Electrochemical Technology in Pollution Control
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Lecture – 32
Batteries and fuel cells

Greetings to you all. Let us meet again and today I want to talk to you about Batteries and battery technology. As I had already explained to you in my last ending remarks in my last class battery technology has grown into a enormous field with lot of improvements and applications starting from rural areas to space.

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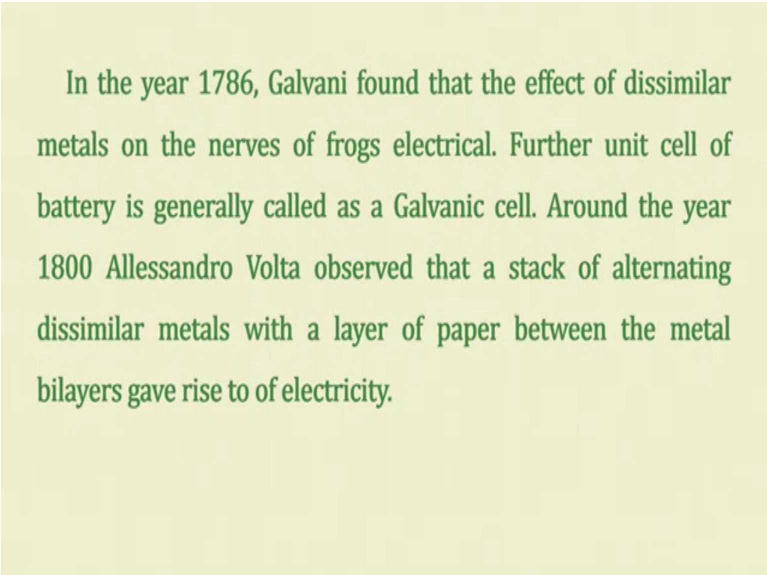

So, first of all a little bit about the history, and history is same as electrochemical technology is as old as electrochemical technology history of batteries also. So, the first effect was by Galvanic Italian scientist, who found that the frogs legs moved a little bit here and there when the electrical metals were connected to the nerves of the frogs. And he showed that, they there will be electrical impulse that can affect the that can be the root cause of movement of the frogs nerves, further based on his first observation our unit cell of battery is generally called as a Galvanic cell.

Around the year 1800, the Volta Allessandro Volta observed that a stack of alternating dissimilar metals with a layer of paper in between their metal gives rise to electricity. This is a very simple observation, but it does not mean that what a Volta observed is now is not out of the ordinary, but at the same time it was a very important discovery at that time that you just connect the 2 metals with a paper in between the metal by layers giving rise to electricity was something phenomenal at that time.

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Later Michael Faraday after intensive work for years together from 1830, discovered that the chemical reaction at each electrode was the source of electricity produced by a battery. It is for this reason that his name is used to describe electrode operation as a Faradaic process.

For the rest of 19th century, batteries were almost always used for experiments in chemistry and physics Laboratories. The batteries used to in early periods were voltaic piles. they consisted of a series of zinc and copper plates fastened back to back to form high voltage, low current source.

So, later Michael Faraday of course, he is a known very well known scientist, without him nothing much moves in scientific circles, is regarded as great as Newton and he worked for number of years on the electricity. And probably he was the first to discover the chemical reaction in around 1830, that the chemical reactions where the source of electricity produced by a battery.

So, it is for this reason that his name is used to describe electrode operations as Faradic processes, Faradaic processes or Faradic processes both I mean the same, f a r d i c or d a i c. So, for the rest of the 19th century batteries were almost always used for experiments in chemistry and physics laboratories only. They came into the market later and when they came into the market the batteries used to be nothing but voltaic piles, that is one after metal after another connected with a separate with a separator in between.

So, they consisted of a series of zinc and copper plates fastened back to back to form high voltage low current source.

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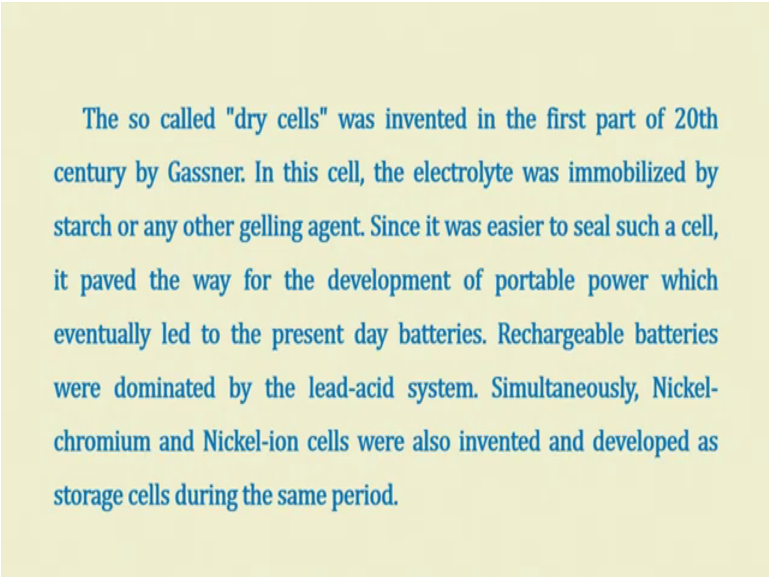

So; obviously, low current was a problem. And subsequently in the early part of 20th century dry cells were invented, that is by Gassner. In this cell the electrolyte was immobilized by adding a little bit of starch to the electrolyte, I think most of you must have seen dry cells in the shops and markets and what I what it contains it contains a shell outside with a tip at the bottom and a tip at the at the top where the wires are to be connected isn’t it.

So, inside what goes must be 2 electrodes and the electrolyte ok. So, the point is if it is liquid it will spill, corrode and do lot of things to the metal plate outside what you see it as a cylinder, and for that what he did was he added a little bit of starch to the electrolyte. What made the starch conducive for dry cell is, it is nonreactive it does not take part in the reaction, but it makes a gel, so the gel will not spill out of the battery cell.

So, that gelling agent was the invention of Allessandro Gassner, and since it was easier to such a seal to seal such a cell it paved the way for the development of the portable power, which we normally carry in all our mobiles and this that and then torch cells; many portable power requirement and are met with these cells. And you are all aware of the present day batteries, we use them in different formats in our computers, mobiles, then radio equipments and then in automation automobiles dry batteries present day batteries lead acid system is one of them oldest one lead acid system.

But, most extraordinarily sustainable lead acid system, you will be surprised to know that even though lead is a an environmental not desirable element in the environment, lead acid system has survived and continues to thrive because of its capability for automation for automobiles.

For almost all automobiles still carry lead acid system as battery source, you need the battery to run during nights to give you headlights this that etcetera electrical systems in the car all of them run on lead acid battery systems, very recently only since last 20 years things are changing a little bit, for Nickel cadmium batteries and simultaneously a nickel ion cells Lithium cells lithium battery cells and they are all invented and developed as storage cells during the same period.

But, lead acid still retains its pride of place because of the simplicity of the manufacture and operation maintenance, simplicity of maintenance. You do not have to do anything except sometimes acid may leak you throw away the lead acid battery put another battery almost all parts of the lead acid batteries are re circulated nowadays, including these separators.

So, the advent of dry cells has one can say safely that it has revolutionized, the our modern life.

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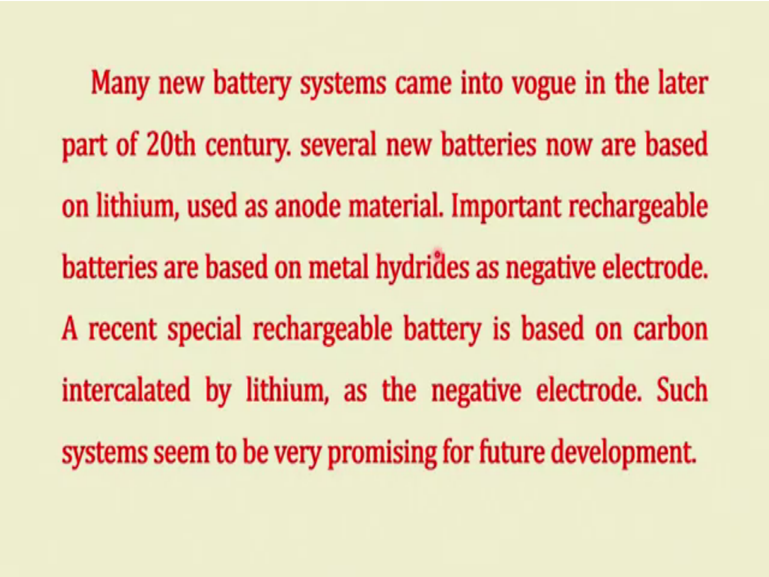

Many new battery systems have come into vogue in the later part of the 20th century and several new batteries are now based on lithium used as anode material, and important rechargeable batteries are there containing metal hydrides as negative electrode instead of metals we use metal hydrides.

And recent special rechargeable battery is based on carbon intercalated with lithium, that is also very important as the negative electrode. This is one of the most recent one such systems seem to be very promising for the future development because they can make the batteries smaller more efficient and easy to carry, and wastage is very less and the charge density and current density are very high compared to their size and myriad applications are available for the use of such batteries.

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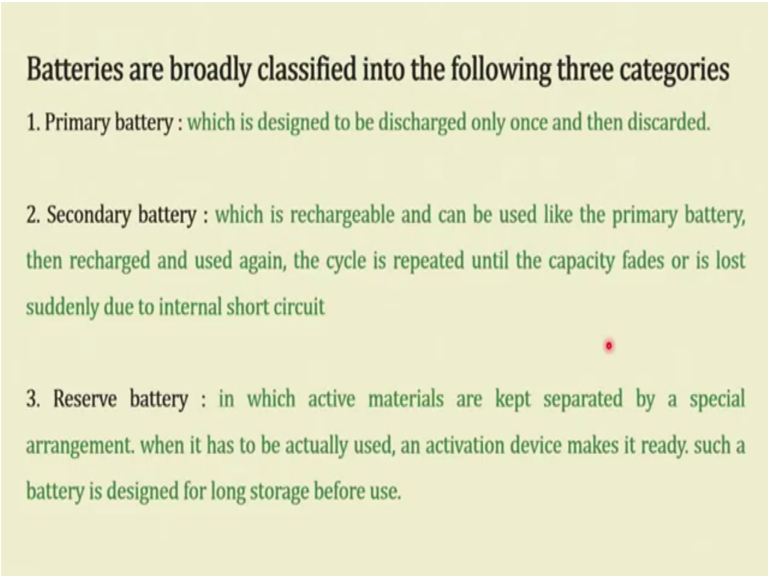

So, let us know a little bit more about the batteries, and batteries are broadly classified into the following three categories. what are the categories? One is primary battery secondary battery and reserve battery. Primary battery is designed to be discharged only once and thrown use and throw primary batteries they cannot be reused.

And secondary battery, battery it is rechargeable it can be used like the primary battery then recharged and used again and again until the recycle is repeated continuously, until the capacity fades or is lost suddenly due to internal short circuit. Nothing else can happen except the internal short circuit in most of these batteries.

And there are reserve batteries in which active materials are kept separated by special arrangement only when you need the active material is released and battery comes into operation. Especially when you want to deploy battery, battery for space applications you do not need to open the battery start working at the moment it leaves the earth surface no not necessary, only when it is deployed there in the orbit probably we want the batteries to open up.

In such cases what we do? We take the electrolyte take the electrodes seal it, but then we have a mechanism to remove the, the separator will be actuated by the by an activation device and then it starts operation. So, such batteries are stored for long storage before use.

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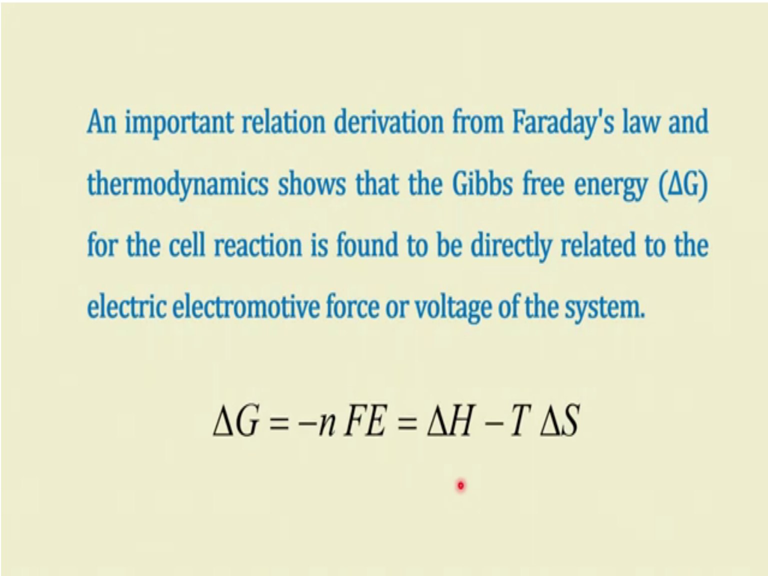

An, important relationship between Faraday's law and thermodynamics, very important Gibbs free energy, I have already described to you number of times this equation that is delta G is equal to minus n into FE that is also equal to delta H minus T delta S where, delta G is the Gibbs free energy n is the number of electrons F is Faraday's and E is the voltage, delta H is the enthalpy change in the enthalpy of course, and T absolute temperature and delta S is change in the entropy of the system.

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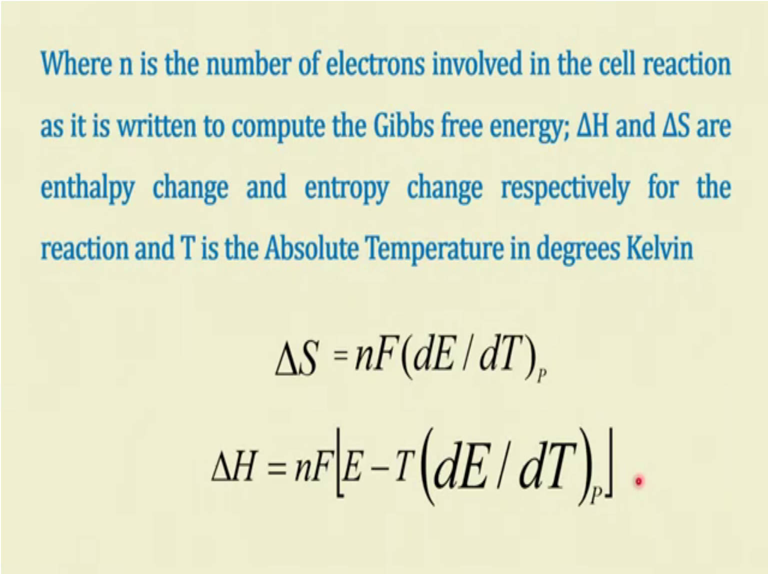

So, delta S is given by n F into delta E by delta T at P, and delta H is given by this expression n F E by E minus T delta E by D by dT at P.

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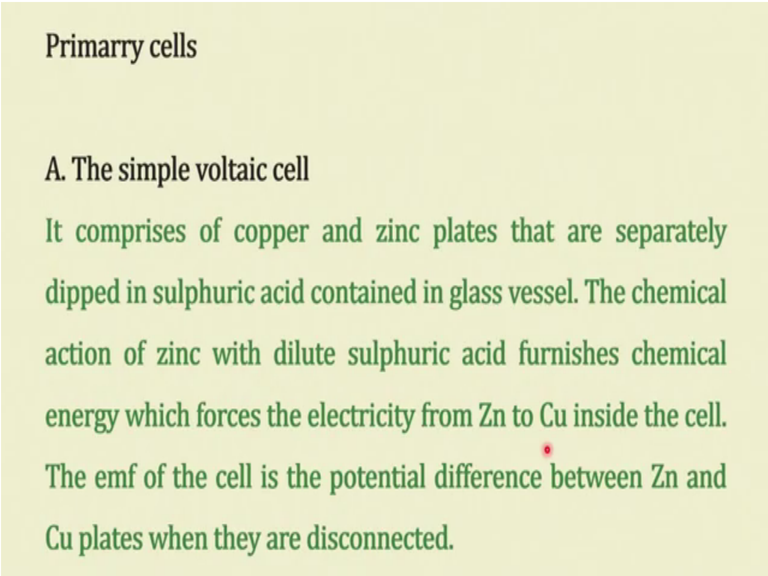

And, that really relation basically is used to compare different batteries, and we will not go into details of these applications except to describe that most of the batteries can be evaluated using the change in heat, change in entropy, and change in the maximum production of the potential.

So, here we are going to discuss a little about the primary cells. Primary cell is nothing, but a simple voltaic cell it consists of 2 metal plates one is copper another is zinc, they are separately dipped in sulfuric acid contained in a glass vessel. The chemical action of zinc with sulfuric acid it produces zinc sulfate is not it, plus 2 hydrogen ions and that furnishes chemical energy which forces the electricity from zinc to copper inside the cell.

So, the emf of the cell is potential difference between zinc and copper plates, this also we had discussed when we were discussing about the fundamentals of electrochemical cells.

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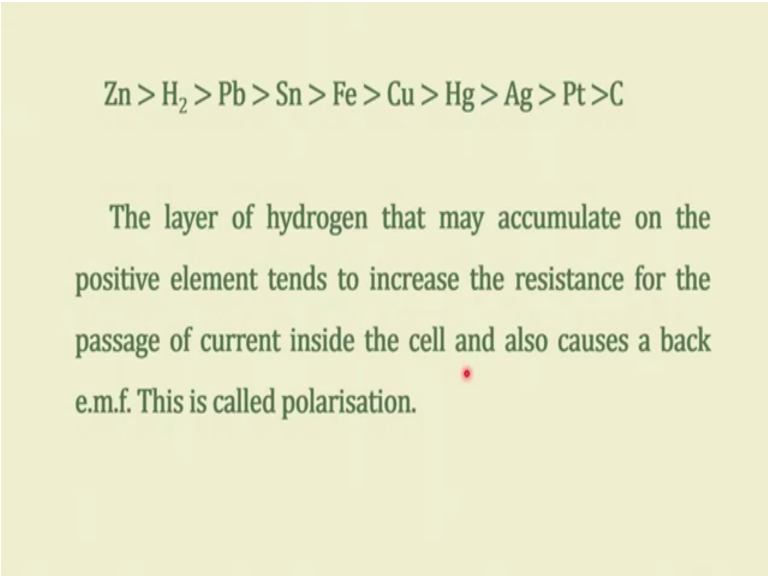

So, here you can see the layer of hydrogen that may accumulate on the positive element tends to increase the resistance for the passage of the current inside the cell, and also it causes a back emf sometimes. So, this is called polarization.

So, the I have taught you earlier that polarization is nothing but the change in the potential from the calculated value. But how does it happen, is given here that is the layer of hydrogen that comes and it accumulates increases the resistance of the passage of the current and emf increases.

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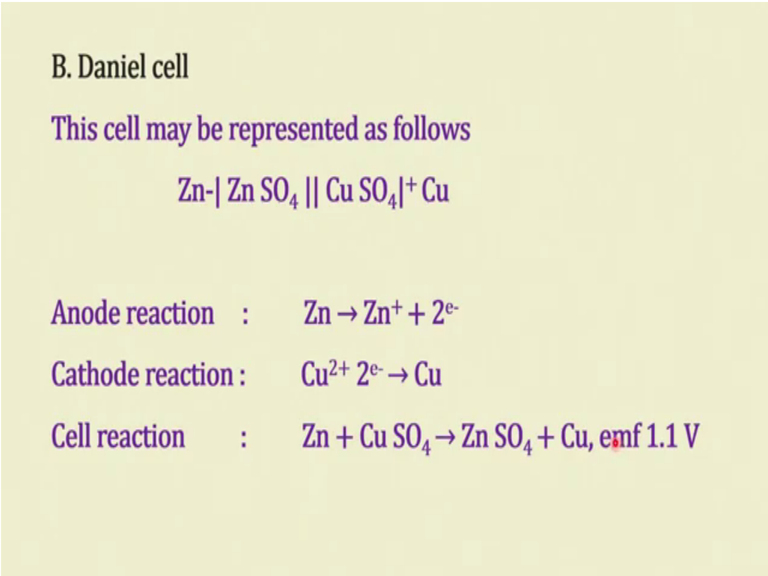

So, the type b, Daniel cell very well known very standard cell and this cell is represented something like this; zinc and then zinc cathode it is negative, indicates cathode and then zinc sulfate in connection with a copper sulfate and copper. Anode reaction is zinc to Zn plus plus 2 e minus Cu 2 plus plus 2 e minus goes to Cu and zinc plus Cu SO 4 goes to Zn SO 4 plus copper the emf is 1.1 volts for this cell.

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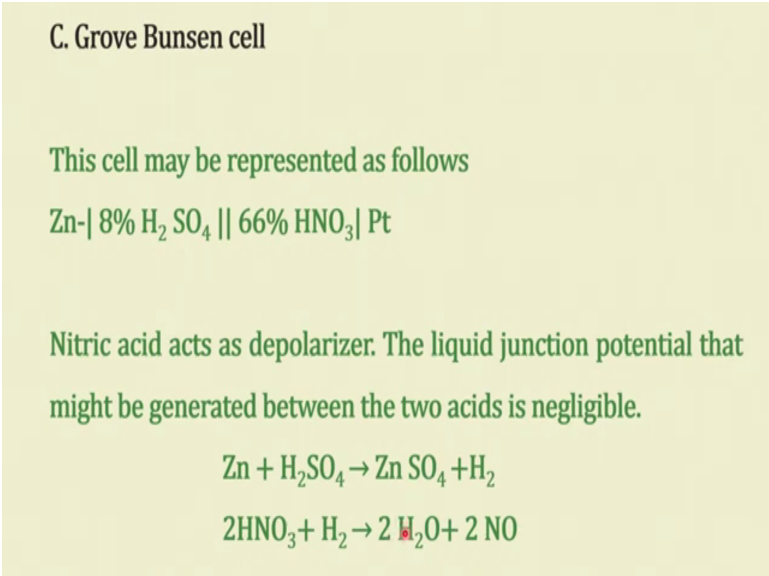

So, Grove Bunsen cell essentially the same thing zinc H 2 SO 4 HNO 3 and platinum electrode. So, here I have H 2 SO 4 and nitric acid together and, but separated in with a salt bridge.

So, nitric acid acts as a depolarizer and the liquid junction potential that might be generated between the 2 acids is negligible. The reactions essentially remain the same zinc and H sulfuric acid to produce zinc sulfate and HNO 3 and H 2 will produce water and nitric oxide.

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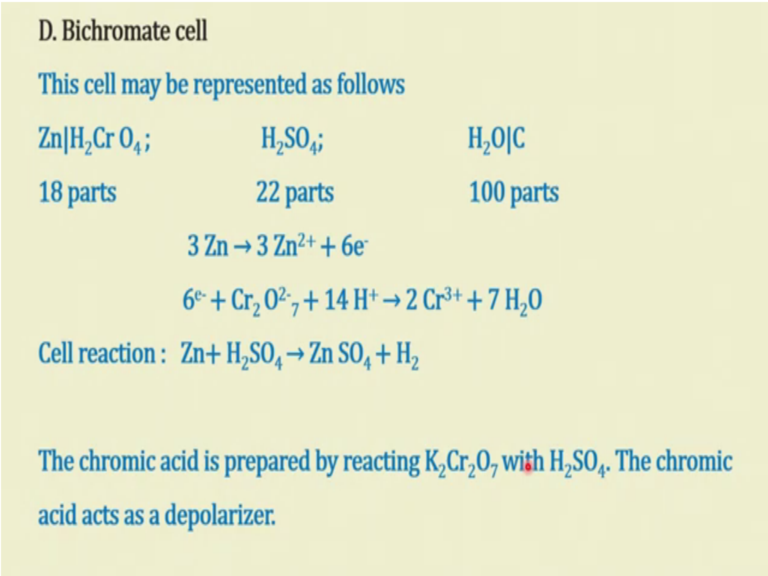

So, in the third one is the Bichromatic cell. So, we use zinc chromic acid and then H2SO4 and water and this is the carbon electrode and zinc electrode here. So, this is 18 parts this is 22 parts and this is 100 parts. So, the reaction essentially same zinc to zinc 2 plus and 3 zinc ions will produce 6 electrons and these 6 electrons are required for potassium dichromate to produce chromium 3, and cell total cell reaction is nothing but zinc plus H 2 SO 4 is going to zinc sulfate. So, the chromic acid is prepared by reacting potassium dichromate with H 2 SO 4. So, here instead of nitric acid we are using chromic acid as a depolarizer

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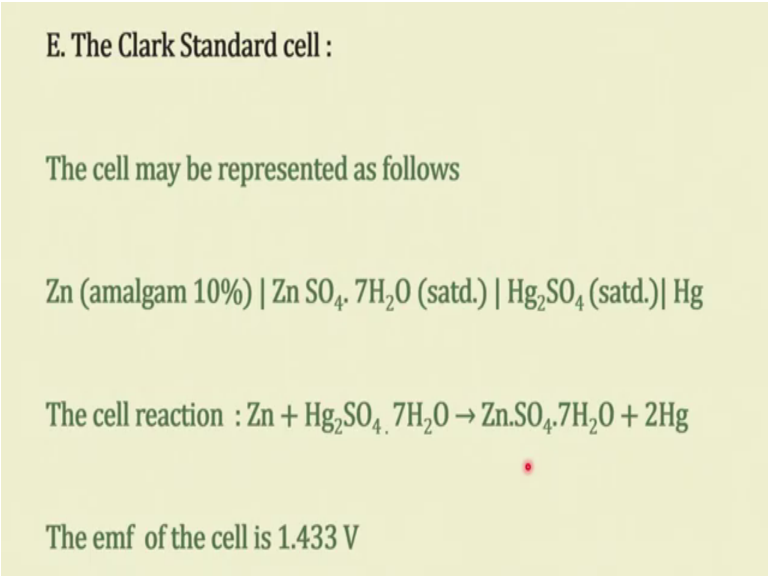

Next one i want to describe to you is The Clark Standard cell, that is represented as zinc amalgam zinc mercury amalgam on they as cathode, zinc sulfate, mercuric sulfate and mercury as anode. Cell reaction is nothing, but zinc and Hg 2 SO 4 going to zinc sulfate and water mercury. Here the emf is 1.433. How much was the zinc original cell? Zinc copper 1.1 volts, now it is just by this arrangement if I go for a amalgam and Hg 2 SO 4 as a anode, I can increase the voltage to 1.4 volts.

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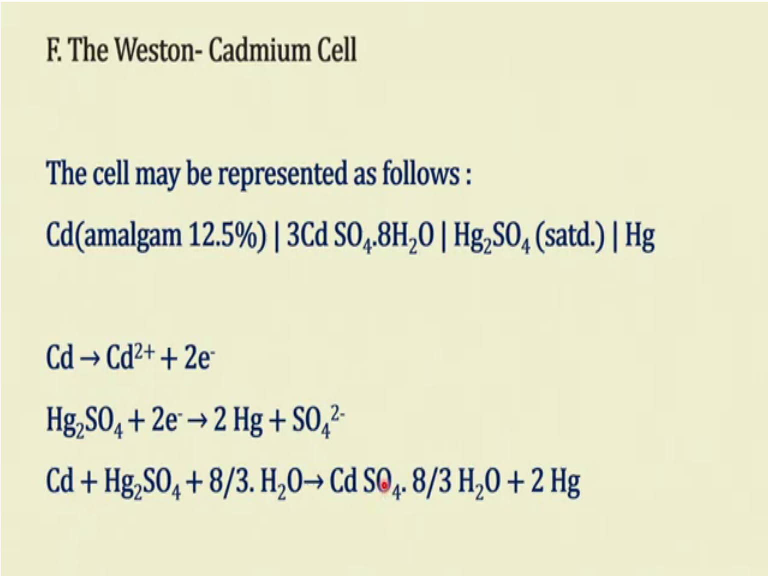

So, this Weston Cadmium cell; again we will discuss a little bit, because this is also a very standard battery the cell may be represented as cadmium as an amalgam and percentage is 12.5 percent, and the cadmium sulfate is the electrolyte Hg 2 SO 4 is the another electrolyte in contact with mercury anode. Reactions are represented simply here the Hg 2 SO 4 goes to Hg, and cadmium cell cadmium will go to cadmium sulfate that is the product.

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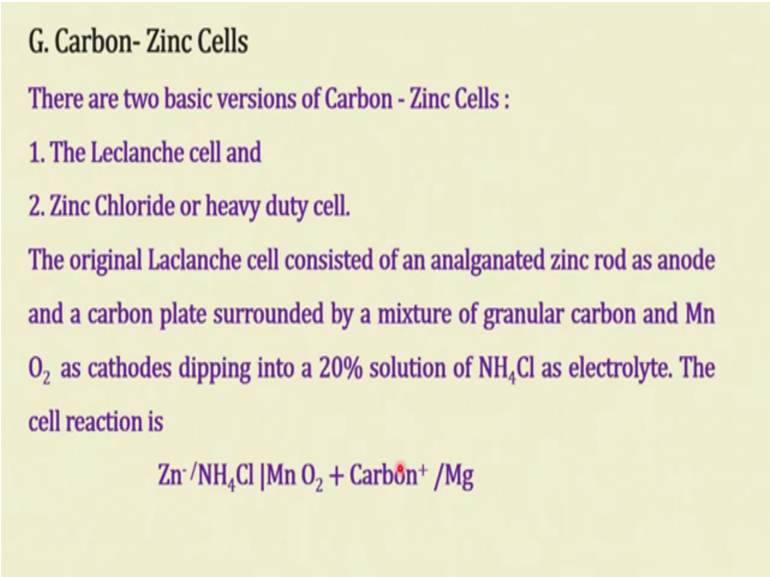

So, Carbon Zinc cells are very popular there are two basic versions of carbon zinc cells, one is Leclanche cell and another is the Zinc Chloride or heavy duty cell. The original leclanche cell consisted of simple amalgamated zinc rod, you know just a simple rod as anode and a carbon plate surrounded by a mixture of granular carbon; that means, carbon rod put some granules around it seal it, so that carbon granular carbon was there and MN O 2 manganese dioxide.

So, that will act as a cathode dipping into a solution of about 20 percent ammonium sulfate as electrolyte. See you so what is the reaction? Carbon is there ammonia is there MN O 2 is there and ammonium sulfate is there zinc is there. So, the cell reaction is zinc, will be reacting with ammonium chloride MN O 2 and then there is reduction the anode in this case is magnesium rod a simple magnesium rod.

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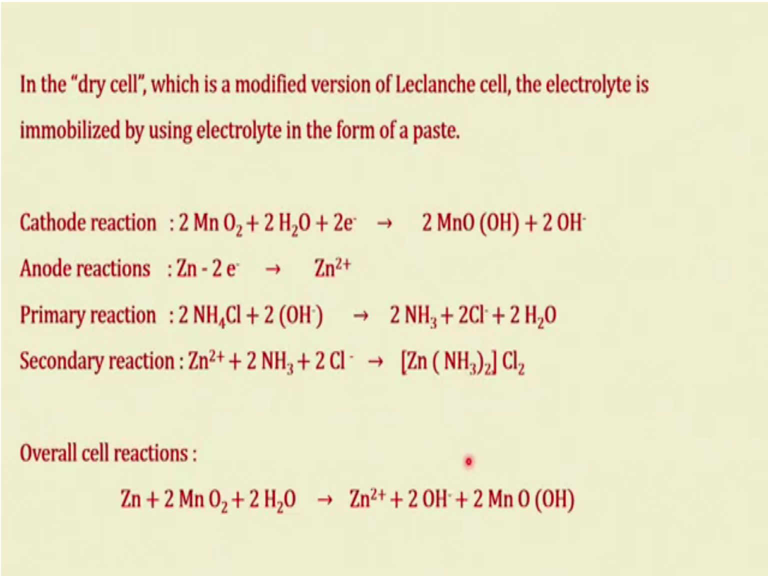

So, in the dry cell which is a modern version of Leclanche cell the electrolyte is immobilized by using electrolyte in the form of a paste you can put this, starch or any other material to form a paste. Here we have the cathode reaction 2 Mn O 2 plus water in presence of 2 electrons it will produce Mn O OH manganese hydroxide, and then anode reaction zinc will dissolve giving you zinc 2 ions. A primary reaction is 2 NH 4 Cl plus 2 OH minus going to ammonia, plus 2 chloride and 2 H 2 O. Secondary reaction is zinc will react with this ammonia, to produce zinc ammonium chloride that is a complex actually so, zinc ammonium complex is the end result.

So, overall cell reaction we can represent it like this; zinc plus MnO2 plus 2 H 2 O going to zinc 2 plus plus 2 OH minus plus 2 Mn O OH minus. You must remember this kind of expressions especially if I ask in the examination. So, I am giving you a hint that please do not ignore cell reactions in the battery chapter, please study them well so, you will be benefited by knowing the basic reactions.

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Anode reaction :

$$Mg + 2\,(OH)^{-} - 2e^{-} \rightarrow 2\,Mg\,(OH)_2$$

Cathode reaction :

$$2\,Mn\,O_2 + 2\,H_2O + 2e^{-} \rightarrow 2\,Mn\,O\,(OH) + 2\,(OH)^{-}$$

Overall cell reaction :

$$Mg + 2MnO_2 + 2\,H_2O \rightarrow 2Mn\,O\,(OH) + Mg\,(OH)_2$$

And the anode reaction coming back to our discussion, magnesium 2 plus will react with magnesium will react with 2 OH minus ions to give magnesium hydroxide. So, the overall cell reaction is magnesium plus 2 Mn O2 plus 2 H 2 O going to two Mn O OH and plus and magnesium hydroxide, that is the overall reaction.

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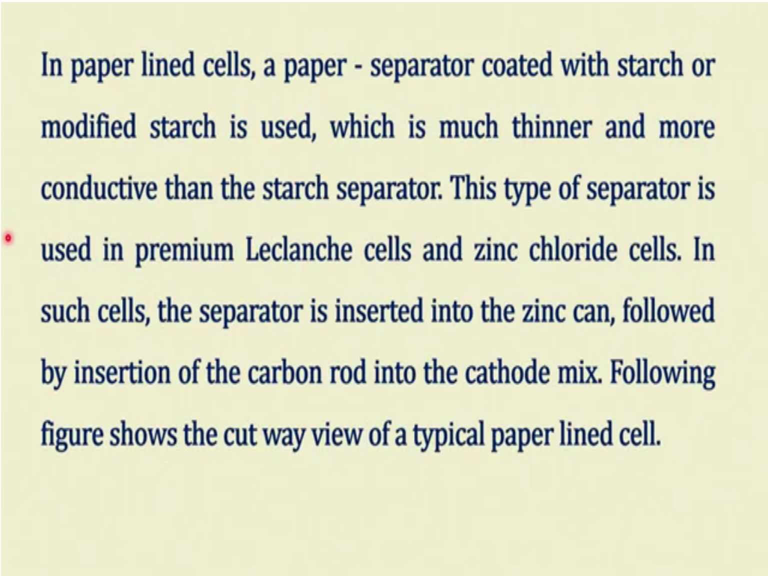

So, in paper lined cells; that is Leclanche cells a separator coated with starch or modified starch is used, that is much thinner and more conductive than starch separator alone. So, this type of separator is used in premium Leclanche cells and zinc chloride cells, in such cells the separator is normally inserted from the top into the zinc can followed by insertion of the carbon rod into the cathode mix.

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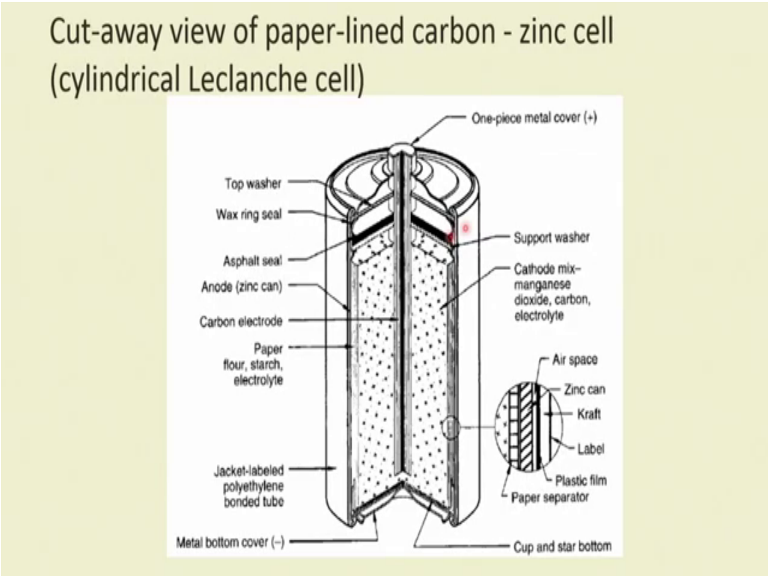

So, you can see the cut away section, that we have a carbon electrode here ok, and then I have a top washer here and then wax ring seal is here, one more seal asphalt seal and then anode is there here at the edge, here near this thing it extends to the almost to the middle of this reaction, of this length. Then we have Jacket labeled polyethylene blend a bonded tube to give a finish nice finish here outside the cell.

So, in the bottom we have a metal bottom cover and cup and star bottom on the other side so, they can be closed like this ok, they can be closed like this for sealing and then you will see a seal in between. So, when it is sealed there is some airspace here and zinc can is here craft paper is here label and plastic film and paper separator. So, here again I have a support washer Cathode mix manganese etcetera this is the electrolyte. What is the cathode mix? Cathode mix contains manganese dioxide carbon and electrolyte. So, this is a readily available across the shelf Leclanche cell.

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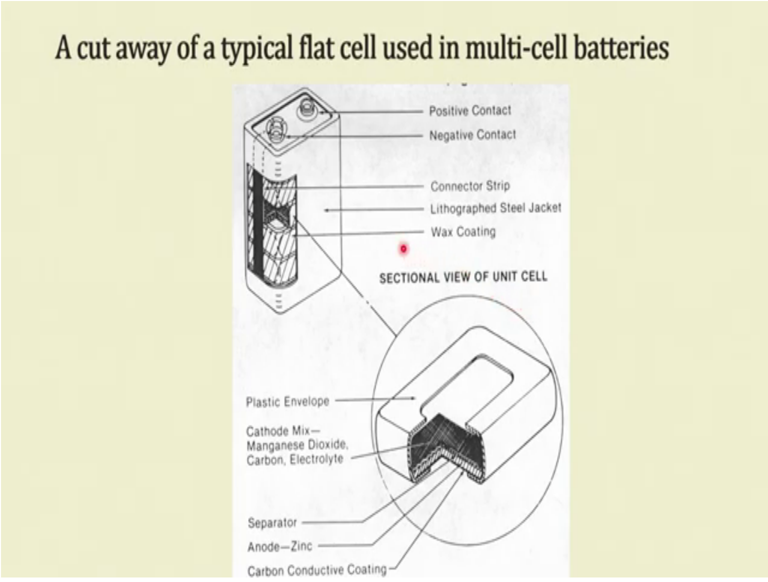

And we you must have seen a lot of cells like this flat cells, here I have a positive contact here I have a negative contact and then a connector strip is there throughout this length, that one then lithographed steel jacket is here this one, then wax coating is here inside outside and sectional view will normally show that the outer top plastic envelope you will automatically see, cathode mix you will not see this, but this dark portion which i am showing here contains manganese dioxide and carbon electrolyte.

And then there is a separator here again as usual, and anode is there zinc and carbon conducive coating is at the other edge. So, but such cells are also quite useful and they have a longer life.

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H. Ruben- mallory Dry Cells

In the Ruben- Mallory dry cells, Zinc is used as anode while the cathode consists of a paste of carbon and Hg 0 (depolarizer). The elecrolyte is a 40% KOH solution saturated with pottasium zincate absorbed in cellulose of gelled with carboxy methyl cellulose.

Anode reaction : $Zn + 2(OH^-) \rightarrow 2e^- \rightarrow Zn(OH)_2$

Cathode reaction : $Hg0 + H_20 + 2e^- \rightarrow Hg + 2(OH^-)$

Overall cell reaction : $Zn + Hg0 + H_20 \rightarrow Zn(OH)_2 + Hg$

Then I want to describe to you Ruben Mallory dry cells, here zinc is used as the anode well the cathode consists of a paste of carbon and mercury, mercuric oxide actually. So, the electrolyte is a 40 percent KOH solution saturated with potassium zincate. See in all these new cells the most of the materials are highly researched and kept in such a way that the chemicals will not leak out, that is one of the prime requirement.

And it must operate for longer time and new materials instead of starch, what else I can use? I can use CMC carbon carboxymethyl cellulose, it is a very simple white powder that can be mixed with water and made into a paste and then connected. So, that is how the such cells are constructed and pastes and electrolytes they are all kept in the confinement so, that things can be sealed from the bottom and top etcetera using washers and sealers.

So, anode reaction, basic chemistry remains the same. So, anode reaction zinc and 2 OH minus goes to zinc a hydroxide and it forms zinc ion and then Hg O plus H 2 O goes to mercury and overall cell reaction zinc plus Hg O plus H 2 O goes to zinc hydroxide and mercury.

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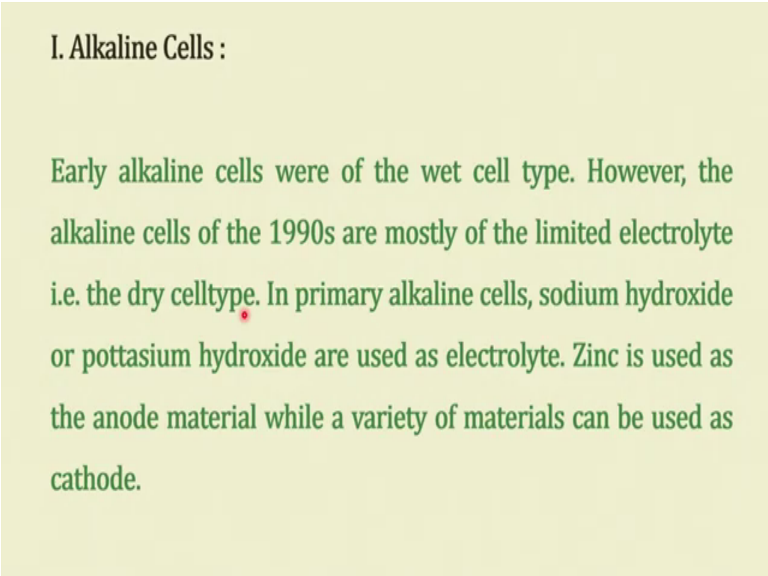

Then, we have couple of things like Alkaline cells. Alkaline cells you must have heard you know whenever you go to any mall or metro you will see whenever you want to buy cells for your mouse or computer or something batteries torches etcetera, you look for alkaline cells because they can be reused recharged and reused.

So, early alkaline cells where of the wet cell type early ones; however, alkaline cells of 1990s are almost limited electrolyte that is dry cell type, in primary alkaline cells sodium hydroxide and potassium hydroxide is used. But zinc is used as the anode material well a variety of materials can be used as cathode.

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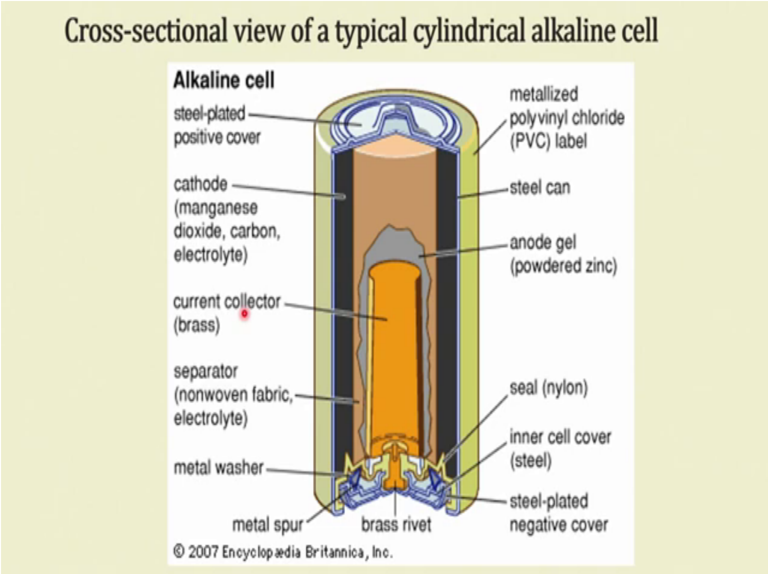

So, this is the construction of a cross sectional view of a typical cylindrical alkaline cell, here you can see that I have a brass rivet here, then I have a connector here steel plated positive cover and then cathode is here at this edge round it is cylindrical basically ok.

So, cathode is made of manganese dioxide carbon and electrolyte; that means, it is like a it is like a paste and here, I in the center I have a another plate brass plate, brass plate is screwed here and this brass plate you see this cylindrical this is cutaway section so, brass plate acts as a collector.

You can see the yellow line here in between and that is a cylindrical operation here, and the separator I have that is a nonwoven fabric and then in the electrolyte, a metal washer now you know what is I hope you know what is washer, washer is a metal seal it is a thin metal plate.

So, metal spur is there to connect and disconnect, brass rivet is there then steel plate at negative cover inner cell cover seal anode gel powdered zinc that is anode gel above this and then steel can, this is the steel can long one and metalized PVC label that is outside. So, polyvinyl chloride coated with metal that is electroplated, we have discussed about such things in the last class.

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The alkaline cell derives its power from the reduction of the MnO_2 cathode and the oxidation of the zinc anode.

Anode reaction : $Zn + 2\,OH^- \rightarrow Zn\,O + H_2O + 2\,e^-$

Cathode reaction : $2e^- + 2Mn\,O_2 + 2H_2O \rightarrow 2\,Mn\,OOH + 2\,(OH)^-$

Miniature alkaline cells are small, button shaped cells, which use zinc anodes, alkaline (NaOH or KOH) electrolyte and a variety of cathodic materials eg. Mn O_2, Hg OM or even air (in case of zinc-air batteries).

So, the alkaline cell derives its power from their reduction of the Mn O 2 cathode and the oxidation of zinc anode. What is the anodic reaction? Very simple zinc is there OH is alkali is there, so it has to form zinc oxide and water. In the cathode reaction manganese is there manganese can get reduced to Mn OOH it is a very standard reaction this reaction Mn OOH.

Usually we write with bracket, MnOH O outside and OH in the bracket, but the overall cell reaction remains the same and miniature alkaline cells we can make very small cells, button cells and there we use zinc anodes; and alkaline cells electrolyte we using Na OH and KOH small quantity. If you 1 or 2 ml or may be 0.5 ml and a variety of cathodic materials can be including Mn O 2 mercury on, a mercuric oxide and metal and even air zinc air batteries so all these things can be used as cathode materials.

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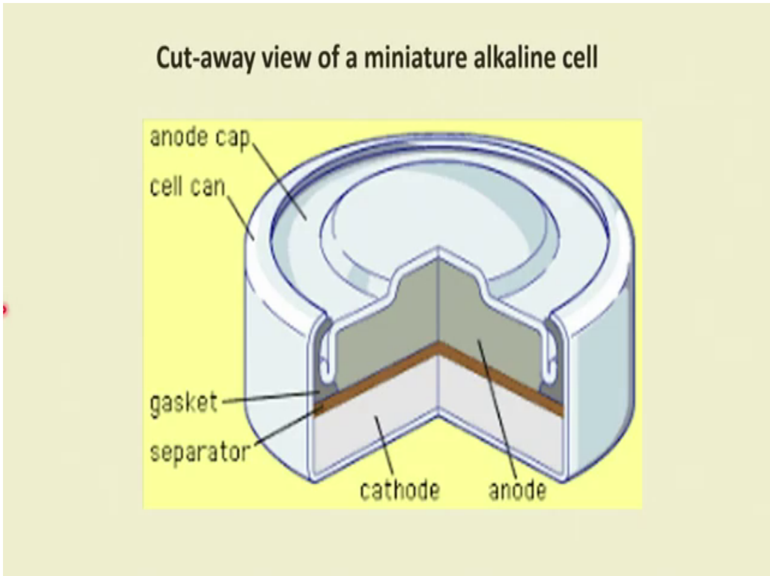

So, miniature alkaline cells is what you see in your watches and other things that cutout figure is here, this is an anode cap this is cell can this is a gasket here and a separator here this is the separator that brown piece, and then a cathode and that is a base plate and anode is this plate.

So, very simple construction, but very small if maybe a few milliliters you would have seen in your watches such cells.

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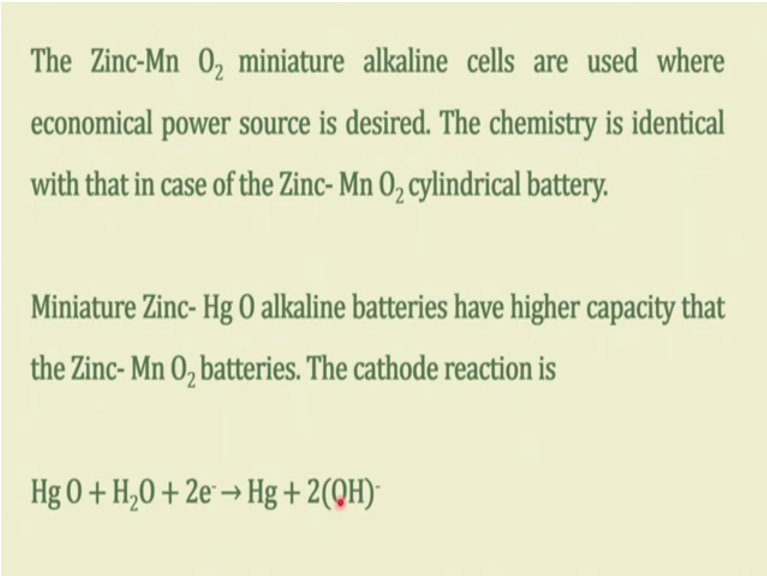

So, the zinc manganese oxide miniature alkaline cells are used where economic power sources require, very small quantity is required to run your watches. So, the, but the chemistry remains identical with that of the zinc and manganese oxide cylindrical battery.

So, they have higher capacity than zinc manganese oxide batteries, so, the cathode reaction is again essentially same resolution of mercury oxide to mercury that is the reduction removal of oxygen is reduction.

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Miniature zinc-silver oxide batteries have high energy density, almost as high as that of mercury cells. They operate at higher voltages than mercury cells but for somewhat lesser time. The cathode reaction is

$$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2(OH)^-$$

Miniature zinc-silver oxide batteries are made with KOH or NaOH as electrolyte. However, KOH- containing batteries operate more efficiency at high current drains, whereas Na OH- containing batteries are more resistant to leakages and easier to seal.

So, miniatures zinc silver oxide batteries they have high energy density, almost as high as mercury cells. See when we say high energy density we should know what are the mercury cell density it is. So, I request you to go and find out what is the energy density for zinc silver oxide and mercury cells.

They operate at higher voltages than mercury cells, but for somewhat lesser time higher the current we draw less is the time the battery will be in operation it would not be efficient for long time, but large current you can draw. So, the basic reaction is Ag2 O plus H2O going to silver. Miniature silver oxide batteries are normally made with KOH or Na OH as the electrolyte and; however, what happens is batteries operate more efficiently at high current drains whereas, Na OH containing batteries are more resistant to leakages and easier to seal.

So, KOH are not so, easy to seal, but sodium potassium know so, they are one below the other in the periodic table so, the capacity to gel is better for sodium than magnesium. So, the leakage will be less in the case of sodium hydroxide then potassium hydroxide, potassium hydroxide can seep through easily.

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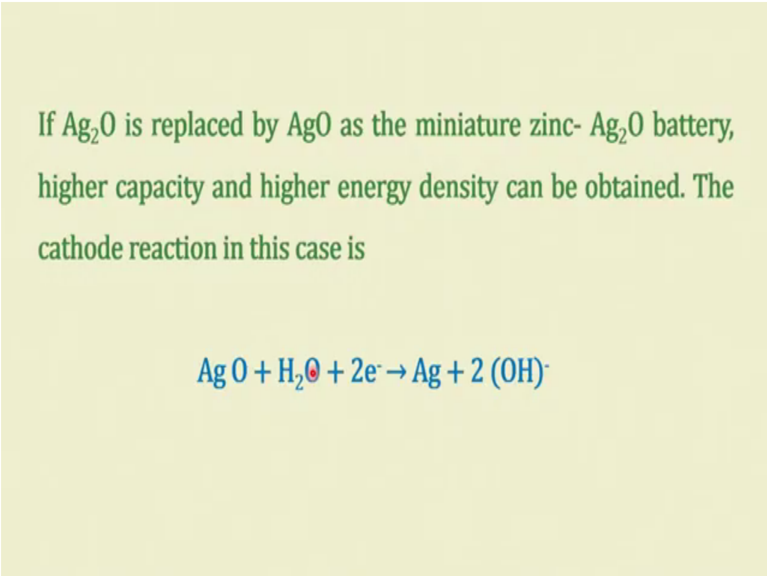

So, if I replace Ag 2 O with silver oxide, silver can have different compounds the in the miniature higher capacity and higher energy density can be obtained and the cathode reaction in this case is Ag O plus H 2 O going to 2 Ag going 2 Ag plus 2 OH minus, essentially reactions are always cathode reactions must always end in metal on the right side. If you remember that you can write many chemical reactions if you know what is the cathode.

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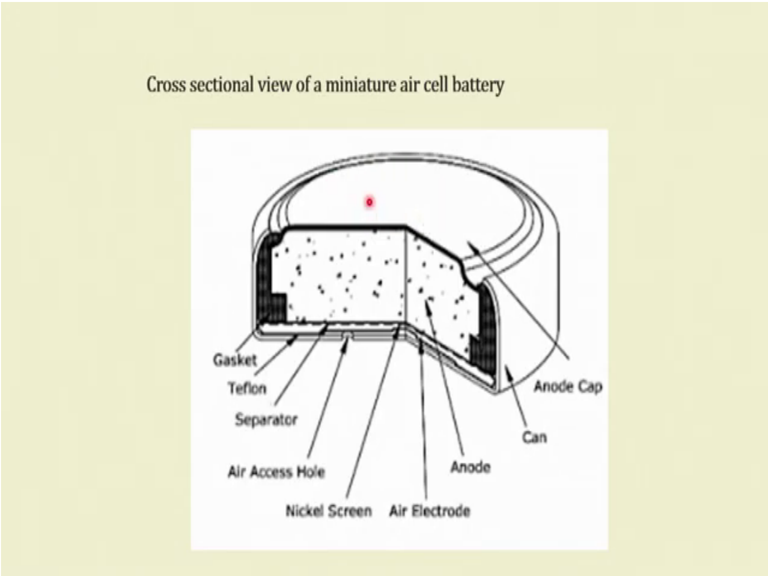

So, cross sectional here is a cross sectional view of the miniature air cell battery that is, again you can see that it is almost similar gasket, Teflon, separator, air access hole, nickel screen, air electrode, anode and here is the can and here is the anode cap, this whole cap will act as a connector from the top and the cathode will be at the bottom.

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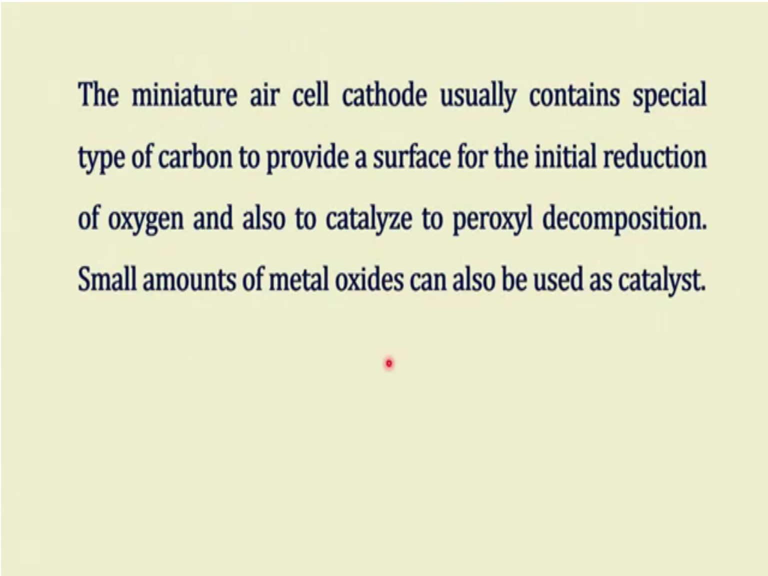

So, miniature air cell cathode usually contains special type of carbon to provide a surface for the initial reduction of oxygen and also able to catalyze peroxyl decomposition.

So, what is this peroxyl decomposition we will study in the next class on the batteries, in the next class I will try to conclude about the batteries because I do not want to teach you more about batteries but the battery cell waste are quite a few because millions and millions of small battery cells are there in the environment containing lithium and other things, we have to know about it how to handle those things.

Thank you very much, we will continue our discussion in the next class, have a nice day.