Physics of Renewable Energy Systems
Professor Amreesh Chandra
Department of Physics
Indian Institute of Technology, Kharagpur
Lecture 34
From Material to a Supercapacitor Device

Welcome. So, based on the lectures which we have given to you over the last two weeks and the first lecture of this week, I hope you understand what are lithium ion batteries, how do we move from lithium ion batteries to super capacitor technologies and the two techniques, which are very useful in characterizing these two kinds of devices. We have also discussed with you, the importance of materials aspect to obtain high performance lithium ion batteries or super capacitors.

In today's class, let me give you the strategy or the protocol, which has to be followed to choose a material, characterize the same and then obtain a high-performance energy storage device. Because, there can be n number of combinations which are possible. How will you choose the proper combination, so that you get a device as per as your requirement?

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So, in today's lecture, I will give you the idea by which we choose a material. A material which is going to act as the active material in the device, which you are going to fabricate. I have taken super capacitor as the example; the same kind of discussion can be extended to lithium ion batteries. Once I have chosen the material, how do we synthesize those materials?

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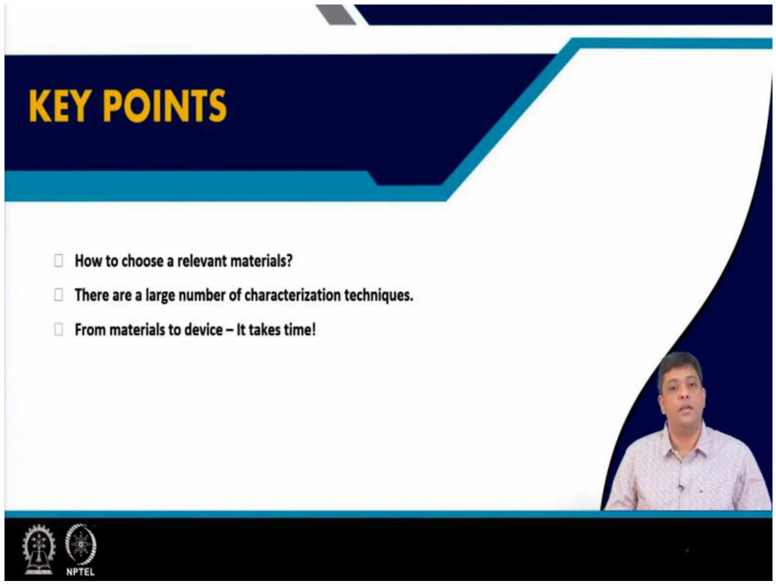

And once I have synthesized those materials, you will also understand that there are large number of characterization techniques, which are there. And those must be used to characterize a particular material, before we even start thinking of using the material in a device. And it is therefore the reason, that if you want to take a material from lab to market, then it takes a lot of time.

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So, let us start with this lecture, where the main idea is to talk about choice of material, its synthesis and how do we characterize the device, which is fabricated using this material.

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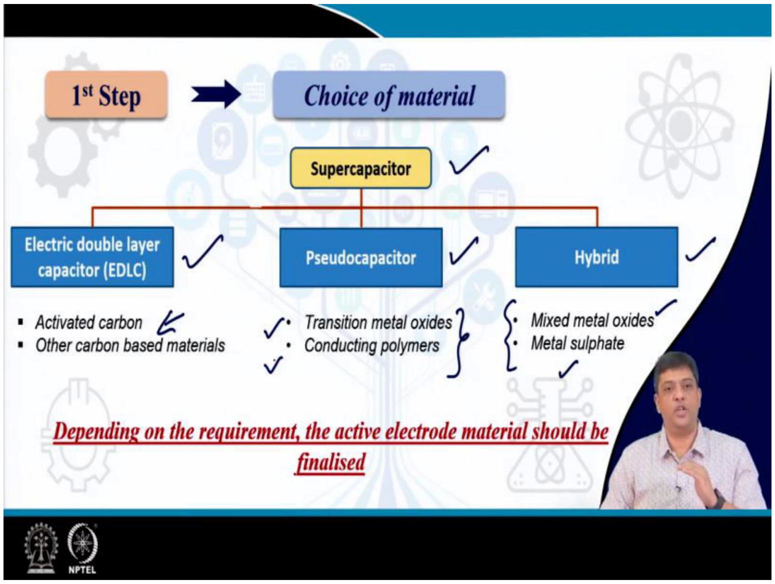

So, let us start and take an example of an electrochemical energy storage device. I have chosen super capacitors. There are three types of super capacitors, which I discussed with you. What are those? The first one was the EDLC type, the electric double layer capacitors. The second was pseudo capacitors. And the third one was the hybrid types of capacitors. We had seen that the EDLC's were mostly fabricated using carbon-based materials.

Pseudo capacitors were fabricated using transition metal oxides or conducting polymers. Whereas the hybrids were using a combination of these two types of electrode materials. So, you could either use mixed metal oxide with any other carbon-based materials or you can use metal sulfates within the carbon-based materials or you can have any other suitable combination. So, if I tell you, that please give me a protocol by which you can get a pseudo capacitive.

Then what type of material will you choose? Will you choose carbon? The answer is no. What type of material will you choose? Either you will choose transition metal oxides or you will choose conducting polymers, as simple as that. So, the choice of material depends on the end user requirement or the specifications given by the end user.

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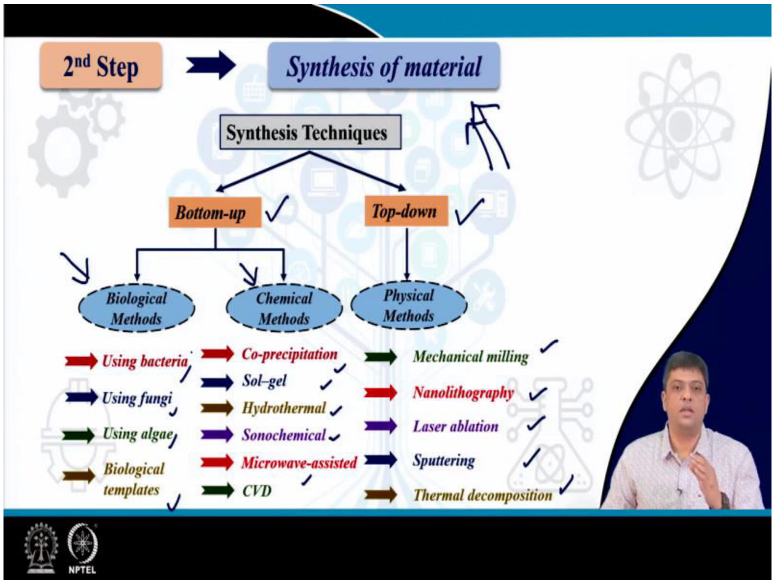

Once I have decided the type of material I am going to use, I must synthesize that material. So, the next step is synthesis of the material, but which type of synthesis protocol will you use? There are n number of techniques which are available. There are bottom up kind of techniques or there are top down kind of techniques. So, even in the bottom up techniques, you can use biological methods, chemical methods of various other sub classifications can be given.

I have just chosen some of them, because these were the ones which we had discussed or mentioned earlier also. If you look into top down that means, I have a material of a larger size particles, then I want to reduce the size of the particle. Then I have the molecular formula and the materials there. But, I am going to reduce the size of the particles in these materials. And so, that is called top, top down.

And in bottom up, what do you do? You start with initial reactants then they react and then there is a new creation, where the particles start to form. And then you grow in size and after a certain time, you get the desired particles of the shape and size, which is required. So, bottom up or top down. So, even if I consider these two very broad subheadings, then there are various techniques which are there.

So, which one will you use? The main idea is that, each of this technique is used or is associated with the temperature range in which it will be working or the pressure under which they have to be performed or other conditions, which are associated with each of these synthesis protocols. As you change the thermo dynamical pressure, parameters such as pressure, temperature or volume, what do you get? You get different kinds of particles which will stabilize by minimizing the Gibbs free energy.

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Different kinds of particles which will stabilize, what do I actually mean by this? I mean that the morphology of the particles would be very different. So, if I have a very large brick and I compare it with a very small size pebble, then obviously, they may look very similar, they may still be rectangular in shape, but their surface areas could be different. If I then crush it further, then the shapes can change, then you can introduce porosities.

In addition, you can change the nature of the voids or the particle itself as if you induce inner cavities, which we had mentioned while we were discussing the hollow structures. And all these things are associated with particle size. So, depending upon the synthesis protocol, which you choose, you will get different kinds of particles. And they would be associated with different characteristics.

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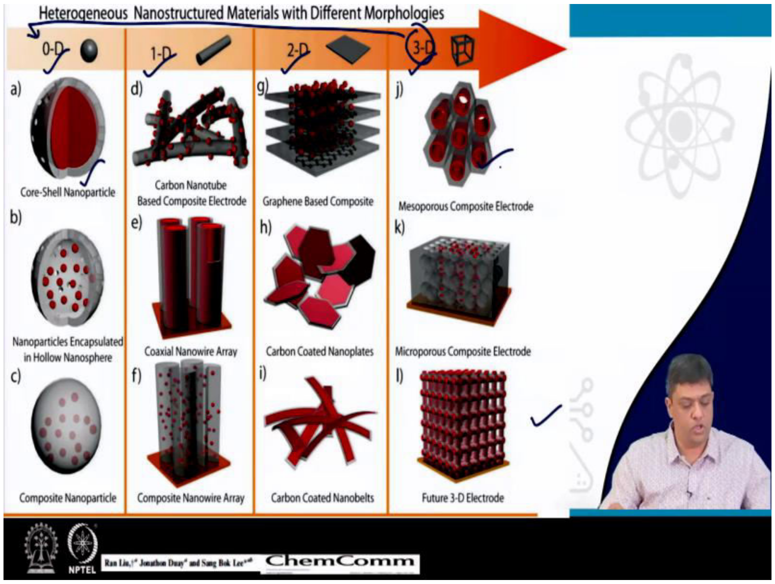

So, as I mentioned in the discussions, when we were talking about the use of nanotechnology in energy devices, I had said that nanotechnology will play an important role. And nanomaterials can be of different shapes and sizes depending upon the confinement. So, you can go from bulk to quantum dot type structures. So, in 0 D structures, what are we talking? We are talking about confinement of free charges in all the three directions. So, you are looking at different kinds of morphologies. So, obviously, the morphologies are very different.

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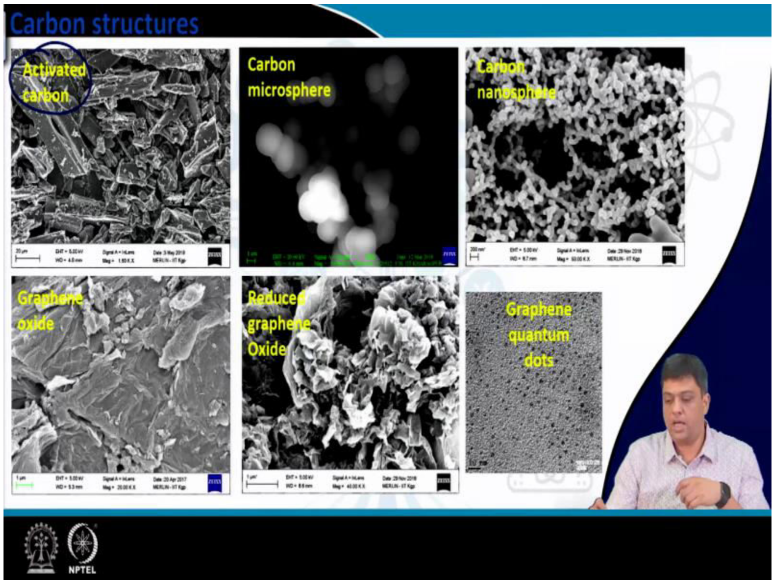

If you look into carbon structures, you can just compare activated carbon. And you can go to very small size carbon nanospheres or you can go into layered structures, in graphene oxides.

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Similarly, if you look into this slide, this is just the slide which is showing the various kind of metal oxides, be it be vanadium oxide, be it be copper oxide, be it be cobalt oxide, the sodium manganese phosphates or you can have nickel iron oxides, they are very different. You can clearly see one is cauliflower type, the other is cactus like. So, you can get very very different morphologies.

And because of this, the surface area associated with the particles are very different. And as the surface areas are different, you will have different electrochemical performance. Because the effective surface area plays the role in giving the double layer formation and also the nature of the redox activity associated with these materials, would be very different.

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We had also talked about the next generation materials, which are coming into picture which are the hollow structures. And you can clearly see that, they have a hollow cavity in the middle. So, then you have the inner cavity, which is going to take part into the electrochemical reaction and also the outside surface of the cavity, which will take part in the electrochemical reaction. So, you can get various kinds of morphologies. And these are obtained by changing the synthesis protocols, and the synthesis conditions.

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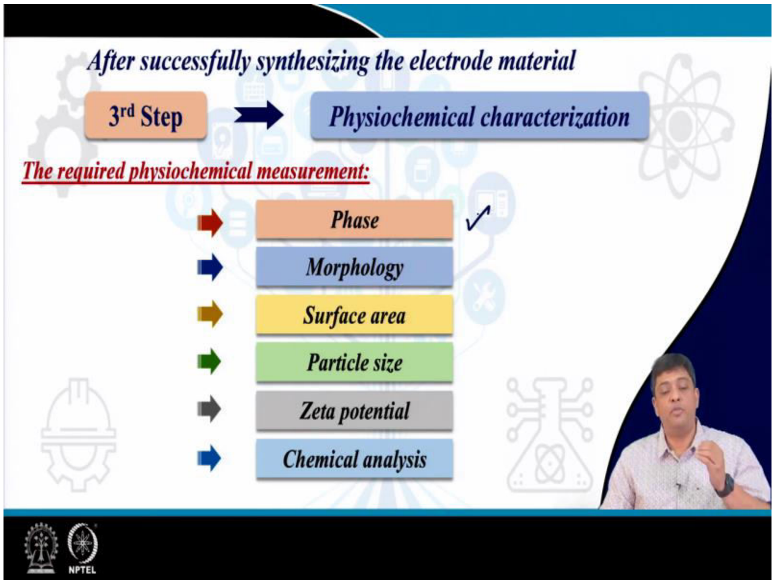

So, now, what I have done? I have chosen the material, I have synthesized the material. Once I have synthesized this material, how do I know whether I have the material which is going to give me the desired performance? So, I have to then characterize these materials, using a large number of techniques. So, phase characterization or determination of phase, we would be using XRD, morphology you can use SEM, TEM, the scanning electron microscope or the transmission electron microscope. Surface area, the Brunauer Emmett Teller technique, that is the BET technique, particle size or zeta potential you can determine using the DLS based techniques. You can determine the chemical analysis of the material using the SAD patterns or the elemental mapping techniques. So, there are a large number of techniques, and all these techniques have to be used to determine the characteristic of a material before even I start thinking of using it in an electrochemical device.

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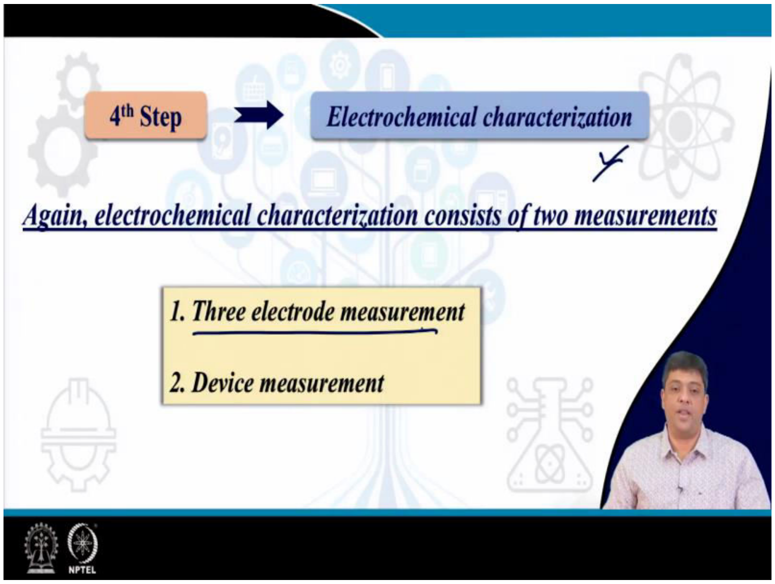

So, material is chosen, it is synthesized and then we start, we have characterized the material using the various techniques and then only I can talk about the electrochemical characterization. Even electro chemical characterization, I have to first perform the three-electrode measurement, why? Because three electrode measurement is going to give me the information of the material. And then only I can make the final device. So, a lot of steps are involved, before I can take a material from lab to market.

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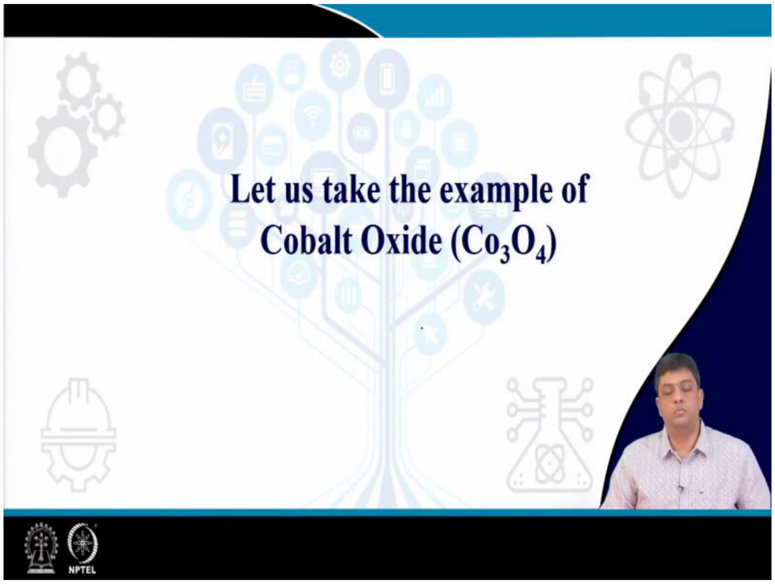

Let us take the example of cobalt oxide, I have chosen this example randomly. Because cobalt oxide is extensively used electrode material, in this kind of devices. So, I have chosen this example.

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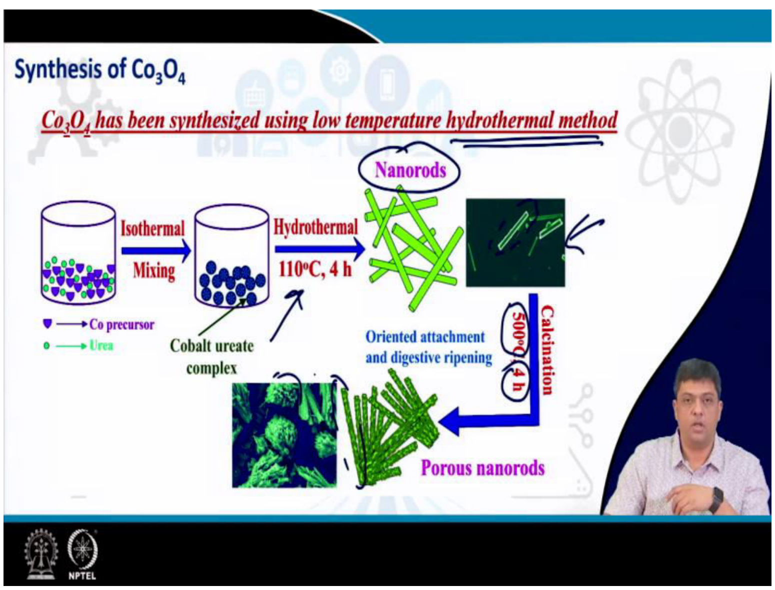

For example, we have synthesized these materials in a hydrothermal jar. That means, I think, take the reactants in a jar, where you can increase the pressure and as well as the temperature. So, you take the reactants and when you heat this reactant, let us say the cobalt uric acid complex at 110 degrees for four hours, you can obtain the nano rod type structures of cobalt oxide. And subsequently you can sign the material, what is calcinations?

Calcination is the process by which you ensure complete reaction and formation of the single-phase material. So, I have ensured that the reaction is complete and the molecular unit is formed in the desired stoichiometry. So, I have CO_3O_4 formed after calcination of these particles, which were having the nano rod type morphology. And the calcination temperature was 500 degrees and again it was heated for four hours. So, you were heating the powders at 500 degrees for four hours. What do you obtain? You actually obtain the porous type nano structure. So, you have nano rods with porosities on the top.

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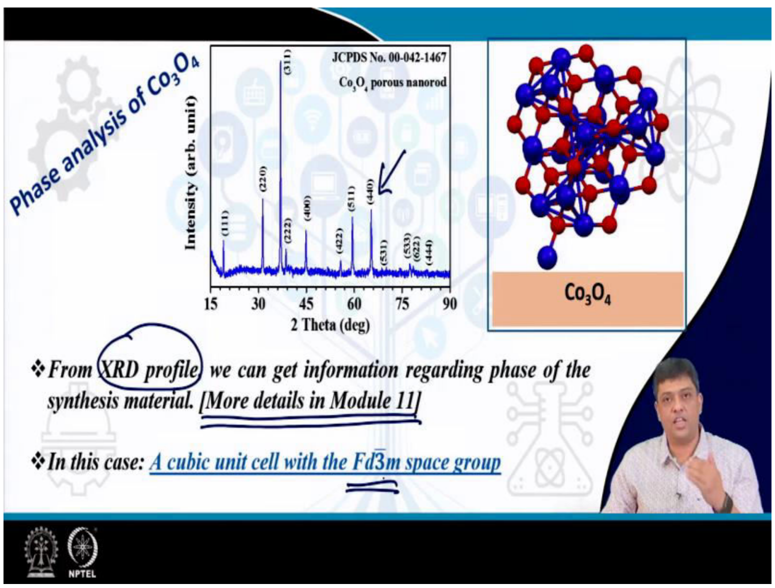

Copper, cobalt oxide has actually, I will just repeat this line. Cobalt oxide has actually formed, how do I find out? The most common technique which is used is the x ray diffraction technique, which is used to get information about the phase. And a couple of lectures are going to be given in module 11, which will tell you the process of performing the XRD studies of these kinds of materials, and what all information you can obtain using this technique.

But, I hope that most of you have understood that x ray diffraction technique is used to find out the crystal structure of cobalt oxide. And if you have the crystal structure of cobalt oxide in a given let us say, unit cell then you can find out the lattice parameters. If you can find out the lattice parameters, then I have obtained a b or c. And if you are talking about a cubic unit cell, then you have found out a.

And from there you can calculate the band structures everything which we discussed in the third module, where we were talking about the free electron model. So, just by finding the lattice parameters, I can get many more information about the material.

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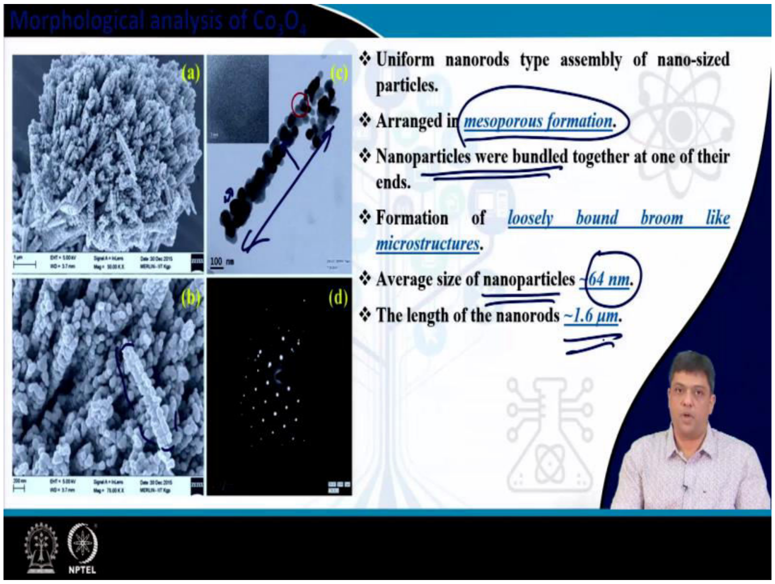

We have already talked about, that you get the nanorods, what all can I infer? I can see that they are mesoporous. So, they are porosities and porosities are of such nature, nature that they can be called as mesoporous. The classifications of microporous, nanoporous and mesoporous would be again described bit later, but this is what it is. That the structures are not very dense, but this you can clearly see that they have voids in between, and they are called as pores.

But these nanoparticles are bundled together. And you can see that, they are forming a rod like or pillar like structures. The average size of nanoparticles and is, if you calculate the particle size of each nanometer it is approximately 64 nanometers. And the length of the rods are 1.6 micrometers. So, nanometer sized particles coming together and forming a very large sized particle. So, this is what you have seen.

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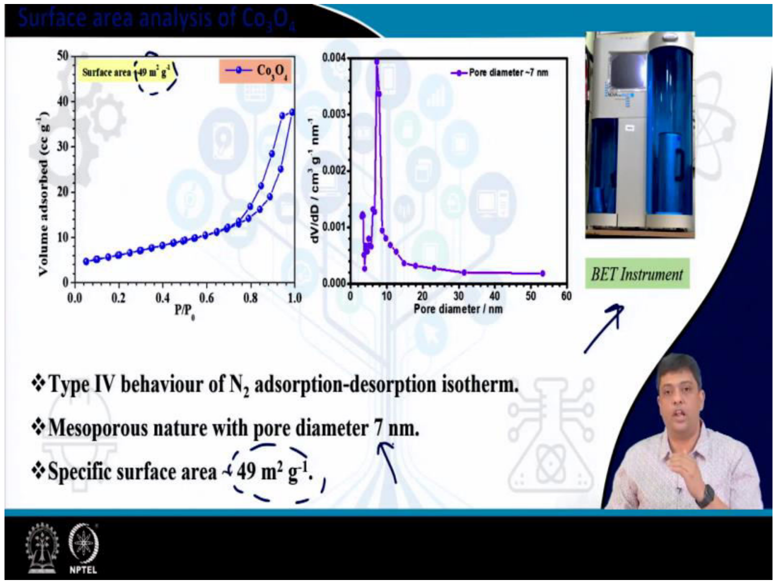

Then what is the effective surface area? You perform the BET measurement. And you can obtain the specific surface area for these kinds of materials. In this case it was approximately 50 meters square per gram, with the pore diameter of 7 nanometers. So, the pore between the two particles are of the order of 7 nanometer or so. So, these pores indicate that here also the electrolyte can move in and then you can have the formation of double layers in this feature.

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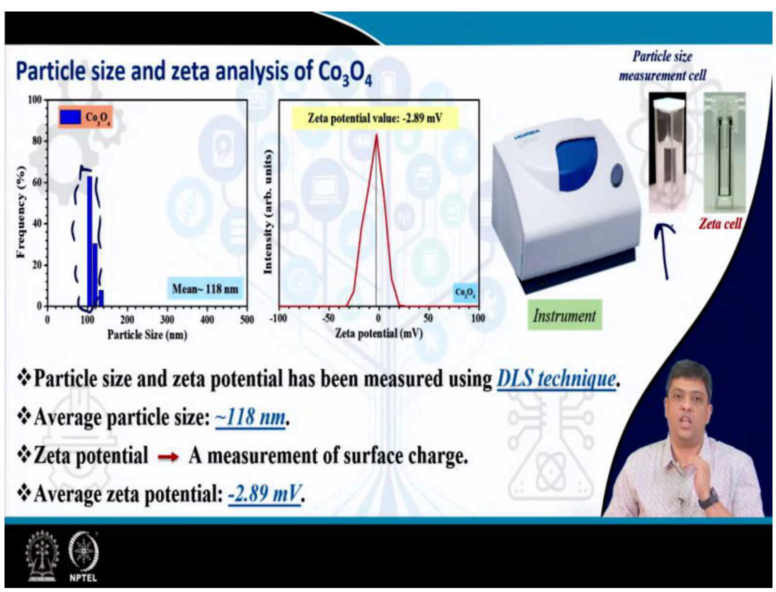

Once I have obtained the surface area, then do we have uniform size distribution of these particles or you have in homogeneous distribution? That you have some particles which are of 17 nanometers and are bundling together to get 10 micrometer sized rods. Some particles are of 20 nanometers and then giving a rod of only 1 micrometer or you get particles which are of similar size. And then you are getting similar sized rods.

You see that most of the particles are in the range of 100 nanometers or so. This data gives you slightly higher value than what you saw in the microscopic picture. Because this is already, you are seeing the agglomeration taking place when you have the dynamic light scattering based measurements in a colloidal solution.

So, this will also be discussed, but it for the time being, you see you have a homogeneous distribution of particle, you have porous material, you have single phase material, you have large surface area material. All these things indicate that the material is going to be very useful for energy devices.

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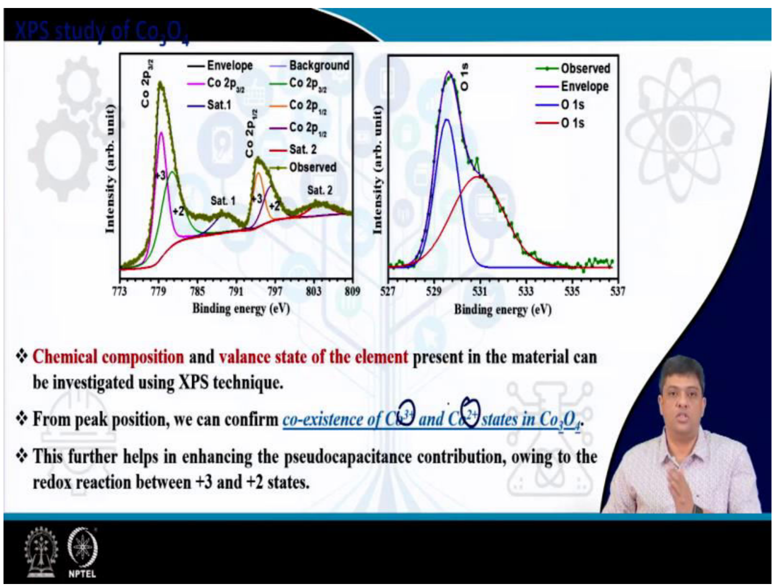

Now, electrochemical performance, you must have elements which can take part in oxidation or reduction processes. So, they can have multi valence states. So, cobalt can exist in 3 plus or 2 plus states. So, during charging or discharging, you can see the change from plus 2 to plus 3 state or plus 3 to plus 2 state. And you will reach the pseudo capacity type behavior.

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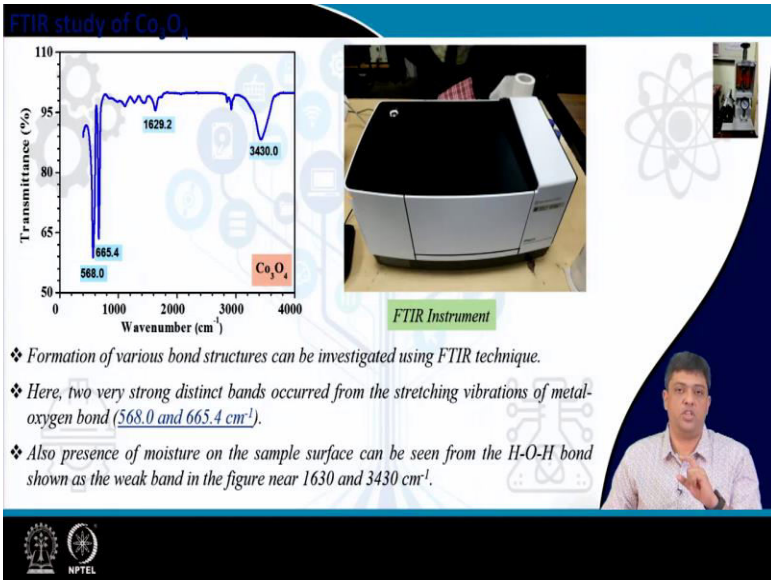

Before we take the next step, it is also useful to characterize this material, by techniques such as FTIR the four year transform infrared spectroscopic techniques, which can indicate the nature of bonds. And if there are absorbed water on these kinds of materials. Because, if you take materials which are all really having absorbed waters, then you will get limited voltage window of these materials. And then you must ensure that the materials are not having moisture in them. So, you use these kinds of techniques.

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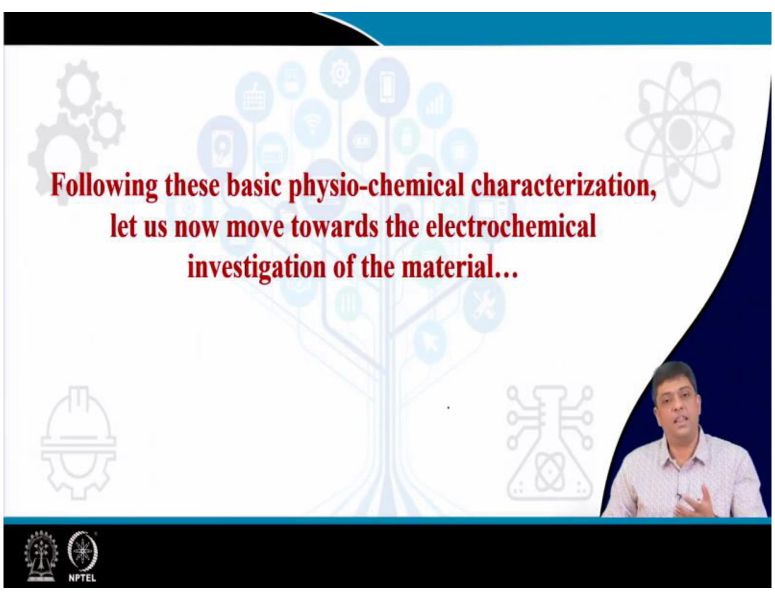

So, what has been discussed? We have chosen a material, we have characterized the synthesize materials. And we have characterized just the basic techniques have been used and that too, turns out to be 8 to 10 techniques. And still we have not reached to the point, where we are talking about the device.

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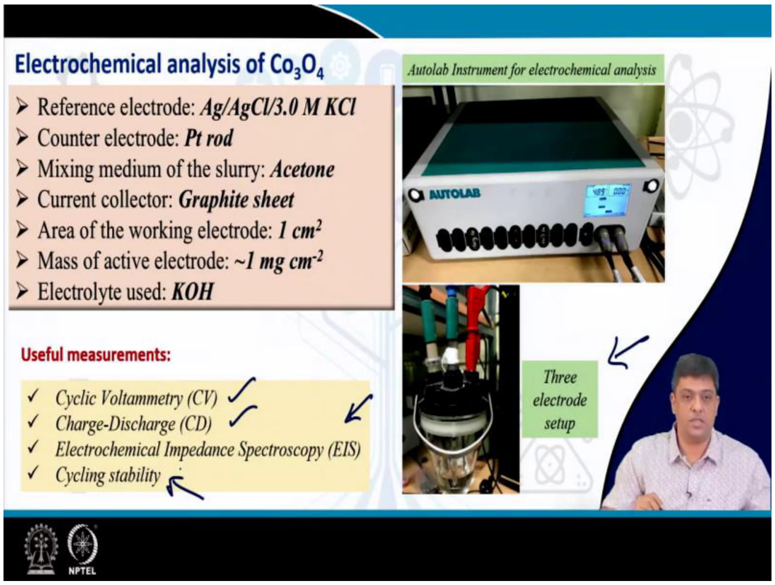

So, now we have cobalt oxide with desired performance, which performance? The physical characteristics look useful for application in electrochemical device. But we have still not tested its electrochemical performance. So, what are we going to do? We are going to use the techniques, which were discussed in the previous lecture that is CV and CD. So, first you use CV, CD techniques in a three-electrode setup to determine the electrochemical performance of cobalt oxide.

You also use the electrochemical impedance spectroscopy to talk about or determine amount the IR dropping these kinds of materials. And then, how long you think that this material is going to be stable? Before you take this material to a device, you perform the cycling stability of the material itself in the three-electrode assembly. So, we are still not at the point, where we are talking about the device.

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Let us see how do we prepare the electrode? So, you take the material and from here you are going to mix it with polymer, then you are going to add the activated carbon, make a slurry. After making a slurry, then you will coat it and then cut into a required dimension.

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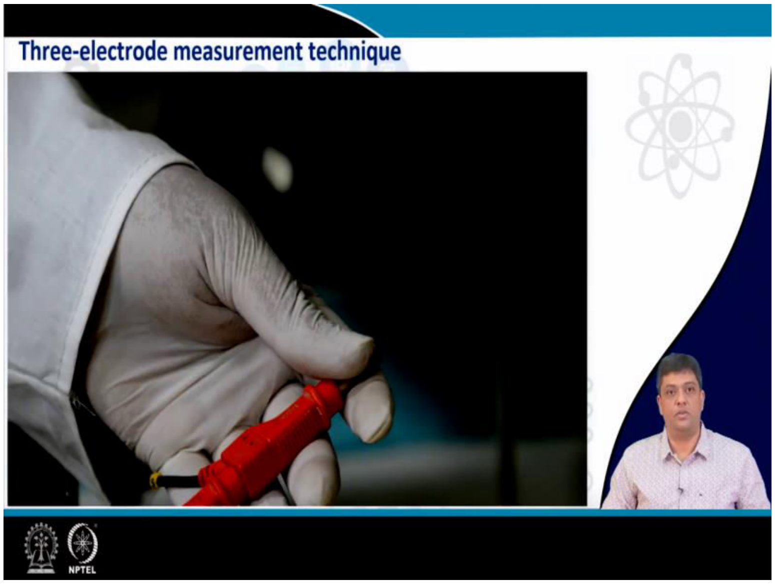

Subsequently, you will take the data for three electrode measurements.

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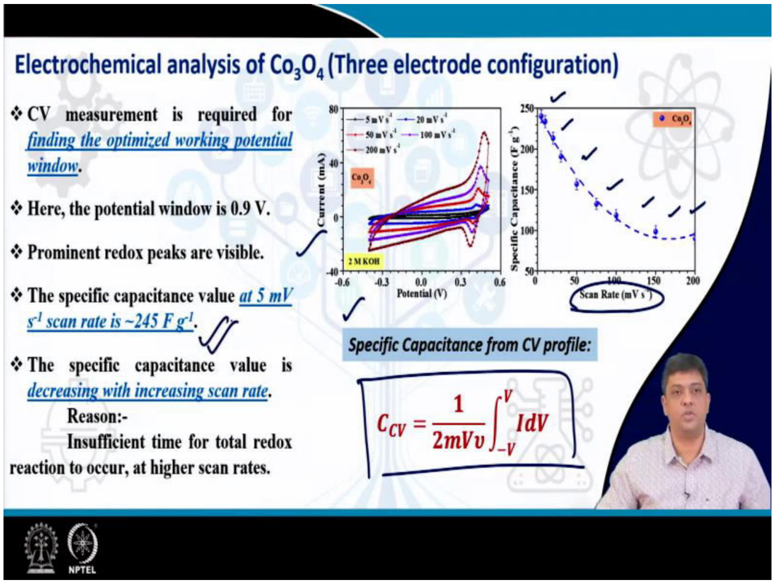

This is a typical CV data for the cobalt oxide in three electrode configurations. And you can find that as a function of changing scan rate, you have different values of these specific capacitance, which is determined using the formula given on the right-hand side of this curve. Why do you actually see scan rate dependent changes in the specific capacitance?

See, if you introduce the iron or, the electrolyte is such that it is intercalating and then inducing along with it, you have the solid ions which are forming the double layers. Then you must ensure that the double layer get enough time to stabilize. And you get a capacitive component dq by dv. But if you are changing the directions very fast, then what happens? You do not have enough time for the stabilization of the double layer.

So, at very fast scan rate like means, you are going to maximum voltage bring it back to zero, going to maximum voltage bringing back to zero, or in the reverse direction going to my plus, going to plus v to minus v plus v to minus v. So, you send in the electrolyte and then extract it. Then what happens? You do not give enough time for the formation of double layer. And hence, the values decrease significantly at very fast scan rates. So, you will get scan rate dependent variation in the specific capacitor. So, we have calculated the specific capacitance using the CV.

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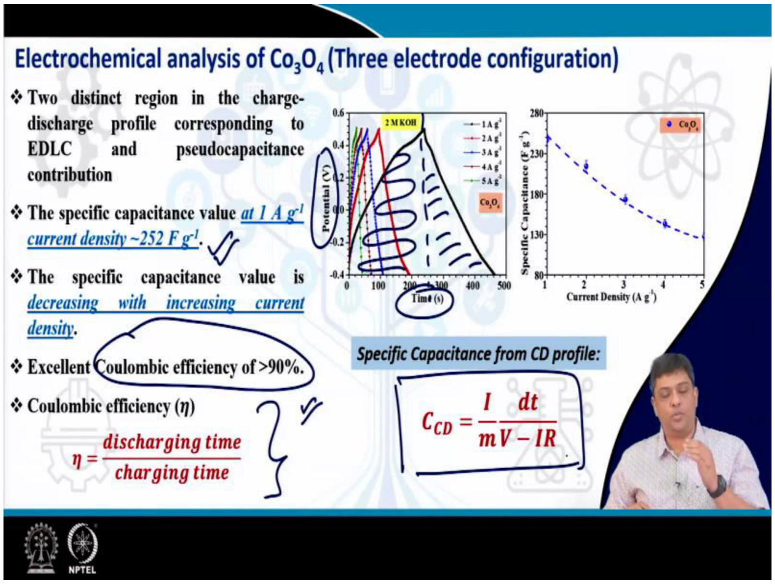

Similarly, you can get the value for specific capacitance using the charge discharge curve. If you considered the area under the discharge cycle and area under the charging cycle, you can take the ratio and you find this will give you the columbic efficiency. If you have devices, which are giving you more than 90 percent columbic efficiencies, they are then they are considered to be quite satisfactory for integration in the end application.

So, for this case, you can easily find out that the columbic efficiencies were more than 90 percent. So, now, I have obtained the material, which is giving me the desired electrochemical parameters. And this can be taken to a device.

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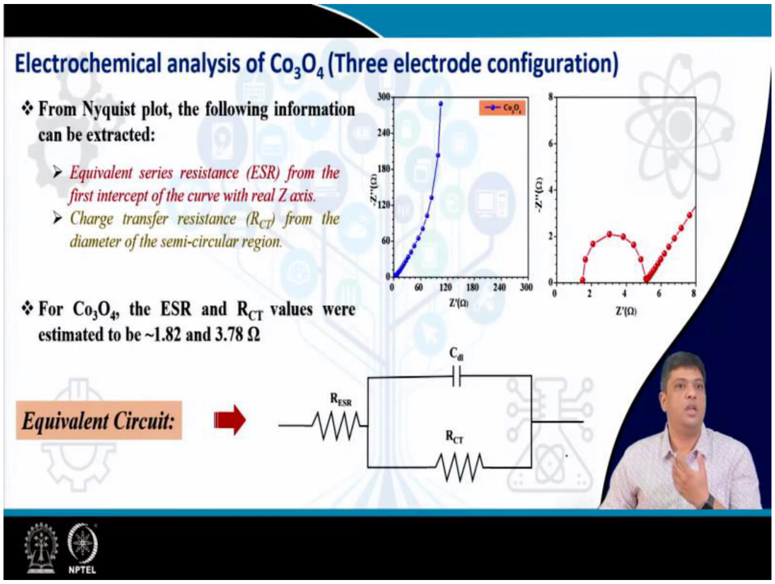

And when you are going to take them into a device, there is an additional factor which comes into picture, that is the IR drop or the what is the resistance drop in these kinds of materials, which can be because of the charge transfer resistance or the, the equivalent series resistance in these materials. So, I get what is a typical IR drop. So, that is going to give me the voltage drop I into R. So, that is the kind of voltage I am going to see as dissipating in the device.

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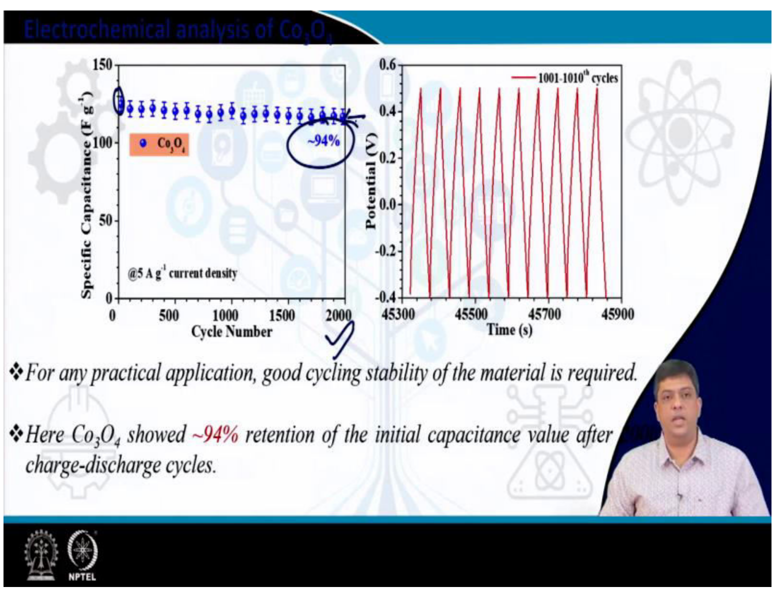

So, once I have obtained the materials, for how long will it be stable? Let us say I check for 2000 cycles, I find that the retentivity is 94 percent. So, if I start from this value, then the value which

I get after 2000 cycle is around 94 percent of the initial cycle. And this kind of written retentivity is quite acceptable. So, the material itself is indicating that it can give me the desired performance in the device.

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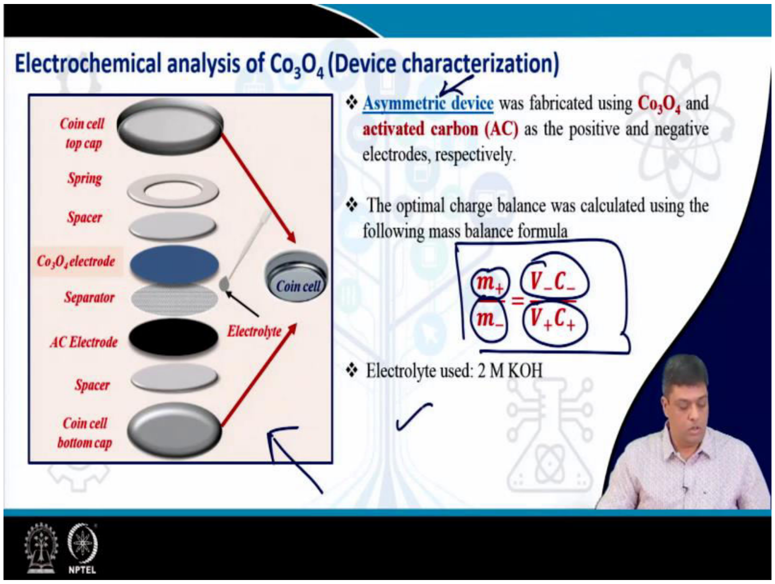

So, now I have a material, I form a device using the protocols which we had discussed earlier. But, please remember that you must ensure mass balancing before you make the two electrodes. Why? Because if you choose materials let us say, you have an asymmetric device. You choose cobalt oxide in one side and carbon on the other. Then the material required to store the charge, which is being released or which is developing at this interface of cobalt oxide and the electrolyte must be very similar to that at the other electrode.

So, you must ensure that the volt V minus into C minus divided by V plus into C plus is equal to the mass of these two materials. So, how much materials you should take? So, that both are able to store the similar magnitude of charges.

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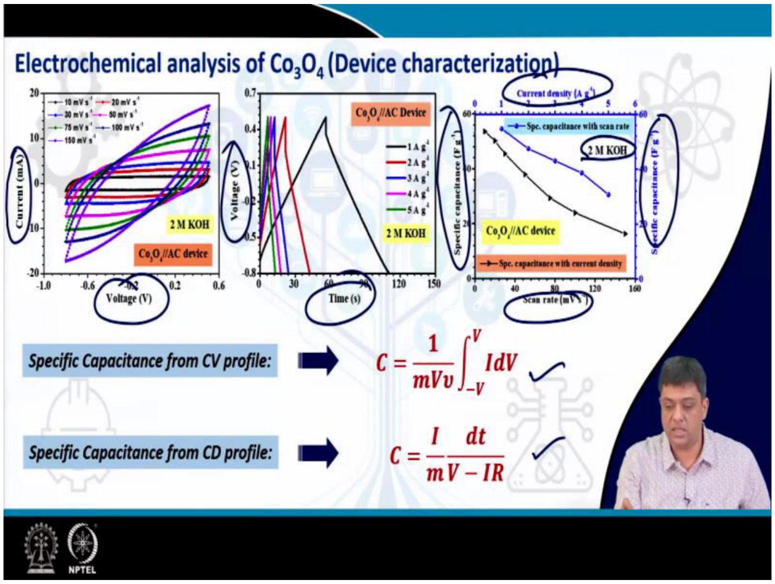

Now, I have found the device and the similar measurements are performed. So, you have the CV measurement, the CD measurements and then you can plot the specific capacitance. Either as a function of scan rate or as a function of current densities. So, you will get the variation in values depending upon the electrolyte. So, if you change the electrolyte, everything will change.

You change the, the carbon which you are using in the other side of the asymmetric device, that was fabricated with copper cobalt oxide is one of the electrodes, the values will change. So, various combinations are possible. But you can see, that you are able to get specific capacitances which are as high as 55 to 60 Farads per gram. So, you can get very high values.

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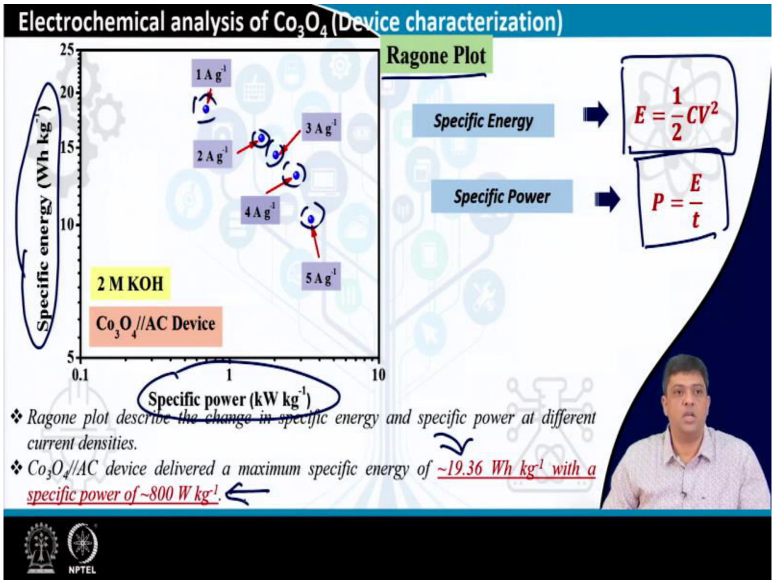

And finally, if you plot the Ragone plot, the Ragone plot which gives you the variation of specific energy, which is what our per kg with respect to specific power, that is let us say kilowatt per kg then you will get the values. And these values also change as a function of current densities or scan rates. Because of the reason discussed earlier. Specific energy, half CV squared and specific power E by t, where E is the specific energy.

And if you look into these values, they are quite high. So, you have specific energies which are of the order of 20-watt hour per kg. And specific power which is nearly 800 watt per kg. So, you can store a lot of energy using these materials.

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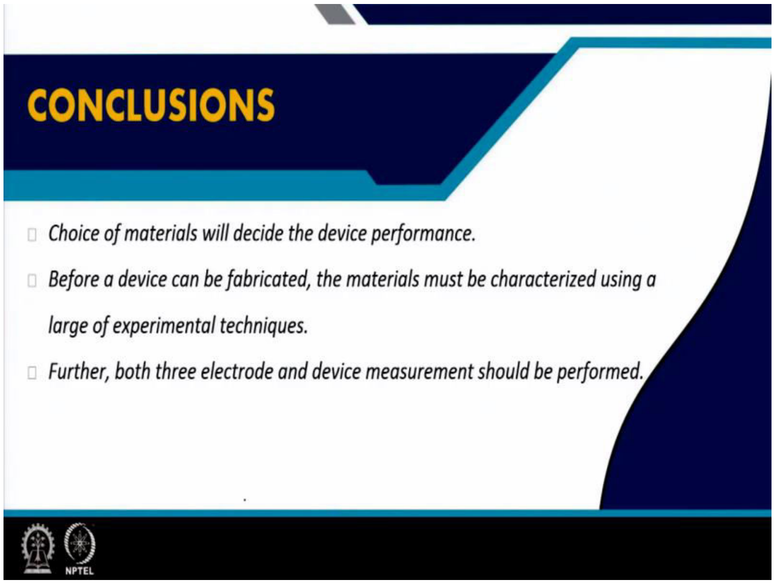

I hope using this lecture, you can actually initiate independent work towards the development of a high-performance super capacitor. I have given you the way you should choose the material. There are a large number of techniques and most of these techniques, of synthesizing these materials have actually been discussed either in your class 11th or 12th or initial years of your bachelor's program.

So, you already know them, it is just about utilizing them. And then there are large number of characterization techniques, which are available. We will also explain in detail about these techniques bit later in this course. But they are easy to understand, if you are having these instruments. Then you can perform the measurement and extract the data and relevant information will be in front of you.

After you have made the material, you can develop or fabricate the device and characterize the same. Once you get a high-performance device, you can pass it on to the industries for mass production or scale.

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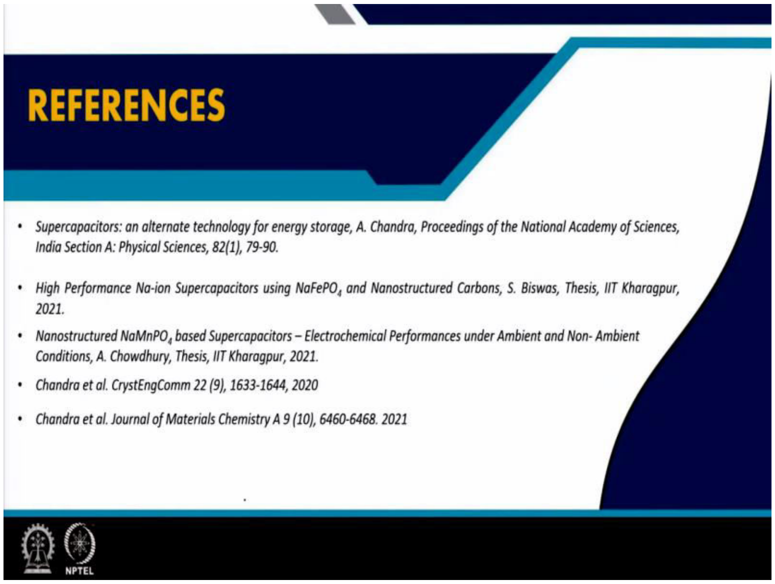

These are the major references, where we got the data from. And you can refer to these references to get more information. And I thank you for attending today's lecture.