Physics of Renewable Energy Systems
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Lecture 24
Introduction to Li-ion Battery

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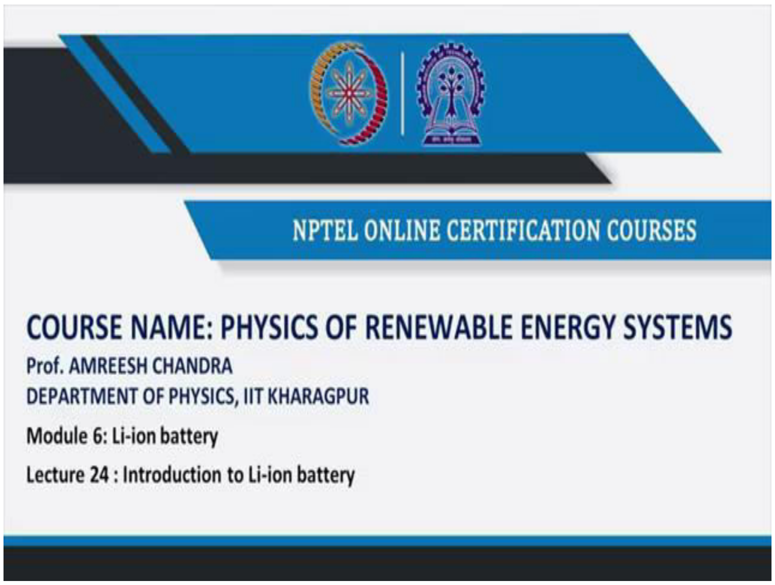

Welcome. Welcome to the first lecture of the 6th week of this course on Physics of Renewable Energy Systems. Till now we have talked about the generation of energy using various renewable based technologies then we moved on to discuss the need for energy storage technologies and then discussed the solar and mechanical based energy storage technologies. As I said in the previous lecture that was the last lecture of the previous week that I know that all of you are interested to learn about lithium-ion batteries.

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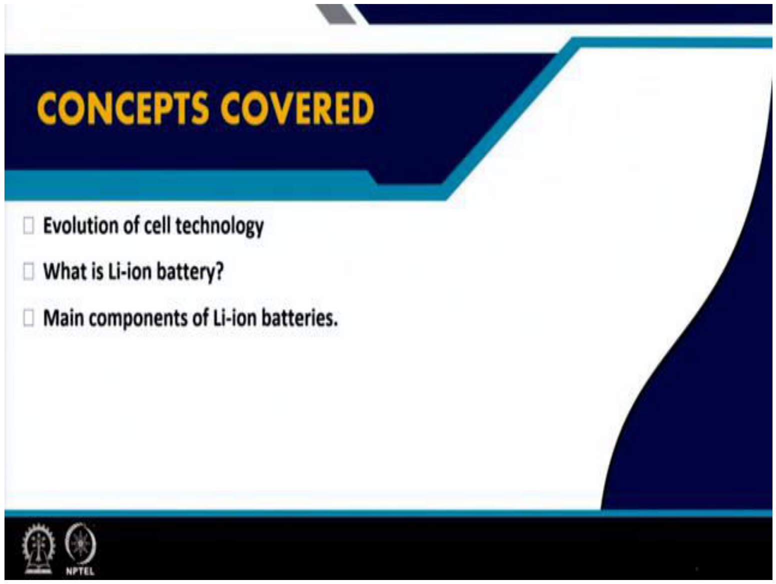

So, in this lecture let us start with our first lecture on lithium-ion technologies and to build our knowledge we will start by getting some information on the evolution of cell technology. Then what is actually lithium-ion battery and in today's lecture we will at least like to introduce to you the main components of the lithium-ion batteries. The details of each of them will be discussed in the subsequent lectures.

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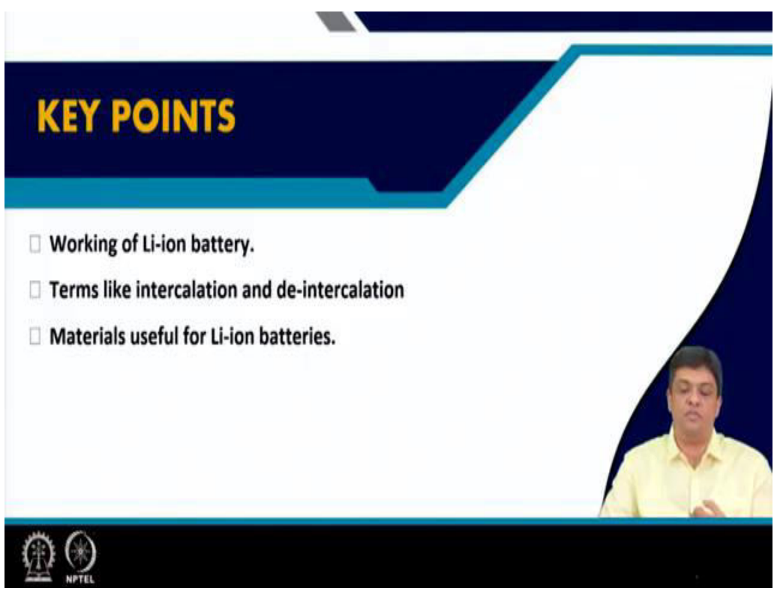

So, after understanding today's lecture you will be understanding the working of the lithium-ion battery, terms which are very relevant to the discussions which we will have over the next couple of weeks. Terms like intercalation, de-intercalation, insertion, de-insertion so these kinds of words would be explained and you will understand that the development of lithium-ion battery is directly linked with the development of smart and functional materials.

And the future of this technology is being driven by the fact that nanotechnology and nano materials have become an integral part of this technology which has led to the significant improvement in the performance.

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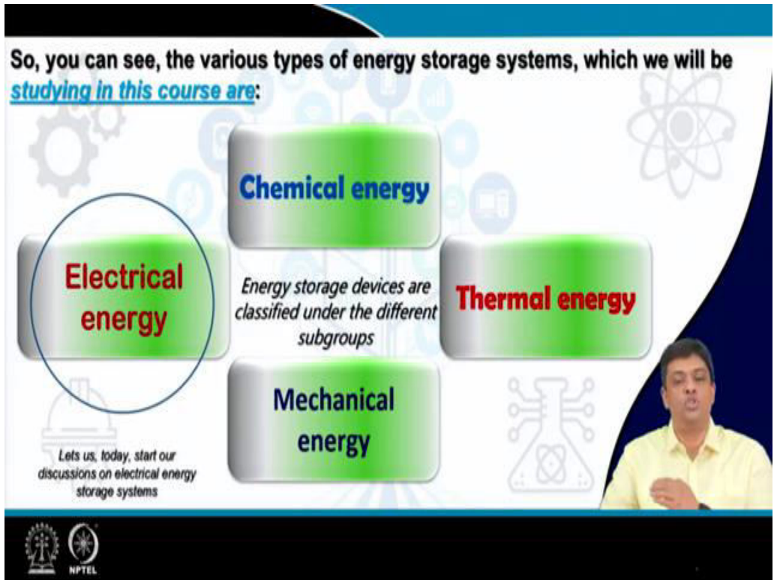

As I said we have already understood for the need for storage technologies and the way the storage technologies are classified under four broad headings. Energy storage technologies which can be classified under chemical energy storage technologies or thermal based energy storage technologies or mechanical based energy technologies but let us today start with our discussions on electrical based energy storage technologies.

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And the importance of this sub area which we will be starting today to discuss is driven by the fact that this area let us say the area of lithium-ion batteries has brought in massive change and had impact on our lives which is evident all around. Because of this the massive impact that I am talking about three scientists; Professor Goodenough, Professor Whittingham and Professor Yoshino were awarded the Nobel prize in Chemistry for the contributions they have made in the development of lithium-ion batteries.

And you will see that they were awarded this Nobel prize in Chemistry because it is about the chemistry of materials which is driving the whole research and the advancement of this technology.

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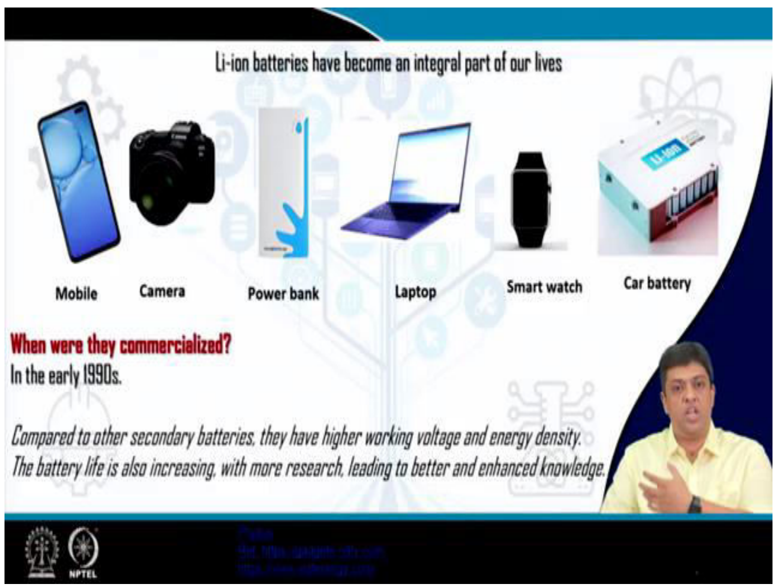

If you look around you will find that the lithium-ion batteries have become an integral part of our lives. Can we live without a mobile phone? Can we survive in this world where we are so much dependent on online classes or online meetings and work from home culture without a technology such as laptop or country like India which is moving towards e-vehicles we would require the batteries which would be driving this E-vehicle.

So, you are talking about mobile phones to car batteries, smart watches to cameras all these are being driven by the use of lithium-ion batteries. So, it is a massive technology which has actually penetrated each and every facet of our lives.

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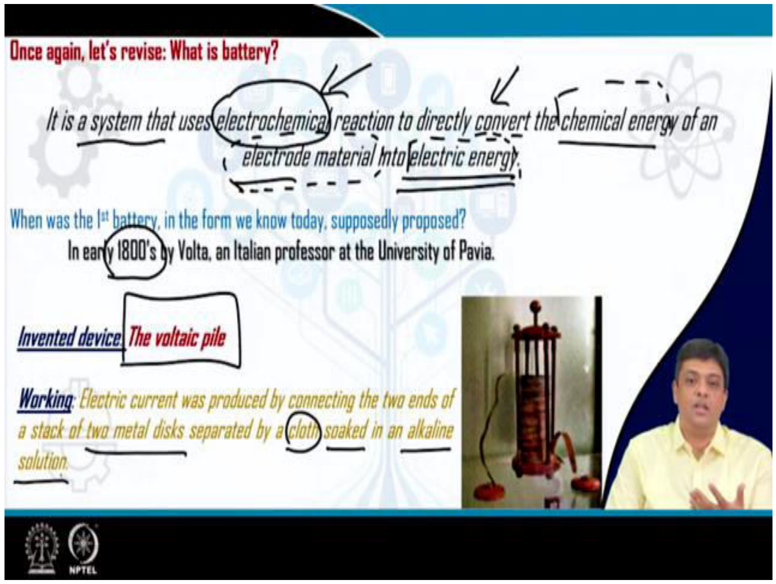

We have been defining batteries right from our school days. Let us very quickly revise a broad definition for a battery, what is a battery? It is simply a system that uses electrochemical reactions. So, we are talking about electrochemical reactions which lead to direct conversion of chemical energy to electrical energy, chemical stored where chemical energy of an electrode material into electrical energy or electric energy.

So, if you look into the main terms which are defining the battery system it is the electrochemical reactions, conversion processes, how do you store chemical energy and the efficiency by which you can convert chemical energy to electrical energy or electric energy and finally and the most critical if I may say the electrode materials. The materials which are used to fabricate either anode or cathode.

Somebody may ask is it like that in 1990s when the lithium-ion batteries were discovered that was the time when you actually discovered the batteries? No. Again right from the first lecture onwards we have been discussing that it takes time for a technology to mature and then become relevant to the society and most probably the first battery in the form or at least using the characteristics or electrochemical reaction based system which we know in today's lives as batteries was discovered in early 1800s, it was discovered in early 1800s by an Italian professor; Professor Volta.

And the device was called the voltaic pile. Very simple concept continues to be similar to what we have been using for the next couple of centuries. It is produced using two electrodes which we are saying here as metal discs separated by a cloth. So, you have one metal plate, the other metal plate and in between you have a cloth, a cloth which is soaked in an alkaline solution which is now understood as an electrolyte.

Why cloth? Cloth is used because it electrically insulates two metal discs because if you do not have a cloth and if the two metal discs come together there will be a short circuit and the concept which you are going to utilize to develop the potential difference would be lost. And therefore, the cloth soaked in alkaline solution can be renamed as if a separator which is soaked in electrolyte. So, that is how we explain in today's world but initially it was called as if two metal discs separated by a cloth which was dipped in alkaline solution.

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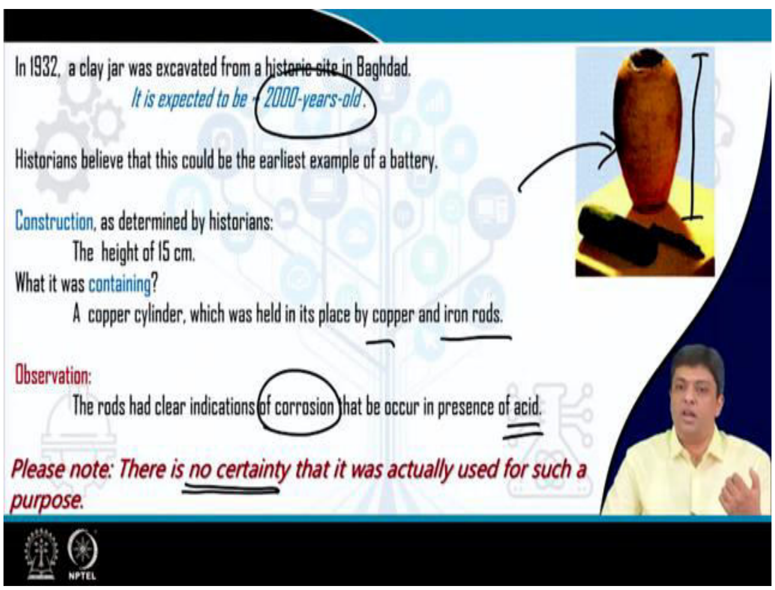

Historically if you look around then you have excavations going on at various place and in Baghdad in 1932 there was an excavation which was done and a clay type system was obtained. A clay type system was the clay jar.

And historians believe that this could be one of the earliest example of a battery or at least a proposed system which has similar performance or similar characteristics. It is a simple construction using a clay jar a compartment made of clay, the height is approximately 15 centimeters or so and you find that it contains a copper cylinder inside which was held in its place by copper and iron rods.

So, it was placed in a jar which was made of clay. So, a clay jar, a copper cylinder which was fixed in place using copper and iron rods. Now how did the historians actually predict that this could have been used as a battery like system? They found that the corrosion on the rods had similar features that could occur when you have a rod of iron or copper dipped in acids.

So, if you have a system which has two electrode plates and you could have a possibility of an electrolyte which was acidic in nature then you could probably develop a potential difference and that could lead to a battery like device. But please note there is no certainty that actually says that this was used for such a purpose. There is no certainty in this inference but the system actually looks like a battery.

Why am I saying these things? Because you should realize that this jar is dated to be around 2000 years old. So, most probably the concept of an electrochemical reaction driven system that could lead to appearance of a potential difference may be known to our predecessors. So, that is how people are still finding new systems or proofs which indicate that the battery technology has been a part of our lives for many-many-many centuries.

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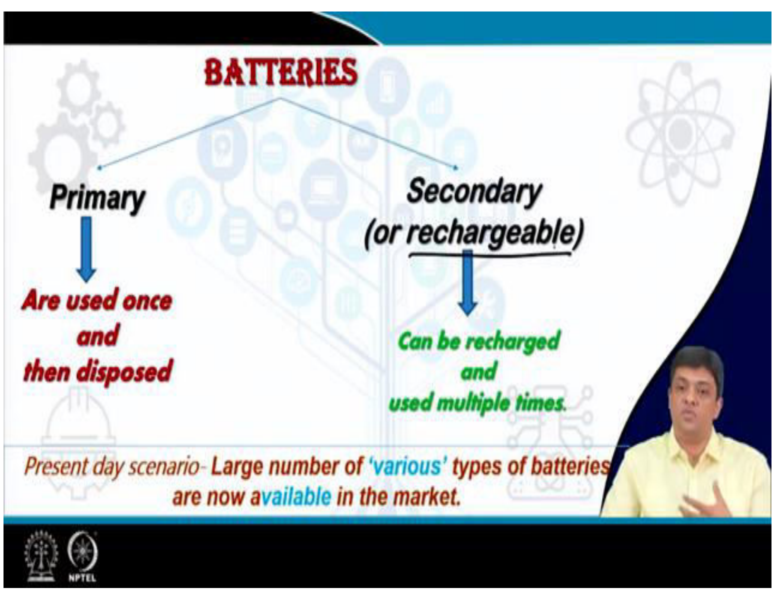

Batteries; if we talk about how they are classified in today's world then there are two types of batteries: either primary batteries or secondary batteries. Very simple way to distinguish the two types of batteries. Primary batteries are used once and once they fully discharge they are lost that means they cannot be recharged to be used again.

So, primary batteries are used once and then they have to be discarded whereas secondary batteries are also known as rechargeable batteries. And can you immediately give an answer to what this kind of secondary battery would be looking like if I have given you the hint while I was discussing the primary battery? I suppose yes you can, what is a secondary battery? A secondary battery is a battery which can be recharged and used multiple times.

So, primary battery and secondary battery these are the two classifications for the batteries that are available to us in today's world. And do we have batteries which are only you have only one primary battery and one secondary battery; do you only have lithium-ion based primary battery and lithium-ion based secondary battery? No. We all know that we have large number of batteries and batteries of various types which are available in the market.

We have various types of primary batteries and we have various types of secondary batteries. And new battery technologies are coming to the forefront with each passing day. I am saying each passing day because if you see the published literature which is coming out you find new and novel results being reported on daily basis which talk about improvement or new technologies which can come up in years to come.

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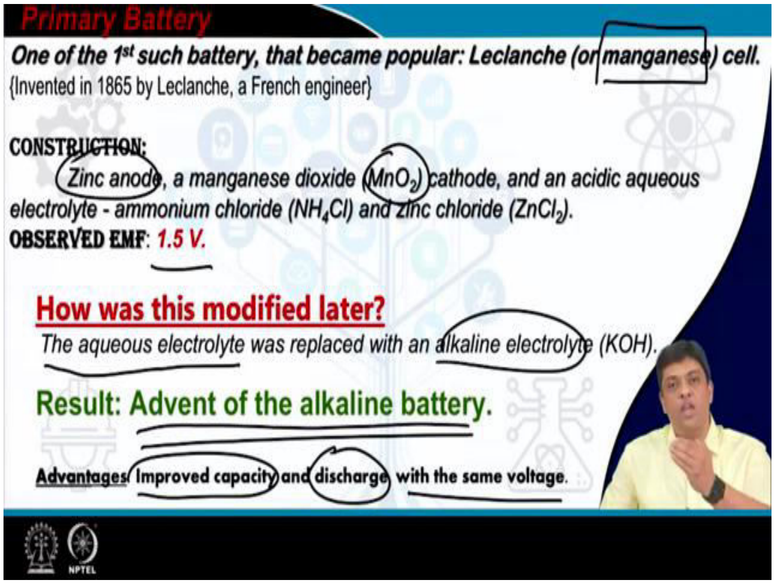

The primary batteries were first proposed by a French engineer Leclanche around 1860s and it is also known as manganese cell, why manganese cell? Because it uses manganese oxide-based cathode and it can also it uses the zinc-based anode and has an acidic electrolyte which is aqueous that is you are talking about liquid electrolyte and more so the electrolytes which were dissolved in water. So, water based acidic electrolytes.

You have an observed EMF the potential which was observed or in the range of 1.5 volts. If you see this cell is also called manganese cell, why? The reason is that the performance of the cell is extremely dependent on the nature and type of manganese diode based cathode which you are using. You would ask what does it mean; manganese oxide is manganese oxide? There is only one manganese oxide then how does it change.

It actually changes if you remember we had talked about the crystal structure, we had talked about the band gap, we are talked about the semiconductor nature and how do these nature change? They change by changing the crystal structure, the lattice parameters you can have different synthesis protocols, you can have particles of different shapes and size there that would result in a change surface area.

Change in the surface area means what? The surface which is exposed to the electrolyte and which would take part in the electrochemical reactions of reduction or oxidation. So, if you have particles of different shapes and size and dimensions and pores and pore volumes then the nature of the cathode itself changes and that has a direct impact on the battery characteristics. And that is why it is also called a manganese cell.

Because you are using acidic electrolyte it had its limitations, we will talk about the limitations of using acid electrolytes bit later when I start giving you the details about the anode materials, the cathode materials, the separators and the electrolytes but you can for the time being believe that acidic electrolytes can lead to degradation of the metal based cathodes.

Then what is the option? The option is to modify the electrolyte or best case scenario replace the electrolyte and that was done bit later where the aqueous electrolyte based on the acidic mediawere replaced by alkaline electrolytes such as KOH and this was the advent of alkaline batteries. And the advantage which were associated immediately with the alkaline batteries were: the improved capacity, improve discharge rates or discharge with the same voltage.

So, you could operate around the same voltage of 1.5 volts but the discharge characteristics were much improved because it is not the charging characteristic which matters because charging means you are supplying energy to the battery that is the amount of batter energy the battery has taken. What is the battery going to give to you depends on the discharge of the battery.

And therefore, it is the discharge cycle which matters and the efficiency of the battery is calculated by analyzing the discharge cycle of the charge discharge measurements. These things will become clear but just for the initial discussions we are giving you the hints as to how the battery technologies moved on and what were the reasons why we move from one battery to the next battery system.

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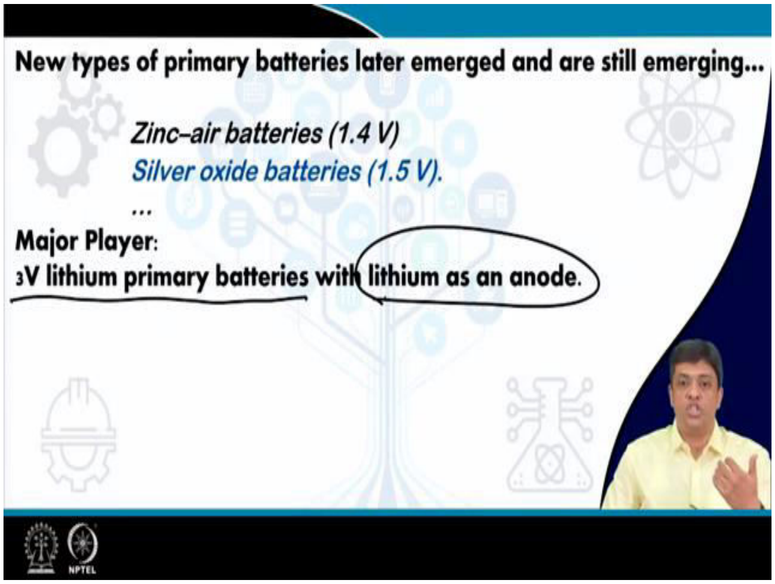

So, the new types of primary batteries which are emerging can be based on zinc, zinc air means you have air being taken by the electrode and then you are driving the electrochemical reactions or you are using silver oxide as the electron material and still lot of work is being performed to improve the performance of these batteries because they have their advantages in various applications.

But as of today, the 3-volt lithium primary battery where lithium is used as an anode has become the major player. So, it is not only the lithium based secondary battery which is a major player in the battery technology used around it is also the lithium based primary battery which is quite prevalent.

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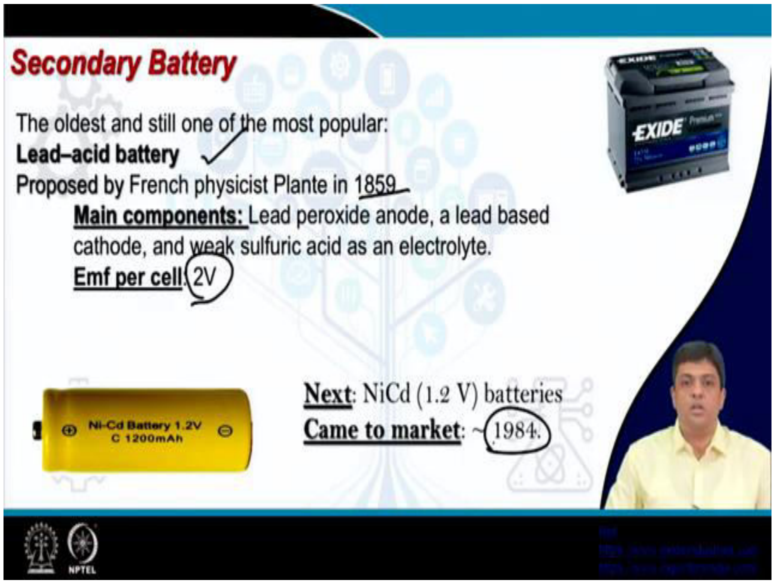

Secondary batteries as we know are already part and parcel of our lives oldest and still one of the most popular are the lead acid batteries, proposed by a French physicist Plante in 1859 uses what it is fabricated using a lead-based cathode lead peroxide based anode and weak acidic electrolyte.

And this technology can give you an EMF per cell in the range of 2 volts, subsequently you have obtained nickel cadmium based batteries and it actually came in market around 1980s mid 1980s or so. But because of the environmental impact of cadmium this nickel cadmium batteries had limited use but they are still there.

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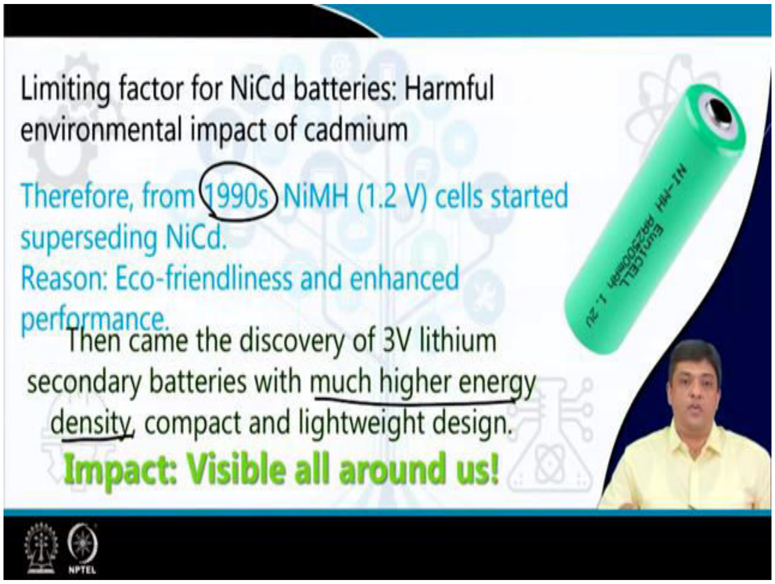

Following the nickel cadmium batteries, you had the advent of nickel metal hydride-based systems which came into the market in early 1990s and they started superseding the performance of nickel cadmium based batteries and the advantage of these were they were more eco-friendly and also had better performance than the nickel cadmium batteries.

Then came the discovery of 3-volt lithium secondary batteries, 3 volts with much higher energy densities. What does this mean? The concepts of energy density, the capacity, the power densities will become clear in the next lecture but for the time being let us see how do you define for a system energy density where you are talking about the capacity is half C V square.

So, it is the square of the voltage which controls the energy of a capacitor or the storage technology. So, if you go from let us say you are having a voltage of 1 V then for the same capacity C you will be having energy of 1 by 2 into C but if you go to 3 volts now then you have E is equal to 1 by 2 9 C so just by increasing the voltage window you have actually increased the energy densities by 9 times or the you have increased the energy which can be stored by such system. So, it is the voltage window if you can enhance that then the performance is immediately enhanced and that is what this technology did to the battery technology.

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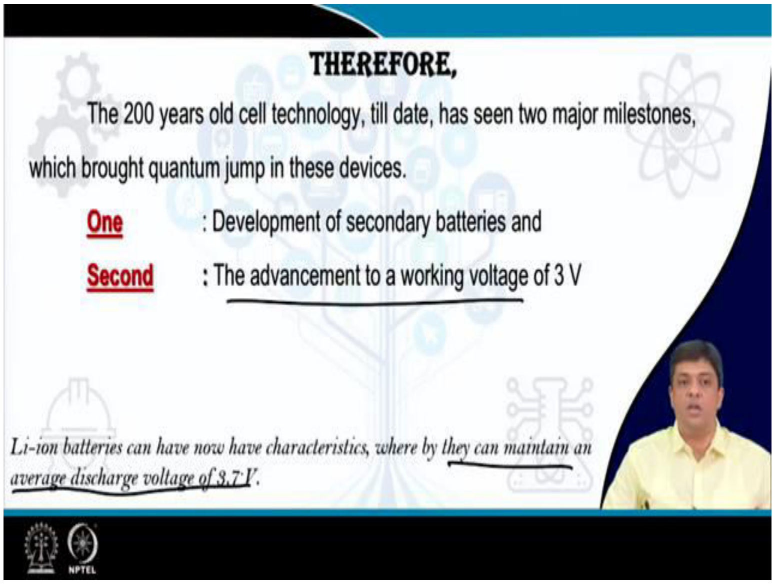

So, if you look around from 1800s from the discovery of the Leclanche cell then there have been two major developments which have changed the course of batteries first one was the discovery of secondary batteries that means batteries which could be recharged and reused.

And the second thing was the advancement to a working voltage of 3 volts. So, you could improve the working voltage window to 3 volts and sometimes people just use the term voltage window. The lithium-ion batteries if you take their performance today then they can actually maintain an average discharge voltage of 3.7 volts.

So, you still have improvement in the voltage window which is being observed or at least the average discharge voltage is quite high and the usable voltage may be slightly lower because of effect such as polarization that would be discussed bit later but at theoretically, they still have very high average discharge voltage.

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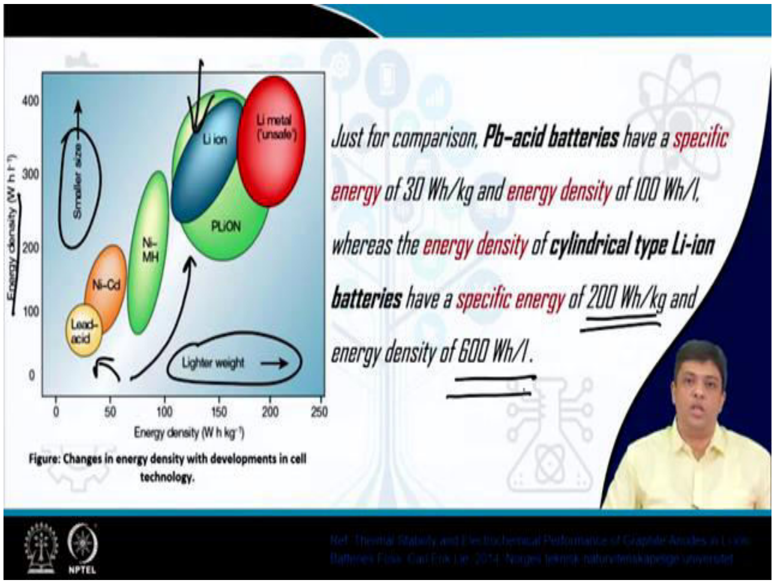

So, if I show the same discussion in graph then you would find that what has lithium done it has actually increased the energy density while ensuring smaller size and lighter weight but many fold increase in the energy density if you compare with the lead acid battery then we have seen a massive increase in the performance characteristics.

Just for comparison the lead acid batteries have a specific energy of 30-watt hour per kg and energy density of 100-watt hour per liter, whereas the energy density of cylindrical type lithium-ion batteries have a specific energy of 200 watt hour per kg and energy density of 600 watt hour per liter. So, that is what has changed and we have seen massive improvement in the performance.

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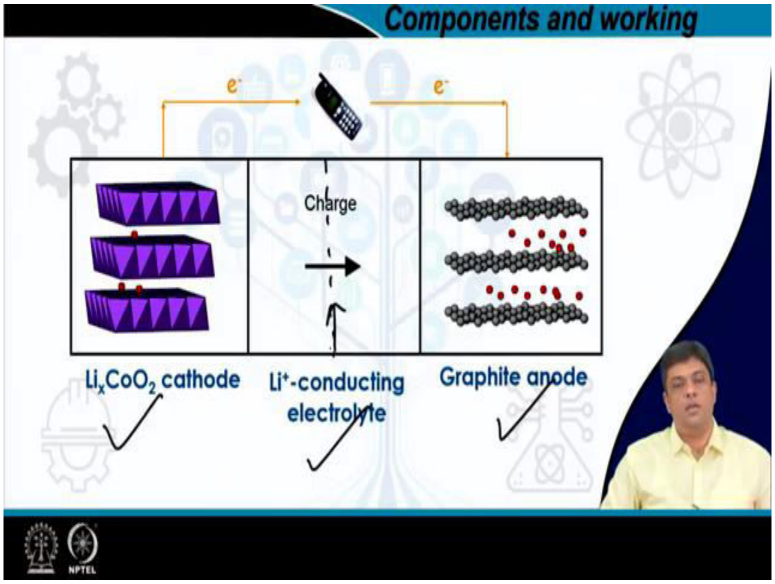

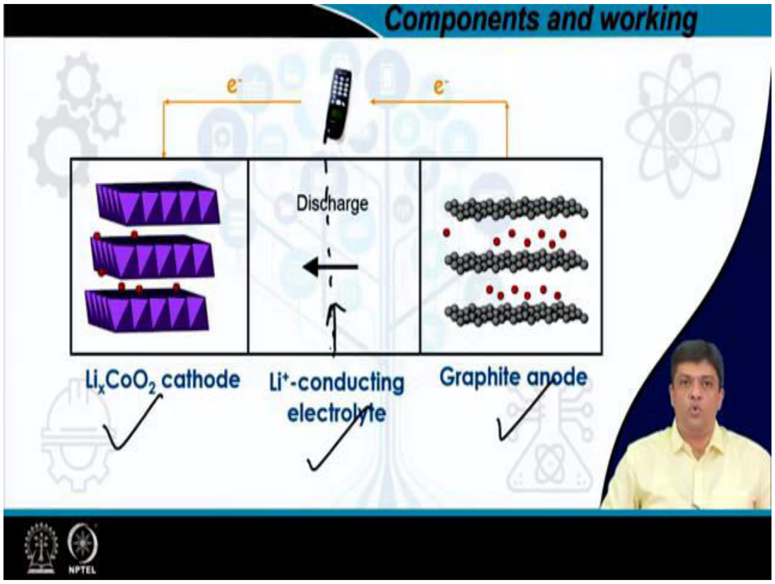

Let us see what a lithium-ion battery looks like. You have a cathode; you have an anode and you have a lithium-ion conducting electrolyte or you can also have a separator mentioned here. So, if you look into this slide, these are the two things which I showed, one is the charging cycle and other is the discharging cycle. Let us try to understand what happens in both the cases.

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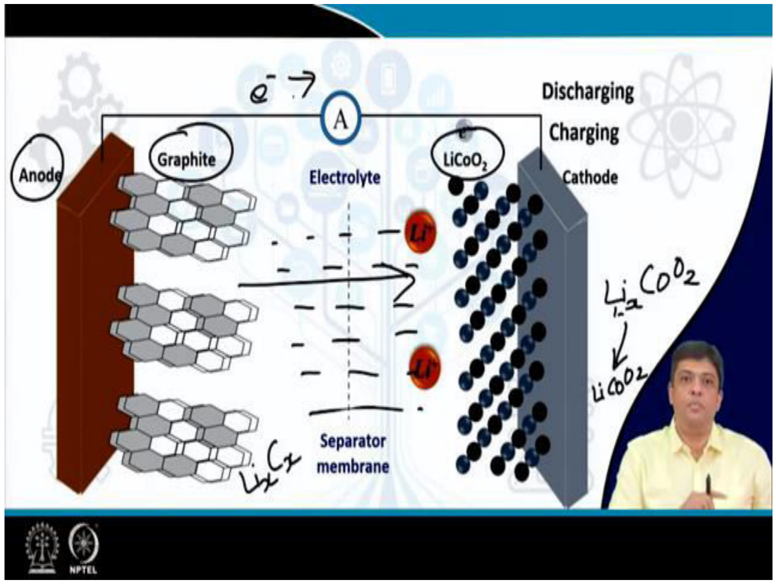

So, let us see we have an anode, we have a cathode for example we have lithium cobalt oxide-based cathode material then you have the electrolyte then you have the electrolyte this is not the way electrolyte is flowing I am just explaining so please do not take this as the as if electrolyte is flowing you have a separator which is soaked in electrolyte, okay, so you have a cathode you have an anode, anode mostly made of layered graphitic based structures, layered graphitic based structures.

So, when you charge the battery what happens lithium from lithium cobalt oxide leaves this lattice and is able to move from lithium cobalt oxide-based cathode through the electrolyte which is allowing the flow of lithium-ion and that lithium-ion gets inserted into the graphatic based layered structure. Why layered? So that lithium-ion can go inside intercalate and when it goes out it is D intercalation or insertion and then D intercalation.

When this happens, this is charging the electron is flowing from the outer cycle, so when it is charging the electron is actually moving and then through the current collector it reaches so that the overall state of the anode is the material at the anode is again the charge neutrality condition is maintained.

And what you are left is lithium 1 minus x cobalt oxide and here you form a complex of lithium x carbon x. During discharging what happens when you have an external load lithium moves back, lithium moves back goes into the lattice once again, you get a material bag lithium cobalt oxide and the electron then flows through the external load.

So, this is what you are doing lithium leaving the lattice entering the layered structure forming a complex during this change it then moves back to its original lattice and so I will just repeat, charging you have lithium from cathode to anode and during discharging lithium-ion back from anode to cathode.

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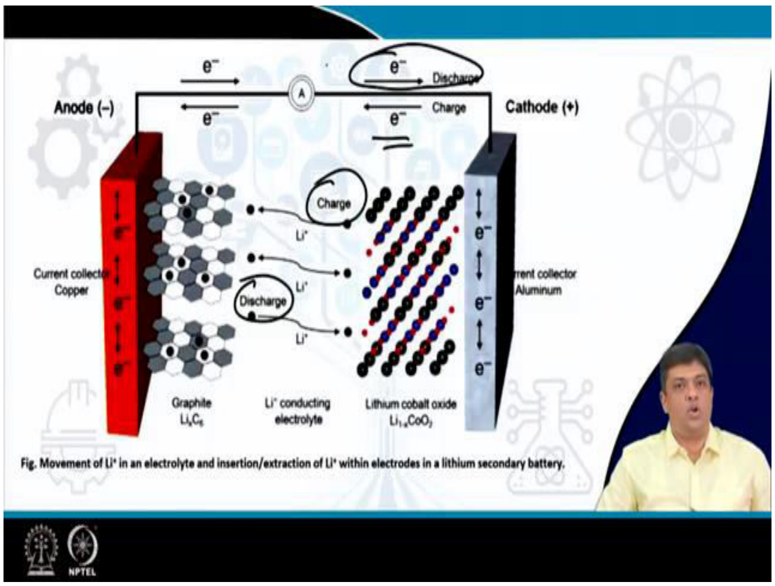

And this is what a typical curve looks like to explain the motion of lithium during the charging cycle or the discharging cycle. Charging cycle electron, the flow of electron is shown by the arrows and during the discharging cycle the flow of electron is reversed.

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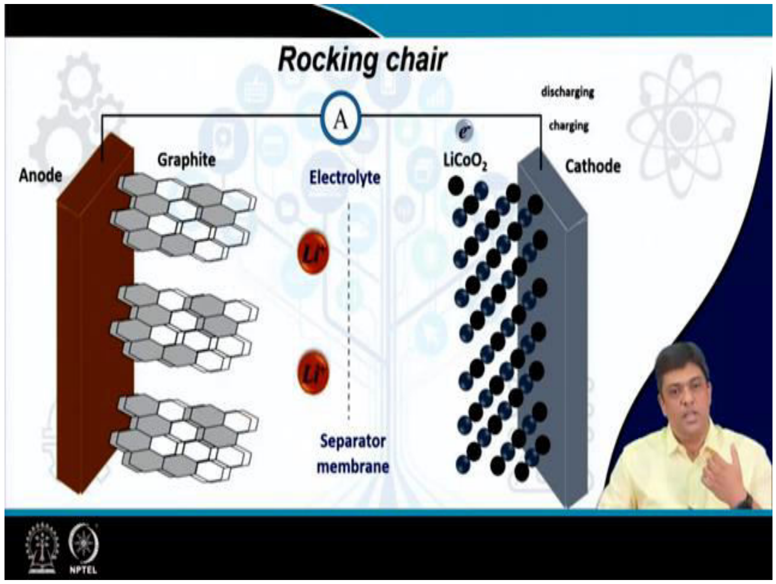

And if you need the battery which is able to perform cycle after cycle after cycle then the battery would be what it would be a rechargeable battery and, in that case, you are talking about the Rocking chair type mechanism charging first cycle charge reuse it when the battery again discharges then you charge again and then reuse sometimes this kind of curve becomes easier to understand what is actually happening.

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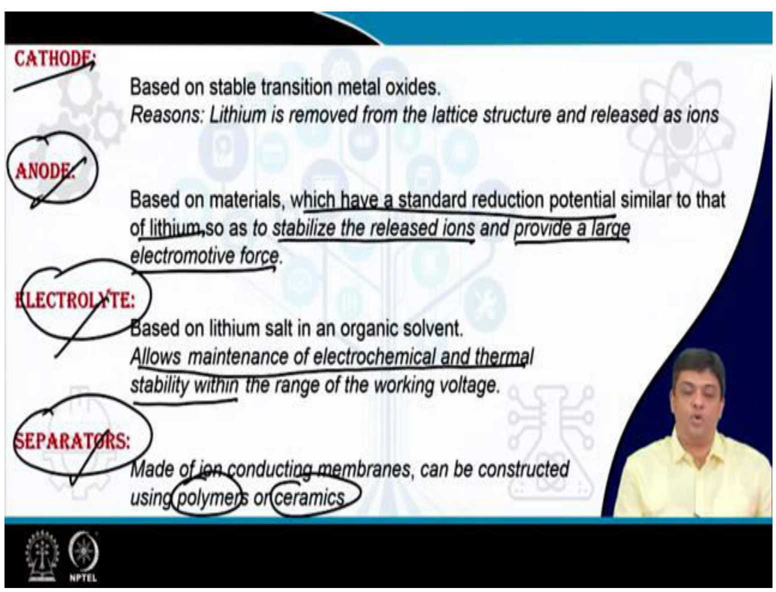

I said four main components. What were those? If you remember and if you have understood till now, you would be easily answering this question. Cathode, anode, electrolyte and separators. What is the role of cathode? It supplies the lithium-ion from its lattice, this lithium-ion moves through where through the electrolyte across, what? Across a separator to reach where, to reach an anode.

So, this is what the four major components are the separators have to be such that their characteristics are defined in a way that they are ionically conducting but electronically they are insulating, so they do not allow the flow of electrons but only allow the flow of ions and they can be constructed using polymers or even ceramics.

Electrolytes it allows maintenance of electrochemical and thermal stability within the working voltage window. Anode, what is the purpose? They are the ones which have the same standard reduction potential similar to that of lithium, why? Because they need to stabilize the released ions, released ions from where the ions which were released by let us say lithium cobalt oxide lattice.

And these released ions are reaching anode and therefore the more ions can reach anode the more ions it can store it will lead to the electromotive force and depending upon the ions which are actually being stored at the anode you will have the magnitude of the electromotive force.

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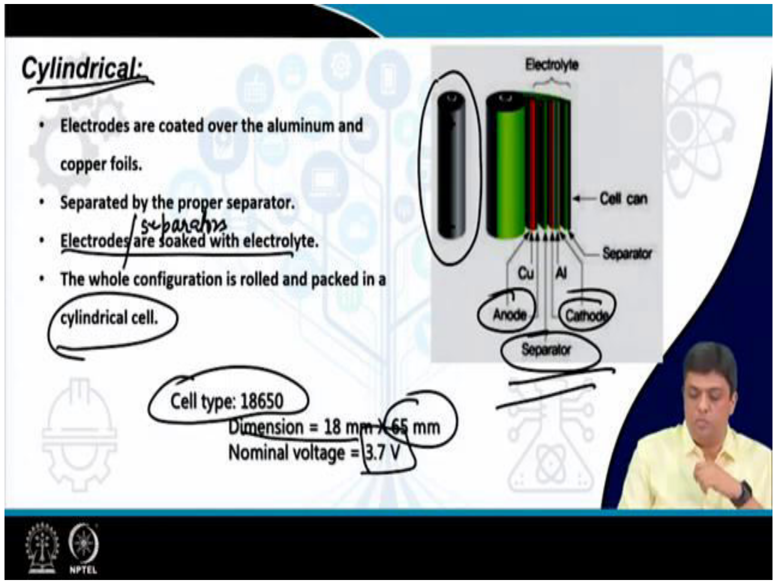

There are various types of batteries that is lithium-ion batteries which have been commercialized and you can find them when if you go and search even in the E markets you can find just if you try type cylindrical type lithium-ion battery so they are the batteries which would be coming as the pictures.

The first one is the cylindrical type batteries, so that why because they are in the shape of a cylinder. How are they made? The construction is shown, so you have a cell can, so the outer can, what are the things which should be there? You should have an anode, a cathode, copper and aluminum, what are they doing, current collectors and then you have a separator.

So, electrodes are coated over aluminum and copper foil so that these substrates act as the current collectors on which the active materials are actually coated, active materials means what? The materials which are going to take part in the electrochemical reactions, they are separated by a separator more so in such kind of systems we are using the iron conducting polymers.

Electrodes or the separators are soaked with electrolytes because if the system or the electrodes or the separated dries then that means you will not be having the flow of the ions and the whole configuration is rolled and packed in a cylindrical form, so you can have electrodes or the separators which are soaked with an electrolyte. The typical ones are the 18650 type cells which have the dimensions of 18 millimeters and the height of 65 mm and the nominal voltage is 3.7 volts.

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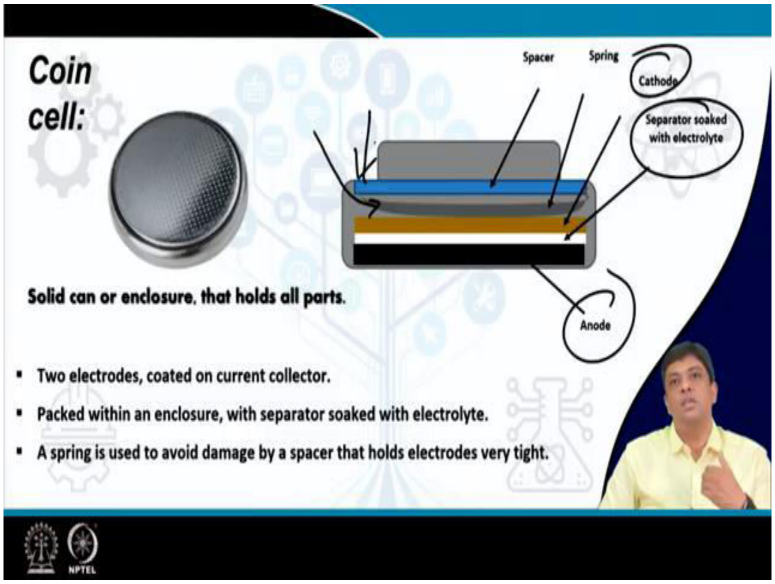

The next one is Coin cells these are mostly used to determine the performance of the electrode materials or the batteries at the laboratory scale not at the commercial level but at if I am doing a research then at the laboratory scale I fabricate coin cells and then analyze the performance of the battery.

Here you again have the cathode, the anode, the separator, soaked with electrolyte this is now compressed in a form of a coin, so you have a two coin covers then between them the whole system is compressed in but here you just have an additional component that is a spacer that is a spring separated spacer. This spacer is there what does it do, it actually ensures that your system is not getting compressed or there is no short circuit taking place between the two sides of the coin which can be made of aluminum or any kind other covers.

So, you have a spacer and the spring ensures that the spacer is not compressing the anode cathode and separator-based region which can lead to the damaging of the whole configuration. So, you have additional components which are spacers and spring.

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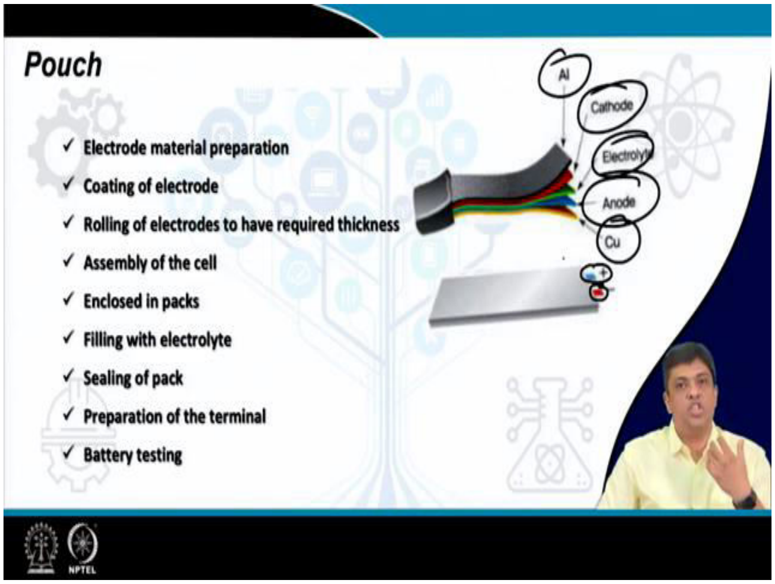

The third one is the Pouch cell it looks like a pouch where again you have the current collectors and the three components and I would not repeat the construction you can easily now see what it looks like the only thing which you see here which is additional that you actually bring out two more sets of protruding electrodes which act as the positive and the negative terminals. So, this is what you are talking about when you have the construction of a pouch cell.

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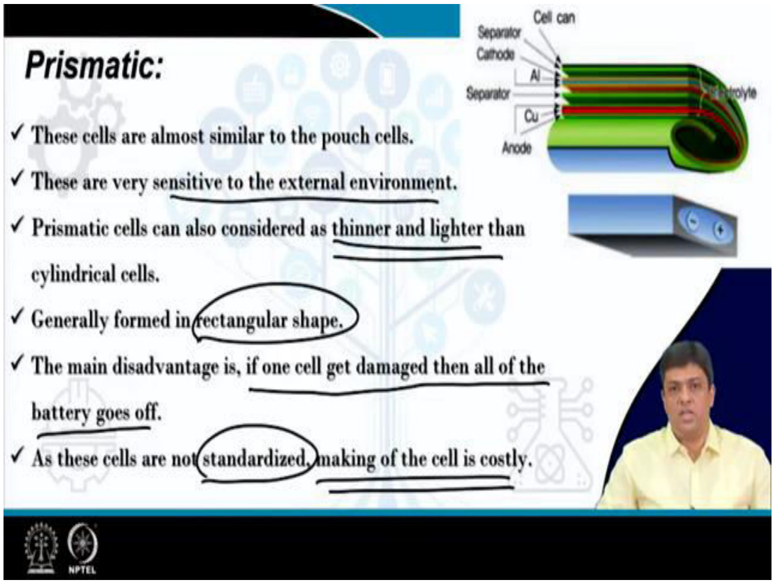

And the more recent one is the Prismatic cell which is very similar to pouch cell but they are much thinner and lighter. They are generally in a rectangular form and you can make many such cells together the problem with such kind of prismatic cells could can be if any one cell gets damaged then the whole battery goes off. As these cells are still not standardized the cost is still on a higher side along with an additional disadvantage that these are very sensitive to external environments.

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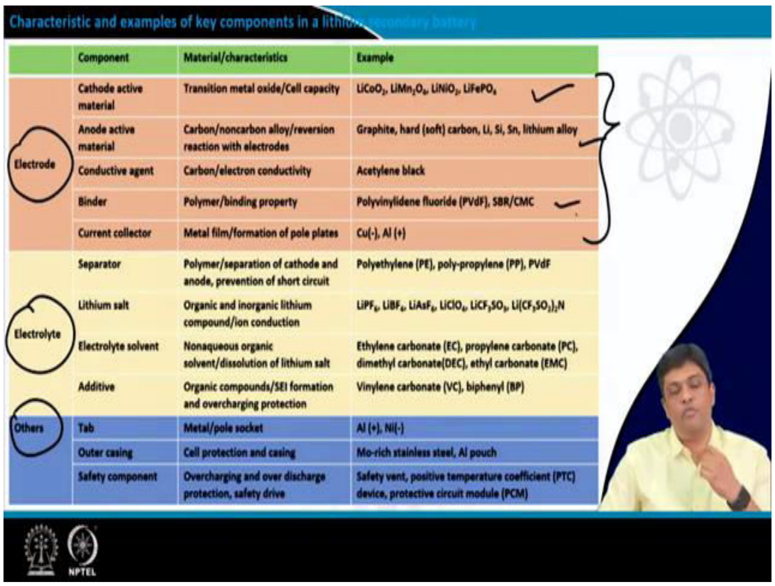

You will see in subsequent lectures that there are large number of electrode materials or various types of electrolytes along with that you have different kind of configurations which can lead to massive variation in the performance of the battery which you are going to fabricate. In this table we have just listed some of the materials which can change the performance of the battery.

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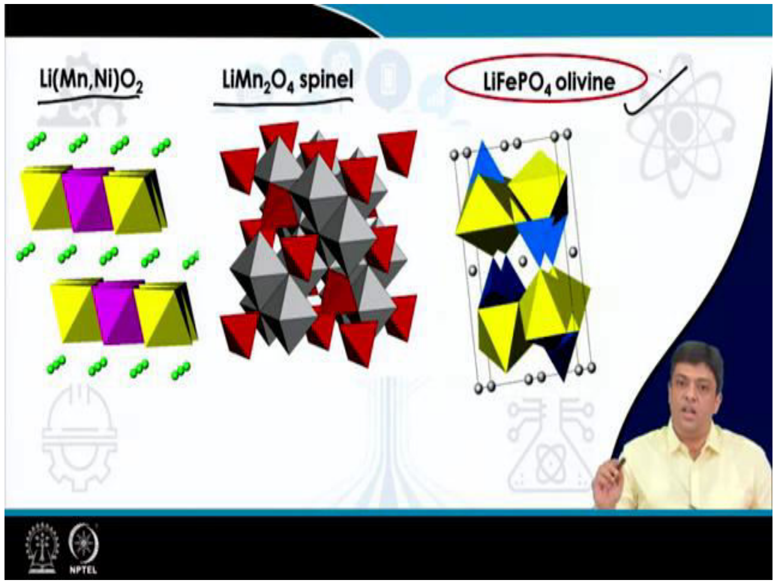

Just to show you why they will change the performance, for example if I take lithium manganese nickel oxide or lithium manganese oxide or a more recent and a more fashionable material like lithium-ion phosphate you can clearly see that the crystal structure of these materials are different along with that the channel which allows the flow of the lithium out or lithium in are also of different size and nature.

And therefore, the ionic conductivity or transparence or transport of lithium-ion from these materials are of different order and of different nature and that has a direct impact on the battery performance. All these things will become in the clear in the next lecture.

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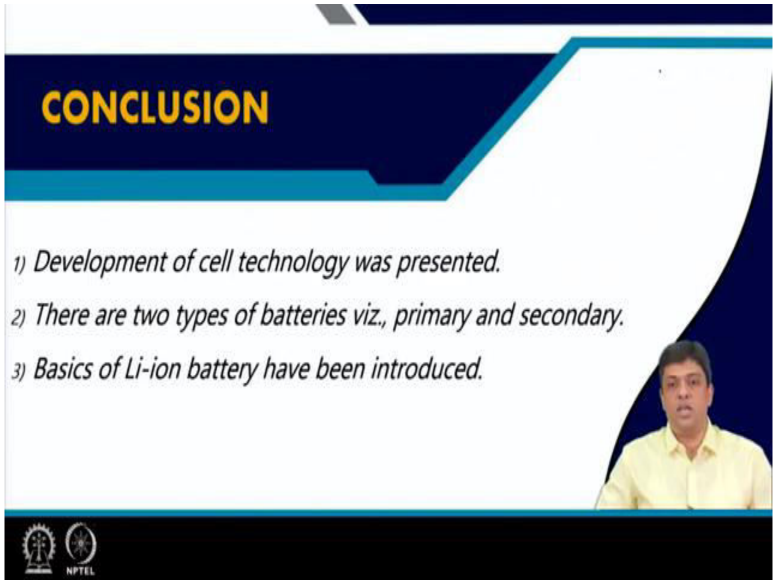

And hopefully after hearing today's lecture one thing is clear that there are various types of batteries, they are classified under primary and secondary type batteries, primary use one throw away secondary batteries rechargeable batteries can be used for many times after charging when they have discharged. And we have also introduced to you the very basic information about the lithium-ion batteries and lot of details will be discussed in the next lecture.

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These are the books which were used as reference books, also the papers from where I have taken certain data are also mentioned in these slides and I thank you for attending today's lecture on lithium-ion batteries and in the next lecture I will give you more details about the materials and the parameters which are used to define the performance of lithium-ion batteries. Thank you very much.