Physics of Renewable Energy Systems
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Lecture 27
Anode Materials for Li-ion batteries

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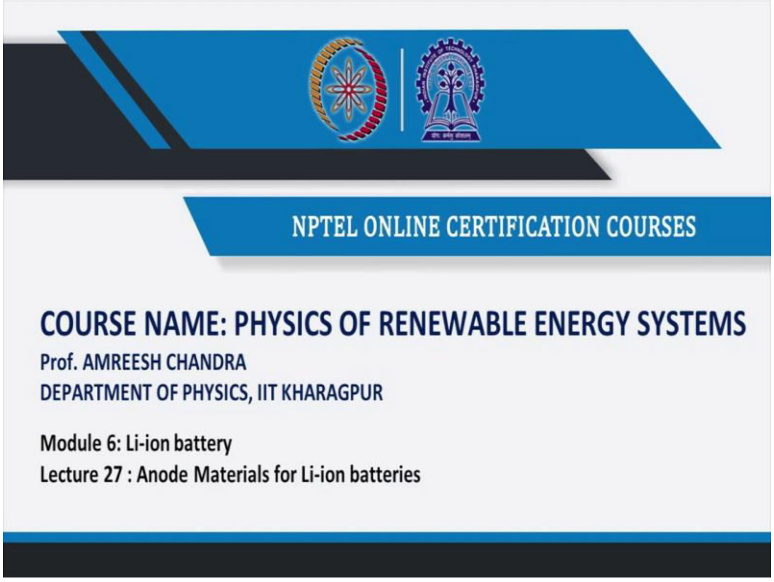

Hello! So let us continue with our discussion on lithium-ion batteries. In the previous lecture, I had discussed with you about the cathode materials, what are the cathode materials, which are being used and we had also given you the important parameters which should be considered while you choose the optimal cathode material.

At the end of the previous lecture, I had also mentioned that the nature of the anode material also plays an important role to, while ensuring the high performance lithium and battery fabrication. So, in today's lecture let us start our discussion on anode materials which are used in lithium-ion batteries.

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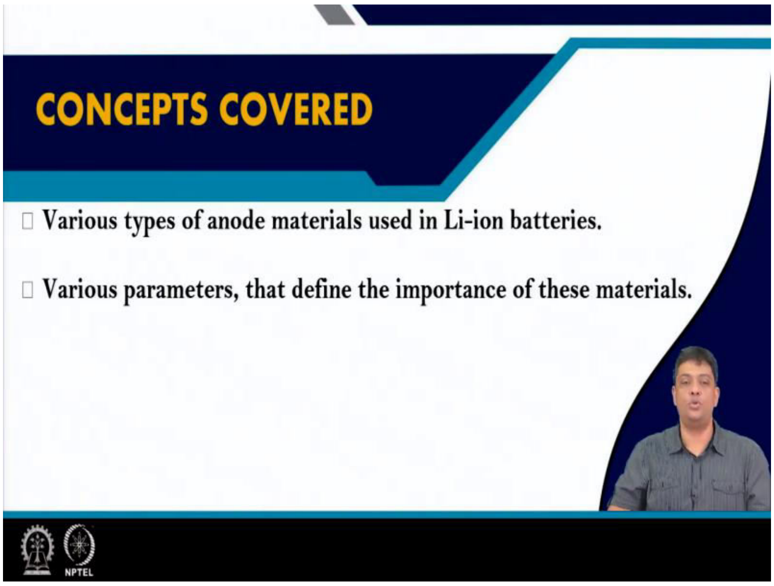

Similar to the way we moved in the previous lecture, in today's lecture also, I will talk to you about the various types of anode materials used in lithium-ion batteries, and the parameters that are used to define the importance of these materials.

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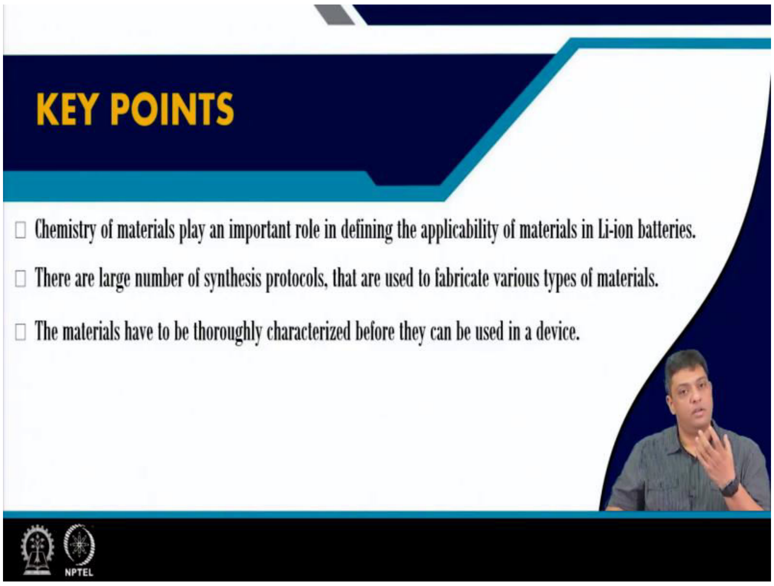

You will be again understanding, the role of synthesis protocols in obtaining these materials and, how you can choose amongst the various protocols to obtain different types of anode materials. This information or the key points are very similar to what we had mentioned in the previous lecture. Why? Because the role of synthesis protocols and characterization techniques are very similar when you are obtaining or fabricating the anode or the cathode materials. It is only the target materials which change but the associated chemistry or physics remain the same.

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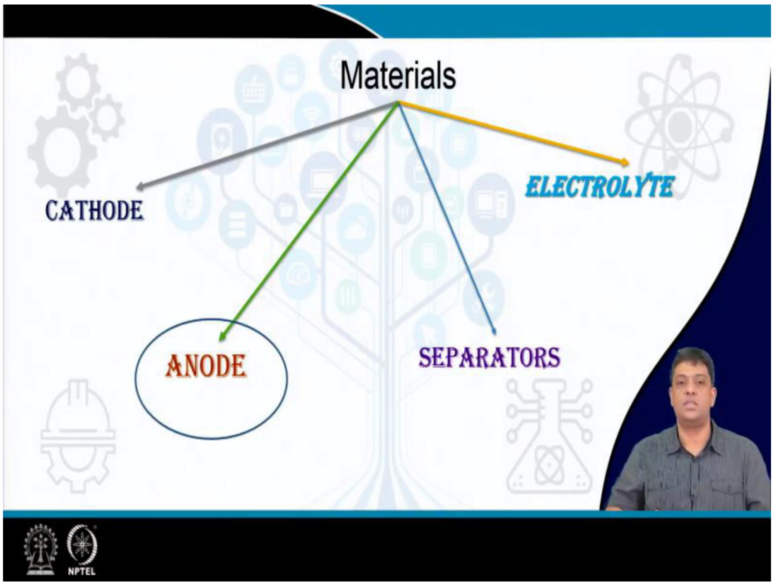

So, in the earlier lecture we had talked to you about the cathode, and in today's lecture let us start our discussion on anode materials.

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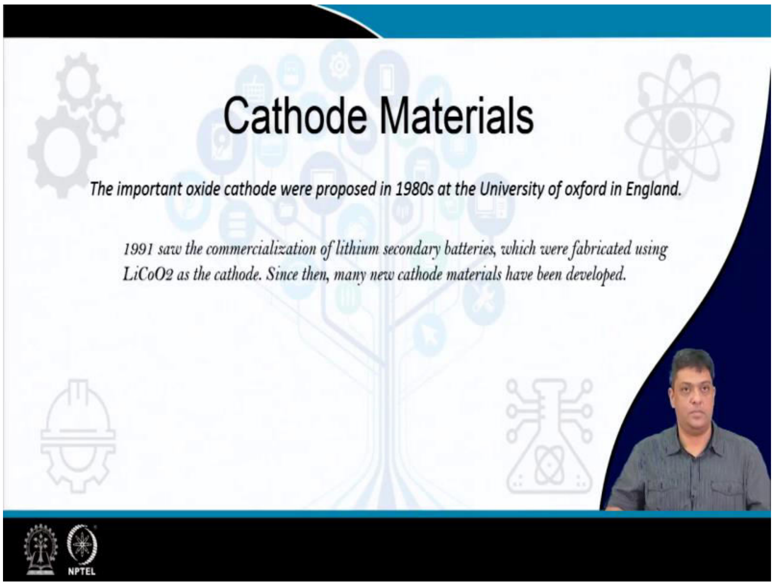

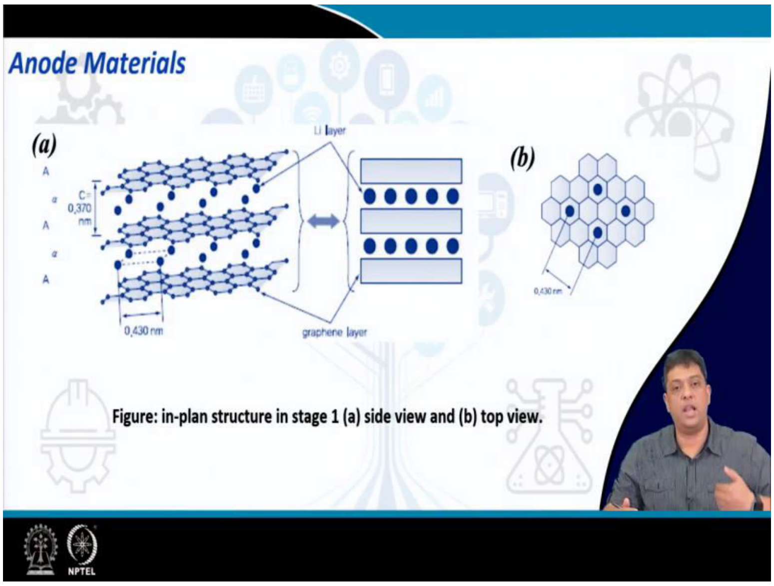

As I said that lithium-ion come out of the lattice of what? Lattice of cathode materials so when they come out, they have to be stored at some places. Which place are they actually stored? They are stored in the layered anode materials. Layered anode materials mean what, it means that you have a material which has layered structures and the lithium-ions are actually going and getting stored in between these layers.

Hence the distance between the two layers play an important role and what is the nature of the channels which take this lithium-ion inside these vacant spaces between the layers and how they come out of these vacant spaces also become quite critical.

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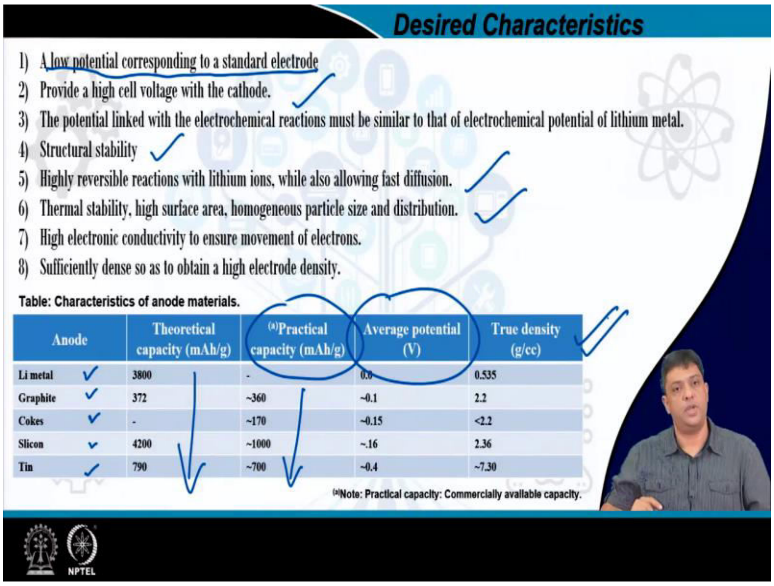

Therefore, similar to the requirement of certain characteristics, while we were choosing the cathode materials, there are also some desired characteristics which are associated for choosing the right anode material. And these are, material which is going to be used as an anode material should have low potential corresponding to a standard electrode, so I should have a low potential with respect to a standard electrode.

Now provide a high cell voltage with the cathode. When will you provide high cell voltage? You should have the capacity to store lithium. The potential of giving or delivering high cell voltage is linked with the electrochemical reactions and this must be similar to that of the electrochemical potential of lithium.

So, if you have electrochemical reactions taking place in the anode then the potential linked with these electrochemical reactions which are taking place in anode should be similar to that of the electrochemical potential of the lithium metal which was being used as the anode materials earlier.

It should be structurally stable, highly reversible for ion intercalation or de-intercalation and should allow fast diffusion. If I charge the battery and I start discharging the battery it should happen as fast as possible and that means it should allow fast diffusion. Similar to the requirements for cathode materials the anode material should have thermal stability, high surface area and homogeneous particle size distribution.

Along with that they should have the characteristic where they are ensuring high electronic conductivity. Why? Because they will either accept the electron from the external circuit or they will deliver the electrons to the external load during charging or discharging cycle respectively. So, their electronic conductivity should also be reasonably high. To ensure high energy density they should be sufficiently dense, so that you can obtain a high electrode densities.

These are the typical anodes which are used but mostly you will find that the commercially available batteries use carbon based structures and they have different advantages and disadvantages. So, they may have different theoretical capacity, but if you have different theoretical capacity then all of them cannot be obtained, you lose the capacity. I hope you remember. Why do we lose capacity?

We had discussed about the concept of polarization in batteries and because of that you have the term practical capacity, which is obtained what is the typical average potential with respect to the standard potential which you are having and the true densities which are obtained. So, you can then choose which type of anode material you will be using to support the cathode material.

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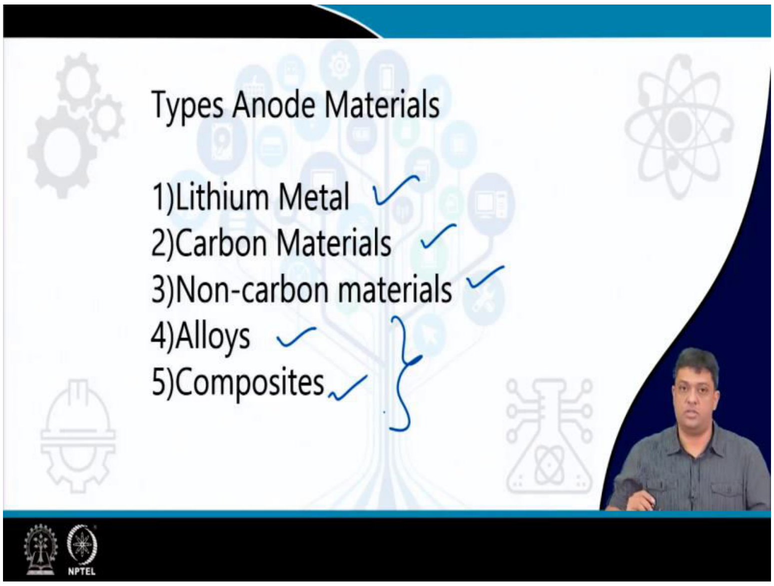

As mentioned in the previous slides, you can have lithium metal, you can have carbon based materials, you can have non carbon based materials, but over the last few decades people are also extensively proposing the use of alloys or composites as anode structures.

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Let us take the example of carbon materials for use in lithium-ion battery, more so for use as an anode material in lithium-ion battery.

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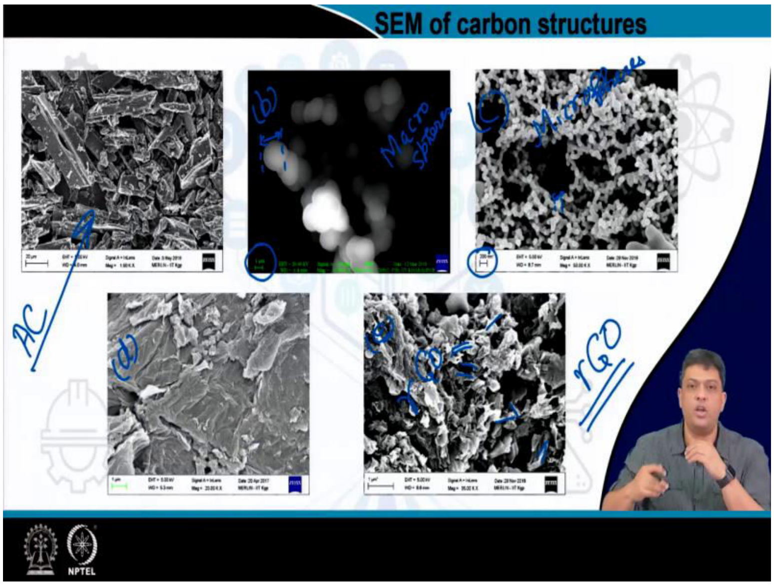

This is a Scanning Electron Micrograph of a carbon structure, which is activated carbon, so this is activated carbon. If I go to the micrograph which I have now written as micrograph b, this is a micrograph which shows the formation or stabilization of carbon spheres, but the macro spheres. Why are we calling it macro spheres? Look at the scale. So, this is the scale which you are going to use to obtain the size of these macrospheres.

So, you can see they are in the range of one micrometer or more, but if I then go to, so macrospheres. If I go to graph c then you can clearly see that the size of these particles is much smaller. They are in the range of hundred nanometers or so, so an order of magnitude lower and these are generally called as microspheres, so you have microspheres.

In the slide d this is your graphide oxide or graphene oxide, while the figure e shows RGO which is termed as reduced graphene oxide, and you can clearly see the formation of a structure which is not like the spheres, but maybe it is like thin papers sitting over each other so you are stabilizing like a layered structure.

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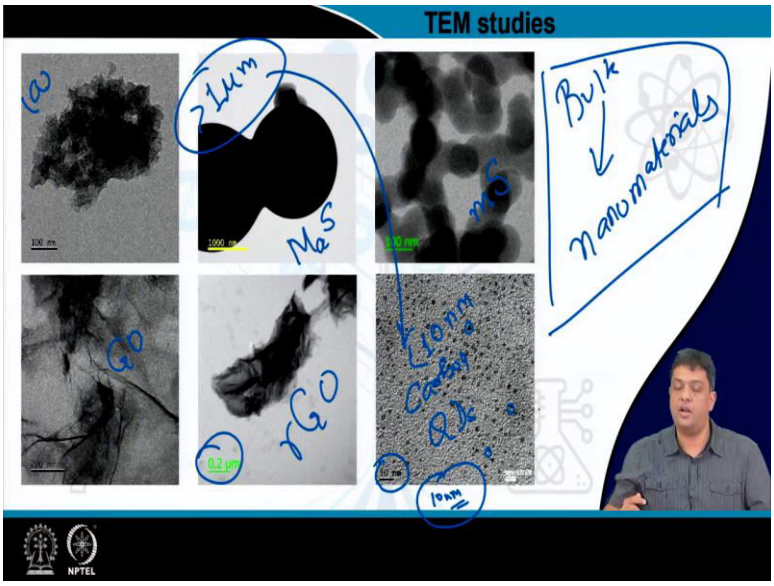

The same thing can be seen here. The figure this is transmission electron microscope, you have the activated carbon, the macrospheres, the microspheres, the graphene oxide, reduce graphene oxide and carbon quantum dots. You can see these are very very small structures the black spots which you are seeing these are very small carbon dots which are forming and the dimensions you are looking at is 10 nanometers or less.

So, you have gone from few micrometers to less than 10 nanometers. Obviously, the performance of both these materials will be very different. For example, if I take a block of brick, complete brick and I compare it with a small, very very small pebble. Are the performances of these two structures similar? Obviously not.

Same thing is there when you talk about these materials, when you change their structures, when you change their morphologies, when you change their size, their electrochemical response are also very different, and that is where you move from bulk to nano materials.

And you will see that the development of these technologies are also directly linked with the development of nanomaterials and you must understand the characteristics and few important features of nanomaterials, if you really want to understand and enjoy the development of these energy storage technologies like lithium-ion batteries, sodium ion batteries, zinc ion or zinc air batteries, supercapacitors, pseudocapacitors.

So, these are all linked with the development of nanomaterials. Hence, we will also have dedicated lectures on nano technology and nano materials, but very relevant points will only be discussed in that lecture, the points which are useful to understand the topics mentioned here.

But for the time being you can just take it as a point that I have reduced the size from 1 micrometer or more and have taken a material which is of the order of 10 nanometers or twenty nanometers. I have taken a brick and else I have also taken a flick and then the properties are very different and that is why you choose the right material.

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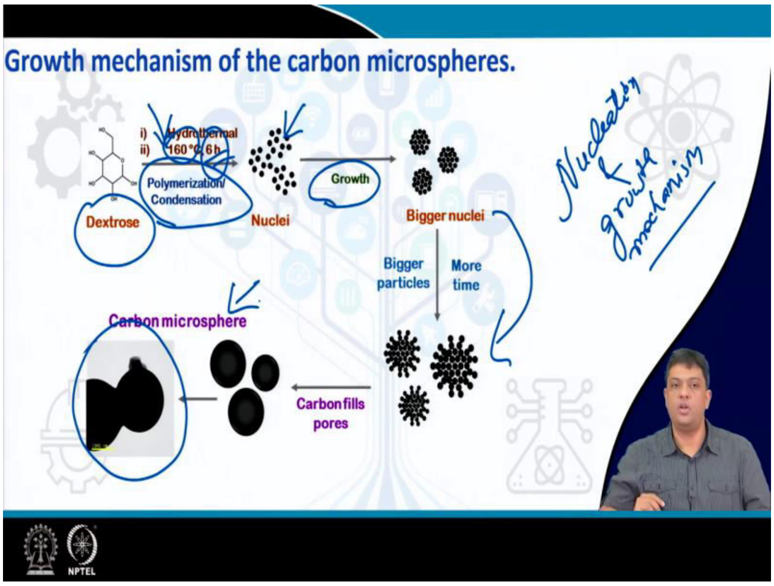

What happens, how do you make a carbon microsphere? Let us give you an example of this; you can start with dextrose in a hydrothermal jar. What is it it is just like a high pressure cell you increase the allow the vapors to appear but they are not allowed to escape that builds the pressure you heat it for certain time you can have polymerization and then subsequent condensation, because of this process you have the nucleation sites.

This nucleation site leads to the formation of nuclei, and if you allow this process to continue you have the growth mechanism taking place and if you allow the different nuclei to grow and then come together then you obtain different kind of size and shapes. This is a typical nucleation and growth mechanism, which is driven by the fact that the system wants to minimize the Gibbs free energy.

And you are driven by the fact that there are two competing energies, the volume and surface area related energies and in different regions and time you have one over the winning over the other. And after a certain times a critical radius is obtained where the growth take place. So, this can be explained as nucleation and growth mechanism.

At this point this is the only information which is useful for you, but you must also understand the importance of this mechanism and hence, when we are talking about the formation of nanostructures we will give you a detailed description about the nucleation and growth mechanism, and things will become very clear after you hear that lecture.

So, what you have seen what, the features which are playing the important role, reaction temperature and time. You may say change the reaction, change the time maybe you will get different kind of structures.

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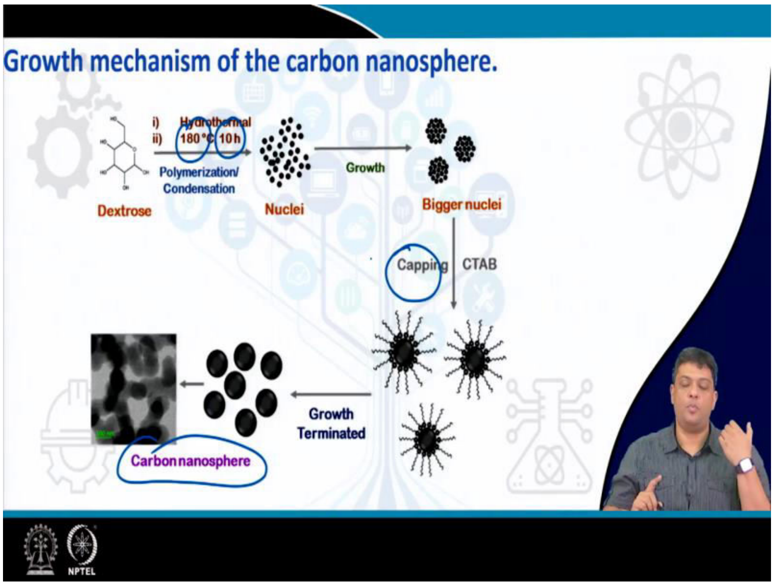

And that is what is done, you can go from carbon microspheres to carbon nanospheres or you can go from carbon macrospheres to carbon microspheres to carbon nanospheres. It is the change in the temperature which leads to different forms of structures. What you saw in the previous slide that you were allowing the particles to come together and then become bigger in size.

So, if I have to maintain a smaller size particle what should you do? You do not allow them to come together and if I am not allowing them to come together, there must be a way to prevent this and that is done using a capping agent. And this actually ripples the two particles, which now have similar charges when they try to come together they are rippled back and then they cannot coalesce or agglomerate.

This is how you can maintain the distance between the particles and do not allow them to agglomerate and the final particles which you obtain are much smaller than the particles you obtain when you are not using a capping agents.

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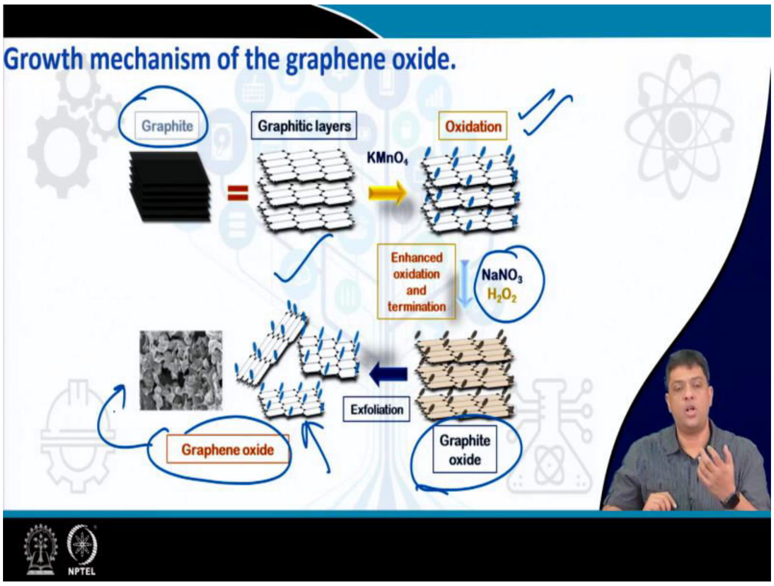

There are ways where you can obtain graphene oxides. This is what similarly is done you can start with graphite then you can sonicate in an ultrasonic path, you can sonicate. You will separate the layers of the graphite so you then obtain graphitic layers. You use the oxidizing agent and then you have an oxidation of these layers, enhance this oxidation and then terminate the reaction using an acid and hydrogen peroxide.

What you obtain is graphitic or graphite oxide many people call it as graphene oxide and then again ultrasonic head then you have the layers and what you obtain is a graphene oxide structures. So, this is the way you can obtain graphene oxide and if you get a single layer of these structures then you are actually obtaining graphene.

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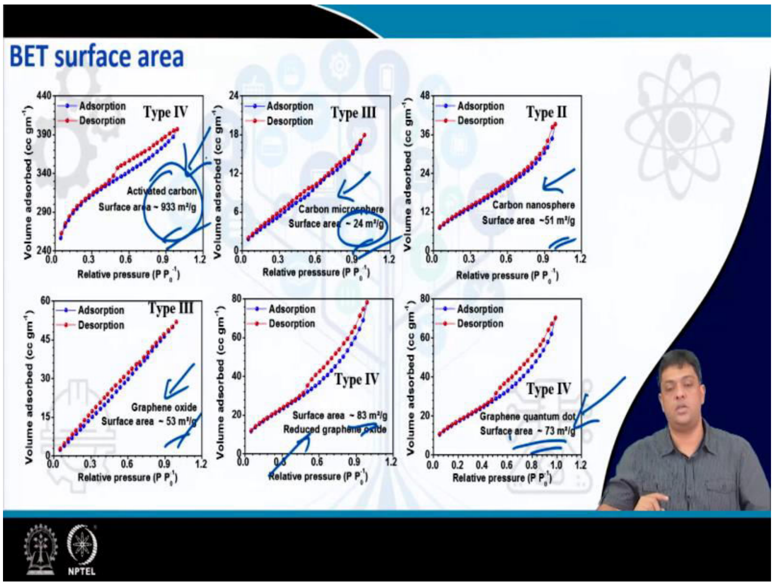

What is the difference if I take activated carbon I have a surface area of 933 meter square per gram, if I go to different kind of structures let us, say microsphere, nano sphere, graphene oxide or I go to reduce graphene oxide or graphene quantum dot then the surface area is changing and hence their electrochemical performances are also quite different.

If I ask you please choose the material which has the highest surface area, you will obviously choose activated carbon. Then if I tell you please choose the material which has the highest electrical conductivity then you will have to perform the electrical conductivity measurements and then determine.

And various permutation combinations have to be optimized so as to obtain the best performing material, which will be collaborating with your cathode material to give the desired performance. Activated carbon may actually be giving you a very high surface area but its channels may be such that it does not allow the intercalation or deintercalation of the lithium-ion.

Then can it work as an ideal anode material, what is your answer? Yes, it cannot be used as an anode material, because it is not allowing the exit of the lithium-ion. Then what type of materials should I use, most probably I should go towards graphite structures which are layered structures and that would be more useful.

But if I use those kinds of materials, do they have the similar surface area, if they do not have the similar surface area then I have to use more materials then the weight will go up. So, you have to choose the right material which gives you the best performance to collaborate with the cathode.

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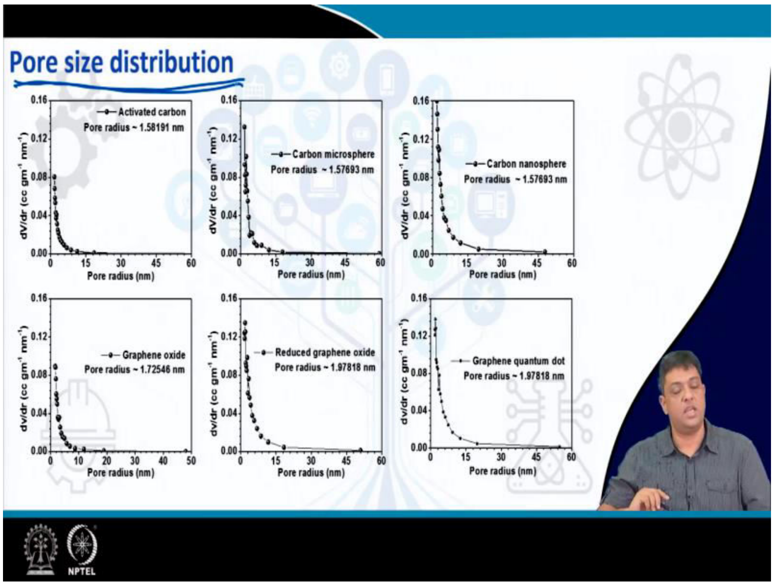

And the next parameter which you will see later is the Pore size which plays an important role. What is this pore? The pore is actually the vacant side which is available in the structure or the material to accommodate the incoming electrolyte ion or the ions which are traveling along with the electrolyte. So, the vacant sides within the material.

So, you should also have a porous material, so that it actually allows the ions to come inside and then undergo the electrochemical reactions. So, this will also be discussed in detail during the characterization week.

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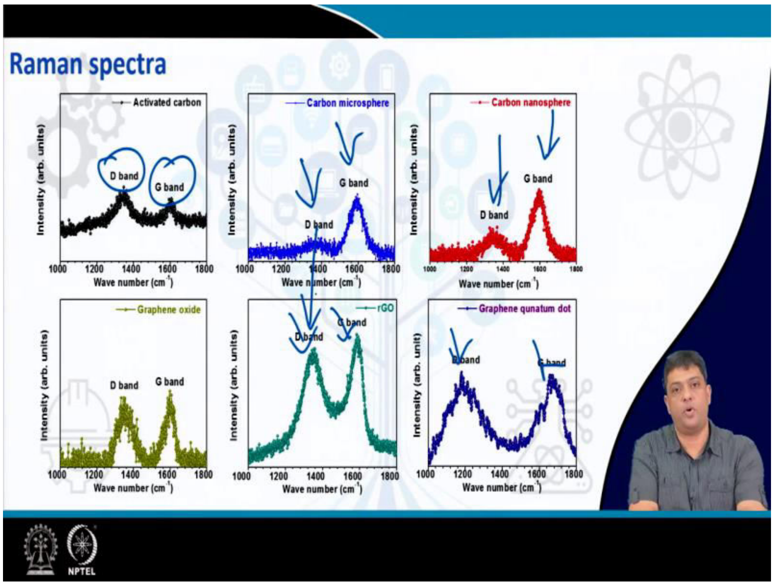

And similar to what we had discussed in the previous lecture about the Raman and the FTIR data, you have to again confirm using the Raman data, whether you are actually getting the characteristic D band or G band. And if they are getting formed then you have actually obtained the carbon structure, but when you obtain this data things are very clear.

Are the intensities of both the bands similar? You can clearly see that they are not and they are of different magnitude. So, if you compare the intensities of D bands of carbon microsphere with that of reduced graphite oxide they are very different. What is the meaning of this? Although you are getting a carbon like structure or a carbon based material which is similar to graphitic structures, but still you have different ordering of carbon in them and their electrochemical performance becomes different.

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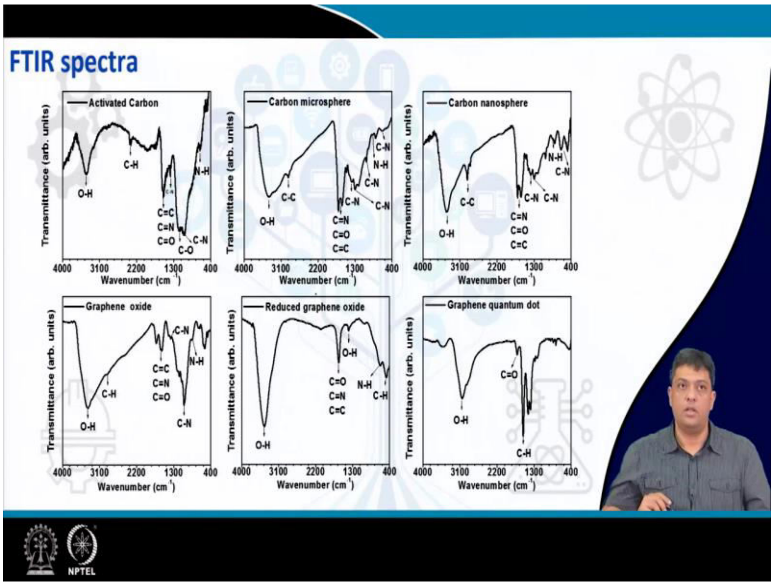

And the same information is obtained using ftir.

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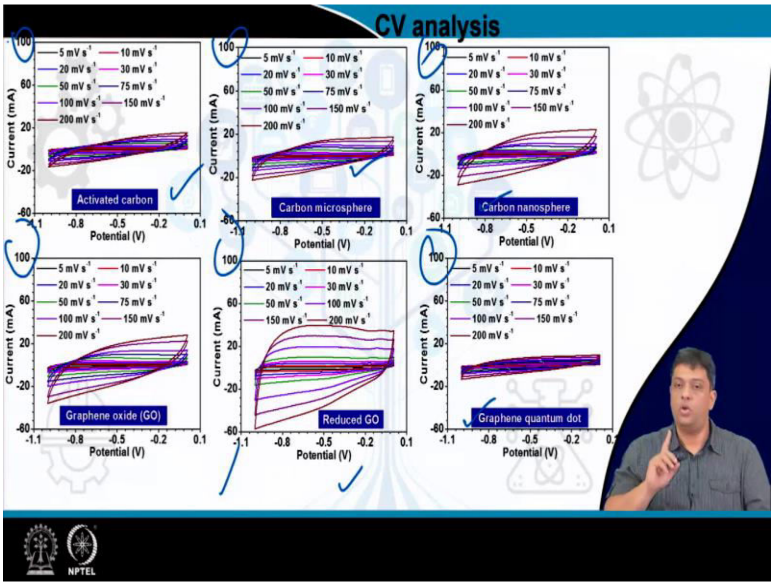

As we moved for cathode material, what next you need to do? You need to analyze their electrochemical performance the cyclic voltammetry and the charge discharge. Cyclic voltometry, how fast they can react with change in current and voltage and how fast the response is there if I want to change the scan rate. At different rates I am putting in the charge and I am extracting the charge at different rates, how the materials are responding.

And you can clearly see if I have drawn the curves to same scale the response characteristics also change. The details about this curve how you interpret will become clear in the later lecture. It is only shown to convince that the electrochemical performance of anode materials can vary significantly, even when they are made of similar carbon like structures. So, you must be very clear on this point.

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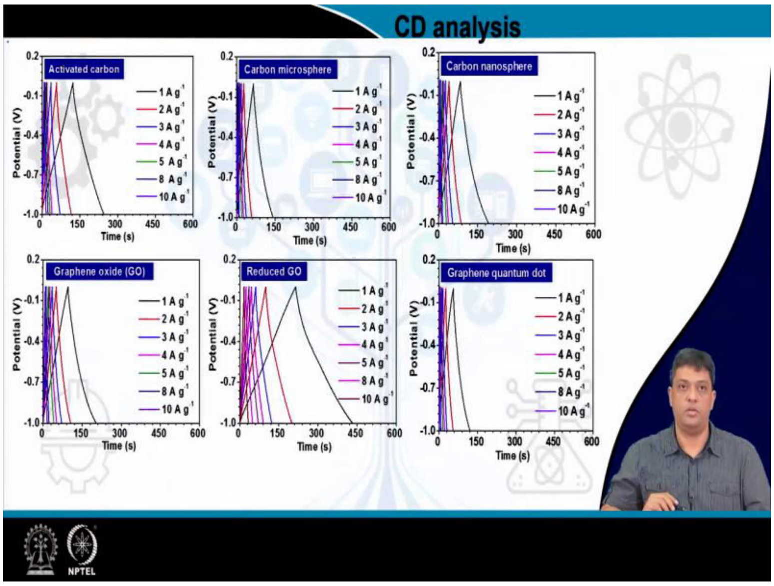

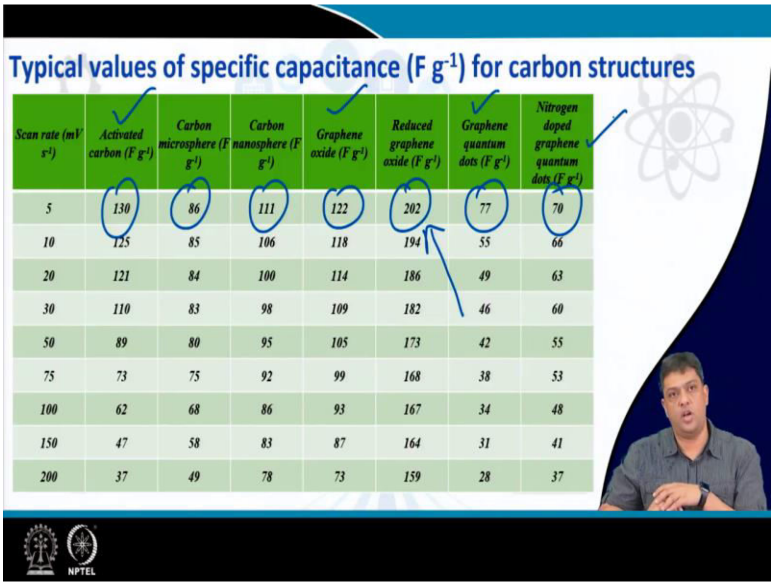

Scan rate (mV s-1)	Activated carbon (F g-1)	Carbon microsphere (F g-1)	Carbon nanosphere (F g-1)	Graphene oxide (F g-1)	Reduced graphene oxide (F g-1)	Graphene quantum dots (F g-1)	Nitrogen doped graphene quantum dots (F g-1)
5	130	86	111	122	202	77	70
10	125	85	106	118	194	55	66
20	121	84	100	114	186	49	63
30	110	83	98	109	182	46	60
50	89	80	95	105	173	42	55
75	73	75	92	99	168	38	53
100	62	68	86	93	167	34	48
150	47	58	83	87	164	31	41
200	37	49	78	73	159	28	37

And in terms of specific capacitance, if you look into these carbon structures you can clearly see that the values are also different this is what was told to you in the earlier slide. So, if I tell you please choose a material which gives you the highest specific capacitance at a scan rate of let us say 5 milli volts per second, which material will you choose if you look in through this slide?

You would like to use a reduce graphene oxide, but I say no please, use a material for two applications but they should have similar specific capacitance at 5 millivolt per second scan rate. Then maybe you can take activated carbon and graphene oxide or you can take graphene quantum dots with nitrogen dope graphene quantum dots. So, depending upon your application you choose the materials.

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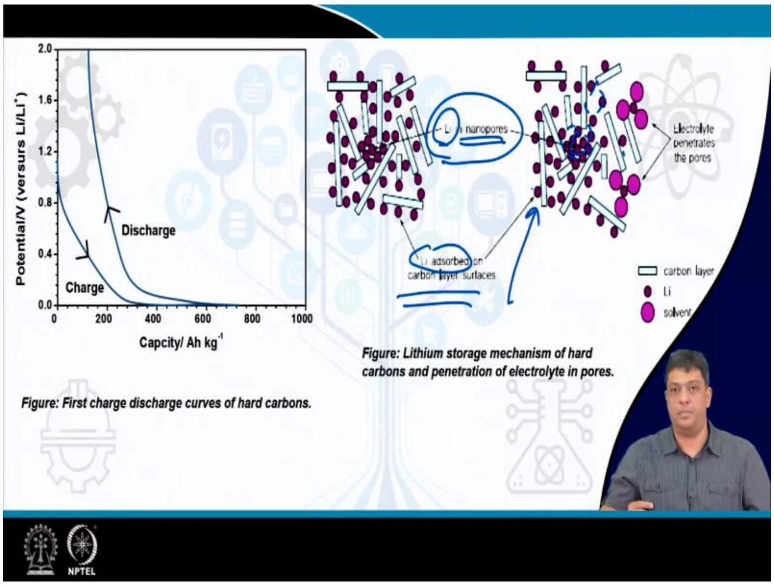

And once again this curve is drawn to show you what happens if you have carbon structures then you are actually allowing lithiums to move into the nano pores. So, these are the vacant sides which are called as pores, these are the places where lithium will also go and get stored along with what lithium getting adsorbed on the carbon layer surface.

So, there is adsorption and there is in the collection in the pores, the nanoporous regions within these structures. So, ideally your structure must be such that it should have porosity, it should have pores and it should also be of layered type and that is where carbon structures have become so important.

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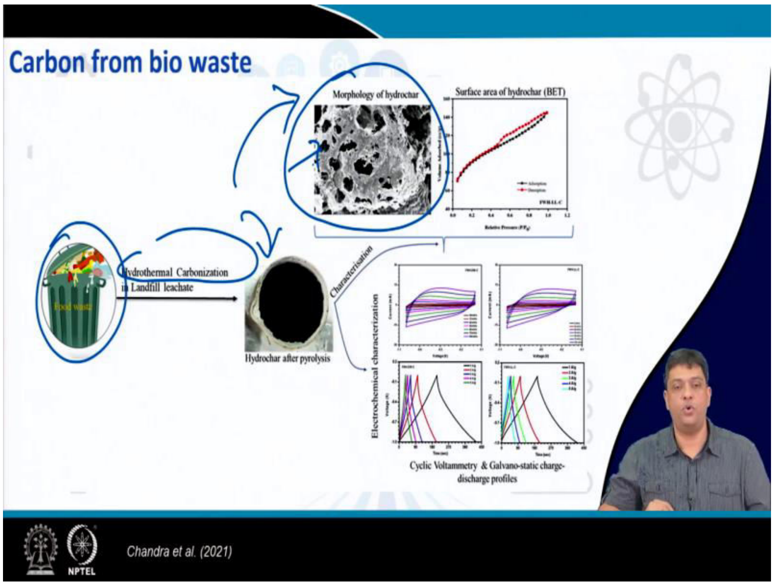

In recent times you may have seen that we are talking about how to manage waste and one way to use bio waste is actually, to use this bio waste and convert into carbon and if you do so you can get carbon structures. So, if you start with food waste just perform the hydrothermal based carbonization, you can get after pyrolysis you can get the hydrocharge which are carbon structures which have all the desired characteristics that you have just mentioned.

What have we mentioned? We have mentioned carbon-based structures, which should be layered structures, which should have high electrochemical performance, which should have porosity. If you look into the scanning electron microscope of this hydrochar which was obtained after pyrolysis this has all the characteristics. So, what have you done? You have taken bio waste and you have converted them into an expensive or at least very useful material and this is where we can come into picture with time.

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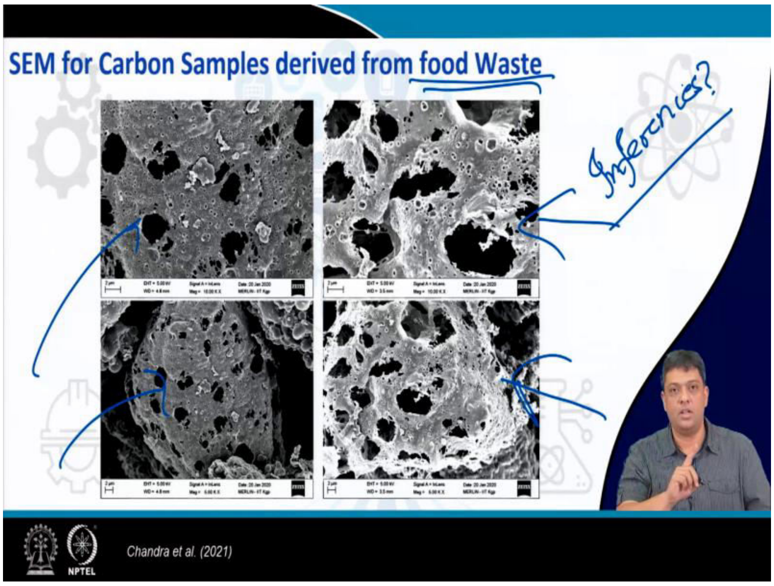

If you want to initiate work from the industrial point of view, you can use various types of wastes be it food waste, but you can get different kind of carbon structures. Can you draw the inferences, and write what all features do you see from this picture which is showing the carbon samples which are derived from food waste? List it and you will find that all the features I mentioned while describing the characteristics associated with the anode material are linked here.

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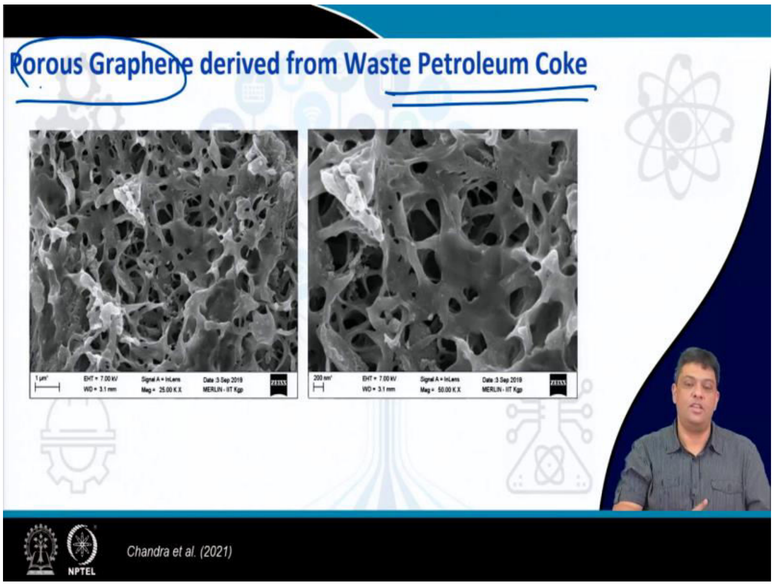

You can use petroleum waste, so if you have waste like petroleum coke you can use the same waste petroleum coke to obtain highly porous graphene structures and they can be used in your battery. So, you are converting waste and you are using for a high-end application.

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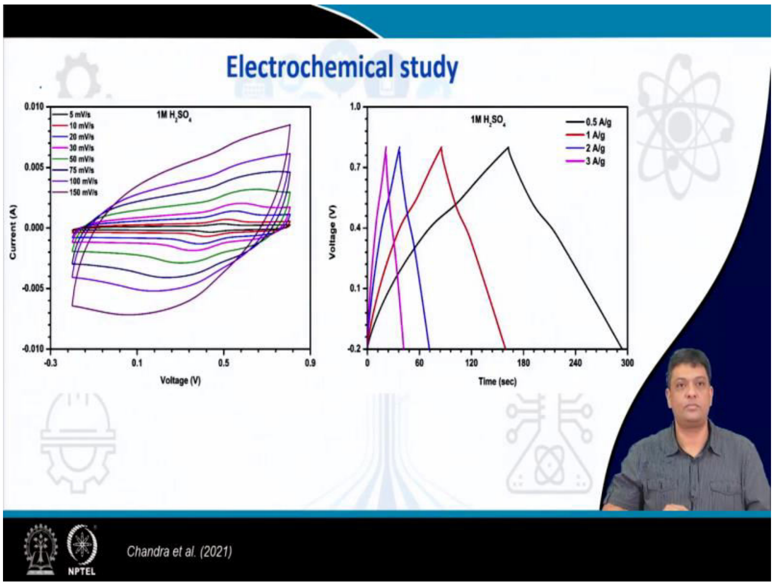

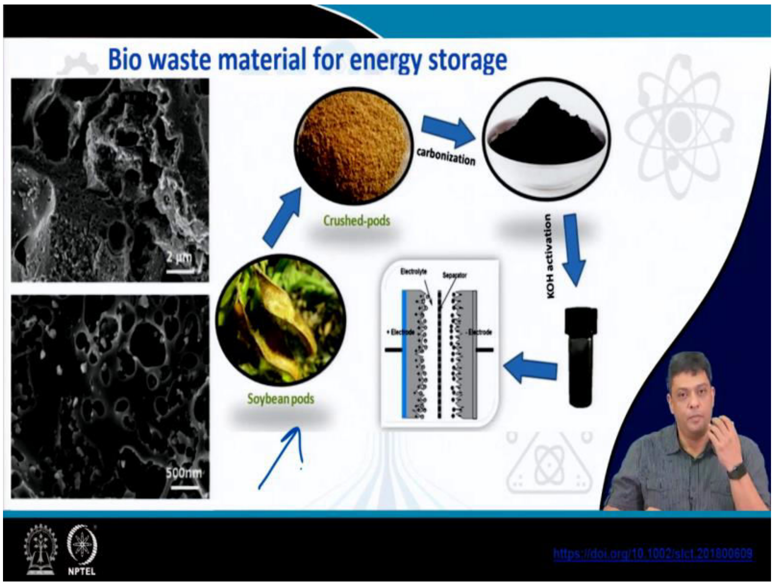

And there are various types of bio systems which are used. For example, I have just mentioned here soya beans, people are using ginger, you are using coconut shells, people are using the leaves, any kind of bio waste which have carbon in it can be used to derive carbon out of it.

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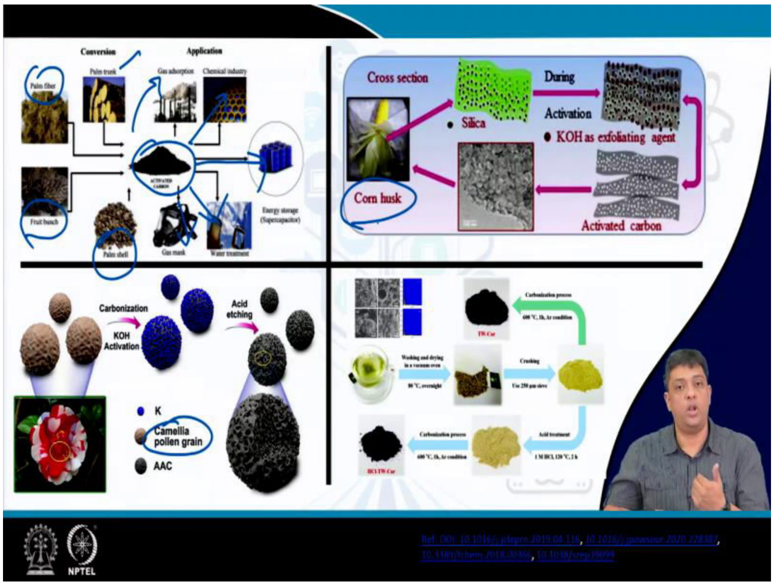

You can use palm fibers, you can use the fruit bunches, you can use palm trunk, you can use palm shells and you can have carbon which can then be used for various application. It can be used for gas adsorption, chemical industry, energy storage, water treatment, gas mass. Similarly, you can even use like a flower to act as the raw material for carbon extraction.

You can use corn husk something which we throw in the dustbin or you can use the rice waste or husks to act as the source for carbon structures. You can rather than burning in air in open fields you can take them into industry, use the hydro thermal jars and then convert into usable carbon. So, something which was a waste can become an extremely useful and to in to an extend quite an expensive material which is used for large number of applications.

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For example, let us take one more thing like you have a caltrop shell. You can get different kind of structures and they have different performance.

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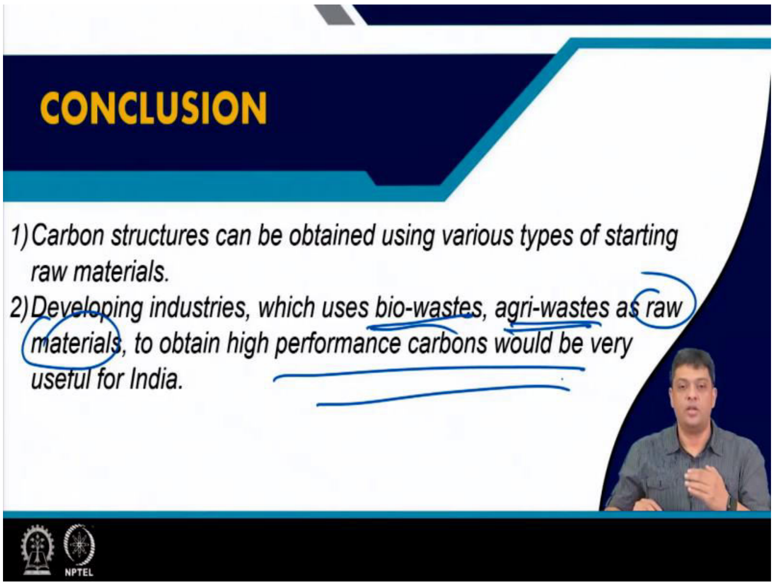

Hence, it must be clear to you that carbon structures can be obtained using various types of starting raw materials. Carbon structures are extremely important why, because they have application in large number of industries. More so if I am talking about lithium-ion batteries most of the commercial lithium-ion batteries use carbon based anodes. Also, if you are talking about next generation sodium ion batteries, they also have carbon based anode materials.

So, if I am talking about our country and if you have to build industries which have to contribute in the progress of lithium-ion battery technology or sodium ion battery technology then we can use and develop industries which are going to utilize bio waste or even agri-wastes as raw materials to obtain high performance carbon which would also contribute in reducing the environmental impact of these waste. And increasing our reliance on our own industry to obtain these materials and we can reduce the cost because then we are not importing these materials.

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These are the references which were used to prepare the lectures today and in the next lecture we will talk about the next three major components. Namely the electrolyte, the separator and then if I can bunch them together the components such as binder, the conducting elements and the current collectors. So, we will talk about the remaining components, which are critical for high performance lithium-ion battery in the next lecture. Thank you very much!