Physics of Renewable Energy Systems
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Lecture 26
Cathode Materials for Li-ion batteries

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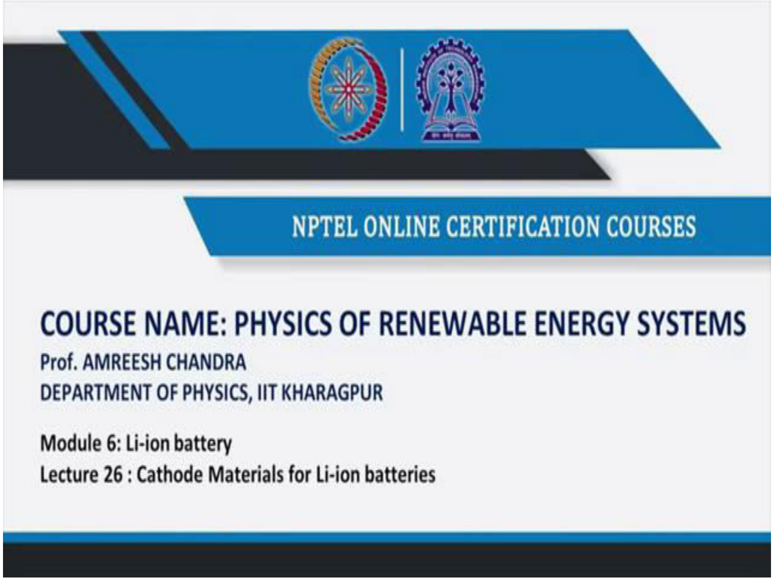

Hello! Let us start the third lecture on lithium-ion batteries. In today's lecture we will talk to you about the cathode materials which are routinely used to fabricate lithium-ion batteries.

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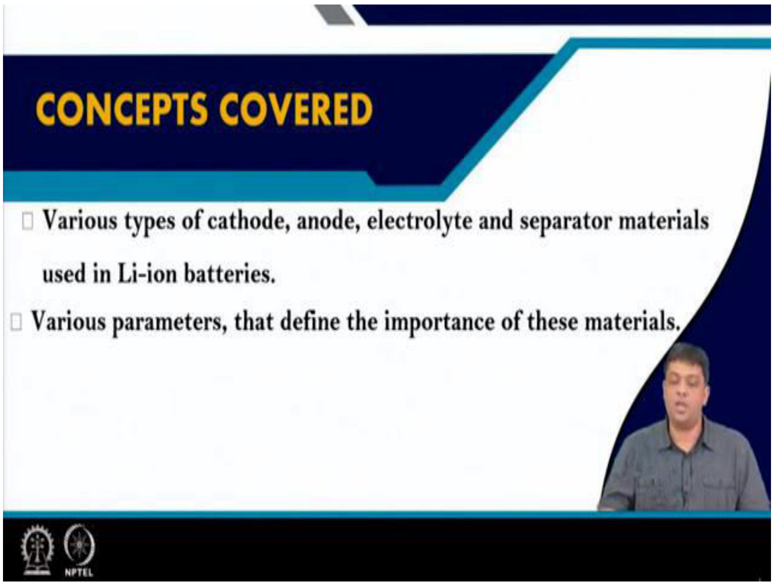

And in today's lecture you will see that there are various types of cathode materials which are used. There are various types of proposed cathode materials which may become useful for future technologies and improved lithium-ion batteries. There are also different types of anode, electrolyte, separator, binder and conductive agents, which are required to fabricate lithium-ion batteries. Each of these materials are associated with various parameters and only after you have optimized these parameters you will see that a high performance lithium-ion battery can be obtained.

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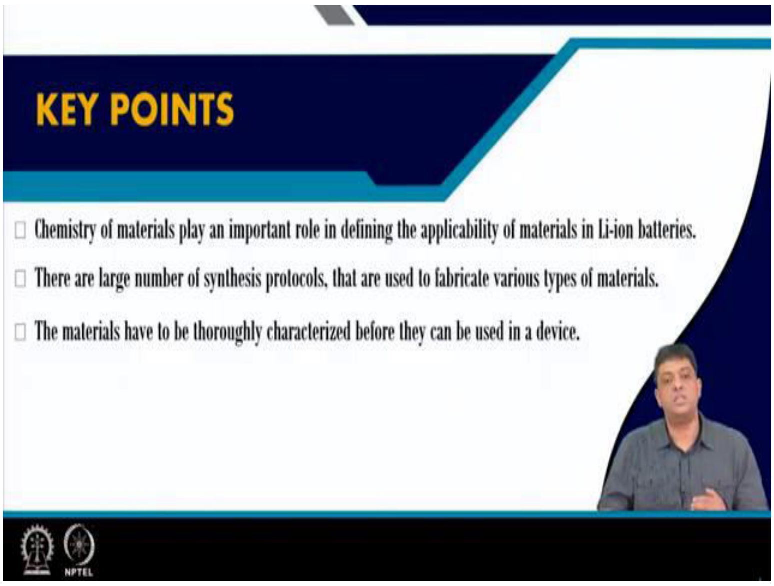

So, as it is said if you want to do good physics get the chemistry right, especially the chemistry of materials and the development of lithium-ion batteries has been directly linked with the development of materials which are used to primarily make cathodes. And then now the research focus is moving towards the development of anode materials, because high performance cathode materials have been discovered and are now available for large scale use.

So, you must make the materials very carefully then only you will be able to develop high performance batteries. The moment I say that you should develop or fabricate these materials I am indicating that out of the various synthesis protocols which you may have heard or you may have been using you have to choose the right synthesis protocol, which would give you a material with desired parameters. What are the desired parameters? Would become clear by the time we finish this lecture and that would be one of the major key points you will take back after listening to this lecture.

Even if you have made the materials, it is absolutely essential that those materials are characterized using large number of experimental techniques, so that you understand the physical as well as chemical properties of these materials before you start understanding their electrochemical performance that is relevant for lithium-ion batteries.

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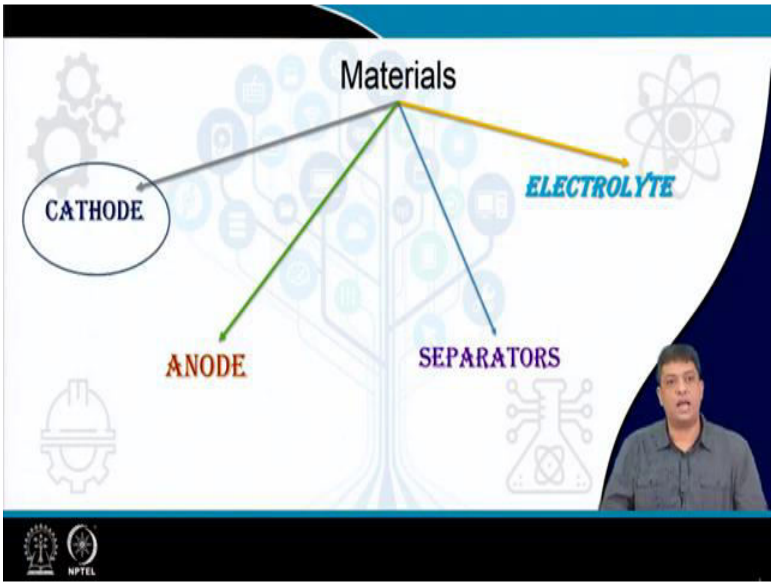

In the previous lecture, we saw that a battery is made up of different components. What were the major ones? You had a cathode, you had an anode, you had a separator in the middle which was separating cathode and anode that means it was preventing any short circuit between the two electrodes and you had an electrolyte which was facilitating the motion of lithium-ions from the cathode to the anode side during charging and during discharge from the anode side to the cathode material back. So, these are the major components which are actually going to be used while you fabricate these batteries.

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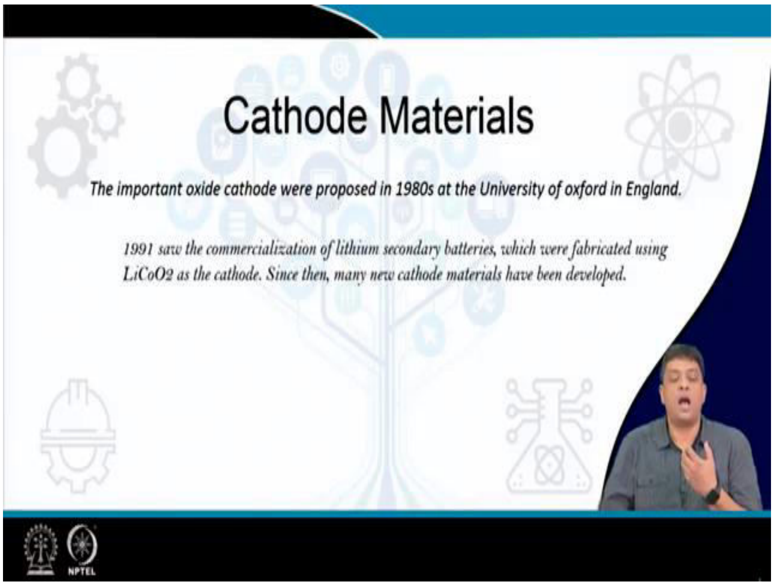

And in today's class let us focus on cathode materials. Cathode materials actually the most important cathode material, which was used in the commercialized battery that came into market in 1990s, early 1990s was lithium cobalt oxide, but since then you have seen that the battery technology has moved on. Moved on means what? You are routinely getting batteries which are available for commercial use but their performance is getting enhanced.

How is the performance getting enhanced? It means that you are using different materials to fabricate the batteries, and the major component or the major material which plays the role in improving the efficiencies and the battery characteristics is the cathode material and there are large number of cathode materials that have been discovered since the discovery of lithium cobalt oxide and the research is still going on to develop even newer materials with very very novel architectures, so that they can give even higher performing batteries.

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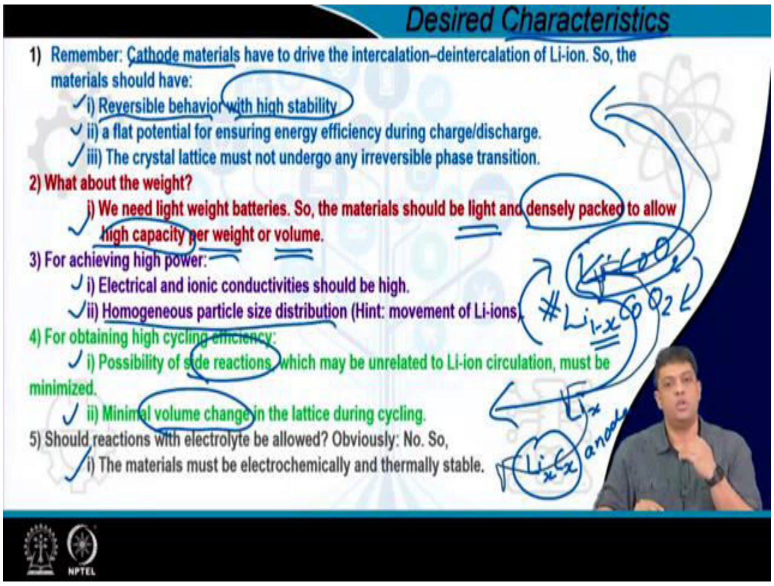

If I say the cathode materials, what should be the characteristics of these cathode materials is the first question which comes to my mind, if I am told please choose a suitable cathode material to make a lithium-ion battery. What have I learned earlier? I have learned that the cathode materials will do what they will deliver lithium-ion while the battery is charged that means lithium-ion will leave the lattice of these cathode materials, travel through the separator using the electrolyte medium, and then they will intercalate into the lattice of anode, which you will see are layered structures and they will get stored there.

This is charging and the reverse happens during the discharging process when you are taking the current out of the battery. So, lithium going in to the anode and then lithium coming back from the anode to the cathode side means what? You should have a material which has a reversible behavior for allowing the lithium-ion to leave its lattice and also accept the lithium-ion back into the lattice and maintain the lattice structure.

It should not degrade during this process. So, you must have a reversible behavior with high stability. Now if I am charging or discharging the potential should be such that it is a flat potential which will ensure the efficiency during charging or discharging process. Now you see when I take an ion out. Let us say from lithium cobalt oxide I have, I am taking an ion out, so what is left?

I am left with 1 minus x cobalt 2, where x, lithium x is going, is leaving the structure of lithium cobalt oxide and it is forming a complex which is something like lithium carbon complex in the anode, this is happening in the anode. Obviously, lithium cobalt oxide is not equivalent to lithium 1 minus x cobalt oxide. There is a new phase which seems to be forming, but what is the structure which you should obtain is lithium cobalt oxide.

Hence when you extract lithium, and at that moment any the phase transition should not be irreversible means when I get back lithium into the cathode we should again get back what we should get lithium cobalt oxide. So, lithium cobalt oxide going to lithium 1 minus x cobalt O2 during charging and during discharging I should get back the material that is what you mean by irreversible transition should not take place.

Now, do you want a battery which is very heavy? Then your mobile phones will become very very heavy, your wearable technologies will become very heavy, your laptops will become very heavy. So, obviously you are looking for batteries with reduced weight. What is the major component in battery?

You have the cathode. So, we should also have materials which are light, they should be densely packed they are light but densely packed, so that in a small volumetric condition you are able to pack enough material so that you are able to obtain high capacity per weight or per volume.

So, your volumetric densities should be high so that you are able to reduce the weight. Now what will happen in terms of power? To achieve high power, you should have electrical and ionic conductivities which should be high, ionic conductivities of the lithium-ion moving in and out of a lattice, so the conductivity of the lithium should also be high and because you are getting electron back into the lattice, when you are discharging the battery during the flow of lithium from anode to cathode that is a discharge cycle then you should also be able to collect back the electrons.

And then you will have the positive ion and the negative charge combining and leading to a charged neutral condition. Hence both electrical and ionic conductivities should be reasonably high. Now if I have particles which are forming the material, so if you take let us say a brick and a pebble. Then the surface area of a brick and a pebble are very different and therefore, the chemical reactions which will take place at the interface of let us say an electrolyte which is near to a brick or to a pebble will be very different.

What would you say to have homogeneous reaction kinetics or reaction behavior throughout the electrode surface you please choose materials which are having particles of similar shapes, dimension and size. And that is what it means that you should have homogeneous particle size distribution. Now you say you want to have a battery which can be cycled for 1000 times.

For having high cycling efficiency what should be avoided there should not be any side reactions which take place, and these side reactions are nothing to do with lithium but there are reactions taking place in the material itself or at the the solid electrolyte interfaces which are of different nature, and that will lead to the loss in cycling stability because the material will undergo phase change and the overall physical or chemical response will also change.

Now, you would also like to have a material which shows minimal volume change in the lattice during cycling. Volume change can occur because of the change in temperature or because of the appearance of vacant space when lithium is taken out of the structure. Then it appears to be a vacancy and vacancy induced that can lead to some volume change, but you should try to have a material which do not undergo volume change during the cycling process.

If I ask you a very simple question, you have an electrolyte which is going to transfer lithium-ion across the separator and deposit them to the anode. Should the cathode react with the electrolyte? Very simple answer everybody will say no, make sure that the electrode is such that it is not reacting with the electrolyte and it is also thermally stable.

That is the points which are written on this slide but then one may look into these points and say for achieving high power why do not you write this point that the side reactions should be avoided then only the conductivities and electrical conductivities will be high otherwise the structure will change and you will form a material which has less performance or lowered performance in the previous case.

And that is exactly what it is, I have just listed these points it does not mean that they are independent of each other. You can see that all these points which are mentioned, which are mentioned can be put at any other heading, under any other heading whichever you like, so they are also related. So, if you change the reversible behavior then your capacity to obtain cycling efficiency will also be lost.

If you increase the weight of the material then your capacity to avoid any kind of volume expansion may also be reduced, so they are all related phenomenas you can write under different headings as per as your understanding but be very clear in which point you want to write these different points and then explain it to anybody who wants to learn from you.

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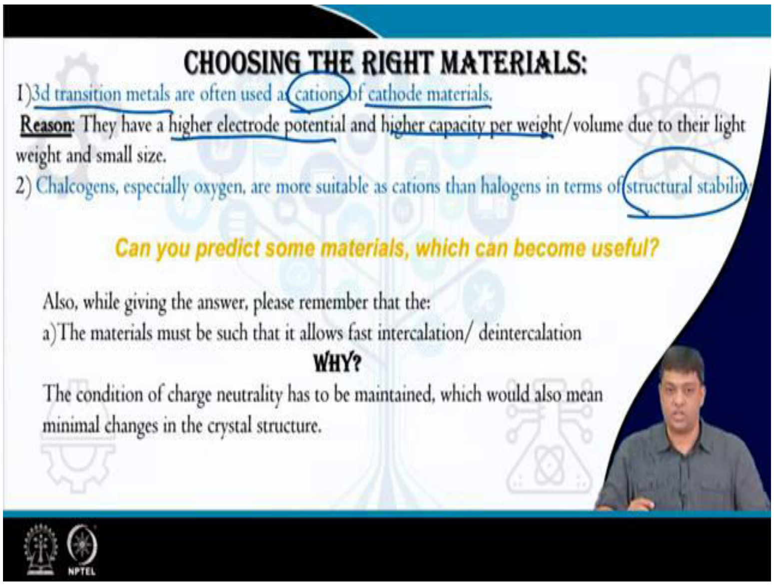

Now, we have got an idea that there are various parameters, which define the cathode materials. So, how do we choose the right materials? It is the 3D transition metals that are often used as cations of cathode materials, why? Because they have higher electrode potential and also higher capacity per weight or higher capacity per volume due to their lighter weight and smaller size.

Along with that to obtain structural stability chalcogens like oxygen have been used as suitable candidates to support the transition metals. Now the moment I tell you there is a transition metal, there is oxygen. Can you predict some materials which can be useful or can you get an idea about the materials which we are talking about oxygen. Are we actually talking about certain transition metal which are 3D transition metal type oxides, when you are having oxygen also you call them oxides.

So, are we moving towards the prediction or choice of material which are 3D transition metal based oxides? Also while you are thinking and giving an answer to this question you should also remember that the material must be such that it allows fast intercalation or de-intercalation during discharging or charging. intercalation means back into the lattice that happens when that is the discharging cycle of a battery.

De-intercalation, it is the extraction of the lithium that is happening during the charging cycle of the battery, because we are talking about the cathode materials please remember, and it should also be such that it has reasonable electronic conductivity because when you either take the lithium out or allow the lithium back into the lattice it should also be able to transfer electrons, so that the overall charge neutrality condition is stable and established within the crystal structure.

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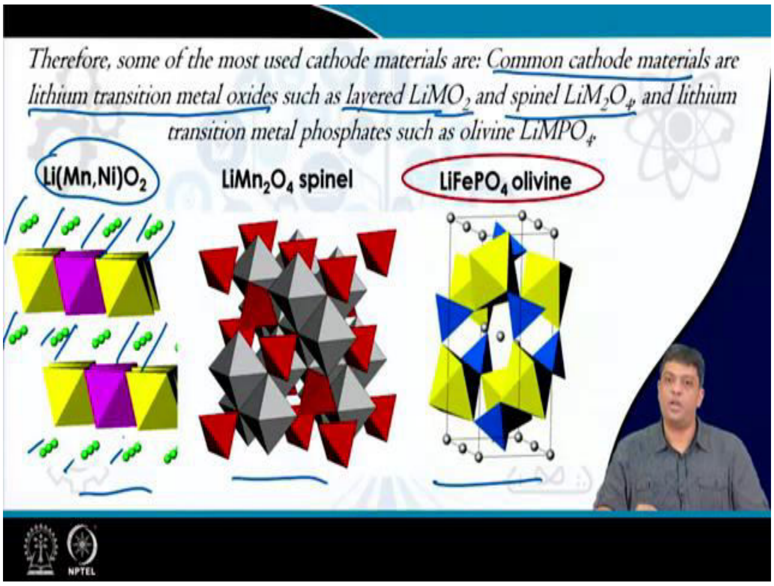

And that is the reason why most of the common cathode materials are lithium transition metal oxides. That is the main reason. Starting from let us say lithium cobalt oxides many other structures have been obtained. They are lithium metal oxides transition metal oxide or spinal type lithium metal oxides. For example, you have obtained lithium nickel oxide or spinal type lithium manganese oxides.

Each of them have their own advantages and disadvantages so to combine the advantages of more than one metal, transition metal there are complex structures which are being tried so you can have lithium manganese nickel oxide, which actually combines the advantages of lithium manganese oxide and lithium nickel oxide and tries to limit their detrimental factors.

Along with this over the last few decades there have been an advent of olivine structures which have actually contributed in the fast development of this technology and they are called as lithium-ion phosphate type structures. Now if you look into these structures you can clearly see that if I am indicating the occurrence of lithium in at the cube or the edges of this structure then you can clearly see that you have different channels from which lithium-ions are going to come out or enter back into the lattice and the shape and the size and the forms of the channels are different.

Hence if the channels are different, so the flow would be different, the diffusion would be different and that would lead to different deintercalation and intercalation processes and hence their usefulness would be of different orders and that is why different types of materials are obtained, they are characterized so that you are always trying to improve about the performance of the materials to get higher performing battery.

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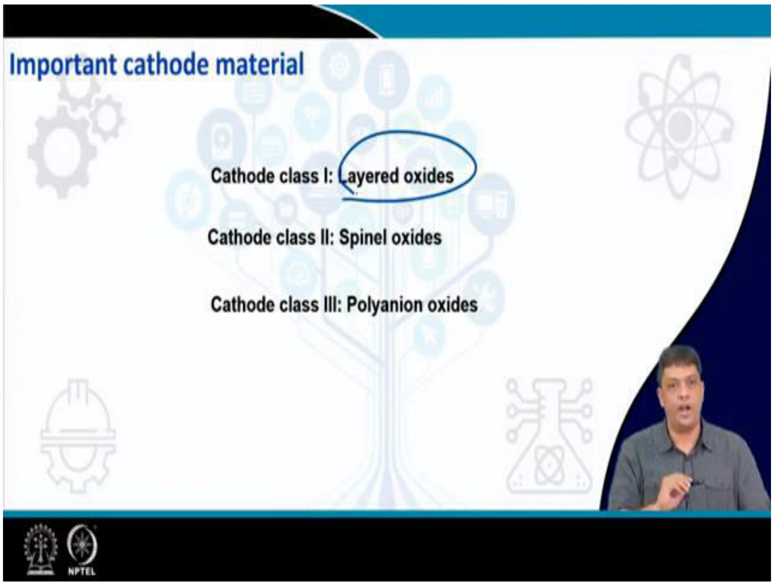

As you saw, you have layered oxide, spinel oxides or polyanione oxides.

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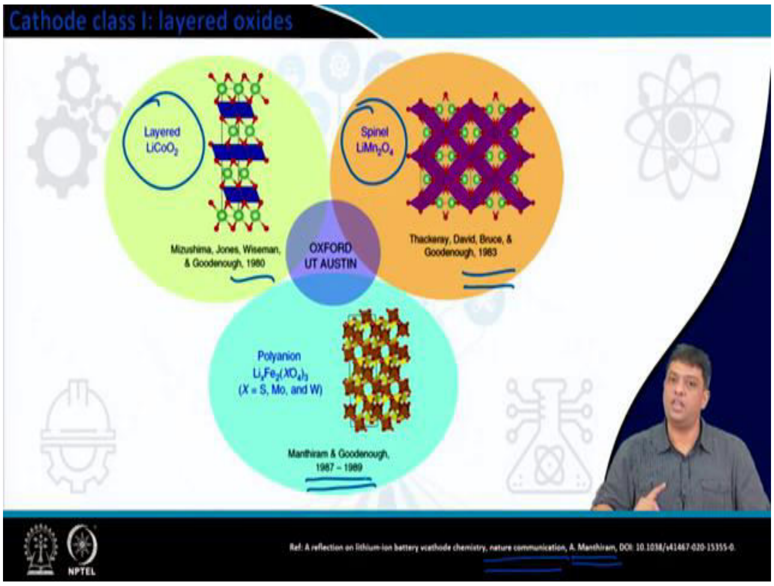

And if you see to this paper which was published in nature communication by the team of manthiram then you will see that the, this picture clearly shows what has happened in the lithium battery cathode technology. So, we started with somewhere lithium cobalt oxide then we have also been working on lithium manganese oxides, 1980-1983 and then came the discovery of polyanion based lithium structures in 87 to 89.

For the massive contribution on these kinds of structures, we saw in the previous slide that professor Goodenough was given the Nobel Prize, because the understanding and synthesis and characterization of these materials were very critical for the advancement of lithium-ion based secondary batteries.

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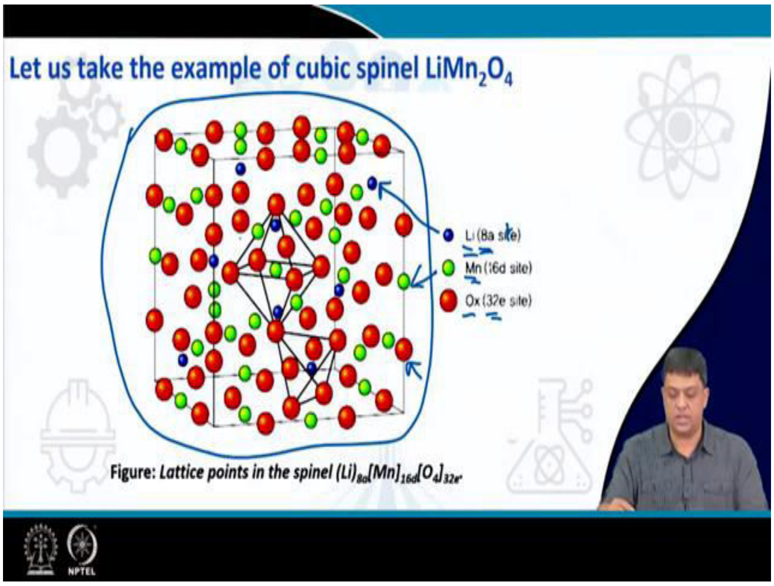

So, let us take an example of a cubic spinel lithium manganese oxide. This is an example I am taking just to explain what all steps in are involved. So, you have a cubic structure where lithium are occupy the 8a wyckoff positions, Mn is at 16d and oxygen are at the 32e wyckoff positions. And you have an arrangement of this nature in this cubic structure of oxygen, manganese and lithium-ions. So, you get a cubic structure something of this type and then you can draw the unit cells.

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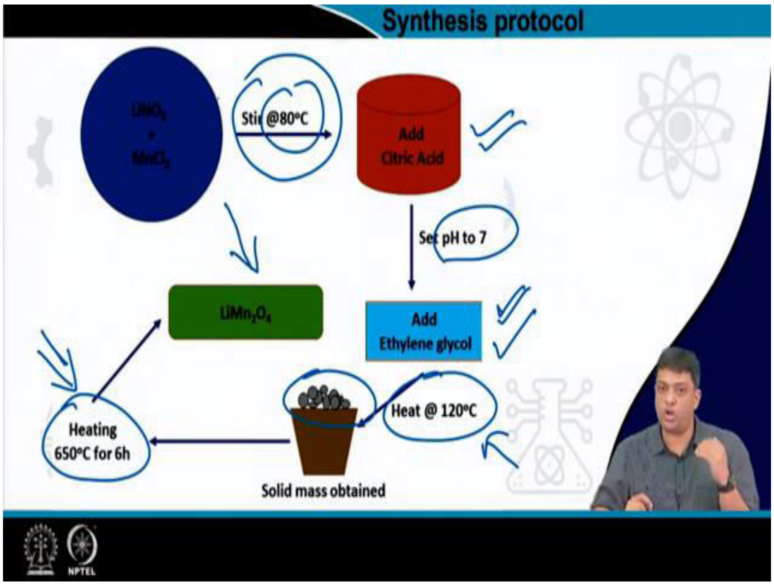

How do you synthesize these materials? For example, let us take lithium nitrate and manganese chloride as the raw materials you mix them and heat at 80 degrees then you use citric acid as the fuel, maintain a pH of 7, add Ethylene glycol, heat again, you will obtain a solid mass. Then calcine these materials for 6 hours, and the material which you will then obtain is $LiMn_2O_4$.

If I ask you just without going any step further, how can you make lithium manganese oxides with different shapes, different size, and different densities? Then you will say okay, what are the parameters I can change? I can change the fuel, I can change the temperature at which the reaction will be initiated, I can change the calcination temperatures or I can again change the temperature at which the complex section is taking place.

So, there are various parameters right from the concentration to calcination temperature which can be varied to obtain a material and that is what different teams and different researchers or different industries do they develop materials with different protocols and the properties of these materials are slightly different from each other and then they choose the best performing material.

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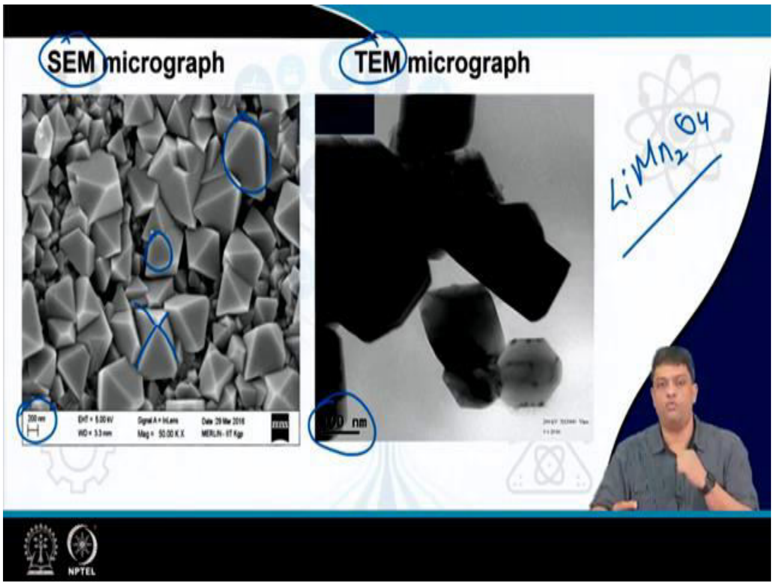

Once you have obtained the material, you look into the structure or the morphologies, because that is what is going to play a critical role. For example, SEM stands for Scanning Electron Microscope and sometimes you call it Scanning Electron Microscopy, if you are looking into the picture. The instrument is Scanning Electron Microscope, and the figure which you see or the graph if you say then you will say the Scanning Electron Microscopy was performed and the SEM micrograph is shown.

So, the technique and how then you talk in terms of explaining the data? You can clearly see we have obtained these are the particles of lithium, manganese 2 oxide. On the right hand side, we have the transmission electron microscope data and the microscopic picture is shown here. You can see that the materials are in the range of 200 to 300 nanometers and from the surface if you just see the back scattered mode of the scanning electron micrograph then you see that the distribution of the particles are quite uniform.

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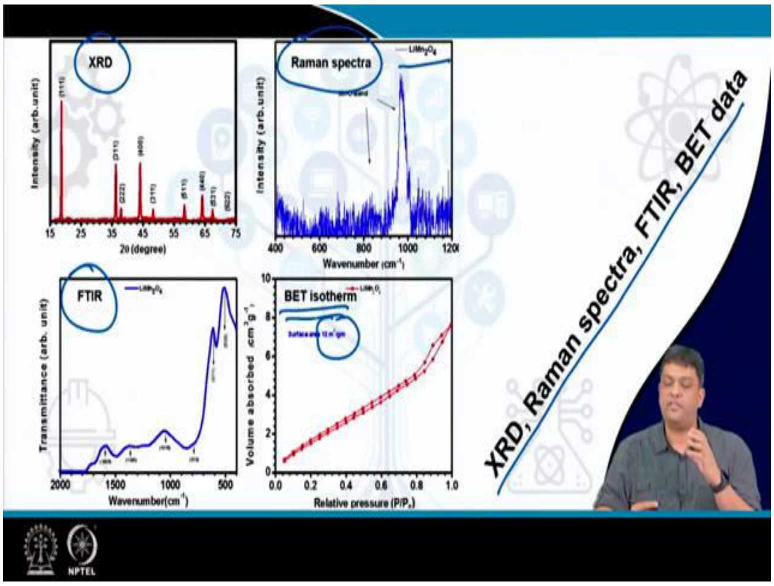

But before I can take this material for the use in a battery, I must find out whether the material has actually formed or not. The common techniques which are used to obtain the data about the structure, about the lattice, about the phase, the phase purity and the unit cell parameters are X-ray diffraction, the Raman Spectroscopy and Fourier Transform Infrared Spectroscopy.

And this is what is performed and then you can interpret the data whether you have the ions occupying the the desired wykeoff positions or not. And if they are having the desired occupancies then you have the associated bonds and the bond lengths and then you can get information about the bonds and their nature from Raman and FTIR Spectroscopy.

And if they are corroborating your X-ray data then you can claim that yes, I have a material which is $LiMn_2O_4$. The details about all these techniques, because these are the routine techniques which are used in these devices will be given to you in week 11 and 12. We will have dedicated lectures to explain each of these data and how to collect the data and also how to interpret the data will be given to you in week 11 and 12.

And the next thing which we saw was the surface area plays the role. Hence, the BET analysis was also obtained and this surface area obtained was something of the order of 12 meter square per gram. To a layman how do I explain? If I have to explain that if I arrange one particle of these $LiMn_2O_4$ and on a surface then one gram of this material would be able to cover 12 meter square area.

But it does not happen in reality, why, because the materials coalesce or agglomerate and then you have bunching and then particles come together and you do you are not getting individual particles they are all forming a global rates and becoming bigger particles. And so you do not have single particles for distributing over the surface, but effectively this is what it means if you have to explain to somebody.

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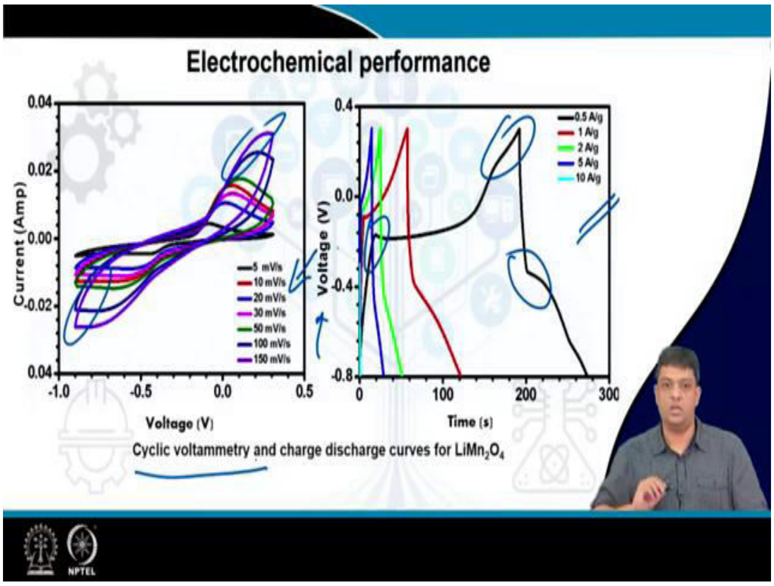

Once I have obtained these materials then you perform these electrochemical measurements, specifically the cyclic voltmetry where you measure the change in current as a function of voltage and or the charge discharge cycle where you measure the change in voltage as a function of time with varying current densities or in cyclic voltammetry, you have the change as a function of changing scan rates.

And then you can get information about the electrochemical reactions which are taking place and what is the maximum specific capacity I can obtain from these materials. Again, electrochemical performance is critical new information which I should have about the material and therefore the details about these measurements need one or two dedicated lectures which would be given in the final week of this course.

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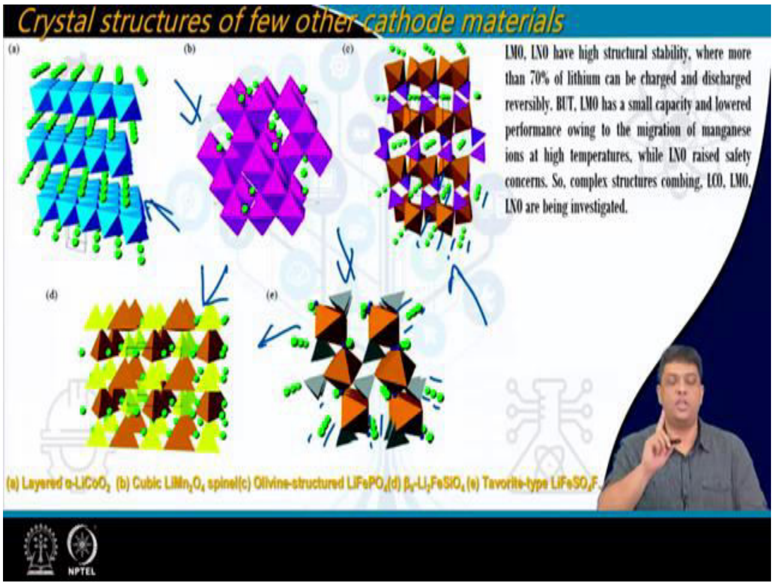

Similarly, you can see that there are various other types of materials which have been formed and you can now see if I draw the, a unit cell or based crystal lattice then you can see that the channels through which the lithium is coming out of these structures are different, the natures are different and hence their performance are also quite different. This is what I meant when I said earlier that the channel is different and hence the performance will be different and I hope that things would be clear by now.

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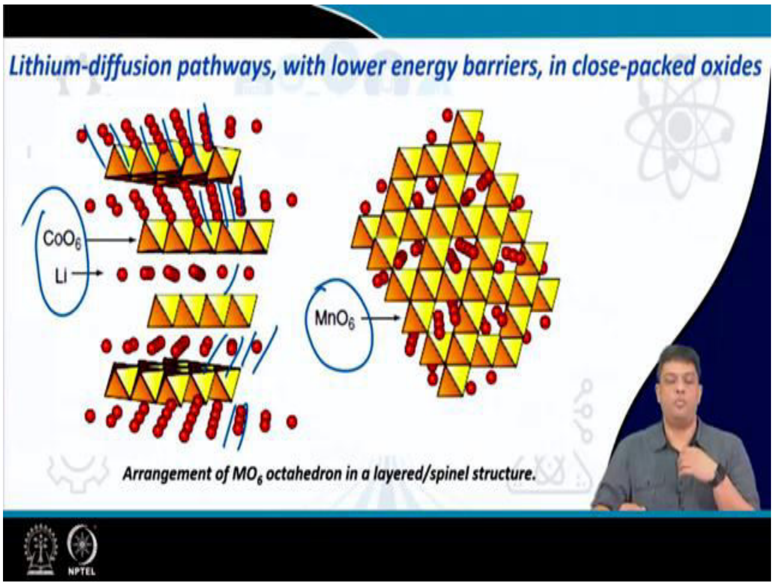

This is the comparison of change in performance in the initial material, which was lithium cobalt oxide and then the spinel type material which was $LiMn_2O_4$. Clearly the same information is visible from this curve, because of the change in the diffusion pathways or diffusion means the channels through which ions are going in or coming out are different and as if the channels are different you will have different kind of energy barriers being felt by the ions.

So, they would be either going out or coming back with different ease, so if you have ease in going out and easy facilitation of the ion back into the lattice your electrochemical performance will be much more enhanced, and that is what it means.

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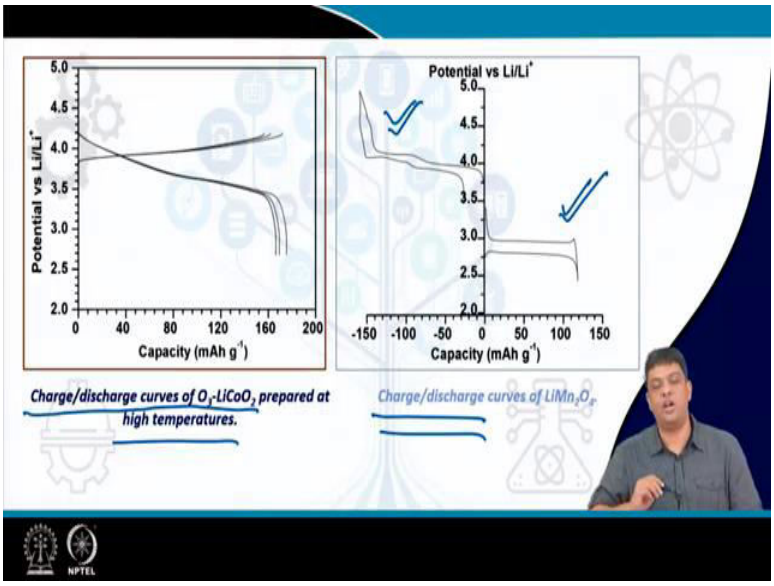

This is words which I said in the previous slides can become clear from the curve shown here. So, if I just compare the discharge curves for the two structures you can clearly see that if this is for the tetragonal structure of lithium manganese oxide and this is for the cubic structure then you can clearly see that you are working in different voltage windows and if you are working in different voltage windows, if you have a higher working voltage window your energy densities would be much higher. This is what it is meant when you say that the materials have different electrochemical performance.

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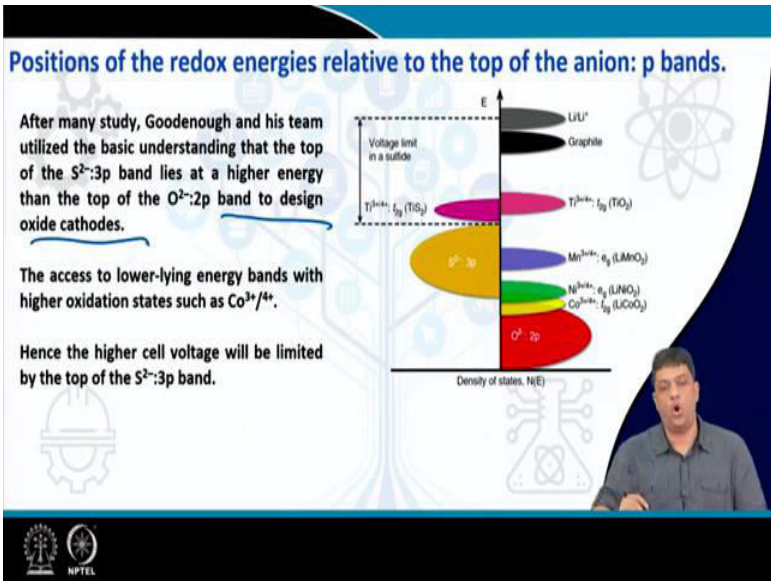

All these things can be explained by understanding the energy levels and how they are placed the most important thing is you must be so designing the materials that the structures are giving you the maximum voltage window to operate.

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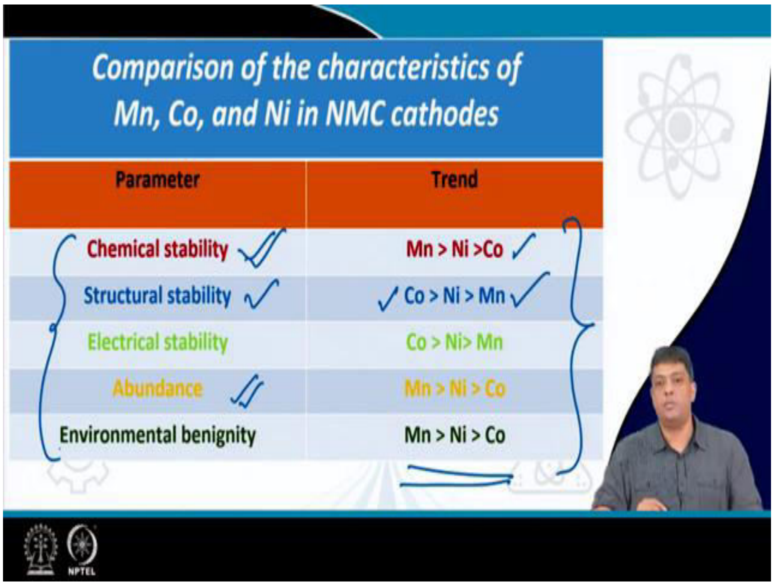

Hence, the characteristics of different materials will it be lithium manganese oxide, lithium nickel oxide, nickel lithium cobalt oxide or lithium nickel manganese oxides, base cathodes what are the parameters? So, if you look into the chemical stability then manganese based structures are more stable than cobalt and lithium is the intermediate, but structurally maybe cobalt based materials are more stable than manganese based material.

In addition, you can have the consideration for abundance because you want to avoid in today's world the geopolitical issues of import and the environmental impact. So, there is no one material which is on the top when you consider each parameters, You have to therefore choose the optimal material which can give you the desired performance while ensuring chemical stability, structural stability, electrical stability it is abundant in your country.

It may be abundant in somebody else's country, but if I have to be independent if i have to be self reliant then the material should be abundant in your country you should not be dependent on the imports. And while you make these materials these materials should not impact the enviornment in a negative manner.

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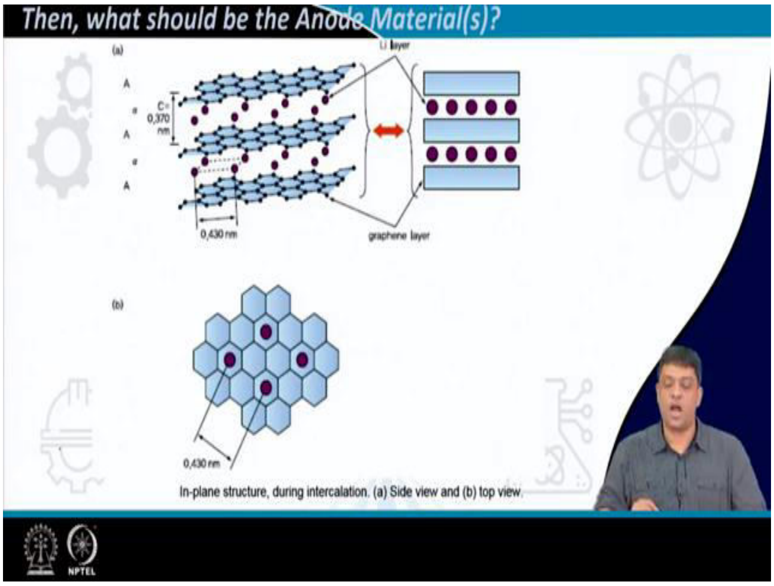

Now, I have obtained a material, and I have obtained a stable material from where lithium is going to be transported to anode, lithium is going to be transported to anode. What is the nature of anode material that should be chosen? Because I may send out lot of lithium-ion, but I choose an anode material which accepts the lithium-ion, but during the discharge cycle it does not send back the lithium into the initial cathode material then will your battery be working? No, it will not work. Therefore, the choice of anode material also becomes extremely critical and this is what we are going to start in the next lecture.

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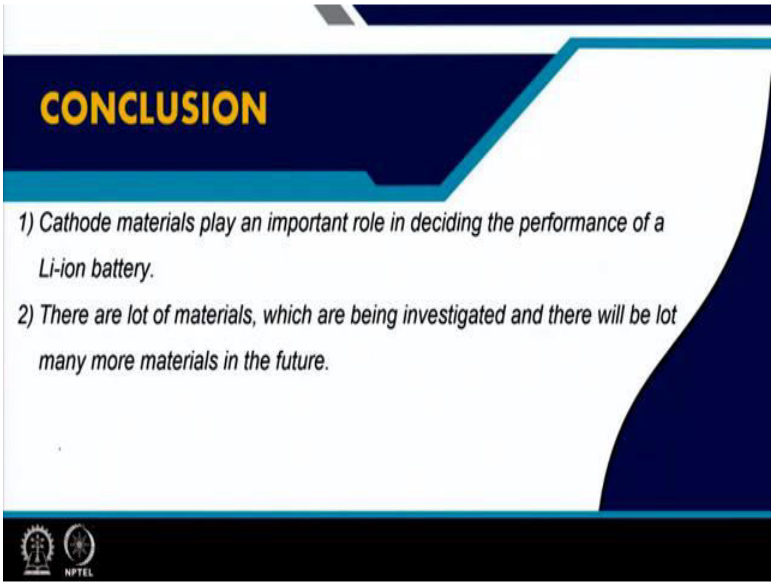

And hopefully in today's lecture it is very clear that cathode materials play an important role in deciding the performance of a lithium-ion battery. There are large numbers of cathode materials which have been investigated, which are being investigated, and there are many many more materials which will come into the forefront in future.

And that is where we should come forward and try to contribute in the development of new materials so that India can start producing those materials and you obtain high performance lithium-ion batteries, which are actually made in India.

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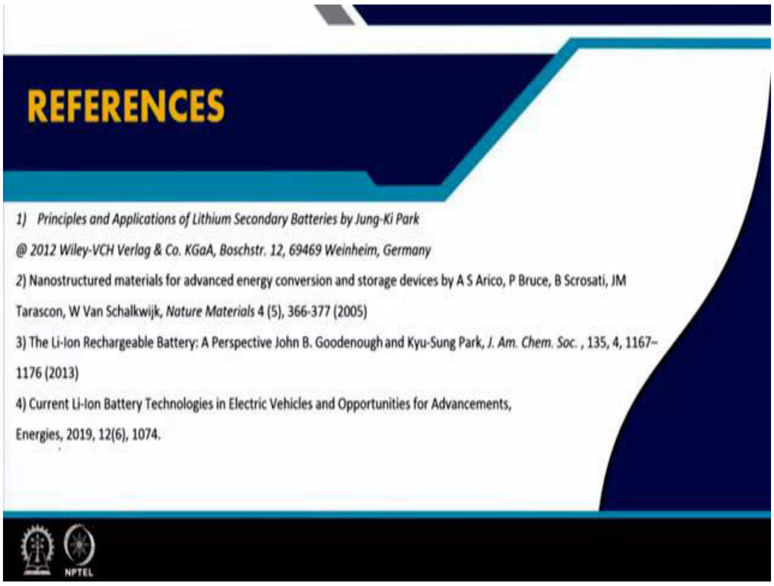

These are the references which were used for preparing the slides and obtaining the relevant data, and I thank you for attending lecture number 3 on lithium-ion batteries. Thank you!