Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture- 17
Electrochemical Energy Storage (Batteries)

Hello my friends, in this particular lecture, we are going to discuss about the Electrochemical Energy Storage, which is nothing but the batteries, because the electrochemical applications or maybe rather I can say on the mechanisms of the electrochemical basically the batteries works. So, that is why you are calling it as a electrochemical energy storage.

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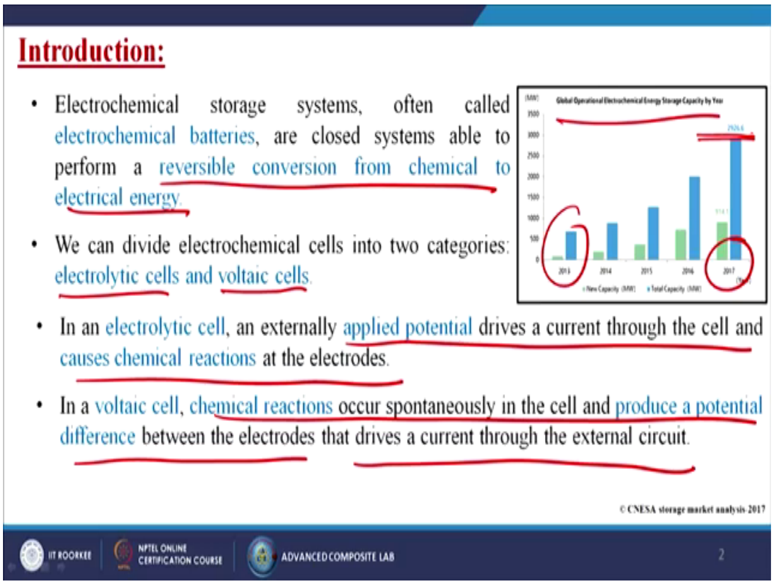

So, electrochemical storage systems, often called the electrochemical batteries, are enclosed systems able to perform a reversible conversion from chemical to electrical energy. So, that means, you can understand that we are having some materials, which will react each other and they will generate the electricity. We can divide electrochemical cells into two categories; one is called the electrolytic cells, another one is called the voltaic cells.

In an electrolytic cells, an externally applied potential drives a current through the cell and causes chemical reactions at the electrode cell. In a voltaic cell, chemical reactions, occurs spontaneously in the cell and produce a potential difference between the electrodes that drives a current through the external circuits. So, just it is the vice versa one.

So, this is the total scenario of today's world. So, basically if you see that in 2013, we are having that new capacity are very less, and total capacity also it is not up to the mark. When in the year of 2017, we have reached up to this much level. So, now, you can understand that how much basically, we are believing on this particular technology to increase the storage. So, basically you can understand that earlier days, when we are using certain our cameras, so simple we are using the batteries. And in that particular battery maybe we are taking some few pictures after that batteries gone dead and then again we are replacing the new batteries. After certain time it has come that recycle will battery has come into the market.

So, in that case we are taking certain pictures and then when the batteries is drained out, then again we are charging it for certain times and then again we are using. But one thing minutely you can understand that charging time was quite high for that particular purpose. It takes almost ten to some few hours or maybe the day. But nowadays, in our mobiles or may be in our cameras or may be in torches, you can see that charging time has been reduced drastically, maybe within few hour or maybe within a hour, you can get the 100 percent charge of that particular system. So, now you can understand that how or maybe in what capacity we are relying on this particular technology.

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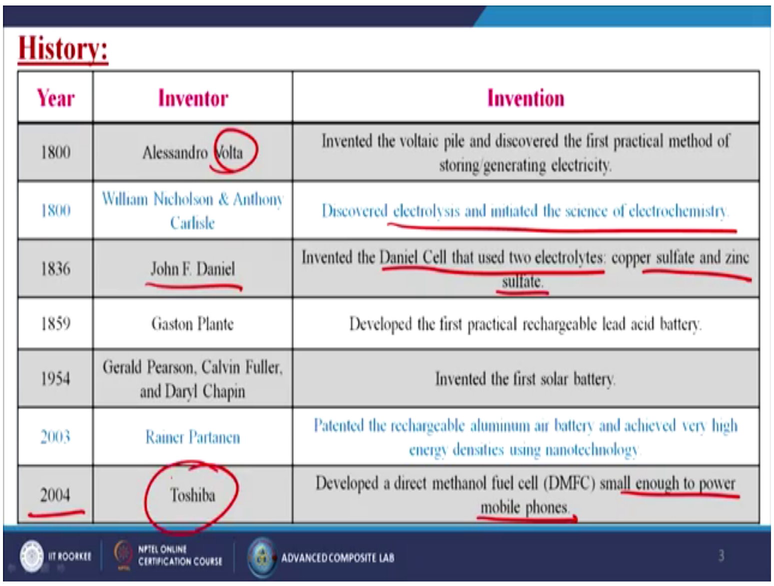

History:

Year	Inventor	Invention
1800	Alessandro Volta	Invented the voltaic pile and discovered the first practical method of storing/generating electricity.
1800	William Nicholson & Anthony Carlisle	Discovered electrolysis and initiated the science of electrochemistry.
1836	John F. Daniel	Invented the Daniel Cell that used two electrolytes: copper sulfate and zinc sulfate.
1859	Gaston Plante	Developed the first practical rechargeable lead acid battery.
1954	Gerald Pearson, Calvin Fuller, and Daryl Chapin	Invented the first solar battery.
2003	Rainer Partanen	Patented the rechargeable aluminum air battery and achieved very high energy densities using nanotechnology.
2004	Toshiba	Developed a direct methanol fuel cell (DMFC) small enough to power mobile phones.

So, now, if you go to the history, in we can see that in the year of 1800 by Alessandro Volta by whose name that Volt has come basically, invented the voltaic pile and discovered the first practical method of storing or maybe the generating electricity. Then 1800, William Nicholson and Anthony Carlisle discovered electrolysis and initiated the science of electrochemistry.

Now, you can see that there is a specific branch, which deals with this kind of technology and that are dealing with all the electrochemistry kind of things. In 1836, John F. Daniel, invented the Daniel cell that used two electrolytes copper sulphate and zinc sulphate. Like this way we had come in the year of 2004 by Toshiba developed a direct methanol fuel cell small enough to form the mobile phones. So, basically in his name that Toshiba company which was very famous and renowned company, they were making in the camera or maybe any kind of digital things. So, they have invented this particular battery or maybe the energy storage system.

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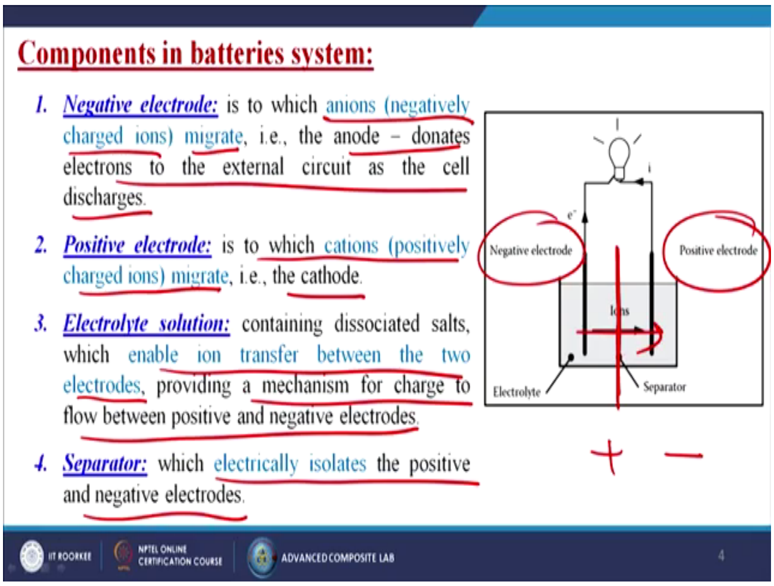

Now, let us know that what are the components in the basical when we are preparing any battery system. First one is call the negative electrode is to which anions negatively charged ions migrate; the anode, donates electrons to the external circuit as the cell discharge. So, in this particular case what happened? We are having one negative electrode, we are having one positive electrode over there. And this is the electrolyte solutions. So, this electrolyte solution is basically divided into the plus ion and the minus ion.

Now, I will come later. Next is called the positive electrode is to which cations positively charged ions migrate, that is called the cathode. Electrolyte solutions containing disassociated salts, which enable ion transfer between the two electrodes providing a mechanism for charge to flow between positive and negative electrodes. And the next one is called the separator, which electrically isolates the positive ions and the negative electrodes.

So, basically in this particular case you can see that is in between there is one barrier which is nothing but known as the membrane or maybe the separator. So, in this particular case, what happened, that separator it is allows the positive ion to go from one side to another, but it abstract the negative ions to go through it. So, where the negative ions will go? So, that is why the negative ion is going in this particular manner, when we are doing the short circuiting, and through this simple we are taking out the negative ion which is nothing but your electric charge.

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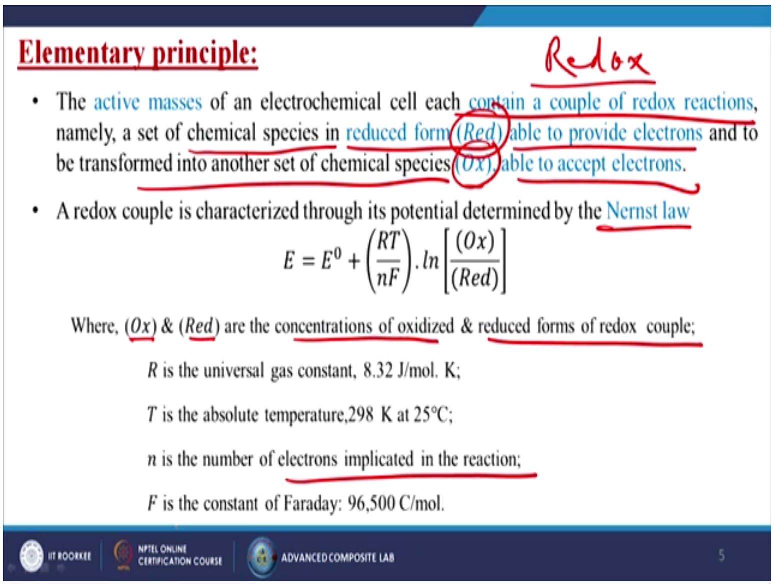

Now, what is the elementary principle over there? The active masses of an electrochemical cell each contain a couple of redox reactions, namely, a set of chemical species in reduced form Red able to provide electrons and to be transformed into another set of chemical species Ox, able to accept electrons. So, that is why this is called the Red and this is called the Ox. So, that means, the whole term is Redox. So, that is why the redox has concept has come. Redox couple is characterized through its potential determined by the Nernst law, which is nothing but the capital E is equal to E0 plus capital R T by n capital F into ln Ox by Red.

So, in this case, Ox and Red are the concentrations of oxidized and reduced form of redox couple. Capital R is the universal gas constant which is nothing but the 8.32 Joule per mole Kelvin. T, capital T is nothing but the absolute temperature which is nothing but 298 Kelvin at 25 degree centigrade. Small n is the number of electrons implicated in the reactions, and F is constant of the Faraday that is 96,500 coulomb per mole.

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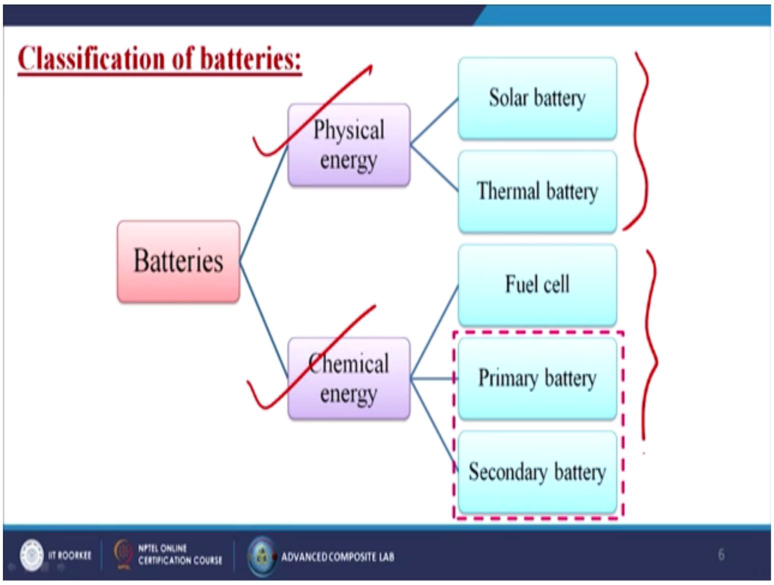

Now, let us do the classification of the batteries. So, if I do the divisions of the batteries, it has been divided into two parts; one is called the physical energy, another one is called the chemical energy. Then the physical energy is divided into two parts; one is called the solar battery, and another one is the thermal battery. And if we talk about the chemical energy, then it is fuel cell primary battery and secondary battery. So, basically in this particular lecture we are going to discuss about the primary battery and the secondary battery this two only.

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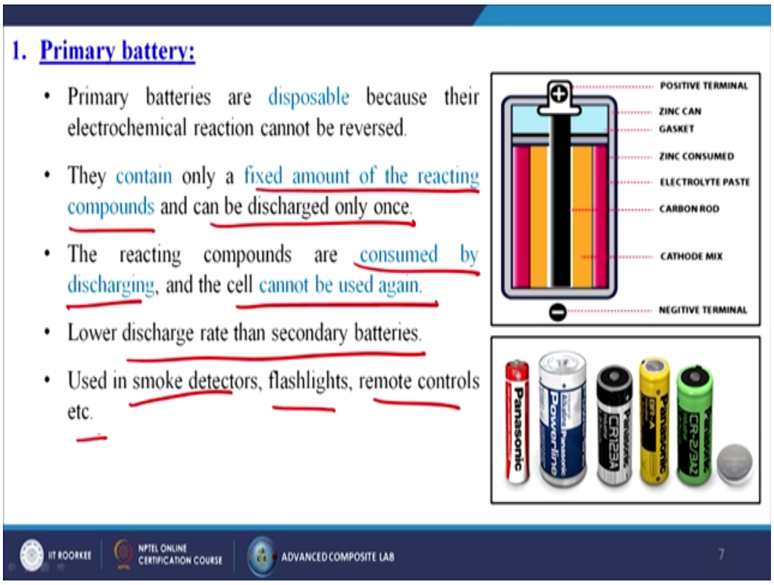

So what is primary battery? Primary batteries are disposable because their electrochemical reactions cannot be reversed. So, it is not a reusable battery, it is only one time. So, they contain only a fixed amount of the reacting compounds and can be discharged only once. So, when the full reaction of the material will be completed, then after that new generation of energy is not possible that time we have to throw that particular battery, so that means, it is not the rechargeable one. The reacting compounds are consumed by discharging and the cell cannot be used again. Lower discharge rate than secondary batteries; used in smoke detectors, flashlights, remote controls, etcetera. So, in this particular case, these all are the examples of the primary battery.

So, where, we are having a one carbon rod. So, one end is positive, another one is the negative terminal over there. We are having that cathode mix, then we are having that electrolyte paste, then we are having the outer cell or maybe the body. So, here in this particular case, you can see that this is the zinc consumed, then I am having that zinc can, and then gasket or maybe the layers are they are in between these two.

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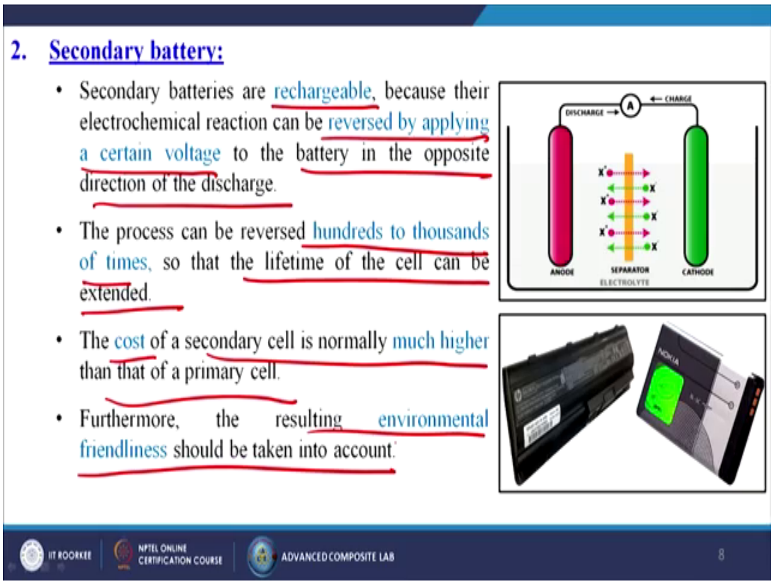

Next, come to the secondary battery. So, secondary batteries are rechargeable, because their electrochemical reaction can be reversed by applying a certain voltage to the battery in the opposite direction of the discharge. The process can be reversed hundreds to thousands of times, so that the lifetime of the cell can be extended. The cost of a secondary cell is normally much higher than that of a primary cell; it is almost maybe the double or maybe the thrice. Furthermore, the resulting environmental friendly nature should be taken into account.

So, in this particular case, when the full reaction will be completed, so battery will be drained out then we have to give the again the energy or may be the store energy into that system, so that again the material will come into its original position and then after that again the reaction will start. So, like this way we can utilize that particular battery for several times.

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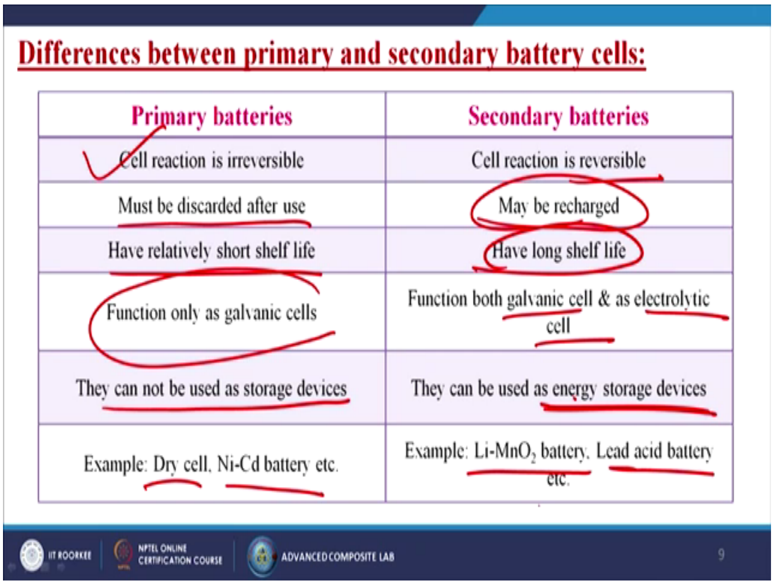

Now, what is the difference between the primary and secondary battery cells? So, if I talk about the primary batteries, the cell reaction is irreversible; in this particular case, it is reversible. For primary batteries, it must be discarded after the use; it may be recharged and so many times. Primary batteries have relatively short shelf life; here it is having the long shelf life. In this particular case, functions only as galvanic cells; for secondary batteries, function both galvanic cell as well as the electrolytic cell. Primary batteries cannot be used as storage devices; in secondary batteries, it can be used for energy storage devices. Examples dry cell, nickel cadmium battery. In secondary, it is lithium manganese dioxide battery, lead acid battery, these all are the examples of the secondary batteries.

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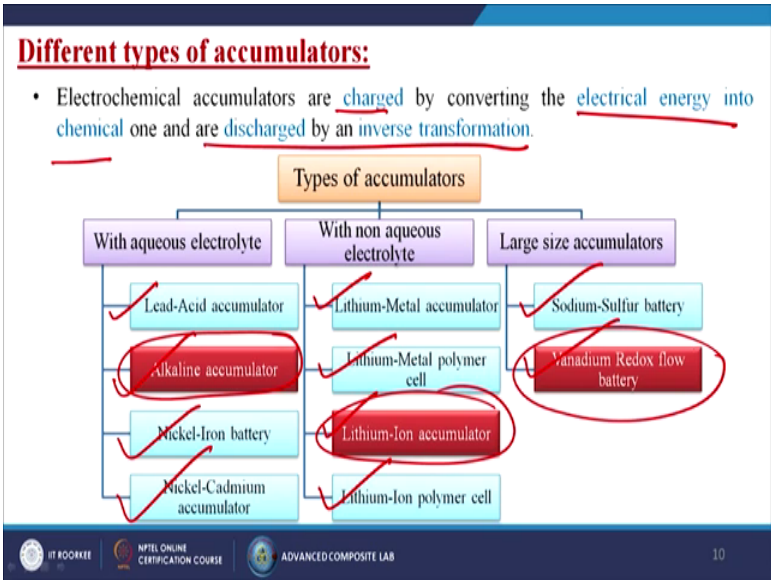

Now, come to the different types of accumulators. Electrochemical accumulators are charged by converting the electrical energy into chemical one and a discharged by an inverse transformation. There are several types of accumulators are present. First is that with aqueous electrolyte that is also like lead-acid accumulator, alkaline accumulator, nickel-iron battery, nickel-cadmium accumulator. If we talk about the non-aqueous electrolyte, maybe sometimes we are calling it as a solid electrolyte basically, so that is known as the lithium-metal accumulator, lithium-metal polymer cell, lithium-ion accumulator, lithium-ion polymer cell.

And if we talk about the large size accumulators, so basically sodium-sulphur battery, vanadium redox-flow battery. So, in this particular lecture basically we are going to discuss about the alkaline accumulators, one lithium-ion accumulator and one vanadium redox-flow battery.

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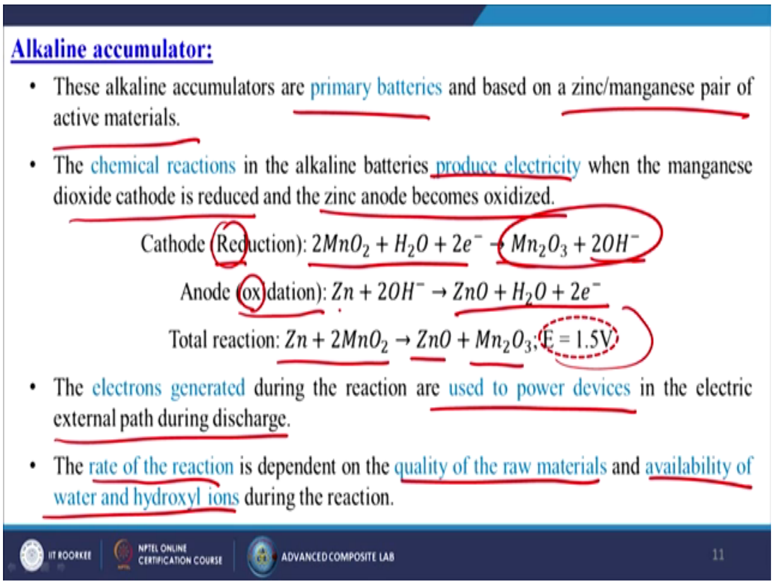

So, if we talk the alkaline accumulator, these alkaline accumulators are primary batteries and based on zinc manganese pair of active materials, that means, it cannot be rechargeable. The chemical reactions in the alkaline batteries produce electricity when the manganese dioxide cathode is reduced and the zinc anode becomes oxidized. So, redox reaction is taking place. Cathode reduction, Red, 2 M n O 2 plus water plus 2 electron, if I give then it will form that M n 2 O 3 plus 2 hydroxyl ion.

In anode, oxide case, so Ox, so Red and Ox – redox, zinc plus these 2 hydroxyl ion will form the zinc oxide plus h 2 O plus 2 e minus. So, total reactions is Z n plus 2 M n O 2 from that zinc oxide plus M n 2 O 3, and it is produced that 1.5 electro volt. So, the electrons generated during the reactions are used to power devices in the electric external path during the discharge. The rate of reaction is dependent on the quality of raw materials and availability of water and hydroxyl ions during the reaction.

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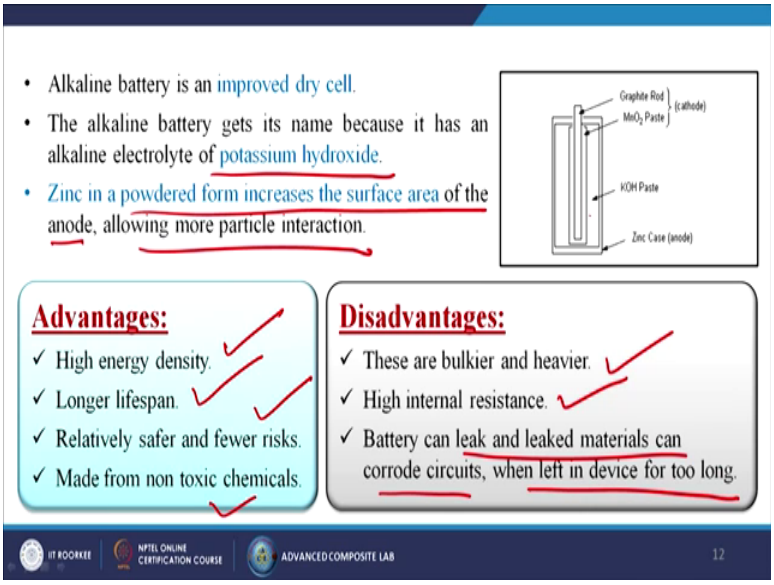

Alkaline battery is an improved dry cell. The alkaline battery gets its name because it has an alkaline electrolyte of potassium hydroxide KOH. Zinc is a powdered form increase the surface area of the anode allowing more particle interaction. So, in this particular case, you can see, this is fully by the KOH or may be the potassium hydroxides paste. In this particular case, we are having that manganese dioxide pastes and we are having that graphite rod as a cathode materials and we are applying the total outer cell made by the zinc, which is nothing but acting as anode material.

Advantages, high energy density, longer lifespan, relatively safer and fewer risks, made from non toxic chemicals. Of course, there are certain disadvantages, what are those? These are bulkier and heavier, high internal resistance; battery can leak and leaked materials can corrode circuits, when left in device for the too long because we are using some paste materials if the case by any reactions or may be any degradations will be leak. So, automatically the paste material will come out. So, that is why in our home you can see that if we keep this kind of batteries for a longer time, you can see some Red colour kind of liquid materials are coming from the battery itself, that is nothing but the inside paste materials are coming out.

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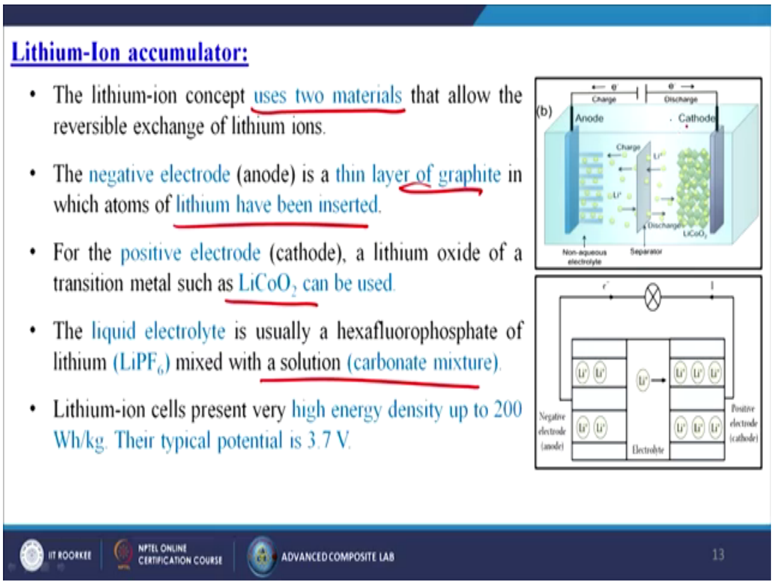

Now, let us discuss about the lithium-ion accumulator. The lithium-ion concept uses two materials that allowed the reversible change of lithium-ions. The negative electrode anode is a thin layer of graphite in which atoms of lithium have been inserted. So, in this particular case, what happened, the negative electrode which is nothing but the anode, so this is the anode materials over there. For the positive electrode cathode, a lithium oxide of a transition metal such as Li Co O 2 means lithium cobalt oxide can be used. So, in this particular case, you are using the lithium-cobalt oxides and in this particular case we are using the graphite materials.

Now, what happens, the liquid electrolyte usually a hexafluorophosphate of lithium a Li PF 6 mixed with a solution that is nothing but the carbonate mixture. Now, lithium-ion cells present very high energy density of up to 200 Watt hour per kg. Their typical potential is 3.7 volt. So, how it is taking place, now this is the separator over there. So, separator will allow to Li plus ion to go from cathode to anode, but it will not allow the electron coming from here to here. So, in this particular case, what happened, the electron will go by the short circuiting where we are taking out the energy from here.

Now, this is a one kind of rechargeable kind of things. So, in this particular case, again we give the energy, so the whole material will come back to its original positions. And then after certain time when it will be full, again the reaction will start, and we can utilize that battery for again same purpose.

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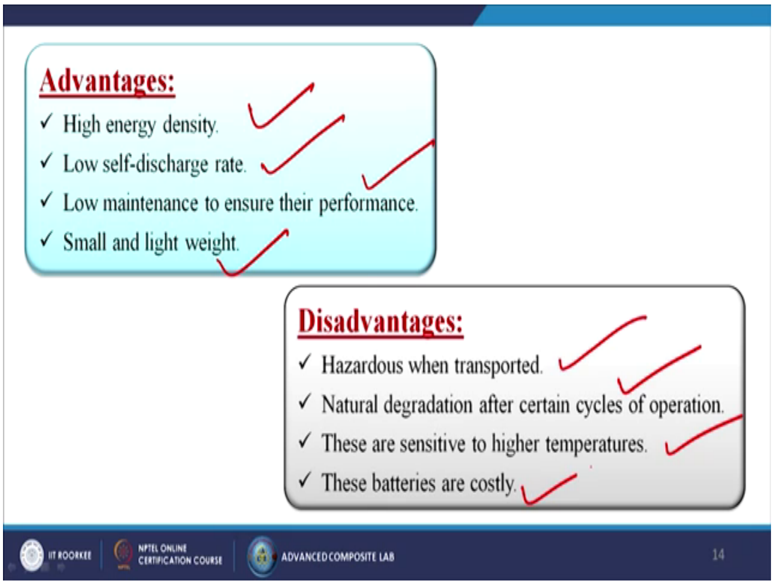

What are the advantages? High energy density, low self-discharge rate, low maintenance to ensure their performance, small and lightweight. Disadvantages - hazardous when transported, natural degradation after certain cycles of operation, these are sensitive to higher temperatures, these batteries are very very costly.

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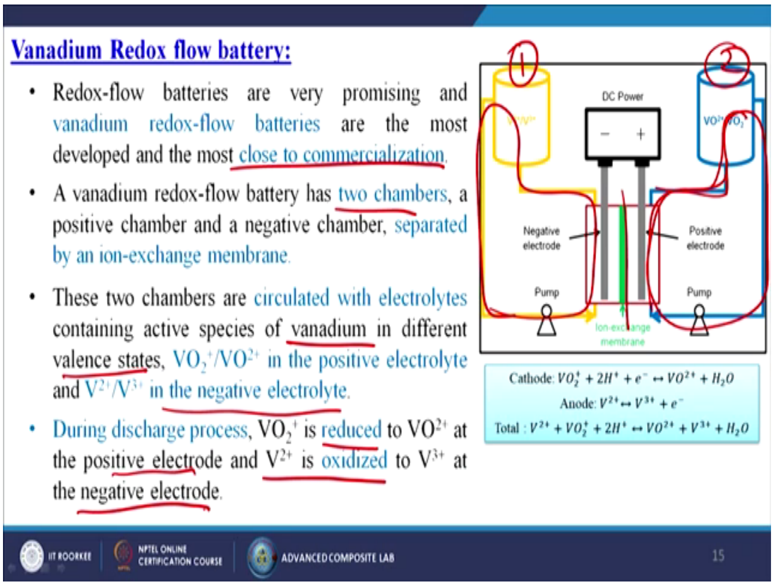

Next, one is called the vanadium redox-flow battery. So, redox-flow batteries are very promising and vanadium, redox-flow batteries are the most developed and most close to commercializations. A vanadium redox-flow battery has two chambers, a positive chamber and a negative chamber, separated by an ion exchange membrane. So, in this particular case, you can see one is this one and another chamber is this one, and it is divided by this ion exchange membrane.

So, automatically some kind of liquid kind of materials basically we are using over there that is why you are utilizing the pump. So, pump the material inside the system. So, this material actually basically will recycle like this. And in this particular case also these material recycle like this.

So, these two chambers are circulated with electrolytes containing active species of vanadium in different valance states that is V O 2 plus, and the V O 2 plus in the positive electrolyte and V 2 and V 3 plus in the negative electrolyte. During discharge process, V O 2 plus is reduced to V O 2 plus ion at the positive electrode and V 2 plus is oxidized to V 3 plus at the negative electrode, so basically this is the concepts over here.

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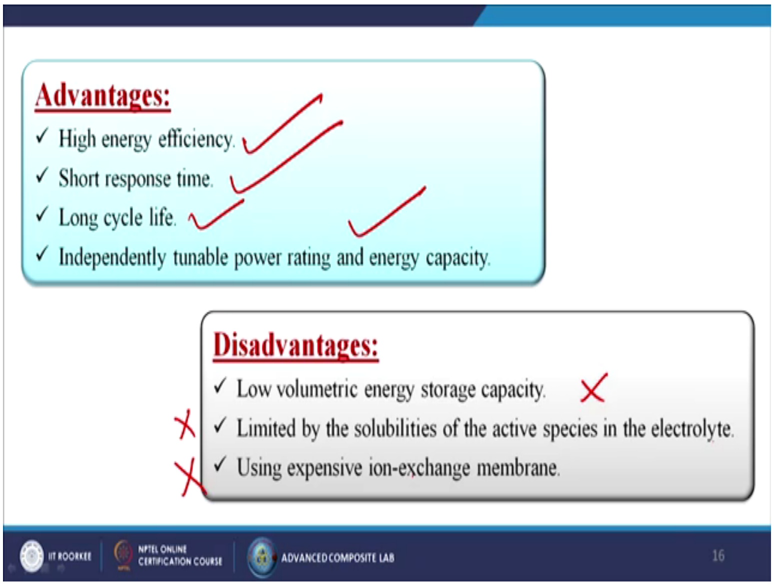

What are the advantages? High energy efficiency, short response time, long cycle life, independently tunable power rating and the energy capacity. Of course, there are certain disadvantages, low volumetric energy storage capacity, limited by the solubilities of the active species in the electrolyte, and the using expensive ion exchange membrane, because sometimes it may happen during that chemical reactions, the increase in heat is taking place inside this particular chamber. So, this ion exchange membrane should capable to withstand that particular temperature, and also it is suspended into some liquid system. So, there is a chance of the swelling, there is a chance of the change in the shape of that membrane, so that is why the cost for this kind of storage systems is little bit higher.

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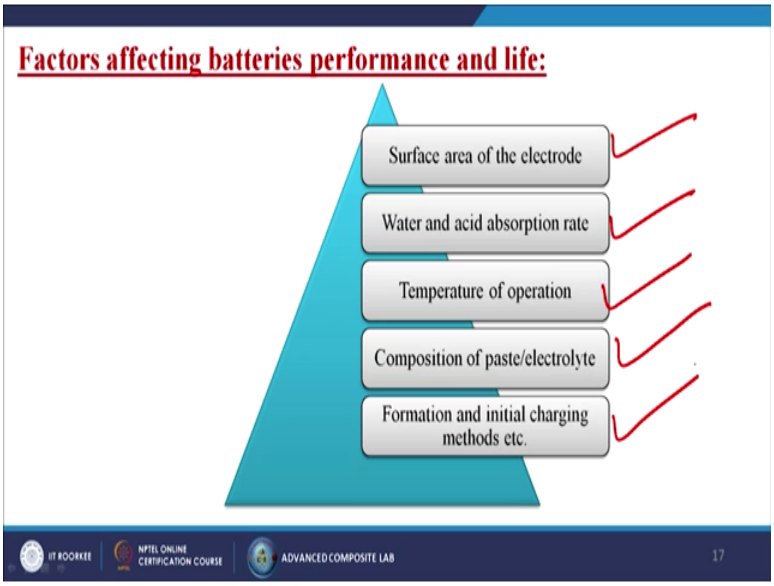

Now, what are the factors affecting batteries performance and life? So, number one is called the surface area of the electrode, water and acid absorption rate, temperature of operations, composition of paste or may be the electrolyte, formation and initial charging methods. So, these all are the five factors which affects the battery life.

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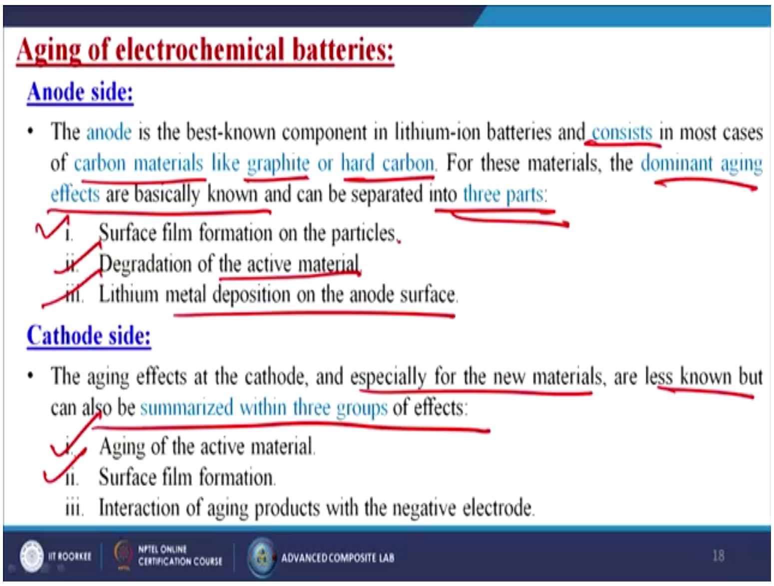

Aging of electrochemical batteries. Anode side; the anode is the best known component in lithium and batteries and consists in most cases of carbon materials like graphite or maybe the heart carbon. For these materials, the dominant aging effects are basically known and can be separated into three parts. What are those? Surface film formation on the particles, because the surface the material can deposit on to that anode side, and it can make a layer, so that the reaction rate cans be reduced. Degradation of the active materials, the material itself can degrade. Lithium metal deposition on the anode surface. So, these all are the drawbacks, which we have to take into the considerations.

Then if we talk about the cathode side the aging affects at the cathode, and especially for the new materials, are less known but can also be summarized within three groups of effects. What are those? Aging of the active materials may be the life of that particular material is not too high. So, material itself can degrade after certain time. Surface film formations, the same problem like anode that there is a layer formations onto the material surface. Interactions of aging products with the negative electrode, so that these all are the drawbacks.

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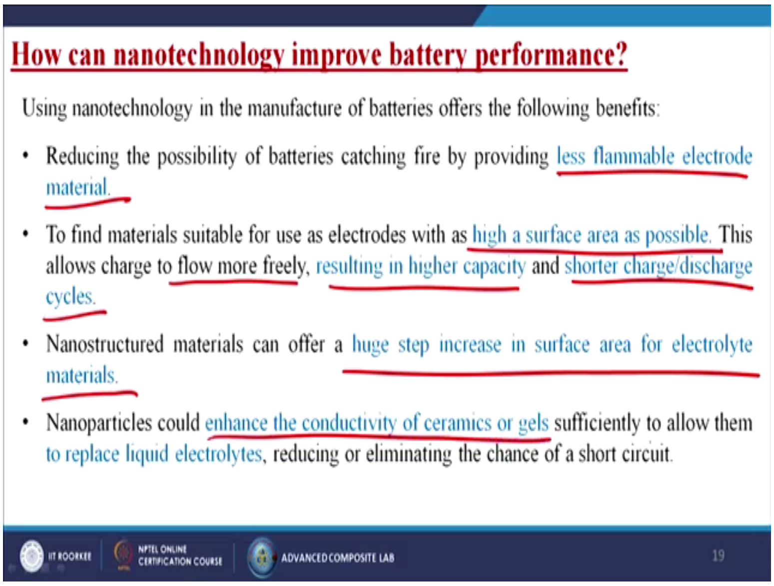

Now, how the nanotechnology has come into the picture to improve the battery performance. Using nanotechnology in the manufacture of batteries offers the following benefits. What are those? Reducing the possibility of batteries catching fire by providing less flammable electrode materials, so that what will happen, this flammability of that cathode materials or maybe the anode materials will be reduced by applying some kind of fire resistant nano-materials. To find material suitable for use of electrodes with a high a surface area as possible, because if the surface area will increase automatically the reaction rate will increase, so that we can generate the maximum energy or maybe we can store the maximum energy inside it.

This allows charge to flow more freely, resulting in higher capacity and shorter charge discharge cycles. Nanostructure materials can offer a huge step increase in surface area for electrolyte materials also. Because every time you can see that electrolyte material is breaking into the positive ion and into the negative ion, and then after certain time again they are coming back and they are the joining each together. So, what will happen, this electrolyte material is having some surface or may be the shelf life. So, after certain time this material can degrade. So, initially we are getting 100 percent efficiency slowly, slowly, the efficiency will go down. So, if we you certain kind of nano-materials which can maintain itself life for a longer period, so that we can utilize that same electrolyte for a longer time.

Nanoparticles could enhance the conductivity of ceramics or gels sufficiently to allow them to replace liquid electrolytes, reducing or eliminating the chance of a short circuiting. Yes, of course, because the reaction is taking place ion is going from one site to another in between that we are having that membrane. So, there is a chance of that short circuiting. Now, if I use certain kind of materials, which will be helpful for the energy generation or may be the storage, but itself is a insulating material. So, automatically it will reducing the short circuiting of the battery inside it.

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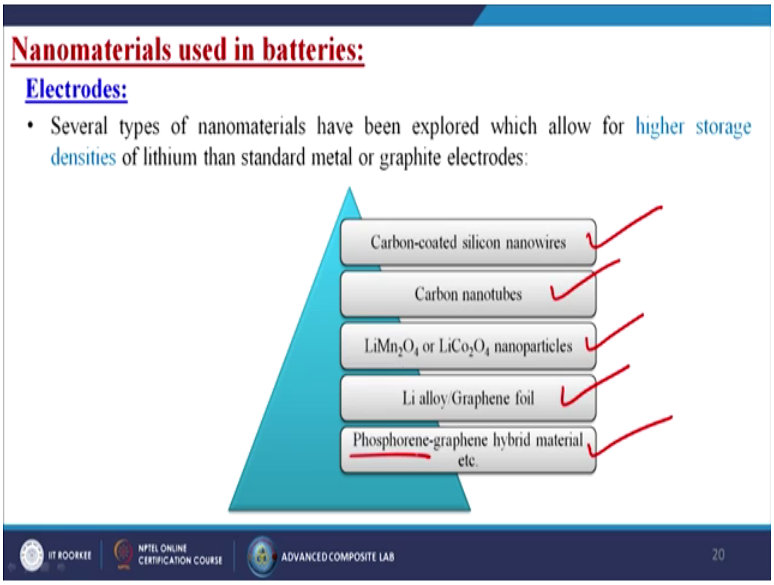

Now, what are the materials basically we are using for making the batteries. If we talk about the electrode, so basically in electrode materials we are using the several types of nanomaterials till today which is having the higher storage densities of lithium than standard metal or may be the graphite electrodes. What are those? Carbon coated silicon nanowires, carbon nanotubes, LiMn 2 O 4 or maybe LiCo 2 O 4 lithium alloy or may be the graphene foil, phosphorene graphene hybrid materials, phosphorene is nothing but we are preparing from the black phosphorus itself. So, these all are the materials basically nowadays scientists are using as a electrode materials.

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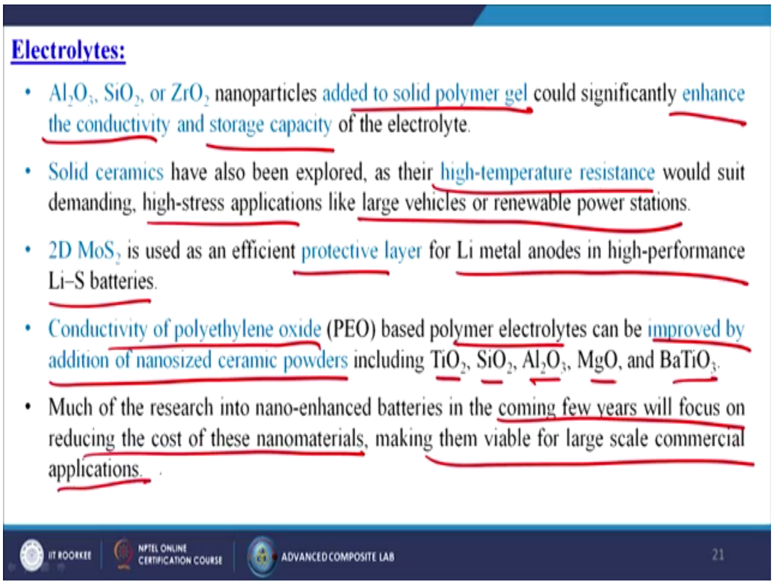

Electrolytes, like alumina L 2 O 3 silicon dioxide or maybe the zirconium oxide nanoparticles added to solid polymer gel could significantly enhance the conductivity and storage capacity of the electrolytes. Now, what I said, I want to use certain kind of ceramic kind of materials like alumina, like zirconium oxides. What they will do, they can sustain in a higher temperature as well as they can keep that electrolytes for longer use.

Solid ceramics have also been explored, as they are high temperature resistance would should demanding, high-stress applications like large vehicles or may be the renewable power stations. 2D molybdenum sulfide is used as an efficient protective layer for lithium metal anodes in high-performance lithium-sulphur batteries. Conductivity of polyethylene oxides basically, PEO based polymer electrolytes can be improved by addition of nanosized ceramic powders including titanium dioxide, silicon dioxide, aluminium, magnesium oxide, or maybe the B a T i O 3.

Much of this research into nano enhanced batteries in the coming few years will focus on reducing the cost of these nanomaterials, making them viable for large scale commercial applications, so that is why the scientists, researchers are working on it tremendously. So, that in near future they will make or maybe invent some kind of materials, which will increase the efficiency as well as which will reduce the cost of that particular system.

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Now, what are the applications? So, basically there are n-number of applications, nowadays we are using. So, like consumer electronics, electric vehicles, renewable energy storage, satellites, walkie talkie, telecommunications. But in our day-to-day life they we are using it tremendously, even if we are using in our smart watch, we are using in our Smartphone any kind of medical devices also we are nowadays using this kind of batteries.

If you see the pacemaker, we are using this kind of batteries, because this kind of batteries is having a very long shelf life. It is not that a today I am putting any kind of pacemaker and tomorrow I am taking it out and then I am changing the battery. So, whatever the pacemaker we are putting at least it should work for 30 to 40 years, so that in a person normal life no need to change the battery, unless and until it will be get rejected. So, these all are the applications, where basically we are using this kind of energy storage devices.

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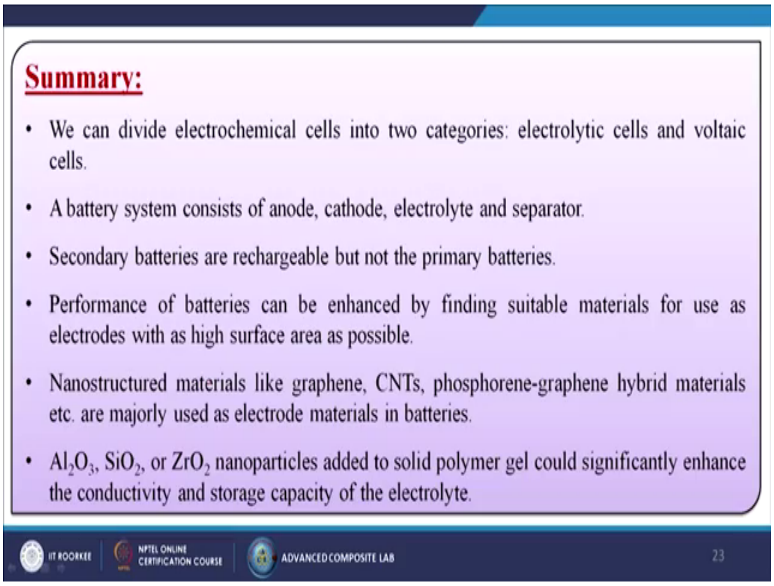

Now, we have come to the last slide of this particular lecture. So, in summary, we can say that we can divide the electrochemical cells into two categories; one is called the electrolytic cells, another one is called the voltaic cells, which is nothing but the vice versa together. A battery systems, contains of anode, cathode, electrolyte and the separators. So, basically it consists by these four different things. Secondary batteries are rechargeable, but not the primary batteries. So, there are two types of batteries, one is only the one time used, another I can use it for a longer time after again and again recharging it.

Performance of batteries can be enhanced by finding suitable materials for use as electrodes with as high surface area as possible, so that what will happen the chemical reaction time will increase or maybe the chemical reaction rate will increase, so that we can generate or maybe the store the maximum energy over there. Nanostructure materials like grapheme, carbon nanotubes, phosphorene graphene hybrid materials, etcetera are majorly used as electrode materials in batteries. Alumina silicon dioxide or may be the zirconia oxide, nanoparticles added to solid polymer gel could significantly enhance the conductivity and storage capacity of the electrolyte.

So, basically nowadays people are using the polymer gel. Now, a people are using the zirconia oxide, silicon dioxide, or alumina or maybe the mixture of these materials, so that this electrolyte material can sustain with high temperature for longer time.

Thank you.