant, maximum current- mass transfer is a limitation. We will come back to this statement in depth later when we will talk about the kinetics. Energy density is the energy that can be delivered per unit volume of the cell. This is volumetric energy density. Specific energy density is the energy that can be delivered per unit weight of the cell. Power density is the power that can be derived per unit weight of the cell, and this is Watt per kg units. Capacity, as I said, is the quantity of electricity involved in the electrochemical reaction.Usually, it is defined in terms of Ampere hour per gram. Cycle life is the number of cycles before the capacity falls to 80 percent. This is also termed as cycleability. So, for primary battery, cycle life does not have any meaning; it is pertinent to the rechargeable type of battery.

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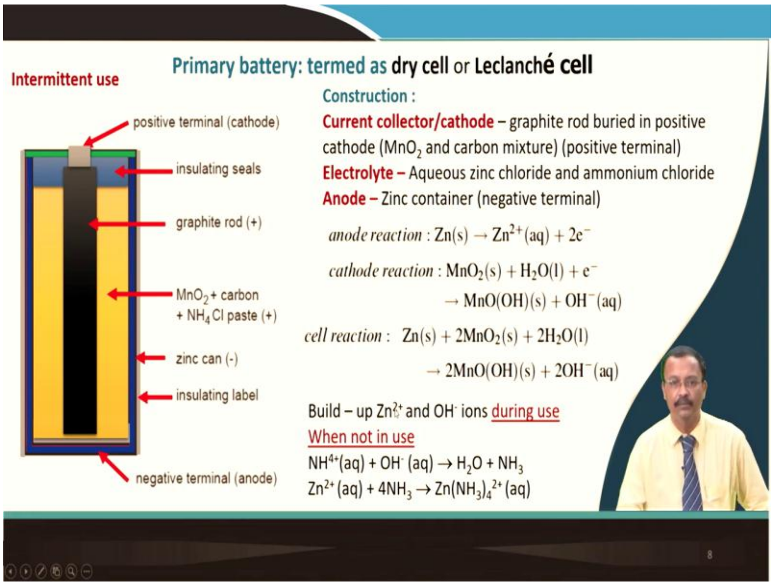

Primary battery: termed as dry cell or Leclanché cell

Intermittent use

Construction :

Current collector/cathode – graphite rod buried in positive cathode (MnO_2 and carbon mixture) (positive terminal)

Electrolyte – Aqueous zinc chloride and ammonium chloride

Anode – Zinc container (negative terminal)

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

$$\textit{cathode reaction}: MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$$

$$\textit{cell reaction}: Zn(s) + 2MnO_2(s) + 2H_2O(l) \rightarrow 2MnO(OH)(s) + 2OH^-(aq)$$

Build – up Zn^{2+} and OH^- ions during use

When not in use

$NH^{4+}(aq) + OH^-(aq) \rightarrow H_2O + NH_3$

$Zn^{2+}(aq) + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}(aq)$

Now, we will talk about three important primary battery, the first one is dry cell or Leclanche cell as it is called sometimes. It should have two terminals, positive and negative terminal. You have the electrolyte right and also, you need to pack everything in a compact form. So, that gives you battery. So, for that you need to have terminals and stuff like that.

So, accordingly, if you just arrange it, you have a current collector cum cathode. In case of this dry cell, graphite rod is buried in positive cathode which is manganese dioxide and carbon mixture. The construction is shown here. If you break a dry cell, you will see these structures and this is called the positive terminal. Electrolyte here is aqueous zinc chloride and ammonium chloride, and it is formed in terms of a paste. Anode is the zinc container itself. So, zinc is a container and we call this is a negative terminal. So, at anode, zinc will get oxidized since zinc is more electropositive according to the standard reduction potential. The cathode reaction is a bit complicated. Overall, the reactions are as follows:

$$\textit{anode reaction}: \mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-}$$

$$\textit{cathode reaction}: \mathrm{MnO_2(s)} + \mathrm{H_2O(l)} + \mathrm{e^-} \rightarrow \mathrm{MnO(OH)(s)} + \mathrm{OH^-(aq)}$$

$$\textit{cell reaction}: \mathrm{Zn(s)} + 2\mathrm{MnO_2(s)} + 2\mathrm{H_2O(l)} \rightarrow 2\mathrm{MnO(OH)(s)} + 2\mathrm{OH^-(aq)}$$

There is one problem for this kind of battery which you may have experienced. If you turn on the torch light for long period of time, you will see that the intensity of the light is progressively reduced. And then finally, the battery stops working. If you wait for some time and again turn it on, then you will see it works again. For the continuous part, zinc ion accumulates in the zinc anode part and hydroxyl ions accumulate in the manganese oxide part. Due to this charge accumulation, this reaction rate reduces and electron flow diminishes. When not in use, the ammonium ion reacts with hydroxyl aqueous ion and zinc ion in the following reactions.

$NH_4^+(aq) + OH^- (aq) \rightarrow H_2O + NH_3$

$Zn^{2+} (aq) + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} (aq)$

Because of this, you can use this dry cell again.

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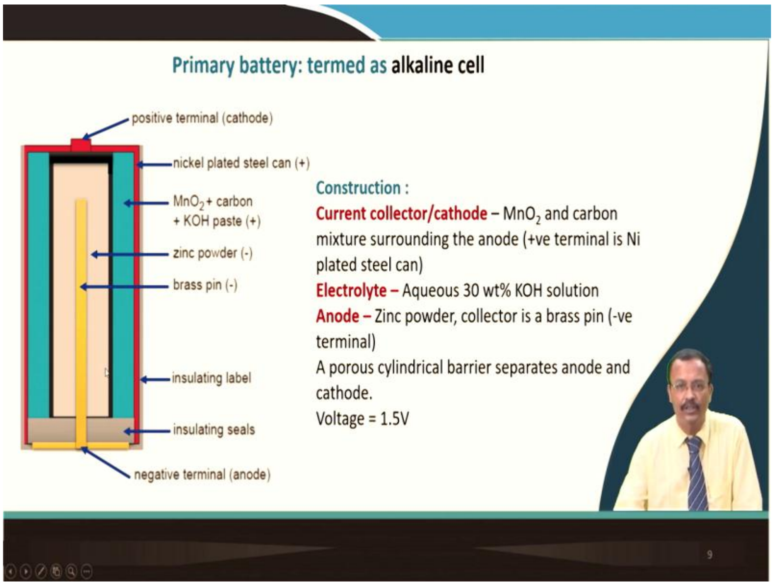

Primary battery: termed as **alkaline cell**

Construction :

Current collector/cathode – MnO_2 and carbon mixture surrounding the anode (+ve terminal is Ni plated steel can)

Electrolyte – Aqueous 30 wt% KOH solution

Anode – Zinc powder, collector is a brass pin (-ve terminal)

A porous cylindrical barrier separates anode and cathode.

Voltage = 1.5V

The construction of the primary battery termed as alkaline cell is a bit different. Here you can see the current collector or cathode is manganese oxide and carbon mixture, which is surrounded by nickel plated steel can. Anode is zinc powder and instead of your graphite rod, there is a current collector which is brass pin. So construction wise, it is a bit different. Electrolyte here is aqueous 30 percent of potassium hydroxide solution. You remember that the electrolyte leaks out of these batteries when not in use or if it is overused. So, one should be cautious of this fact. Once the battery is down, it should be immediately replaced. There is a porous cylinder barrier that separates anode and cathode material. Usually, the voltage for both the dry cell and this kind of cell is 1.5 Volt, decided by the standard reduction potential of the material in use.

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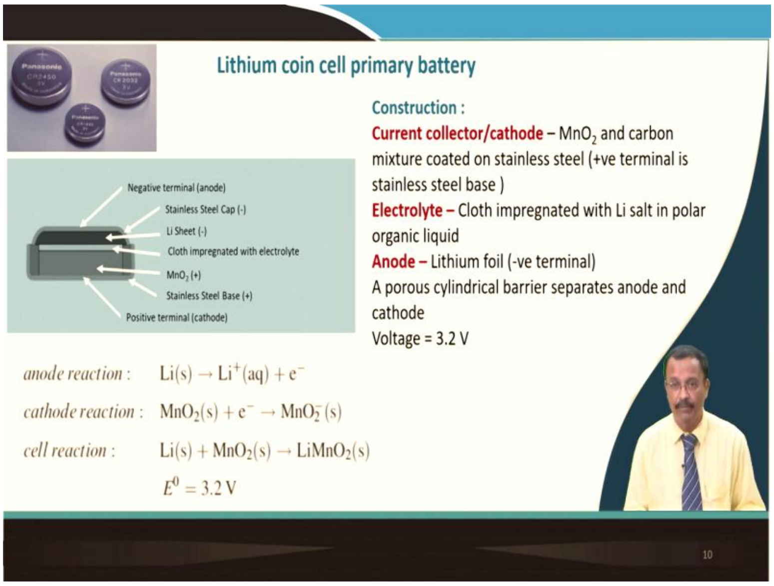

Lithium coin cell primary battery

Construction :

Current collector/cathode – MnO_2 and carbon mixture coated on stainless steel (+ve terminal is stainless steel base)

Electrolyte – Cloth impregnated with Li salt in polar organic liquid

Anode – Lithium foil (-ve terminal)

A porous cylindrical barrier separates anode and cathode

Voltage = 3.2 V

anode reaction : $\mathrm{Li(s)} \rightarrow \mathrm{Li^+(aq)} + \mathrm{e^-}$

cathode reaction : $\mathrm{MnO_2(s)} + \mathrm{e^-} \rightarrow \mathrm{MnO_2^-(s)}$

cell reaction : $\mathrm{Li(s)} + \mathrm{MnO_2(s)} \rightarrow \mathrm{LiMnO_2(s)}$

$E^0 = 3.2\ \mathrm{V}$

You are also familiar with this button cell. They are lithium coin cell primary battery. Here, the current collector and cathode is manganese dioxide and carbon mixture that is coated over a stainless steel. This forms the positive terminal. Positive terminal is the stainless steel base. Electrolyte is a cloth which is impregnated with a lithium-based salt in a polar organic liquid. So, one difference here (from the dry cell or alkaline cell) is that the dry and alkaline cells use aqueous electrolyte. So, the voltage is limited because of water. Water can get dissociated if you go beyond certain voltage. Also, the voltage depends on various other parameters. So, lithium for example, is highly electro positive and that leads to very large, relatively large voltage. The reaction is very straightforward; lithium gets oxidized and manganese dioxide gets reduced and the cell reaction is this.

$$\begin{aligned} &\textit{anode reaction :} && \mathrm{Li(s)} \rightarrow \mathrm{Li^+(aq)} + \mathrm{e^-} \\ &\textit{cathode reaction :} && \mathrm{MnO_2(s)} + \mathrm{e^-} \rightarrow \mathrm{MnO_2^-(s)} \\ &\textit{cell reaction :} && \mathrm{Li(s)} + \mathrm{MnO_2(s)} \rightarrow \mathrm{LiMnO_2(s)} \\ & && E^0 = 3.2\ \mathrm{V} \end{aligned}$$

Lithium reacts with manganese dioxide to form lithium manganese oxide; and here, the standard electrode standard EMF that you get is 3.2 Volt, which is reasonably high in comparison to your dry cell or alkaline cell (typically 1.5 Volt).

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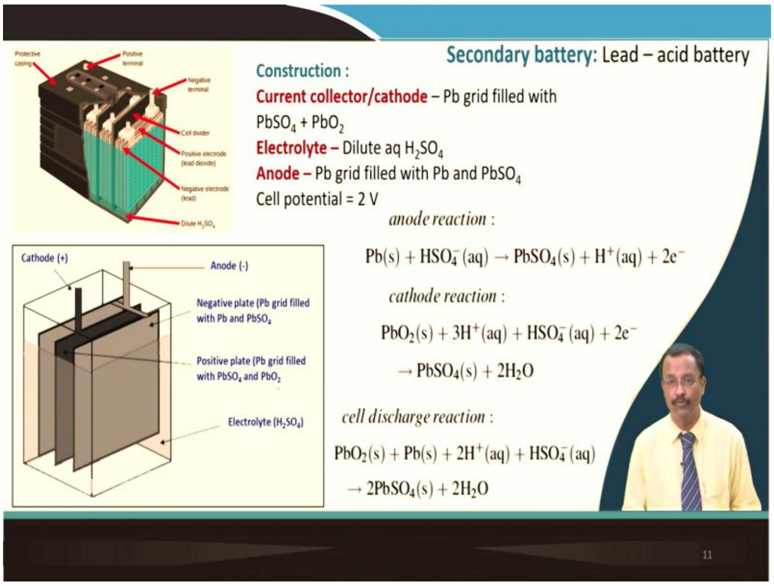

Secondary battery: Lead – acid battery

Construction :

Current collector/cathode – Pb grid filled with $PbSO_4 + PbO_2$

Electrolyte – Dilute aq H_2SO_4

Anode – Pb grid filled with Pb and $PbSO_4$

Cell potential = 2 V

anode reaction :

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

cathode reaction :

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

cell discharge reaction :

$$PbO_2(s) + Pb(s) + 2H^+(aq) + HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$$

Now, we will talk about the secondary battery, where you can recharge it once it is completely discharged. Here, the lead-acid battery is a forerunner. Here, the current collector and cathode is lead grid that is filled with lead sulphate and lead oxide. Electrolyte is dilute H_2SO_4. So, one should be cautious about opening this battery because of the possible acid bond. Anode is the lead grid filled with lead and lead sulphate. Cell potential comes out to be about 2 Volt. So, the charge and discharge reaction here is straight forward as below:

anode reaction :

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

cathode reaction :

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

cell discharge reaction :

$$PbO_2(s) + Pb(s) + 2H^+(aq) + HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$$

So, each of this cell will give you 2 Volts. So, if you want a 12 Volt battery, then you will have to connect several such cell; about 6 such cell in series in order to increase a 12 Volt battery. If you want to increase the capacity of the battery, you will have to connect it in parallel.

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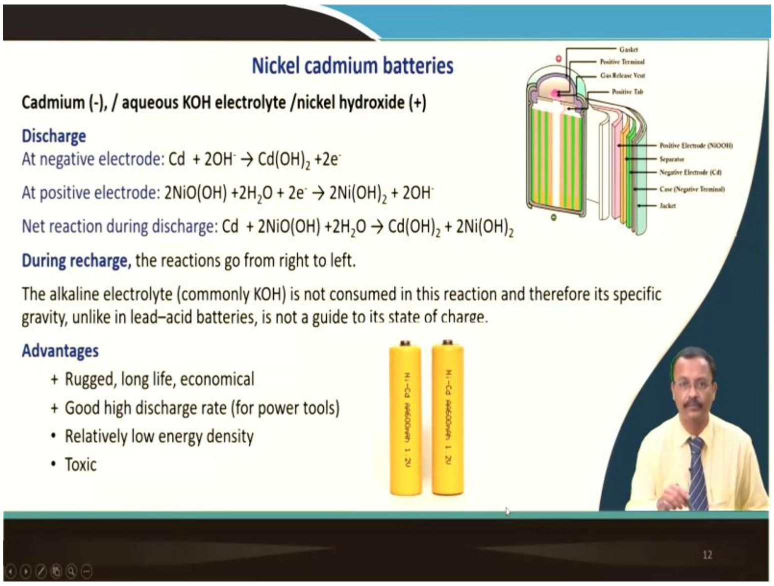

Nickel cadmium batteries

Cadmium (-), / aqueous KOH electrolyte /nickel hydroxide (+)

Discharge

At negative electrode: Cd + $2OH^- \rightarrow Cd(OH)_2 + 2e^-$

At positive electrode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

Net reaction during discharge: $Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

During recharge, the reactions go from right to left.

The alkaline electrolyte (commonly KOH) is not consumed in this reaction and therefore its specific gravity, unlike in lead–acid batteries, is not a guide to its state of charge.

Advantages

- + Rugged, long life, economical
- + Good high discharge rate (for power tools)
- • Relatively low energy density
- • Toxic

Similarly, nickel cadmium battery was quite popular in 90s. This uses cadmium, which is not environmentally friendly. So, their use has been almost discontinued. Aqueous KOH electrolyte is used with nickel oxy-hydroxide. The overall charge and discharge reactions are as follows:

Discharge

At negative electrode: Cd + $2OH^- \rightarrow Cd(OH)_2 + 2e^-$

At positive electrode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

Net reaction during discharge: $Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

During recharge, the reactions go from right to left.

The alkaline electrolyte is commonly KOH is not consumed in this reaction. Therefore, its specific gravity, unlike the lead acid battery, is not a guide for the state of the charge. Advantage is that it is rugged, it has long life, it is economical, and it is having good high discharge rate. That is why it is used for the power tools. But it is toxic, as I said cadmium is involved.

As for the construction of this kind of battery cylindrical cell, you first have anode, separator and cathode. You roll them and pack them inside a cylindrical cell to form this battery. So, I will separately take this battery in relatively more details afterwards. This lecture is primarily aimed to make you familiar with different types of battery. So, do not worry too much about how they are made, what the reaction sequences are, and how the voltages are calculated and stuff like that at this point.

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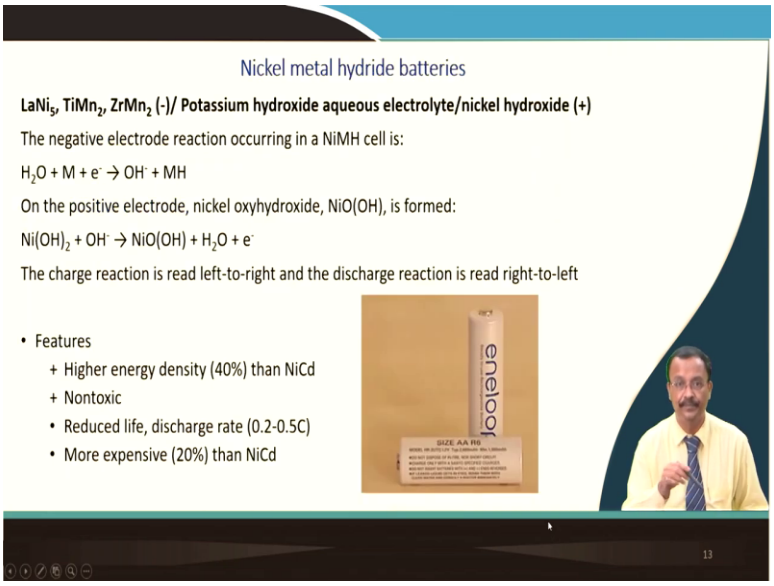

Nickel metal hydride batteries

$LaNi_5$, $TiMn_2$, $ZrMn_2$ (-)/ Potassium hydroxide aqueous electrolyte/nickel hydroxide (+)

The negative electrode reaction occurring in a NiMH cell is:

$H_2O + M + e^- \rightarrow OH^- + MH$

On the positive electrode, nickel oxyhydroxide, NiO(OH), is formed:

$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

The charge reaction is read left-to-right and the discharge reaction is read right-to-left

- Features
  - \+ Higher energy density (40%) than NiCd
  - \+ Nontoxic
  - Reduced life, discharge rate (0.2-0.5C)
  - More expensive (20%) than NiCd

For the Nickel metal hydride battery, the reactions sequences are as follows:

The negative electrode reaction occurring in a NiMH cell is:

$H_2O + M + e^- \rightarrow OH^- + MH$

On the positive electrode, nickel oxyhydroxide, NiO(OH), is formed:

$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

The charge reaction is read left-to-right and the discharge reaction is read right-to-left

So, it is having a high energy density; 40 percent higher than nickel cadmium.

It is non-toxic. It is having reduced life. Discharge rate is usually 0.2 to 0.5 C. One C means that you discharge your battery within 1 hour. So, a rate of 0.2C means that you discharge your battery in 5 hours. It is 0.5C here, which means you discharge your battery in 2 hours. It is more expensive than nickel cadmium battery.

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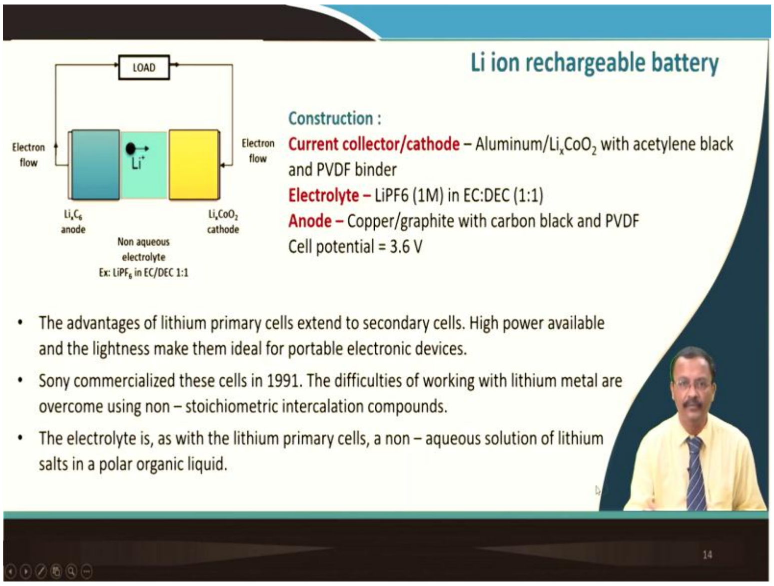

Li ion rechargeable battery

Construction :

Current collector/cathode – Aluminum/Li_xCoO_2 with acetylene black and PVDF binder

Electrolyte – LiPF6 (1M) in EC:DEC (1:1)

Anode – Copper/graphite with carbon black and PVDF

Cell potential = 3.6 V

- The advantages of lithium primary cells extend to secondary cells. High power available and the lightness make them ideal for portable electronic devices.
- Sony commercialized these cells in 1991. The difficulties of working with lithium metal are overcome using non – stoichiometric intercalation compounds.
- The electrolyte is, as with the lithium primary cells, a non – aqueous solution of lithium salts in a polar organic liquid.

Now, we talk about lithium rechargeable battery. The construction is a bit different. Cathode assembly consists of aluminum as a current collector and typical cathode is lithium cobalt oxide mixed with acetylene black and PVDF binder. Therefore, it is a composite electrode inside the electrolyte in this case instead of a metal plate.

Electrolyte is 1M $LiPF_6$ dissolved in EC and DEC 1 is to 1. Anode assembly consists of copper as a current collector with the anode material being graphite with carbon black and PVDF as a binder. The cell potential is pretty high 3.6 Volt, and that is why this batteries are very important. It was commercialized by Sony in 1990.

The advantage of lithium primary cell extends to the secondary cell. High power and low weight can be achieved because of the low density of lithium. It is ideal for portable electronic devices. As I said Sony commercialized it in 1991, and the electrolyte is non aqueous solution of lithium salts in a polar liquid.

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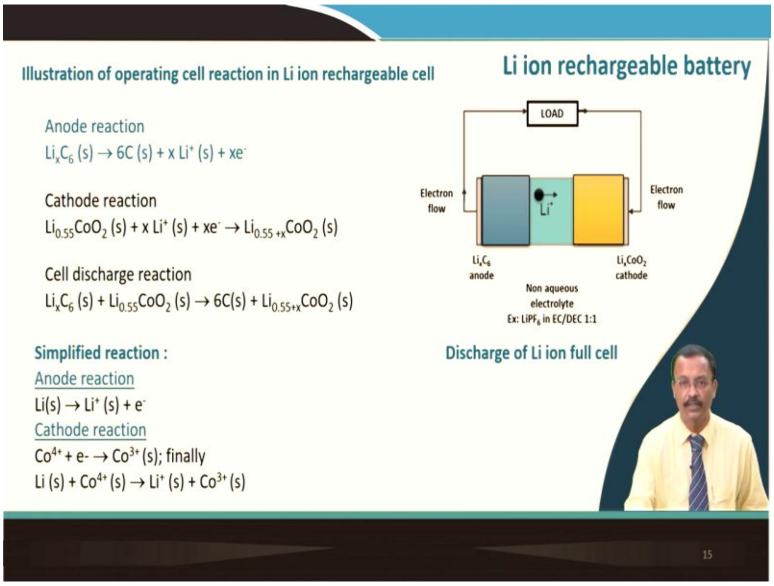

Illustration of operating cell reaction in Li ion rechargeable cell

Li ion rechargeable battery

Anode reaction

$Li_xC_6\ (s) \rightarrow 6C\ (s) + x\ Li^+\ (s) + xe^-$

Cathode reaction

$Li_{0.55}CoO_2\ (s) + x\ Li^+\ (s) + xe^- \rightarrow Li_{0.55+x}CoO_2\ (s)$

Cell discharge reaction

$Li_xC_6\ (s) + Li_{0.55}CoO_2\ (s) \rightarrow 6C(s) + Li_{0.55+x}CoO_2\ (s)$

Discharge of Li ion full cell

Simplified reaction :

Anode reaction

$Li(s) \rightarrow Li^+\ (s) + e^-$

Cathode reaction

$Co^{4+} + e- \rightarrow Co^{3+}\ (s)$; finally

$Li\ (s) + Co^{4+}\ (s) \rightarrow Li^+\ (s) + Co^{3+}\ (s)$

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Now, you can talk about the reaction.

In graphite, lithium is intercalated while from the cathode lithium is taken out during the charging operation. During cell discharge lithium is taken out from the graphite.

So, the simplified relation is that lithium forms lithium ion and electron, and cathode reaction is one of the transition metal cut down. Here, in case is cobalt, which is in plus 4 state, is getting reduced. So, finally, this is the cell reaction.

Simplified reaction :

Anode reaction

$Li(s) \rightarrow Li^+\ (s) + e^-$

Cathode reaction

$Co^{4+} + e- \rightarrow Co^{3+}\ (s)$; finally

$Li\ (s) + Co^{4+}\ (s) \rightarrow Li^+\ (s) + Co^{3+}\ (s)$

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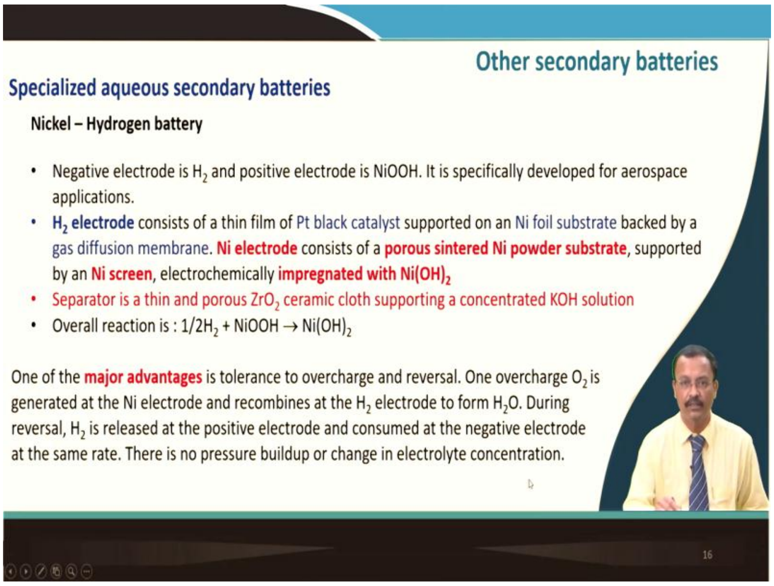

Other secondary batteries

Specialized aqueous secondary batteries

Nickel – Hydrogen battery

- Negative electrode is H_2 and positive electrode is NiOOH. It is specifically developed for aerospace applications.
- **H_2 electrode** consists of a thin film of Pt black catalyst supported on an Ni foil substrate backed by a gas diffusion membrane. **Ni electrode** consists of a **porous sintered Ni powder substrate**, supported by an **Ni screen**, electrochemically **impregnated with $Ni(OH)_2$**
- Separator is a thin and porous ZrO_2 ceramic cloth supporting a concentrated KOH solution
- Overall reaction is : $1/2H_2 + NiOOH \rightarrow Ni(OH)_2$

One of the **major advantages** is tolerance to overcharge and reversal. One overcharge O_2 is generated at the Ni electrode and recombines at the H_2 electrode to form H_2O. During reversal, H_2 is released at the positive electrode and consumed at the negative electrode at the same rate. There is no pressure buildup or change in electrolyte concentration.

So, these kinds of batteries are reusable. Other secondary batteries are nickel hydrogen battery where the negative electrode is hydrogen, and positive electrode is nickel oxygen hydroxide oxyhydroxide. It is specifically developed for aerospace application. Now, hydrogen electrode, they consist of a thin film of platinum black catalyst that is supported on the nickel foil substrate backed by a gas diffusion membrane. And nickel electrode consists of a porous sintered nickel powder substrate supported by a nickel screen and that is electrochemically impregnated with nickel hydroxide. Separator is a thin porous zirconia ceramic cloth, supporting a concentrated KOH solution.

Overall cell reaction you can work it out, but the finally, this is hydrogen and nickel oxyhydroxide, it forms nickel hydroxide. One of the major advantage is the tolerance of over charge and reversal. On overcharge, oxygen generates at the nickel electrode and recombines at hydrogen electrode to form H_2O. During reversal, H_2 is released at the positive electrode and consumed at the negative electrode at the same rate. So, there is no pressure buildup, and change in the electrolyte concentration is also ruled out.

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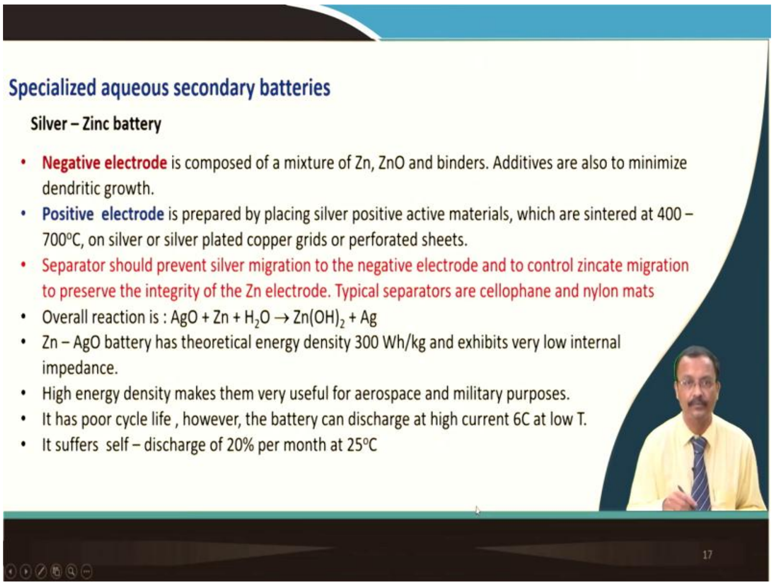

Specialized aqueous secondary batteries

Silver – Zinc battery

- **Negative electrode** is composed of a mixture of Zn, ZnO and binders. Additives are also to minimize dendritic growth.
- **Positive electrode** is prepared by placing silver positive active materials, which are sintered at 400 – 700°C, on silver or silver plated copper grids or perforated sheets.
- Separator should prevent silver migration to the negative electrode and to control zincate migration to preserve the integrity of the Zn electrode. Typical separators are cellophane and nylon mats
- Overall reaction is : $AgO + Zn + H_2O \rightarrow Zn(OH)_2 + Ag$
- Zn – AgO battery has theoretical energy density 300 Wh/kg and exhibits very low internal impedance.
- High energy density makes them very useful for aerospace and military purposes.
- It has poor cycle life , however, the battery can discharge at high current 6C at low T.
- It suffers self – discharge of 20% per month at 25°C

Similarly, we have specialized aqueous secondary batteries in the form of silver-zinc battery. Negative electrode is composed of a mixture of zinc, zinc oxide and binders. Additives are also used to minimize the so called dendritic growth. Positive electrode is prepared by placing silver positive active material which is basically sintered at relatively high temperature on a silver plated copper grid, or a perforated sheet.

So, the separator should prevent silver migration into the negative electrode, and also control the zincate migration to preserve the integrity of the zinc electrode. Typical separators are cellophane sheet or nylon mats. The overall reaction is given like this and zinc silver oxide battery has a theoretical energy density 300 Watt hour per kg. It exhibits very low internal impedance.

High energy density makes them very useful for aerospace and military applications; but it is having poor cycle life. However, the battery can discharge at high current at about 6C, which is an advantage. 6C means that in about 10 minutes it can be discharged. It suffers from self-discharge. So, shelf life is not that attractive.

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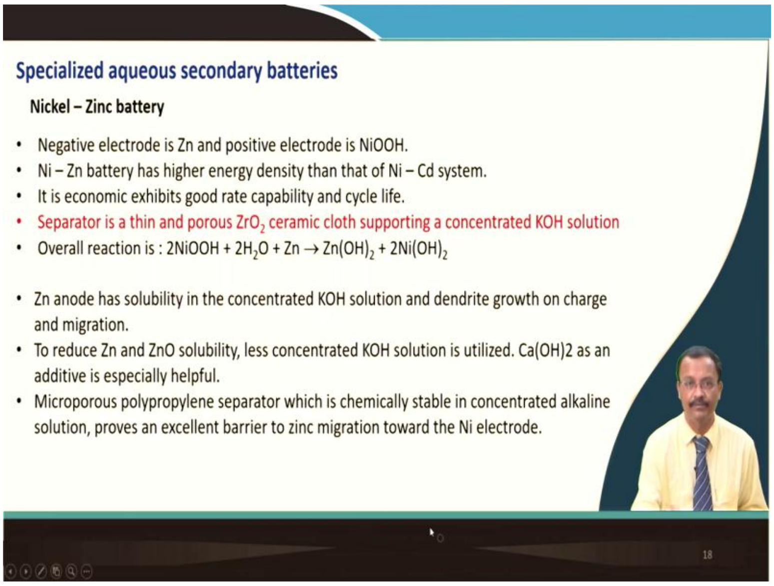

Specialized aqueous secondary batteries

Nickel – Zinc battery

- Negative electrode is Zn and positive electrode is NiOOH.
- Ni – Zn battery has higher energy density than that of Ni – Cd system.
- It is economic exhibits good rate capability and cycle life.
- Separator is a thin and porous ZrO_2 ceramic cloth supporting a concentrated KOH solution
- Overall reaction is : $2NiOOH + 2H_2O + Zn \rightarrow Zn(OH)_2 + 2Ni(OH)_2$

- Zn anode has solubility in the concentrated KOH solution and dendrite growth on charge and migration.
- To reduce Zn and ZnO solubility, less concentrated KOH solution is utilized. Ca(OH)2 as an additive is especially helpful.
- Microporous polypropylene separator which is chemically stable in concentrated alkaline solution, proves an excellent barrier to zinc migration toward the Ni electrode.

Specialized aqueous zinc battery includes nickel-zinc battery. So, negative electrode is zinc and positive electrode is nickel oxyhydroxide. So, nickel and zinc battery has higher energy density than nickel cadmium system. It is economic.

It exhibits good rate capability and cycle life, and its separator is a thin and porous ZrO_2 ceramic supporting a concentrated KOH. So, the overall reaction is given like this and zinc has solubility in the concentrated KOH, and dendrite growth on charge and migration.

- Overall reaction is : $2NiOOH + 2H_2O + Zn \rightarrow Zn(OH)_2 + 2Ni(OH)_2$

So, to reduce the zinc and zinc oxide solubility, usually low concentration KOH is utilized; sometimes calcium hydroxide additive is also added and micro porous polypropylene separator (which is otherwise chemically stable in concentrated alkaline solution) proves to be an excellent barrier for zinc migration towards the nickel electrode.

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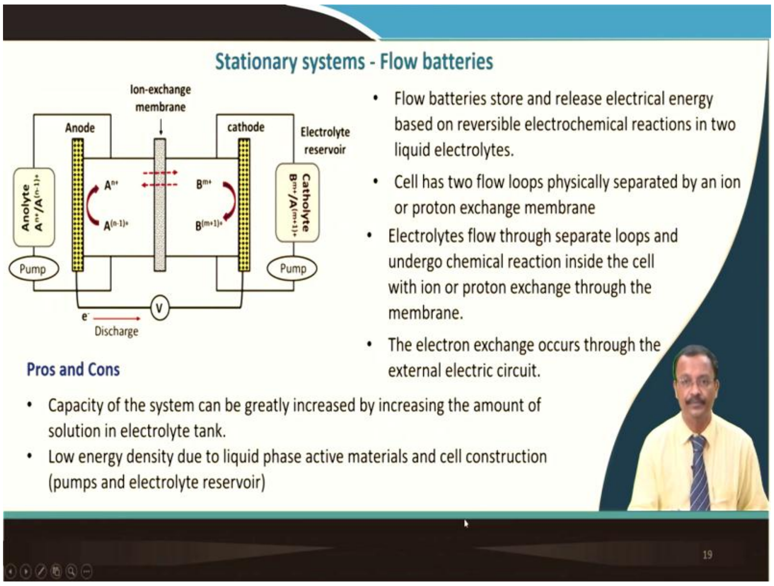

Stationary systems - Flow batteries

- Flow batteries store and release electrical energy based on reversible electrochemical reactions in two liquid electrolytes.
- Cell has two flow loops physically separated by an ion or proton exchange membrane
- Electrolytes flow through separate loops and undergo chemical reaction inside the cell with ion or proton exchange through the membrane.
- The electron exchange occurs through the external electric circuit.

Pros and Cons

- Capacity of the system can be greatly increased by increasing the amount of solution in electrolyte tank.
- Low energy density due to liquid phase active materials and cell construction (pumps and electrolyte reservoir)

In earlier battery also we had a problem of silver migration; silver zinc oxide battery. This is a new type of stationary system. We call it is a flow battery. So, these flow batteries they store and release electrical energy based on reversible electrochemical reactions in two liquid electrolytes.

So, liquid electrolyte is pumped through this chamber and the cell has two flow loops physically separated by an ion or proton exchange membrane. Electrolytes flow through separate loops and undergo chemical reaction inside the cell with ion or proton exchange through the membrane.

The electron exchange occurs through the external circuit due to this process and capacity of this system can be greatly increased by increasing the amount of the solution of the electrolytic tank. So, one can use huge electrolytic tank to increase the capacity; but suddenly, the all the weights will be incorporated here and this will lead to low energy density for this kind of battery.

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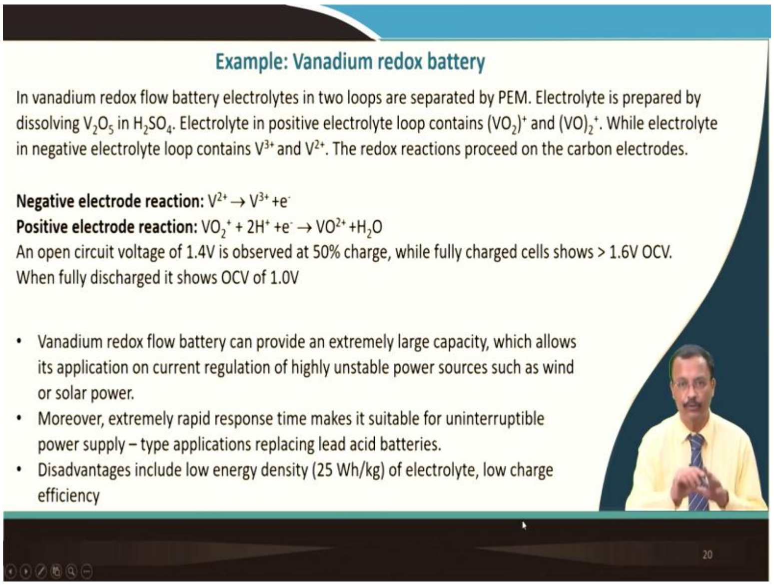

Example: Vanadium redox battery

In vanadium redox flow battery electrolytes in two loops are separated by PEM. Electrolyte is prepared by dissolving V_2O_5 in H_2SO_4. Electrolyte in positive electrolyte loop contains $(VO_2)^+$ and $(VO)_2^+$. While electrolyte in negative electrolyte loop contains V^{3+} and V^{2+}. The redox reactions proceed on the carbon electrodes.

Negative electrode reaction: $V^{2+} \rightarrow V^{3+} + e^-$
Positive electrode reaction: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$
An open circuit voltage of 1.4V is observed at 50% charge, while fully charged cells shows > 1.6V OCV. When fully discharged it shows OCV of 1.0V

- Vanadium redox flow battery can provide an extremely large capacity, which allows its application on current regulation of highly unstable power sources such as wind or solar power.
- Moreover, extremely rapid response time makes it suitable for uninterruptible power supply – type applications replacing lead acid batteries.
- Disadvantages include low energy density (25 Wh/kg) of electrolyte, low charge efficiency

I will cite two quick example which follows this. One is vanadium redox flow battery. In the vanadium redox flow battery, the two loops are separated by a membrane, a PEM membrane. Electrolyte is prepared by dissolving V_2O_5 in H_2SO_4. Electrolyte in positive electrolyte loop contains VO_2^+ and VO^{2+} while electrolyte in the negative electrolyte loop contains only V^{3+} and V^{2+}.

So, vanadium is having various valence states. So, the redox reactions are given below:

Negative electrode reaction: $V^{2+} \rightarrow V^{3+} + e^-$

Positive electrode reaction: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

Open circuit voltage is about 1.4 Volt, observed at 50 percent of charge. Fully charged state shows more than 1.6 Volt OCV. When fully discharged, it shows open circuit voltage around 1 Volt.

So, vanadium this redox flow battery (which I will discuss in details a part of another module), they have extremely large capacity which allows its application on current regulation of highly unstable power source such as renewable energy, wind and solar power. So, this redox flow battery is the solution.

Extremely rapid response time makes these batteries in use for uninterrupted power supply, the type of application replacing the lead acid battery. So, for stationary use, this is the answer. Disadvantage for this is the low energy density about 25 Watt hour per kg, due to the electrolyte. It is having low charge efficiency also (the weight of the pump etcetera that also contributes to this).

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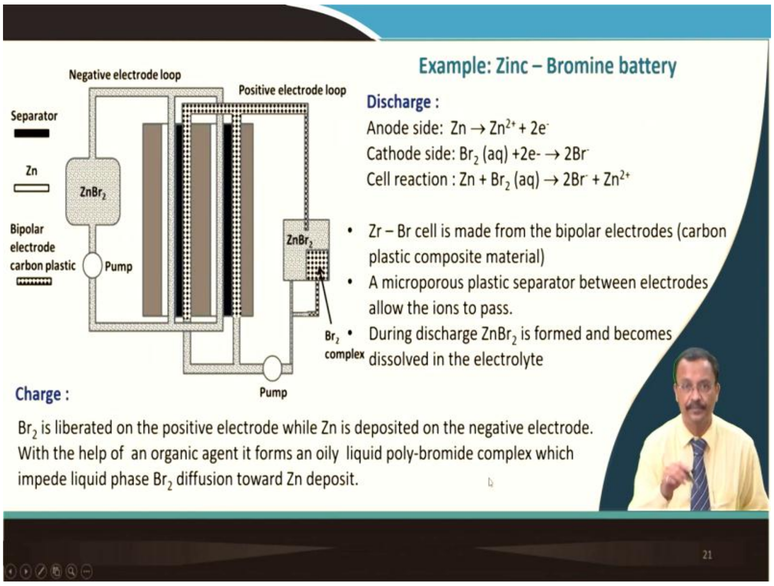

Example: Zinc – Bromine battery

Discharge :

Anode side: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode side: Br_2 (aq) +2e- $\rightarrow 2Br^-$

Cell reaction : $Zn + Br_2$ (aq) $\rightarrow 2Br^- + Zn^{2+}$

- Zr – Br cell is made from the bipolar electrodes (carbon plastic composite material)
- A microporous plastic separator between electrodes allow the ions to pass.
- During discharge $ZnBr_2$ is formed and becomes dissolved in the electrolyte

Charge :

Br_2 is liberated on the positive electrode while Zn is deposited on the negative electrode. With the help of an organic agent it forms an oily liquid poly-bromide complex which impede liquid phase Br_2 diffusion toward Zn deposit.

Zinc bromine battery is another example. So, similar type of construction anode side zinc is oxidized, cathode side bromine aqueous solution undergoes this reaction. The cell reaction is as follows:

Discharge :

Anode side: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode side: Br_2 (aq) +2e- $\rightarrow 2Br^-$

Cell reaction : $Zn + Br_2$ (aq) $\rightarrow 2Br^- + Zn^{2+}$

So, zinc bromine cell is made from bipolar electrode; carbon and plastic composite material. A micro porous plastic, which separates between the electrodes, allow the ions to pass. During discharge, zinc bromide is formed and becomes dissolved in the electrolyte. So, during charge, bromine is liberated at the positive electrode, whereas zinc is deposited on the negative electrode. With the help of an organic agent, it forms an oily liquid; poly bromide complex which impede the liquid phase bromine diffusion towards the zinc deposit.

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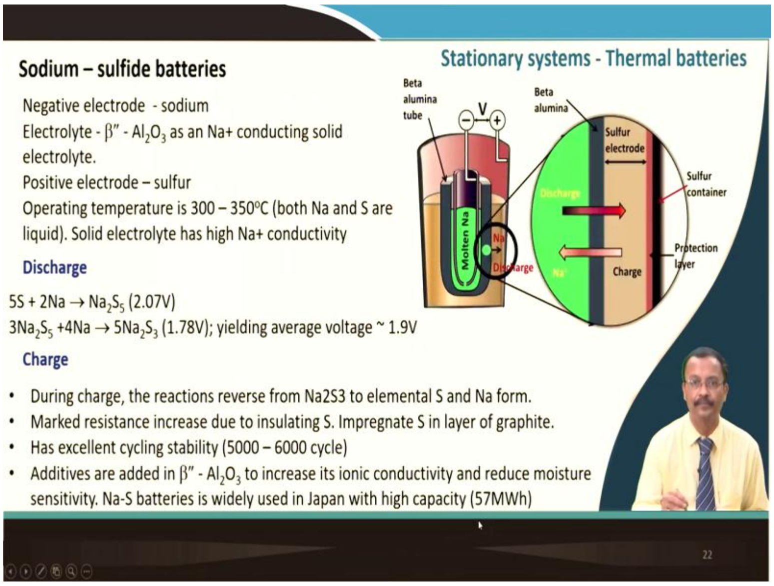

Sodium – sulfide batteries

Stationary systems - Thermal batteries

Negative electrode - sodium

Electrolyte - β" - Al_2O_3 as an Na+ conducting solid electrolyte.

Positive electrode – sulfur

Operating temperature is 300 – 350°C (both Na and S are liquid). Solid electrolyte has high Na+ conductivity

Discharge

$5S + 2Na \rightarrow Na_2S_5$ (2.07V)

$3Na_2S_5 + 4Na \rightarrow 5Na_2S_3$ (1.78V); yielding average voltage ~ 1.9V

Charge

- During charge, the reactions reverse from Na2S3 to elemental S and Na form.
- Marked resistance increase due to insulating S. Impregnate S in layer of graphite.
- Has excellent cycling stability (5000 – 6000 cycle)
- Additives are added in β" - Al_2O_3 to increase its ionic conductivity and reduce moisture sensitivity. Na-S batteries is widely used in Japan with high capacity (57MWh)

Another stationary system is the thermal batteries, sodium sulfide batteries. Negative electrode is sodium; electrolyte is beta alumina. This is a good sodium ion conducting electrolyte. Positive electrode is sulfur. Operating temperature is around 300 to 350 degree Celsius and both sodium and sulfur is in its liquid form.

So, solid electrolyte has high sodium-ion conductivity. The reaction is as follows:

$5S + 2Na \rightarrow Na_2S_5$ (2.07V)

$3Na_2S_5 + 4Na \rightarrow 5Na_2S_3$ (1.78V); yielding average voltage ~ 1.9V

So, therefore, sulfur is impregnated in the layer of graphite. But it is having excellent cycleability about 5000 to 6000 cycles. Additives are added in beta alumina, which is the ionically conducting solid electrolyte to increase this ionic conductivity and reduce the moisture sensitivity. So, sodium sulfur batteries is widely used in Japan and capacity is as high as 57 mega Watt hour.

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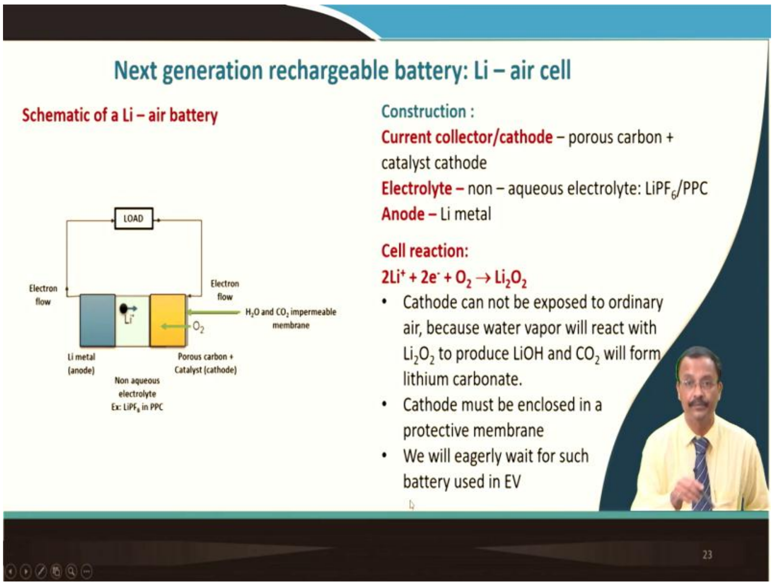

Next generation rechargeable battery: Li – air cell

Schematic of a Li – air battery

Construction :

Current collector/cathode – porous carbon + catalyst cathode

Electrolyte – non – aqueous electrolyte: $LiPF_6$/PPC

Anode – Li metal

Cell reaction:

$2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$

- Cathode can not be exposed to ordinary air, because water vapor will react with Li_2O_2 to produce LiOH and CO_2 will form lithium carbonate.
- Cathode must be enclosed in a protective membrane
- We will eagerly wait for such battery used in EV

Finally, we talk about a next generation rechargeable battery which is lithium air. It is a very simple battery. Current collector and cathode is a porous carbon plus some kind of catalyst, because air is coming in at one end. Electrolyte is a non aqueous electrolyte, same as lithium ion battery; $LiPF_6$ in polypropylene. Anode is a lithium metal.

The cell reaction is as follows:

Cell reaction:

$$2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$$

Cathodes cannot be exposed in ordinary air because water vapor will start to react with Li_2O_2 to produce lithium hydroxide. Carbon dioxide will form lithium carbonate.

So, that is one disadvantage, you cannot use the ambient air for this reaction to take place. You will have to carry the oxygen cylinder. Oxygen cylinder carriage is a problem for mobile applications. Cathode must be enclosed in a protective membrane because of this infiltration of other gases and in fact, we are eagerly waiting for such battery for electric vehicle applications in near future.

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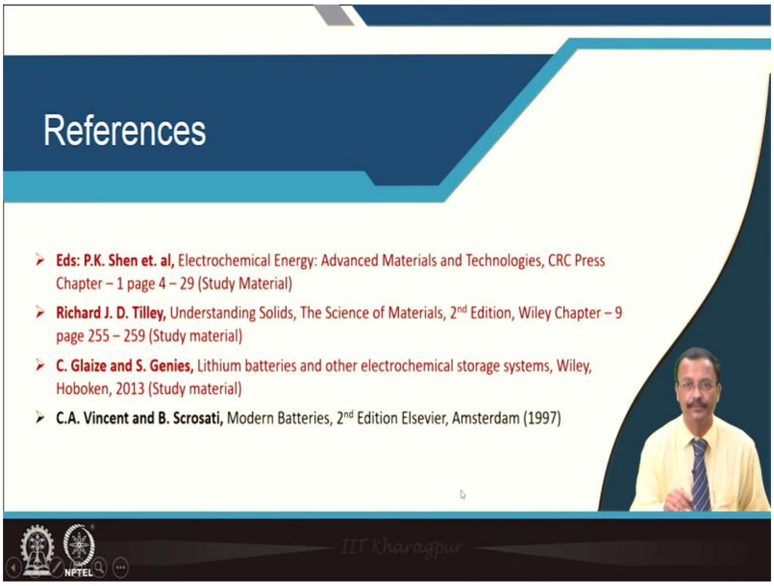

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- **Richard J. D. Tilley,** Understanding Solids, The Science of Materials, 2nd Edition, Wiley Chapter – 9 page 255 – 259 (Study material)
- **C. Glaize and S. Genies,** Lithium batteries and other electrochemical storage systems, Wiley, Hoboken, 2013 (Study material)
- **C.A. Vincent and B. Scrosati,** Modern Batteries, 2nd Edition Elsevier, Amsterdam (1997)

So, the study material for this particular lecture is taken from different sources, which is marked as red and Modern Batteries is an excellent book by Vincent and Scrosati. I would like you to go through the relevant portion.

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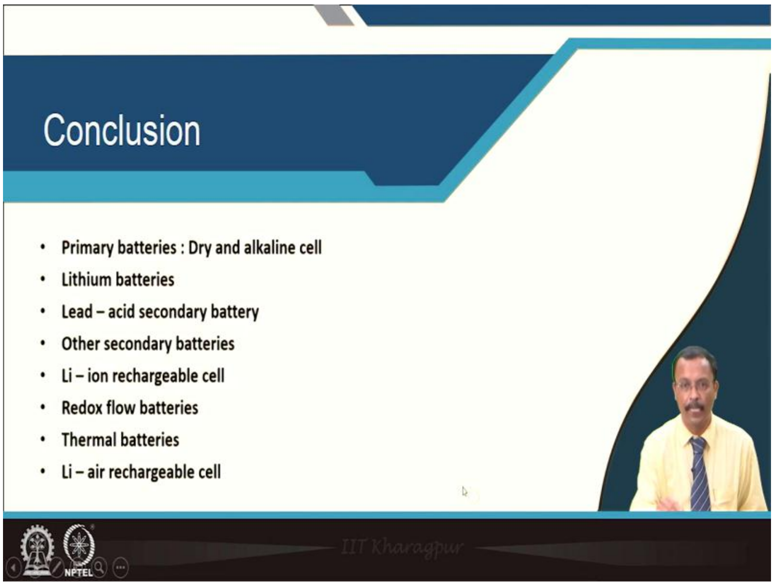

Conclusion

- **Primary batteries : Dry and alkaline cell**
- **Lithium batteries**
- **Lead – acid secondary battery**
- **Other secondary batteries**
- **Li – ion rechargeable cell**
- **Redox flow batteries**
- **Thermal batteries**
- **Li – air rechargeable cell**

So, in this particular lecture, we talked about primary batteries, dry and alkaline cell, then we talked about lithium batteries, then lead acid secondary battery, other types of secondary battery including thermal batteries, then we talked about lithium ion rechargeable cell. We introduced the redox flow battery concept, thermal batteries and finally, lithium air rechargeable batteries.

Thank you for your attention.