**Physics of Renewable Energy Systems**
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**Lecture – 30**
**Construction, Development and Classification of Supercapacitors**

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Hello, welcome to the second lecture on supercapacitors. In today's lecture we will be talking to you about the history of supercapacitors, the types of supercapacitors and the materials which are required or which are being synthesized to obtain high performance supercapacitors. As I have been emphasizing throughout this course; that it takes time for a technology to mature so that it can go to the market and become useful to the end user or society at large.

Therefore, it is very important that we talk about the history of supercapacitors so that you will be able to realize that what has been going on this technology for last five to six decades and it is only for the last two decades that it has become relevant and economically viable technology so that it is going into devices such as e-vehicles, mobile phones any kind of automobiles, where you are going to use them as charge providers during the ignition.

And you will realize that there are various types of supercapacitors which will be discussed today, but it is again the materials aspect which will be very critical and must be understood clearly because that will lead to the development of high performance supercapacitors.

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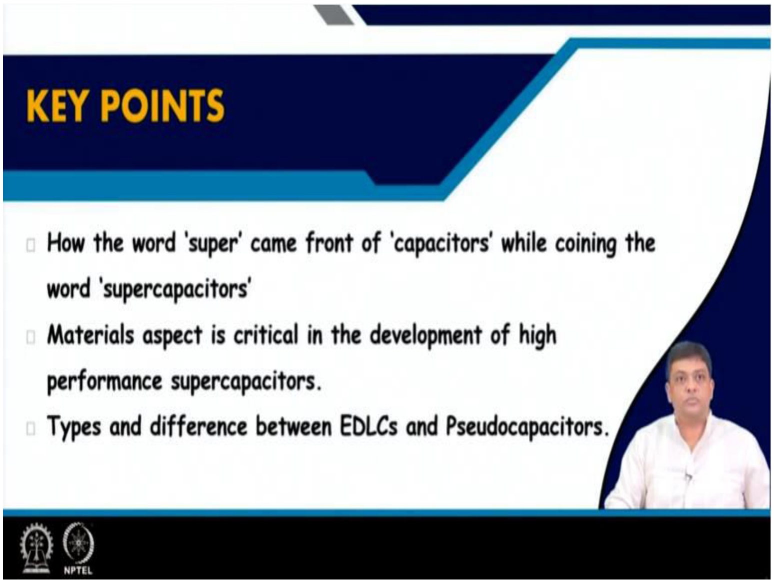


Now you have heard about the word capacitor. Today I will explain the origin of the word ‘super’ before the word ‘capacitor’ so that the word ‘supercapacitor’ came into existence. What was the reason that people started calling these kinds of devices as supercapacitors? So you will be able to understand this clearly. As I just said materials aspect plays a critical role in deciding the final performance of such devices.

And there are two main types of supercapacitors that are being studied as of today, those are the electric double layer capacitors, which have been written as EDLCs here and the second are the Pseudocapacitors. I will also explain bit later why do you call them Pseudocapacitors. Because the word pseudo means something which is actually not there, but it appears to be there this is the word pseudo.

So how come a device is becoming a pseudocapacitor; so that will also be explained and you will understand the difference between EDLCs and pseudocapacitors, clearly by the end of this lecture or the next lecture which is dedicated to Pseudocapacitors. Today we will focus on electric double layer capacitors.

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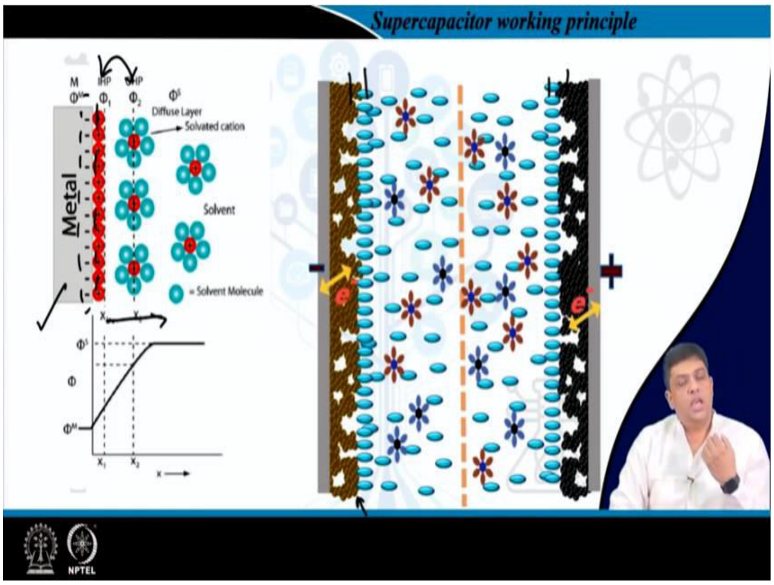


As discussed in the previous lecture where we talked about moving from battery to supercapacitor technology, supercapacitors are the one where you have charge separation at the interface and you get parallel arrays of charges which lead to the formation of layers which are very similar to the capacitor effects.

And this is what it means that you have an electrode where you have the appearance of charge when you apply a voltage and then in the electrolyte you have two layers which form the inner helmholtz layer and the how outer helmholtz layer, which lead to the appearance of capacitance. This figure will become very clear by the time I finish this lecture.

So, I hope you will be able to answer the points which just mentioned and these will be the main key points which you will take back after listening to today's lecture.

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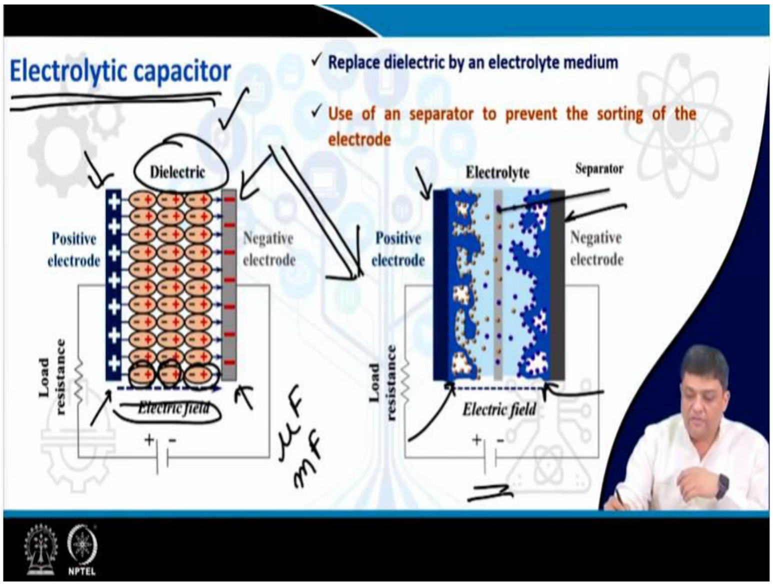


In the previous class, we had discussed about the electrolytic capacitors. What are electrolytic capacitors they these are two parallel plate capacitors made up of metallic plates and in between you have a dielectric and when you apply external potential then you lead to the appearance of charges on these plates and the dielectric media gets polarized.

And you have the arrangement of the electric dipoles, which lead to the appearance of an electric field, which was explained by the concept of displacement current in the maxwell's equations. So these are electrolytic capacitors. And the typical range you were looking at were from microfarad to millifarad, this is the typical range of capacitance which you obtain using these kinds of capacitors that is the electrolytic capacitors.

Now as we want to have devices which have higher energy densities, but you are looking to miniaturize the device that means you are looking to reduce the size of the device. So, what is the way out that you need to develop new newer technologies, whereby you can increase the capacitance value, but reduce the size of the capacitance and this was actually obtained in a device which is now called as supercapacitor.

If you compare the electrolytic capacitors with the supercapacitor technology or the device there is clearly a difference in the construction. What is the difference? You have the current collectors on both these sides. On top of these collectors you have the negative electrode or the positive electrode depending upon the field you are talking about or the potential you have applied and in between you have the separator and this is filled with an electrolyte.

So, when you apply the field you lead to the condition where charges appear on the electrode and the corresponding charges appear in the electrolyte side and you have parallel arrangement or the array of charges and these are two layers, so you call them double layer and similar picture appears on the other electrode as well. This is the difference between the electrolytic capacitors or supercapacitors.

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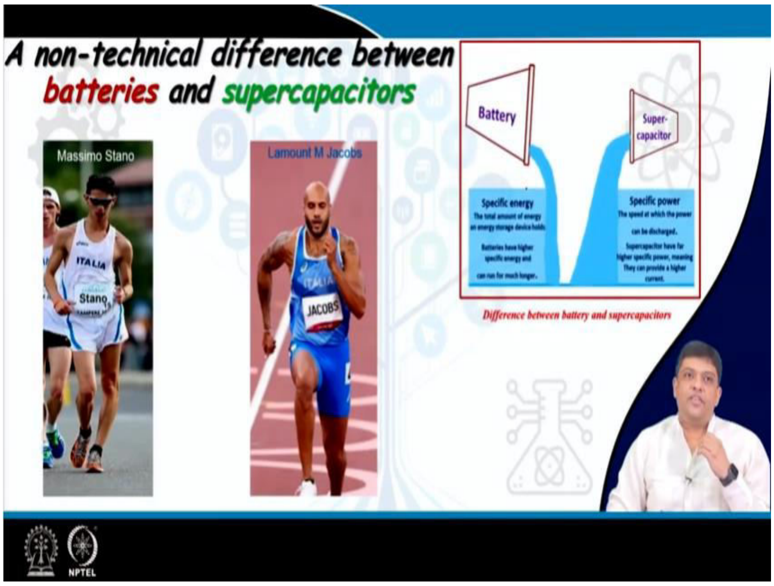


A very non-technical difference between a battery and supercapacitor can be understood from this slide. So, I just took the pictures of the two gold medalists of the recently concluded Tokyo Olympics, where Massimo Stano was the winner of the 20 kilometer walk, whereas Jacobs was the winner of 100 meters race. Now, if I compare these two athletes then do you think that Jacobs would be able to run at the same pace for 20 kilometers?

Obviously, the answer is not possible but Jacobs need lot of energy for short period of time. If I compare Stano, the winner of the 20 kilometer walk, then Stano actually, if he walks at the same pace of walking then obviously, he will not be able to compete in the 100-meter race so, but the pace he maintains for the 20 kilometer distance is similar.

So and it is very slow rate of reduction in the energy which Stano depicts, so maintains similar energy level but for long period of time, whereas Jacobs burst of energy but for short period of time. So that is a non-technical way of understanding the difference between batteries and supercapacitors. Batteries are what? They are high energy density devices, whereas supercapacitors are high power density devices.

That means batteries have higher specific energy and it gives nearly constant energy for a long duration of time, but supercapacitor delivers lot of energy in a short period of time, so this is what do you mean by high power and high energy density systems what is the difference between the two.

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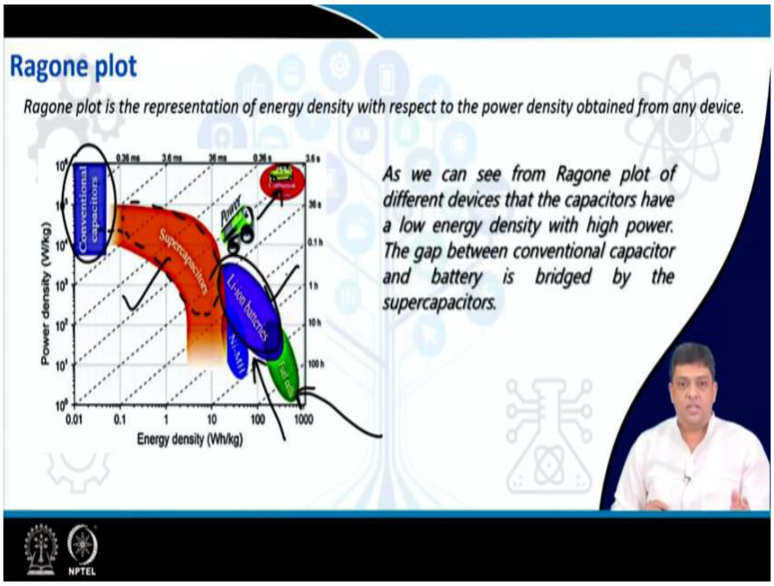


And if you compare the conventional capacitors with batteries or another technology that is fuel cells which we will be discussing in a couple of weeks time supercapacitors actually bridge the gap between the two. So they are giving you higher energy densities than the batteries but you see that there is slight loss in the power densities than conventional capacitors. So, the aim is to move towards a system which can lead to hybrid performance.

That is the advantages of supercapacitors as well as the advantages of lithium-ion batteries are combined together and then you can get a hybrid technology, which will be able to give you high energy density as well as high power densities and that would be an ideal kind of energy storage device which would be useful to us and what is already going on towards development of hybrid storage devices.

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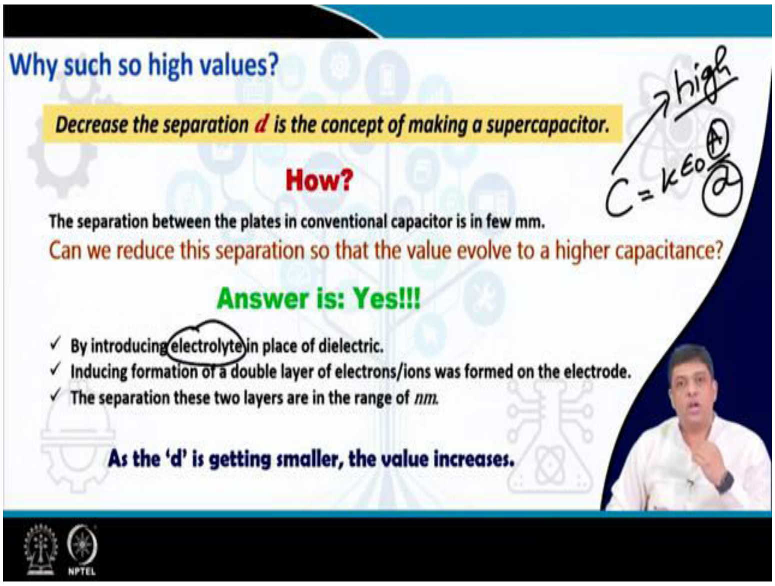


As I said that supercapacitors can obtain very high specific capacitance or the capacity of these devices are very high. What did we see in the case when we were talking about the electrolytic capacitors? We had seen that you are going to write the capacitance as k epsilon naught A by d. Now to increase the value of C there were two main features which we could consider either increase area or decrease d.

And if you increase area then what you see the weight of the capacitors, increase the construction become non-trivial and lot of manufacturing issues come into picture. If you decrease the value of d then the dielectric which is in between the plates then that becomes reduce and if you have dielectric which is not able to be mechanically stable and prevent the short circuit between the two plates the device itself will fail and so there were lot of issues involved when you were looking into this formula.

And thinking how to increase area and decrease d so that I can get high value of C and we will see that this could be achieved by introducing an electrolyte in place of a dielectric medium inducing the formation of a double layer of electrons ions at the electrode interface, use of nanomaterials which actually led to many fold increase in the specific area that was becoming available to you.

And by using this strategy you could reduce the layer between the two parallel arrays of charges which were opposite to each other but stabilizing and facing each other. This separation between these two layers could be significantly reduced and as it could be reduced to a range of nanometers or so the overall capacity could be enhanced by many orders compared to conventional capacitors, so this is what was done.

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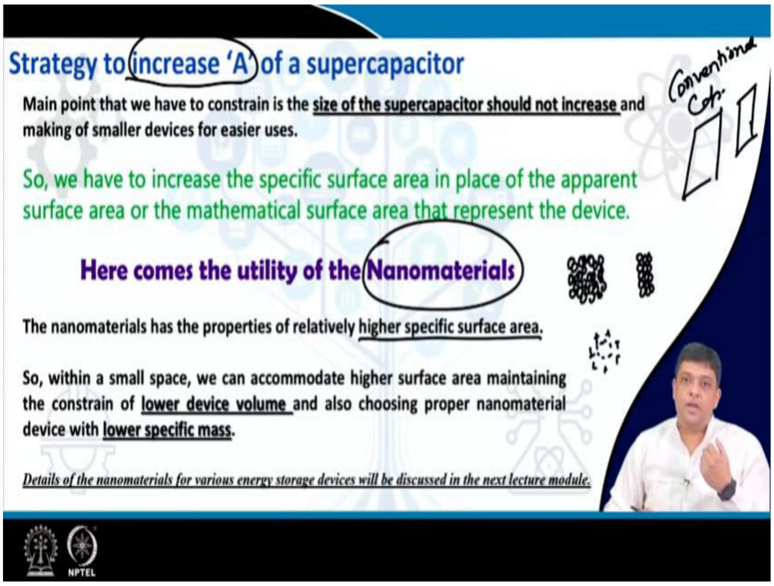


Let us see, strategy number one that is increase area. We should find out the difference in conventional capacitors. Let us say conventional, what were we using conventional capacitors we were using a solid metallic plate and then the other electrode was also the same. How do we change this? That is where came the utility of nanomaterials.

What is the advantage of nanomaterial? It has the properties of relatively very high specific surface area. So, within a given space we can accommodate higher surface area maintaining the constraint of lower device volume and by choosing proper nanomaterial you could also have lower specific mass. So instead of using the solid plates we could use nanomaterials to form a plate and similar with the other side.

So what was happening the charges which were only forming just at the plane parallel to the plane which was defining your metallic plate in conventional capacitors in nanomaterials you would have the charges, so if I have a nanomaterial the charges could stabilize all around because they were giving you accessibility to those areas.

So that was the major advantage which came by using nanomaterials and use of nanomaterials is extremely critical for obtaining high performance energy devices be it be batteries, be it be capacitors or supercapacitors what we are discussing now and therefore we will have a dedicated module on nanomaterials and nanotechnology useful for energy systems.

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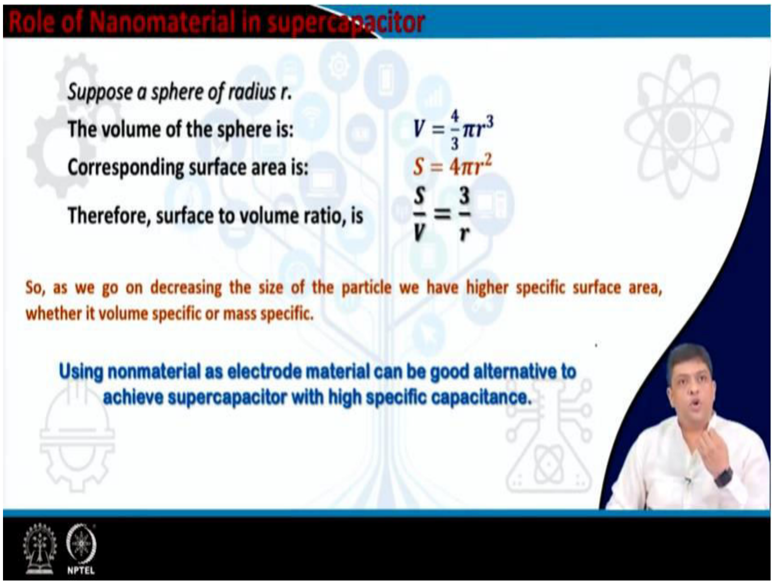


Just to give you a feel how this changes, suppose you have a sphere of radius r, the volume of the sphere is given by 4 by 3 pi r cube. What is the corresponding surface area? Surface area for this sphere is 4 pi r square. Take the surface to volume ratio; surface to volume ratio is 3 by r. So if you want to increase the value of surface to volume ratio, then what is the way out, you can reduce the radius of the sphere.

As you are reducing the radius of the sphere you can that means have accessible surface which is much higher than the point when r is higher. So, what is the way out? Reduce r reduce r means you are going towards let us say from micron region to nano region. Therefore, you could improve the area by using nanomaterials, which are known to have very high specific surface area. Just to give you a definition of nanomaterials these are what?

Nanomaterials are the one which have at least one of the three dimensions in the range 1 to 100 nanometers. This is the most acceptable definition as of today and because of these confinement effect you have different properties which are observed in a nanomaterial compared to a micron size material of the same molecular formula. So, you have the quantum mechanics phenomena coming into picture when you go from bulk micrometer range to nanometer range.

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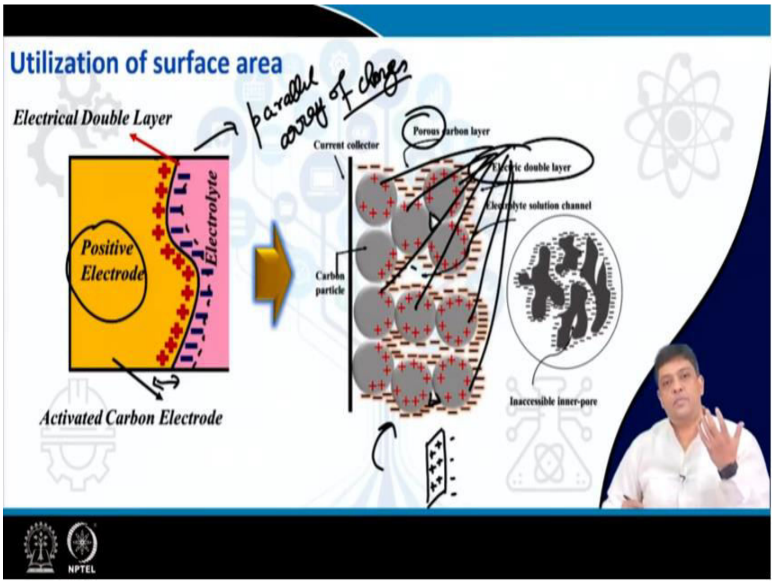


And this is how the double layer actually forms in these kind of surfaces, so you have the positive electrode then in the electrolyte side you have the negative charges stabilizing, so the counter charges stabilizing and then as you see forming a parallel array of charges. In addition, the nanomaterials are known to have the porous structures or pores the voids between two particles, so it can be this space between two particles.

So what happens, if I have to draw a conventional plate then you have, this is what is forming in the conventional capacitors but in the nanometers size particles you have much higher areas which are associated with each of these particles. So, each of these particles take part in the reaction or contribute in the formation of double layer and hence your accessible area becomes very high, your specific capacitance also increases.

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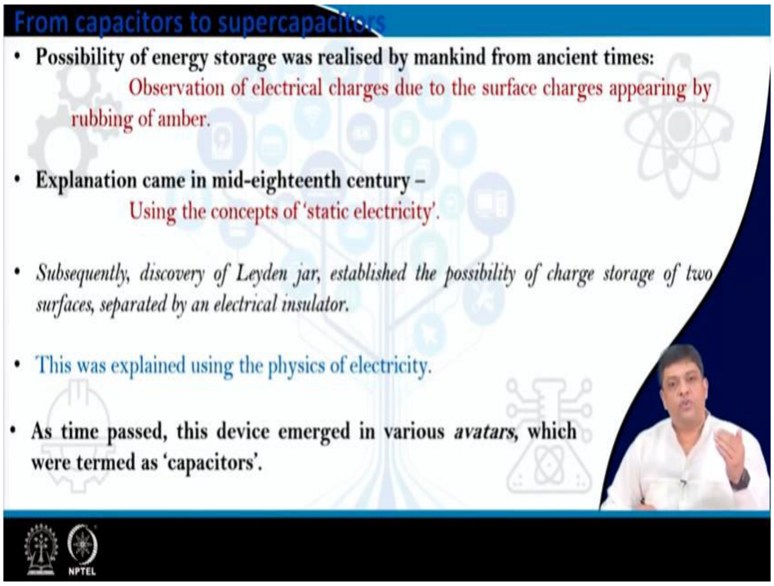


So, we are till now convincing you that there is a way of moving from capacitor that is conventional capacitor to a new kind of technology that is supercapacitor. And the concept of storing charges or electrical charges on surfaces was known to mankind from ancient times. We have all seen the example where surface charges can appear by rubbing amber.

The explanation of this observation came in mid eighty, eighteenth century where the concept of static electricity or static charges was proposed and subsequently you had the discovery of the Leyden jar which established the possibility of charge storage of on two surfaces, separated by an electrical insulator. This was explained only after the physics of electricity was understood and explained.

And that is the reason in the previous class we had spent significant amount of the time to discuss on Coulomb's law, what happens when there are charges which are separated, how do you calculate the energy, how do you calculate the field induced, because those concept were necessary to explain the device which were later termed as capacitors.

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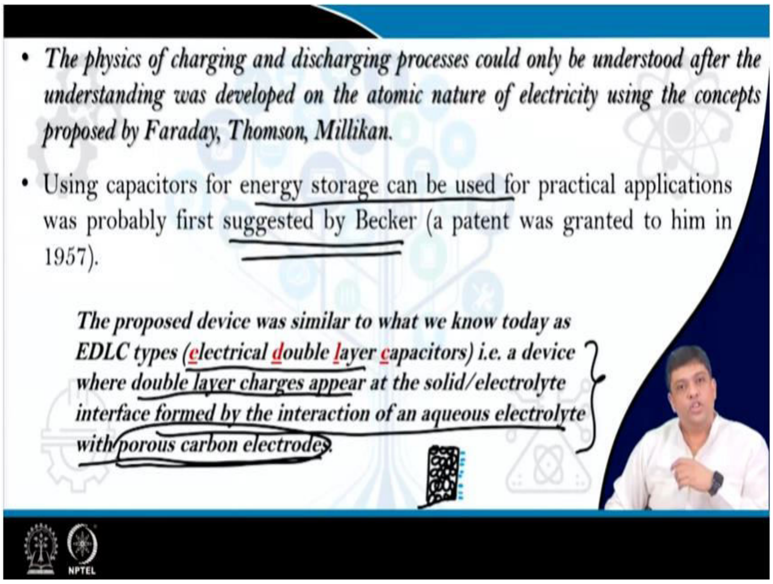


And the physics of charging and discharging processes could only be understood when only after there was an understanding about the atomic nature of electricity, using the concepts of Faraday, Thomson and Milliken. So, lot of physics was used to explain the concept of the charge storage on a surface, then only the devices were called as capacitors.

Using capacitors for energy storage was most probably used around mid 1950s, when Becker proposed this concept and a patent was granted to Becker in 1957 for a device which is very similar to what we call today as electrical double layer capacitors, that is where double layer charges appear at the solid electrolyte interface formed by the interaction of aqueous electrolyte with porous electrodes.

So, if I tell you that just do not go to the next slide try to make a capacitor just with what is written on the slide. Let us see you are looking at double layer formation, electric double layer formation, so you are looking at capacitor. So, that means you have to have two plates, where double layer charges appear, so it is indicating that the double layer is appearing at this solid electrolyte interface.

So, let us draw a solid, so I have drawn a solid. Why I have done this kind of picture because the solid which was used was porous carbon, so the material was porous and electrolyte interface. So, if I draw the electrolyte maybe it is the interface between the solid at the aqueous electrolyte interface where the charges were appearing.

So, solid electrolyte interface that is the boundary between the two systems and that is where the charges appear. This is what was proposed by Becker way back in 1950s and lot of work is still going on, so we have moved on around 70 years and still on daily basis you have research publications which are reporting improvement in these devices.

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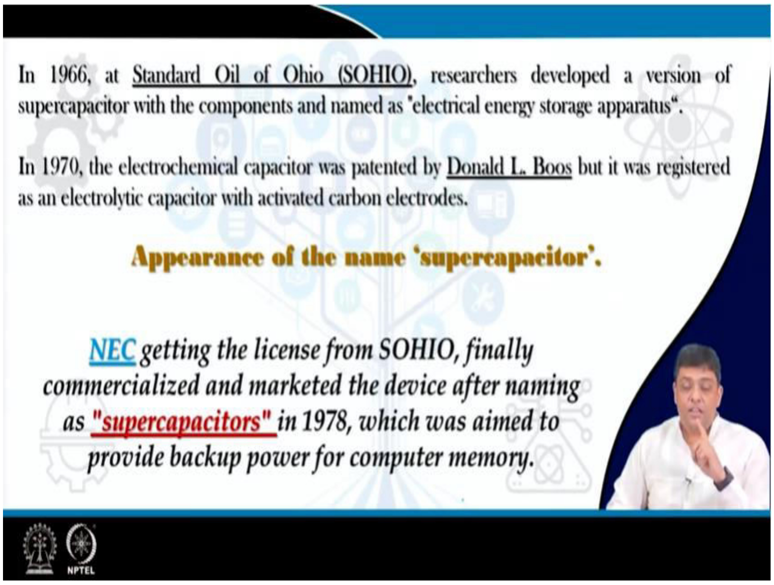


But still the word supercapacitor has not been coined, please note. Similar device was proposed in 1966 at the Standard Oil of Ohio, where researchers developed a similar device and called it as electrical energy storage apparatus. So we moved on from 1950s to 1960s, new version of the device came out and a new name was coined. The new name was electrical energy storage apparatus.

So, it was actually being used for energy storage. In 1970, the electrochemical capacitor was patented by Donald L. Boos, but it was not still registered as supercapacitor, it was registered as electrolytic capacitor with activated carbon electrodes. So, still 1950s, 1960s and we have reached 1970 onwards still the word is not coined.

It was only in late 1970s that the word supercapacitor was coined, where the NEC Company got the license from the Standard Oil of Ohio and commercialized this device and named it in their term supercapacitors which was aimed to provide backup power for computer memories and they called it supercapacitors, they could obtain very high capacities that was the reason they called it supercapacitors.

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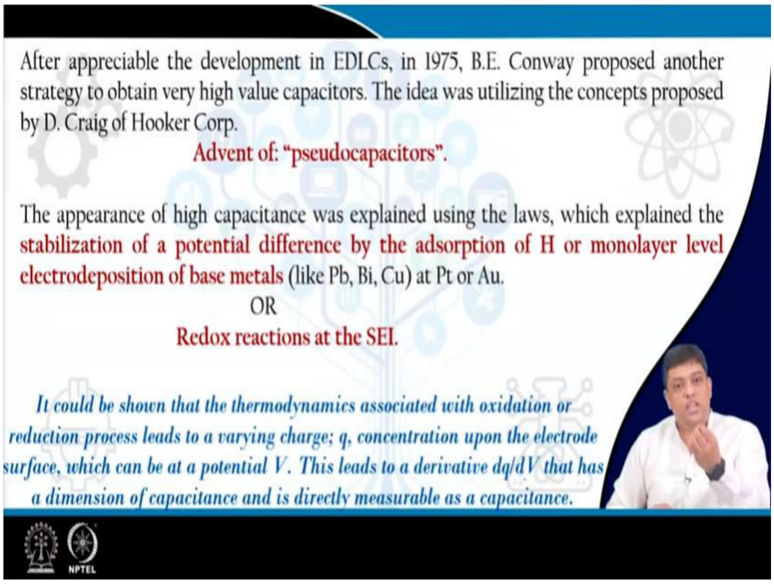


So, we have gone from 1950s to 1960 and late 1970, 70s you get the word supercapacitors. The word supercapacitor has been coined but again in middle of 1970s, Conway came into picture and proposed another strategy to obtain very high value capacitors, so very high value capacitors. They were not utilizing carbon electrodes.

They were actually having a different concept which was leading to a quantity which has the dimensions of capacitance and hence it could be directly measured. So, Conway came into picture and then proposed the concept of pseudocapacitors where you had the variation of dq by dV that has a dimension of capacitance and is therefore directly measurable as capacitance. So you had another technology coming into pictures that was pseudocapacitors.

The appearance of high capacitance in these supercapacitors could be explained using various laws but predominantly the concept was explained by the fact that there was a stabilization of a potential difference by the adsorption of edge or monolayer level electro deposition of base metals on wire at platinum or gold surfaces.

Or the concept of pseudo capacitors was analyzed again and the phenomena could be explained by considering the Redox reactions taking place at the Solid Electrolyte Interfaces. This concept will also be explained in detail in a dedicated lecture.

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These are the two typical kind of devices which we investigate in laboratories and we will therefore focus on them so that if anybody gets interested. You can fabricate them very easily and then try to understand. So you have coin cell looking like a coin and a pouch cell.

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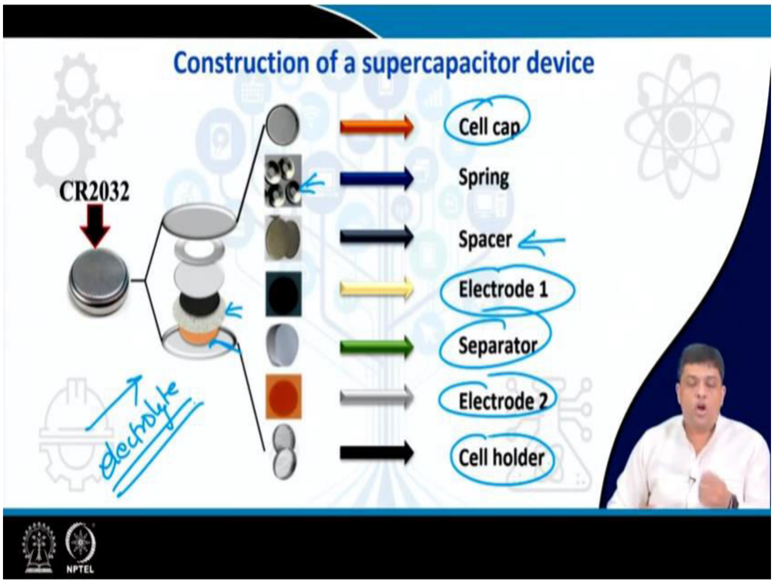


To make a coin cell you have a typical cell cap and cell holders. So, what you do? You take the cell cap then you have the spring we have very similar to lithium-ion batteries, it prevents the mechanical pressure on the electrodes and prevents failure mechanical failures of the electrodes, then you have the spacers which is which goes between the spring and the electrodes then you have the first electrode.

The separator and then the second electrode and what you do you put the whole system in a coin before you are actually closing the cell you soak the electrodes and the separators with electrolyte or you drop the required amount of electrolyte which you may have optimized using various processes. So, this is the construction of a coin cell.

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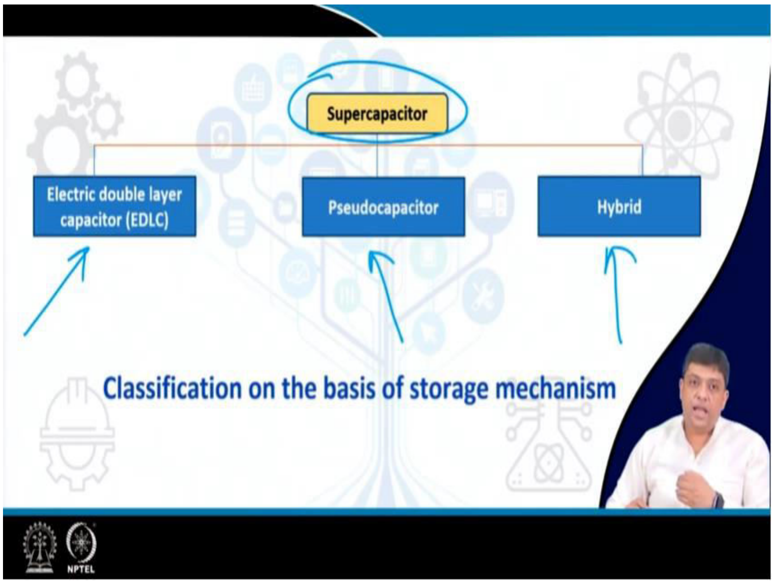


So, if I quickly revise, then there is a device which is supercapacitor. Super, why because the values are extremely high. It can be classified under various subheadings, either the electric double layer capacitors, the pseudocapacitors or the hybrid type supercapacitors, hybrid type which have both high energy densities as well as power densities.

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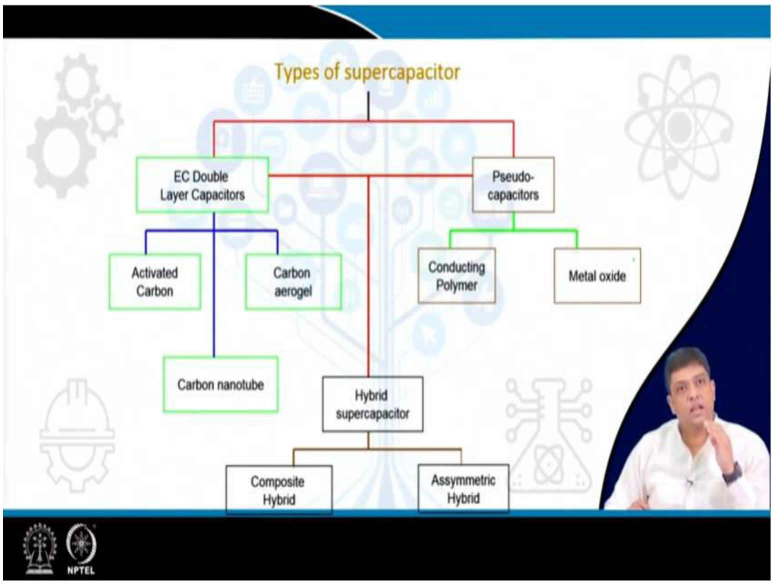

Or you can understand the types of supercapacitors based on the kind of materials they use, so electric double layer capacitors, the pseudocapacitors and the hybrid supercapacitors. Double layer capacitors mostly using carbon based materials. Pseudocapacitors mostly using metal oxides or conducting polymers, whereas hybrid capacitors take the combination of these two kind of materials, so you can have composite hybrids or asymmetric hybrids, but they will be using a combination of two types of materials.

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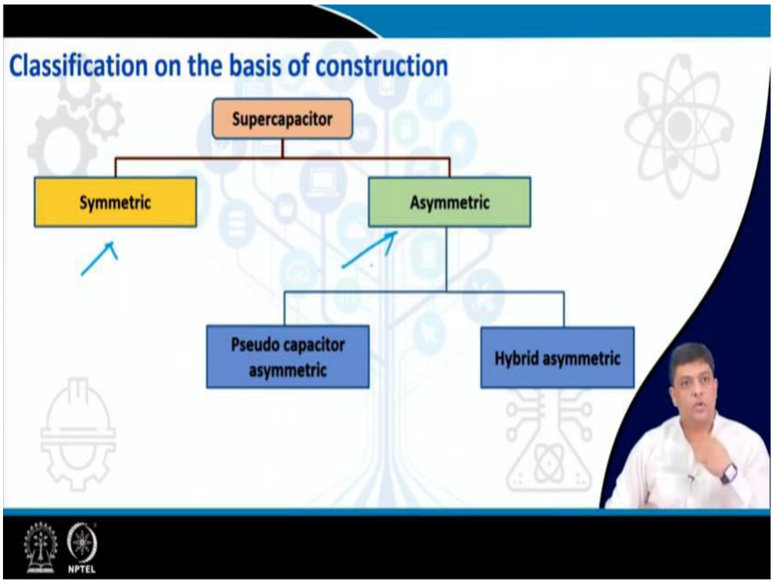


Based on the construction or the configuration the supercapacitors can be symmetric or asymmetric. Symmetric, if both the electrodes are of same materials. Asymmetric, if you have the electrodes which are fabricated using two different types of active materials. The asymmetric materials can be pseudocapacitor asymmetric or hybrid type asymmetric.

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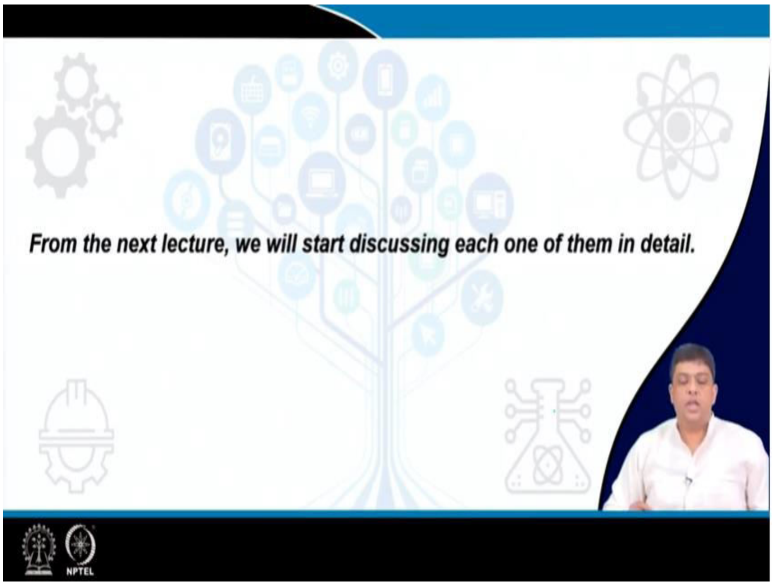


And from the next lecture we will start discussing each one of them in detail.

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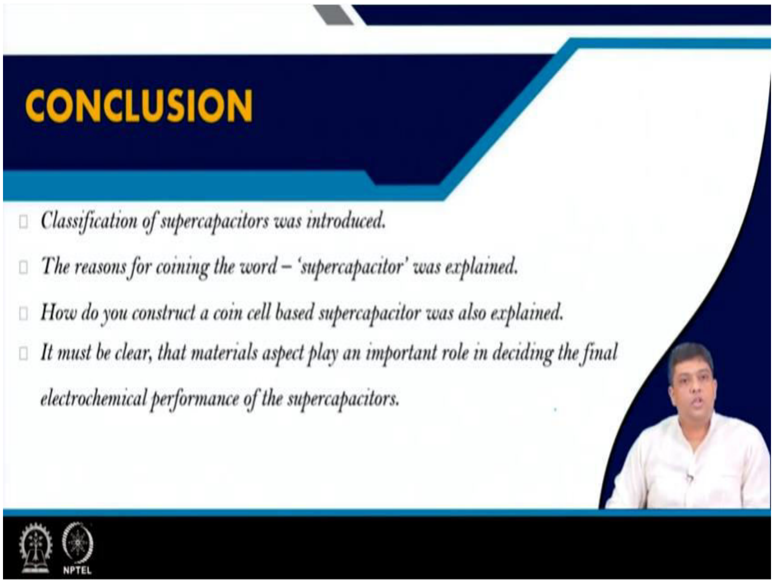


So in this second lecture we have given slightly more detailed introduction about the concept of supercapacitor. We have dedicated two lectures on introducing the concept of supercapacitors because it is a new technology and many of you may be hearing it for the first time. So we have introduced and given you the classification of supercapacitors and how do you construct a laboratory scale supercapacitor. We also understood how do we explain the coining of the word supercapacitor.

So, it is basically combination of the two words supercapacitor because it gives you very high values. Now, we have continuously be talking about separators, electrolytes, electrode materials, similar to batteries which we discussed in the previous module, it is clear that the materials aspect will again play a very important role in deciding the final electrochemical performance of these devices. This will become clear to you in next two lectures.

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These are the major references from where the data was taken and from the next lecture, we will start our discussion on electric double layer capacitors and you will understand how the formation of double layer is actually explained using various theoretical models. Thank you very much!