Non - Metallic Materials
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Module - 06
Optical and Electrochemical Properties of Non - Metallic Materials
Lecture - 31
Electrochemical storage, rechargeable batteries

Welcome to my course Non-Metallic Materials and today, we are in module number 6 Optical and Electrochemical Properties of Non-Metallic Material. And, this is lecture number 31 where I will be talking about Electrochemical storage and particularly rechargeable batteries, this will be introduced.

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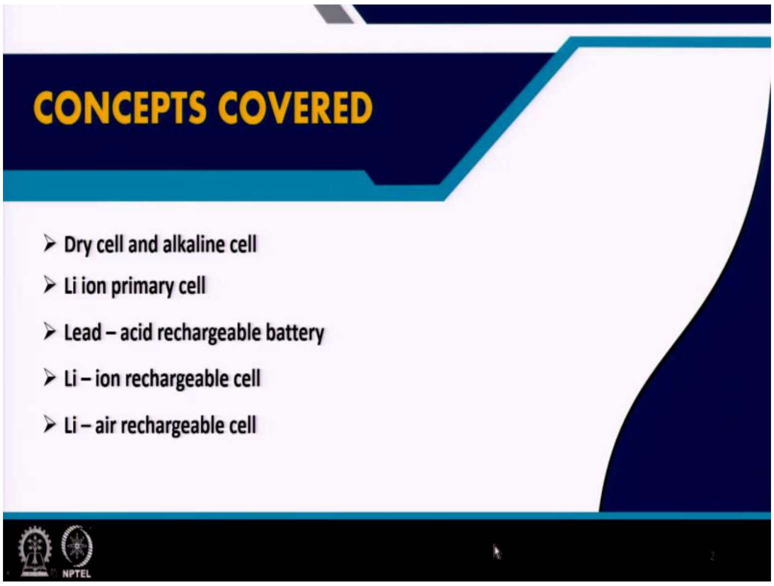

Now, first we will talk about this popular pencil cell we what we call this is dry cell and alkaline cell, what exactly are they. And what are their typical characteristics, fabrication of those kind of thing, construction. And then we will talk about small lithium coin cell battery which are not rechargeable, but they are used for various application, we call it is a button cell. So, what are they?

Then we will talk about rechargeable battery which you can use, in the first two you cannot use neither dry cell, alkaline cell or lithium cell you cannot use, once you are consumed its energy you throw it. And then we have lead-acid battery which is reusable, you use it, it discharges and then again you charge it back. Then we talk about the hot topic of today that is lithium-ion batteries and then finally, some futuristic battery in the form of lithium air rechargeable batteries.

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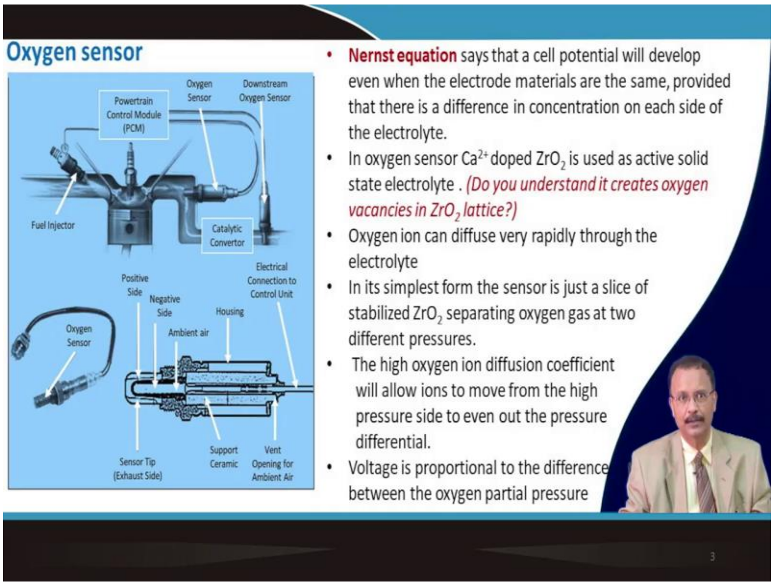

So, I will start with the Nernst equation part of my last lecture where you have learnt that this equation tells that you if you have a concentration difference across a solid electrolyte be that gaseous or other types of concentration dependence difference is there and you have two different dissimilar material.

So, then you generate a small emf; so, whether it is small or large that depends on the type of the electrode material that we are used. Particularly, we talked about this oxygen sensor where there is no dissimilar electrode.

We have porous platinum, but the oxygen partial pressure is different at the two end and you have electrolyte which is in the form of a solid electrolyte. Remember, we talked about calcium doped zirconia which is a good oxygen ion conductor.

And, then you found that even in this condition there is no dissimilar electrode materials are there, only the concentration differences there as far as the oxygen partial pressure is concerned, then you generate emf.

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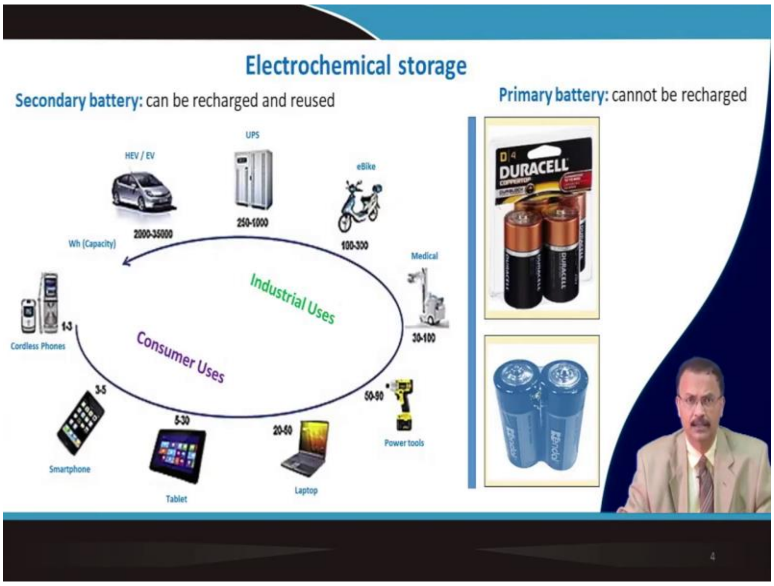

So, we will elaborate this concept to understand the battery. Now, this all you know what are the batteries. This is a Duracell dry cell or alkaline battery. So, these are two different technology and nowadays these are all primary battery you use it and you throw. But, there are lithium-ion batteries or lead-acid battery which are rechargeable and you have plenty of uses. In fact, your mobile communication, the mobile phone, tab, laptop everything nowadays uses lithium-ion battery.

So, you have two application – one is consumer electronics which is shown in the bottom part of this figure and you have industrial application, you can use this battery in UPS. Even you can run your car, you can run scooter, you can run various medical equipments.

Then these are industrial applications of this rechargeable batteries and the consumer electronic application they have almost taken by only this lithium-ion rechargeable chemistry. We will talk about this.

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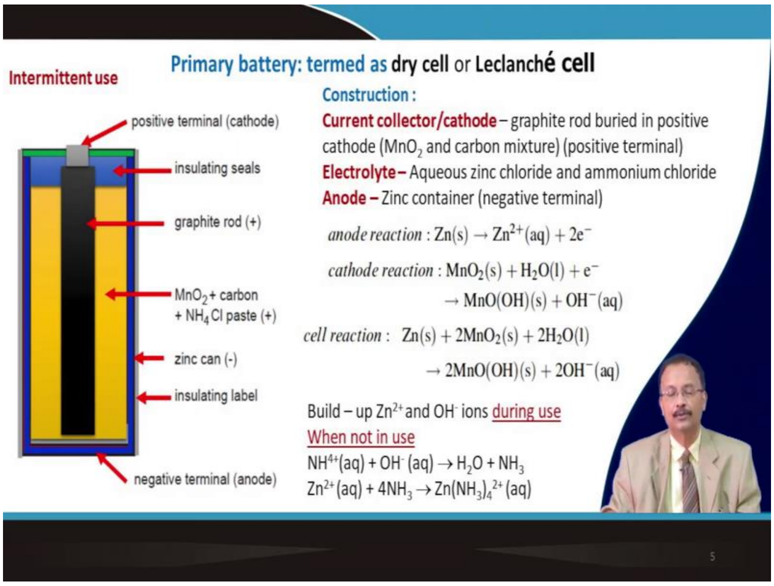

So, first let us see what is the primary battery and in my last lecture we talked about the galvanic cell. So, this is the same concept we have borrowed from this galvanic cell concept and try to understand their application area. So, these cells are termed as dry cell or sometimes they are also called Leclanche cell.

And, if you see the construction it should have a cathode material. it should have electrolyte and it should have anode. So, these two are dissimilar as I have told if it is dissimilar and there is concentration variation other than the standard state, then you will generate emf the voltage electromotive force will be generated. So, exactly you have a current collector and cathode.

In this case, the current collector is a graphite rod which is buried in a positive electrode that is cathode which is manganese oxide and manganese oxide is not electronically conducting.

So, you have to have add little bit of conducting carbon. So, that forms your positive electrode. Electrolyte is aqueous zinc chloride and ammonium chloride. They are mixed in water and form a paste and that is used as electrolyte. And, anode is the zinc container. The container itself is anode so, which is a positive electrode.

So, the anode is oxidized. So, you get electron and this electron can pass through the external circuit to do the relevant work. And, cathode reaction is this manganese oxide and electrolyte is aqueous and it is taking electron. So, it is forming this compound and hydroxyl ion which is also in this aqueous paste. So, you can add up and have the cell reaction as defined by this.

Now, the construction also you can follow based on this reaction and this construction exactly the battery looks like something similar to this, but they are all intermittent battery. You cannot use it continuously. If you use it continuously, then what will happen that zinc iron and hydroxyl ion they will the concentration will built during the use and then eventually the cell will stop working.

So, therefore, it is an intermittent application in a torch light you can use it, but you will you will not like to light the torch for elongated period. So, that is why it is intermittent. Once you stop using it then this ammonium ion is react with hydroxyl which is generated here to form ammonia and water basically NH_4OH is being generated, your zinc iron will react with this to form this compound. So, the concentration of the zinc ion will reduce.

But, as you know that the zinc is corroding so, one time it will happen it will one situation will arise when zinc will no more be corroded so, then the battery is dead. So, this battery always work in the discharge mode and there is no possibility to recharge it. So, once it is done it is it has done its duty you just throw it out.

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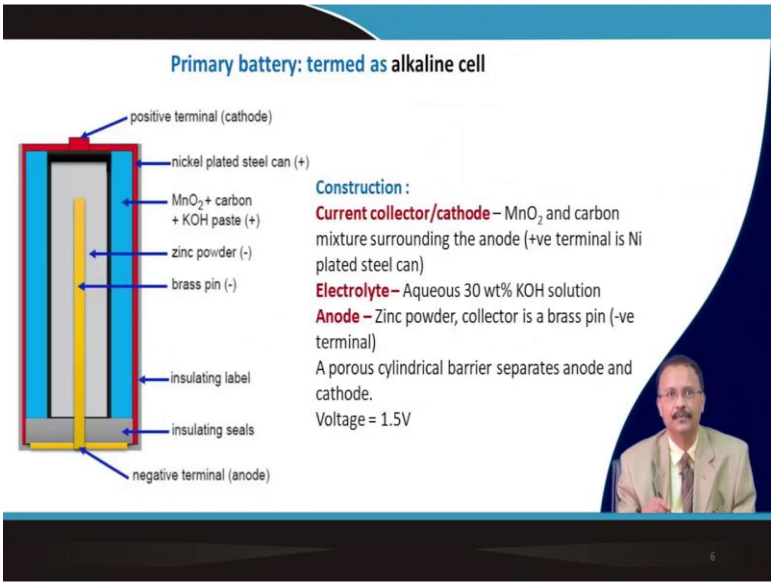

Second one is again the primary battery, but this is alkaline cell; construction is a bit different, as you can see as with respect to the last one. Current collector and cathode here it is manganese oxide and carbon mixture surrounding the anode. So, in the anode it is zinc powder and the collector is brass pin. So, here the zinc powder is in between and this brass pin this one is the current collector. So, of course, this terminal will be negative,

And, then you have manganese oxide and carbon mixture which is the same chemistry; chemistry remains same reaction is a bit different because your electrolyte is different and they are separated by a porous membrane. This black color thing is a porous membrane that separate these two. Typically you will get a emf of 1.5 volt. It is also having the same kind of problem.

And why it is called alkaline cell? Because of the electrolyte which is aqueous potassium hydroxide about 30 weight percent KOH is used in this kind of battery. So, again this is not reusable once it is completely discharged, you throw it out.

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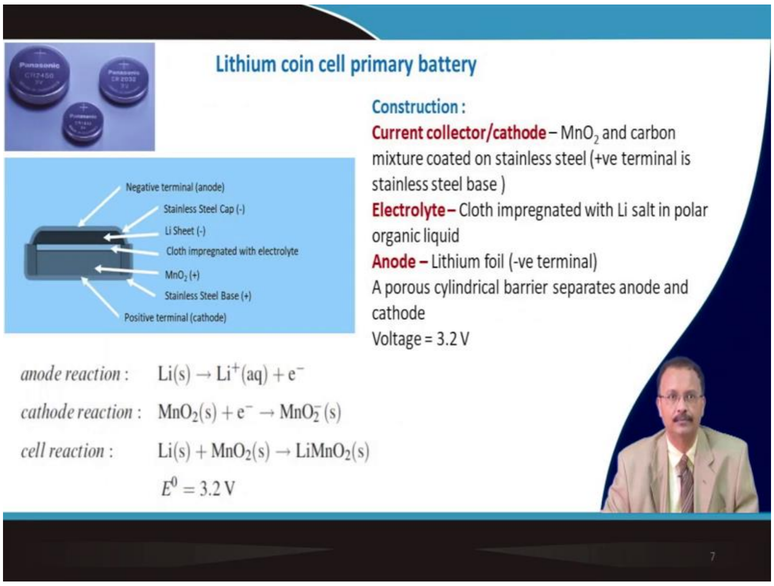

Then there have small batteries, but they are having the standard potential about 3.2 volt and it uses metallic lithium as the anode material and cathode reaction is with manganese dioxide. So, lithium reacts with this manganese oxide to form lithium manganese oxide and this material is in principle you can recycle it, but usually this is not recycled. Because it is extremely difficult to inter collect lithium inside manganese oxide once the compound is formed. It is difficult to take it out and put it back as we do in case of rechargeable battery.

So, once this is over the lithium is corroded you throw the battery out. Now, remember you cannot use aqueous electrolyte unlike the alkaline battery or the dry cell you cannot use the aqueous electrolyte. Because lithium will start to react with this aqueous electrolyte vigorously to form lithium hydroxide. So, basically this is ruled out.

So, you use a separator a separator cloth which separate the lithium with manganese oxide cathode and impregnate it with a lithium salt which is dissolved in organic solvent like EC and DEC. So, that uses that is used as electrolyte material and also in this battery you cannot use aqueous electrolyte because as you know that at such high voltage 3.2 volt you are getting your aqueous base electrolyte is not stable. So, it will also dissociate.

So, in order to avoid that, you will have to use the organic electrolyte for this kind of battery. So, positive terminal is the cathode and negative terminal is the anode material as you can understand.

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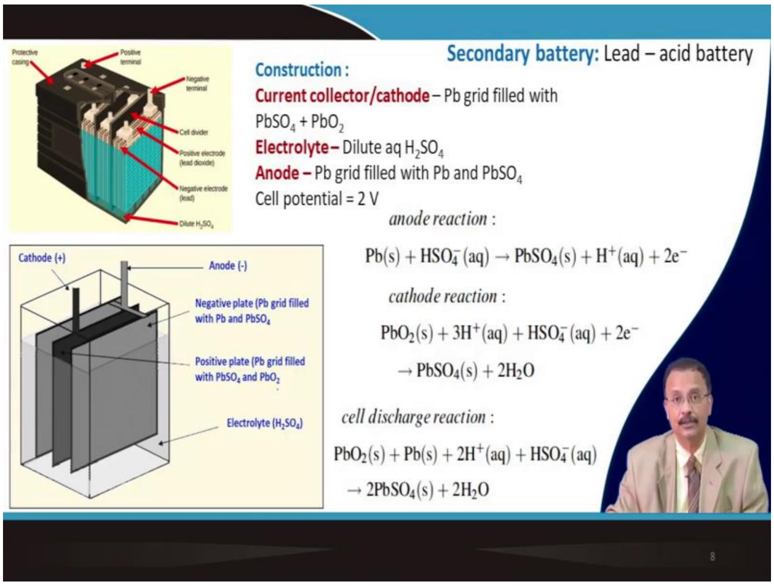

Now, this is also a very old concept in 1896 or something like that this was developed, this is lead acid battery and it is. In fact, is recyclable. And, still today we are using it in our car for lighting and power window and those kind of application, it does not have a very good power density as well as energy density because of its voltage.

The voltage you can calculate out of the Nernst equation if you know the construction of the battery and here it is a typical construction. How exactly the plates of anode and cathode they are oriented, they are organized. And, in fact, this is a one cell and then multiple cells you can connected in series and parallel to increase voltage if you add it in series and if you add it in parallel this cells you will increase the capacity.

So, that is done in a commercial lead-acid battery and the construction is shown here. So, this is a series of plates is connected like this. So, the current collector and cathode here is a lead grid which is filled with lead sulphate and lead oxide. Your electrolyte is aqueous here because the voltage is not that high. Each cell will give you around 1.2 volt. So, dilute H_2SO_4 that is used.

And, anode is again a lead grid which is filled up with basically lead and lead sulphate. Now, see the anode reaction this lead in solid form, it reacts with this an ion and form lead sulphate and hydrogen ion and you get this electron for external wall. So, it is connected to a load in a discharge mode. Cathode is lead oxide. It reacts with the H plus ion along with this and it gets reduced by taking this electron from the circuit form lead sulphate.

So, the total cell reaction you add these two up. So, the total cell reaction is something like this. Now, the thing is important here that it is reversible. Once it is completely discharged then again you put back voltage in the reverse polarity and you will again regenerate this two anode and cathode material. And that is why it is rechargeable in nature.

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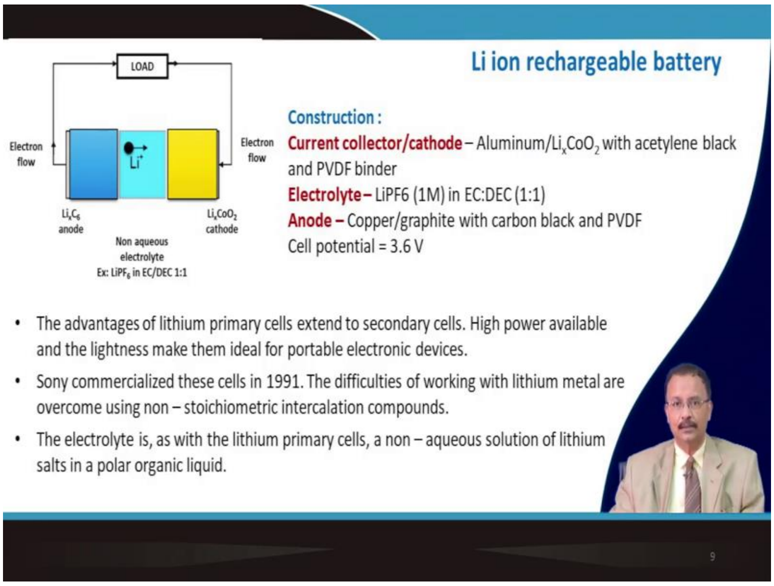

Now, the lead-acid usually they are having very small voltage about 1.2 volt you get out of one cell. So, a 12 volt battery means you will have to connect 10 such cells. So, that is why they are quite bulky. So, the idea is to increase the voltage level. So, if you increase the voltage level. If you from 1.2 volt if you can make a battery which is 3 volt or 4 volt then of course, three cells will be required for you to get 12 volts.

So, that is why people have searched different materials and here in 1990 in fact, this year last year or this year professor Goodenough he got the Nobel Prize because of the invention of the cathode material for lithium-ion battery.

For anode material also one Indian name is involved Professor Samar Basu and who was the faculty member of IIT Kharagpur in Metallurgy Department. And I was fortunate to interact with him. He was the he did pioneer work to use graphite based material as anode.

So, the construction of this battery is the current collector and cathode. So, for the current collector aluminum foil is used and a typical cathode material is lithium cobalt oxide. And this is mixed with acetylene black because as such they are not electronically conducting they are ionically conducting, but not electronically conducting.

In order to impart the electronic conductivity you need to add acetylene black with lithium cobalt oxide and you need a binder which is PVDF that is also applicable for other lithium primary battery as well. You need a binder, so that you can bind this paste on top of the aluminum current collector.

Again, the tape casting is used to make this kind of a cathode composite material. Electrolyte you cannot use aqueous. Electrolyte, but you will have to use organic electrolyte typically lithium base salt for efficient lithium ion conduction that is used LiPF6 and your solvent is EC and DS DEC in 1 is to 1 volume content. So, that is your electrolyte.

So, you can see the electrolyte is here and your cathode material is here, your current collector is here. Then anode material instead of pure lithium here we use graphite. So, that is another intercalating compound I will talk about the mechanism in a short while. And, this also is used with carbon black and PVDF to make a paste and then this is your current collector and this is your anode material and your battery is ready.

The cell potential is 3.6. How it is coming? You can have some kind of idea if you understand nonstick vision and from the electrochemical reduction potential table you can identify depending on the redox how much voltage you are expecting from this battery.

Since lithium is highly electro positive and it is intercalating in graphite, but still it is same lithium. So, the voltage and voltage of the redox of cobalt is quite large and graphite is quite low. So, you get a voltage about 3.6 volt.

So, the advantage of this primary cells are extended to the secondary cells. Because earlier in lithium and MnO_2 this combination you will have to throw the material out, you cannot reuse it and lithium is expensive metal and it is not very heavily available throughout the globe.

So, you need to recycle this part, but this is gun and you are getting the similar kind of voltage. But at the same time you can reuse this battery for your purpose and in fact, the consumer electronic application they are seeing a boom since 1990 because of the advent of this lithium-ion battery. You have good quality laptop with high energy you have a tab, you have a mobile phones and all consumer electronic applications they are due to the advent of lithium-ion rechargeable batteries.

Then Sony commercialized this cells in 1990 and as it is difficult to work with pure lithium metal. Therefore, this intercalated compound as anode that was used and the electrolyte with as you have seen with the primary lithium based material it is not aqueous, but the organic kind of thing.

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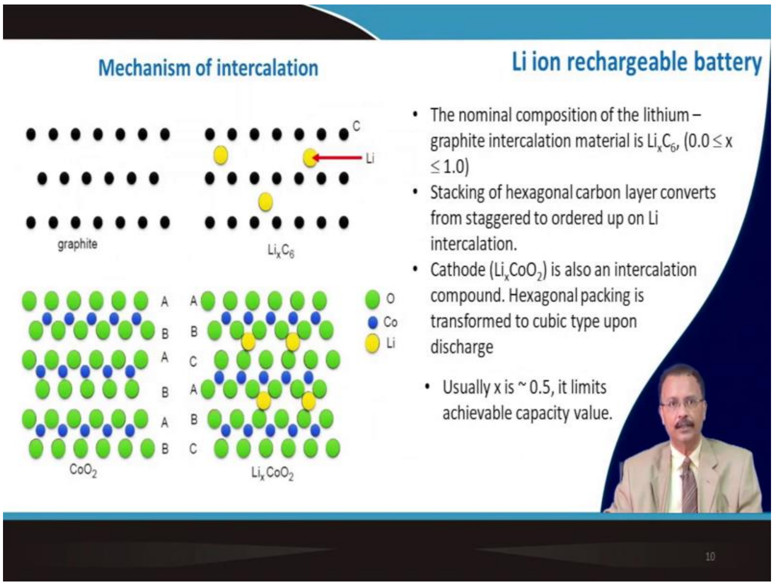

Now, what is exactly happening here? Mechanism of intro mechanism of this intercalation, so called intercalation is quite interesting. You see the lithium-cobalt oxide, here eventually if you take out all the lithium, then cobalt is a transition metal cation. It forms an octahedra with oxygen. So, it sits inside the octahedra.

So, if you take all the lithium out it is nothing, but cobalt oxide which is in their hexagonal kind of arrangement. Now, once lithium is coming you can put lithium inside the structure.

So, the bonding between lithium and cobalt oxide is not very strong. So, you apply a strong negative potential lithium will come out from the lattice right. Although it is not very good for the structure because if you take out all the lithium then the structure will collapse, but it is possible for you to take this lithium out from the structure and put it in.

So, if you have a layer structure we call this is a intercalating compound where you can easily take out the lithium and put it back. So, lithium-cobalt oxide is one such intercalating compound. So, whenever it is in the form of lithiated cobalt oxide, then the structure is ABC; ABC type that is cubic and when you take out the lithium it is a hexagonal structure.

So, there is a structural change that is taking place while you take out and put back lithium which is not really good in some instances particularly for lithium-cobalt oxide it is not a good material. So, although Sony started with that they have shifted with other materials for example, spinel based materials, polyanion base material they are used for cathode materials.

For the anode also we are using graphite which is having a staggered structure as you can see here, but it also can take lithium and once it takes lithium it becomes more organized. So, it is some kind of order disorder kind of transition that takes place upon intercalation. So, the nominal composition the lithium that you can take out from lithium cobalt oxide that is your starting point.

So, when you are taking out the lithium then we call that you are charging the battery and it is going inside the graphitic layer and when you are discharging the battery, you are taking the lithium out from the graphite layer and put it back in the lithium cobalt oxide. So, the composition of lithium cobalt oxide and the graphite it continuously change during charging and discharging.

And, structural change also takes place. As you can see graphite was initially staggered and then it is becoming ordered with lithium intercalation and cobalt oxide although it is not possible for you to take all lithium because then the structure will collapse, this is not a very stable structure.

If something happens to cobalt oxide, all the lithium if you take a take it out then the whole structure will collapse. So, that is not a good idea. So, about 5 mole percent 0.5 mole percent lithium you can take out from this structure.

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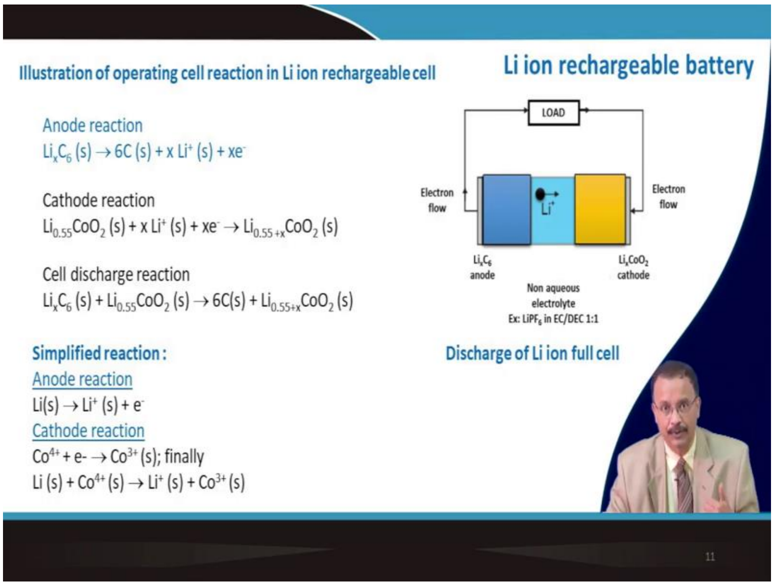

So, these are the equation that I was talking about. So, this is getting oxidized, it is giving electron to the load and the cobalt oxide is basically reduced for this. So, the simplified relation is lithium is getting oxidized and cobalt 3 plus sorry 4 plus is taking electron to have this reduced product. So, this is the actual cell react reaction during the discharge of the battery. So, when lithium is coming back from the graphite layer.

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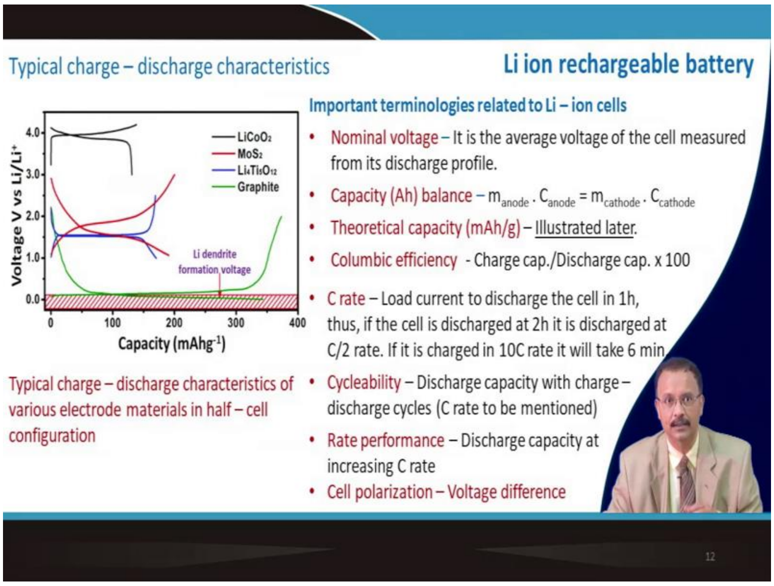

So, if you see the voltage profile of various material is lithium cobalt oxide is not only the material. But if you see all types of material, their graphite is having the potential in this range it is the charge and discharge profile. Lithium titanium oxide is having a very flat profile like this. Then you have molybdenum disulphide this is also giving design charge discharge part and finally, lithium cobalt oxide their voltage is quite high, the 4 volt range. So, that is why this is selected in half cell configuration as well as making the full cell.

Now, you can define a nominal voltage. This is the average voltage of the cell which is undergoing during discharge. So, the capacity I will be coming how to calculate this capacity. So, capacity calculation you need to understand, but the capacity of both anode and cathode should same. So, we call it is a mass balance. So, mass balance is required to make capacity of both anode and cathode in the same scale.

We can calculate the theoretical capacity based on the composition of the material. So, I will illustrate it. Then you have a columbic efficiency the charge capacity and discharge capacity. If they are same, then we call it is a 100 percent columbic efficiency. Then another thing which is very important is the C rate. So, C rate is basically it tells you that in 1 hour the whole discharge is complete.

So, if you discharge it in 2 rate 2 hours then recall that you have discharge as C by 2 rate; if you discharge it at 3 hours accordingly your C rate will change. So, for charging and discharging C rate is very important. Then repeated time you do charge and discharge of this kind of battery then you will see its capacity fades out. So, we call this is a cycleability characteristics of this battery.

Rate performance is defined that if you charge and discharge at different rates progressively higher rates, then you will see that the performance also deteriorates. There are distinct mechanism behind it. So, that is called rate performance.

And, the cell polarization is the difference in voltage between charge and discharge, you see that this cell this particular cell they are polarized because of the internal resistance inside the cell, but as compared to that this lithium titanium oxide is not that much polarized.

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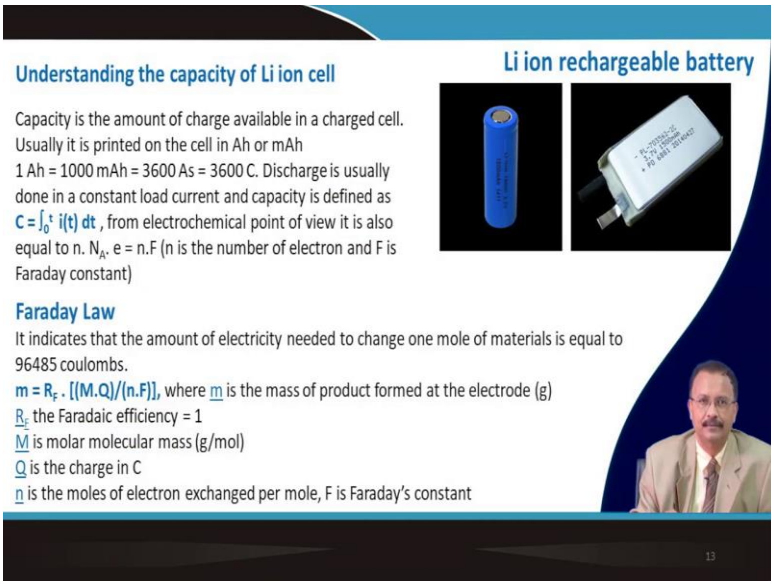

So, you need to understand the capacity of this battery. Usually the batteries are in the form of a cylinder we call this is a cylindrical cell or in the form of a pouch we call this is a pouch cell. And, on top of the cells you see the capacity of the cell as well as the nominal voltage of the cell.

So, here for example, 1500 mili ampere hour that is written along with 3.6 volt; that means, you will get 3.6 volt and you have a capacity about 1500 mili ampere hour. So, the capacity is nothing, but charge right. So, the C is the integration of your profile i t, i as a function of t and if it is galvanostatic, then it is easy because your i is same.

So, you can easily calculate the capacity. So, calculation of the capacity is based on the Faraday law. So, it indicates that the amount of electricity that is needed to change one mole of materials is equal to a certain number 96485 coulomb. And based on that you can have the mass of the product form at the electrode is nothing, but Faradic efficiency which I consider 1.

And molar content molar mass which is in grams per mole and Q is the charge, n is the number of electron that is participating in this reaction and F is Faraday constant.

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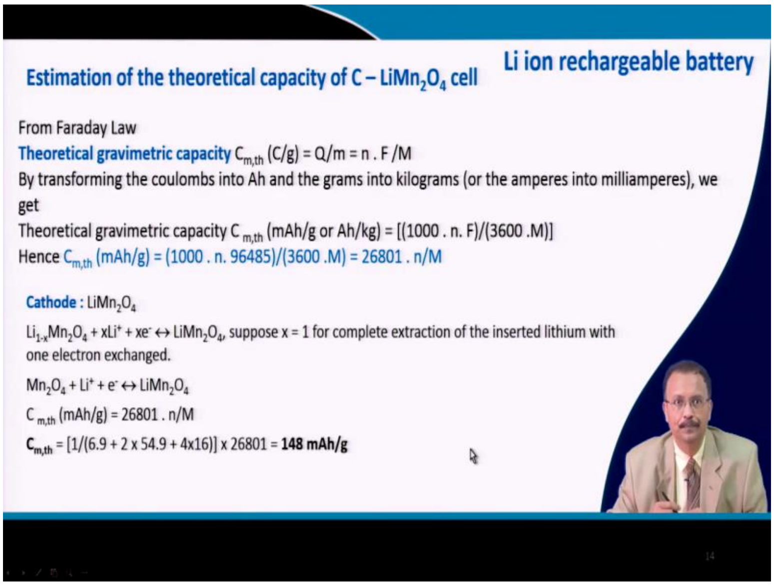

So, if you use this Faraday law then the theoretical capacity this is just you calculate that the m is going in the other side. So, Q by m is the capacity and it is specific capacity, capacity per unit mass this is nothing, but n into F by M. So, then you can just tell that theoretical gravimetric capacity if you calculate in mili ampere hour per gram or ampere hour per kg.

Then you have this factor 1000 into n into F divided by for time this is in hour 3600 into capital M. So, you just work it out and you will get a simple formula 26801 into number of electron and the molar mass of the electrode material that you are talking about.

So, let us consider lithium manganese oxide that is one of the cathode material and you know the reaction is here. So, it is in the discharge state. So, it is taking lithium and eventually you calculate the theoretical capacity 26801 into n into M.

So, here only one electron is getting changed the if I consider the one mole of lithium is going inside the lattice. Then theoretical capacity is coming about 148 mili ampere hour per gram.

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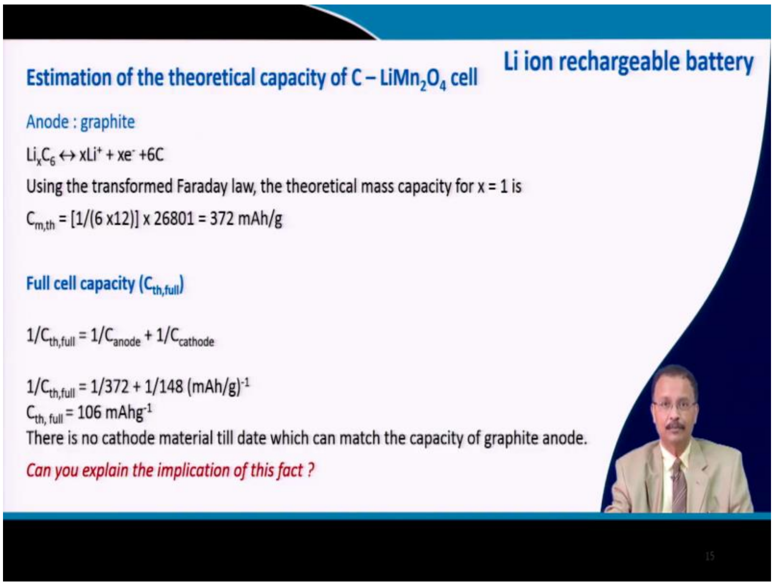

Similarly, you can do for anode material which is graphitic writing this relation and here this is the front part 1 by 6 into 12; 12 is a atomic weight and this factor that will give you 372 mili ampere hour per gram. So, in anode and cathode you are having so, during discharge lithium is going inside the cathode material, right. So, it is getting discharged.

But, at the same time this one the anode is getting charged because your lithium is going out from the lattice. So, one is discharge another one is charged and the total thing the total capacity is two capacitor connected in series. So, you put the respective capacity and you will get in the full cell about 106 mili ampere hour per gram.

Now, you can understand that why it is important to develop good quality cathode material because graphite already is giving you a capacity around 372 mili ampere hour per gram and there is no cathode material which can balance that particular capacity. So, I told that mass balance is required to have the same kind of charge in both the anode and cathode material.

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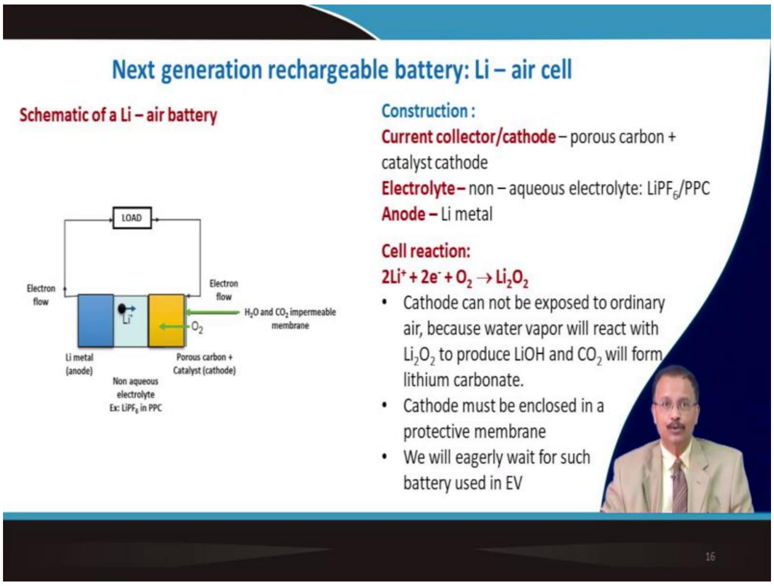

So, it is very important for us to develop a good quality cathode material which is having higher capacity than your anode material. And, voltage and capacity if you increase Q and V both are increased; that means, you are increasing the energy of the battery. So, that is in a brief about lithium-ion battery.

But, in next generation lithium air battery is coming out. So, the construction is pretty straight forward you have a porous carbon. And some kind of catalyst here, but actually it is taking oxygen from the positive electrode site and pure lithium metal is used and here the electrolyte is a non-aqueous electrolyte which we use for lithium ion battery.

The cell reaction is pretty straight forward lithium is reacting with oxygen to form Li 2 O 2 and again it is dissociated in the form of lithium and it breathe out oxygen. But, there are challenges this is very good because you know that oxygen is pretty electronegative lithium is pretty electro positive. So, get good quality of voltage around 4 volt it is a very simple chemistry.

But, cathode cannot be exposed to ordinary air because what will happen carbon dioxide and moisture will start reacting with your lithium to form lithium hydroxide and lithium carbonate which is very very detrimental for the cell life. So, therefore, you need to protect your cathode. It must be enclosed with a protective membrane that will allow only oxygen to pass, but not this external gases.

And, we will really waiting we will be waiting for this battery because this is the ultimate battery. Lithium is very lightweight oxygen is plenty in the ambient. So, in future who knows maybe electric car will be driven by lithium air battery.

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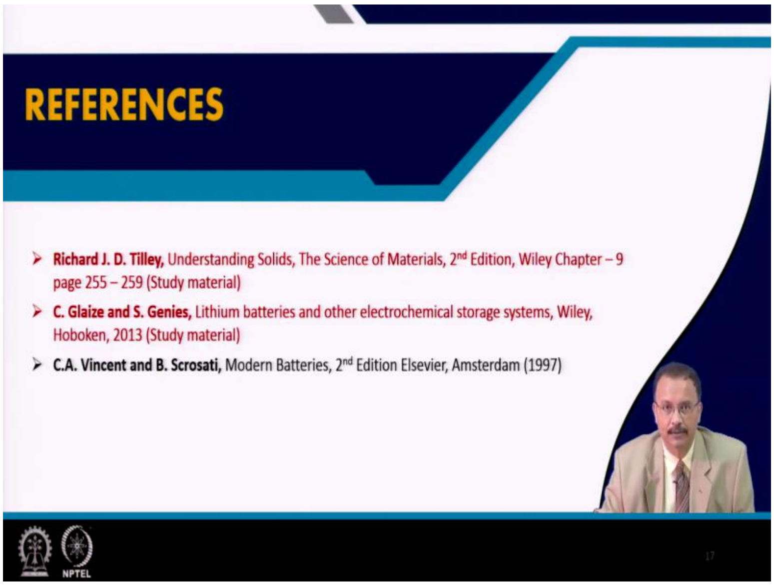

So, the study material is a book by Richard Tilley and also a very good comprehensive book on Lithium-ion battery by Glaize and Genies and also Vincent and Scrosati this particular book on Modern Batteries that is very relevant for the coarse material particularly rechargeable battery is concerned.

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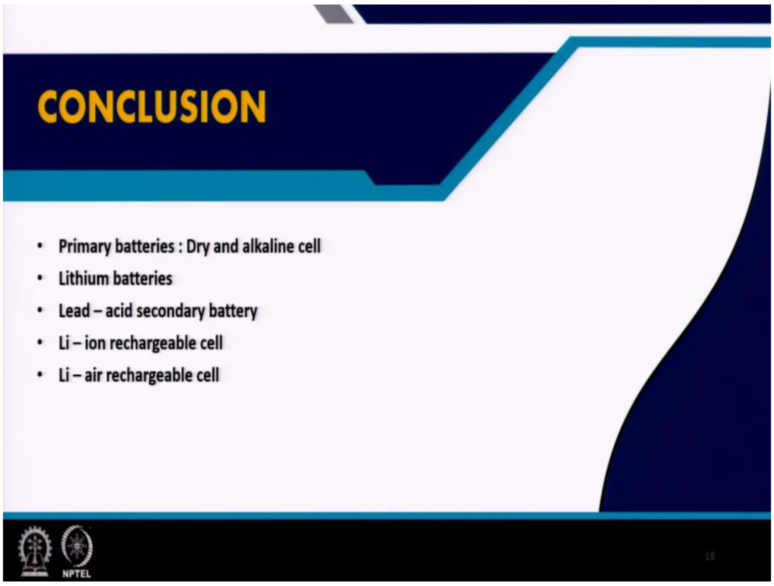

So, we talked about primary batteries dry and alkaline cell, then we talked about primary lithium battery, then we introduce the concept of the secondary battery which is rechargeable one in the form of lead-acid battery, then we will talk about lithium-ion battery understood the various battery terminology and mechanism of intercalation and how to calculate the theoretical capacity and finally, futuristic battery lithium air rechargeable battery is introduced in the course.

Thank you for your attention.