Physics of Renewable Energy Systems
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Lecture – 29
From battery to supercapacitors

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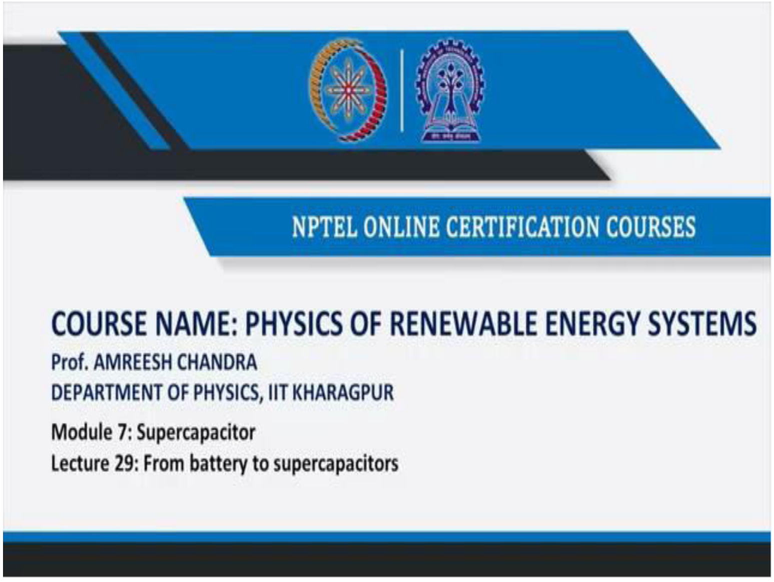

Welcome to the first lecture of week seven. In the previous week, I had talked to you about the lithium-ion batteries and in the area of energy storage technologies which are becoming very prevalent and relevant to the renewable-based energy storage systems. There is another player in the market and that is called as supercapacitors. And in this lecture, I will introduce to you the concept of supercapacitor, how do they differ from capacitors and what are the advantages and disadvantages.

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You will see that there is a clear difference between a conventional capacitor and the device that is now called as supercapacitor or electrochemical capacitor. This difference will also be clear when we talk about the way the two differ in the functioning, how do they differ in the way they are constructed and how do they differ in the kind of materials that are used to fabricate them.

Supercapacitors actually bridge the gap between the battery technology and the capacitors. Capacitors, as you know are known as high-powered as devices, whereas the batteries are high energy devices. What do you want? You actually want a system which can deliver high power as well as high energy density. For the time being, you can understand that supercapacitors lie somewhere in between the two.

And when I talk about the limitations, the advantages, the kind of applications we are looking for the energy storage technologies then you will understand that the future is moving towards hybrid energy storage devices, which combine the advantages of batteries and supercapacitors.

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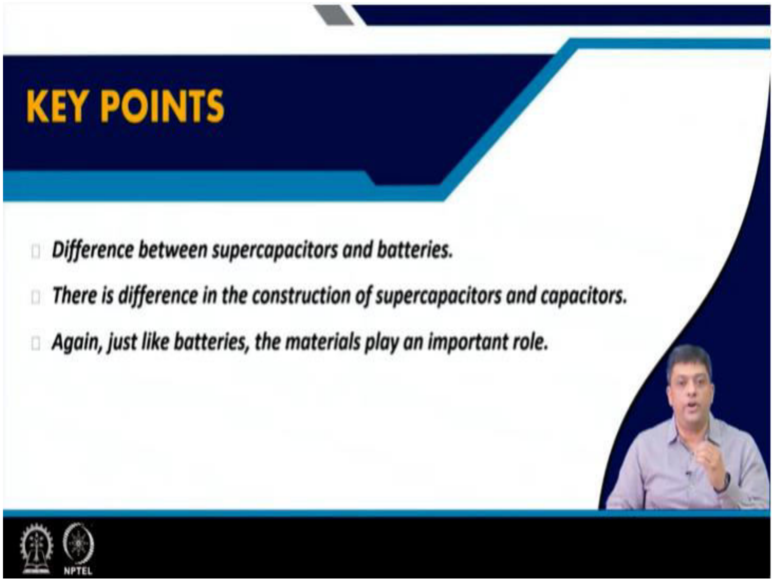

So the key points would be how do supercapacitors differ from capacitors and also from batteries because many a times when we start talking to you about the construction of the supercapacitors, the construction would indicate that they are very similar to batteries, but there are specific differences which must be understood and hopefully, you will be understanding them in today's lecture.

The difference in capacitor and supercapacitors also lie in the magnitude of capacitance which they deliver, conventional capacitors generally range from microfarad to millifarads whereas supercapacitors are now routinely giving energy densities which are much much higher than capacitors and specific capacitance in the range of let us say few hundreds of farads per gram to up to thousands of farads per gram.

So this is where the major difference comes in. It will also be clear that just like what we had discussed during the week when we were talking about the construction, the operation and the components used to fabricate lithium-ion batteries; here too the materials play an important role in deciding the overall physical or chemical response of these supercapacitors.

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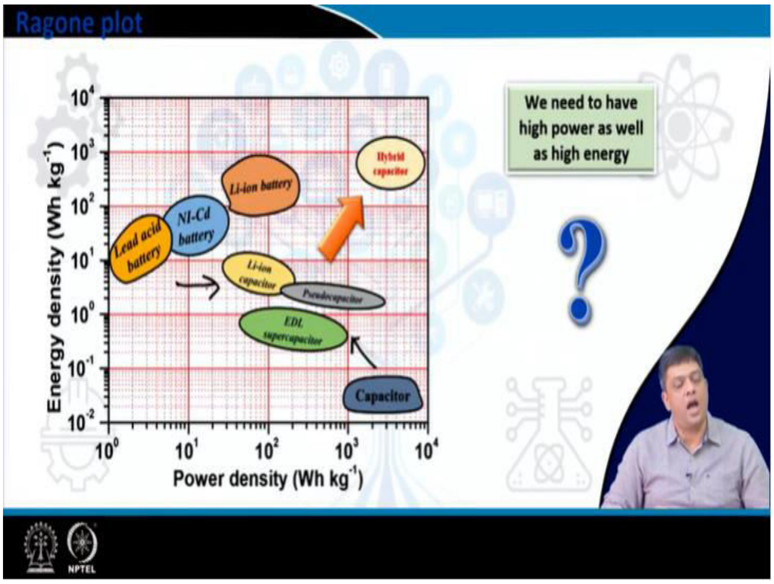

What we have seen till now let us understand from this Ragone plot. Ragone plot is a plot between the energy density and power density of the storage devices which we have studied till now. We started our discussions with lead acid batteries so you can see the typical values of power densities and energy densities which are obtained or delivered by lead acid batteries. Then we moved on to discuss about nickel cadmium, nickel metal hydrides and subsequently we had the discussion on lithium-ion batteries.

So, this is where you have seen that the typical energy densities of lithium-ion batteries are in the region shown in the graph. If you compare with conventional capacitors, you will see that the conventional capacitors give extremely high-power densities; that means, they are able to deliver very large amount of energy in a very short period of time.

In comparison to the capacitor technology, we call the batteries which are high energy density devices. Why? Because they deliver energy maybe at a slightly slower rate, but they can deliver that energy over a sustained period of time, which is much larger than the time we are looking at in capacitors. And that is why one is called the high-power density or high-power device and the other that is the battery technology is called the high energy or high energy density system.

Now, what was happening in the middle there was a gap, so you had one system which was high power the other was high energy and there was a gap and that is where the advent of a new device or a system came and filled this gap and these devices are called as supercapacitors. In the slide we have written the EDLC type supercapacitors or Pseudo capacitors or lithium-ion capacitors but they are clubbed together under the broad heading of electrochemical capacitors or supercapacitors.

Some people also call them as ultra-capacitors these are various types of supercapacitors the electric double layer capacitors, the pseudo capacitors or lithium-ion capacitors. So this is what the reason which was driving the interest in these devices. We needed a system which could have high power as well as high energy.

So you have seen that the power has increased while you are maintaining a reasonable energy density. If I ask a simple question as to where are we heading or what is my wish? My wish would be that please give me a technology which has a very high energy density as well as a high power densities. Energy density is similar to lithium-ion batteries or more and power densities which are similar to conventional capacitors.

And therefore, over the last decade or so there has been advent of new kind of technologies which are called as hybrid capacitors or hybrid systems. These technologies combine the advantages of lithium-ion technology as well as pseudo capacitors or EDLC type capacitors or if we say broadly then they combine the advantages of the battery technology as well as supercapacitors.

And their whole idea is driven by the fact that they combine the two types of different materials, one material which is very relevant to battery like system and the other material which is very relevant to capacitor or supercapacitor like device, then those kinds of materials are brought together and then they give a hybrid characteristic.

So that is the reason why we should understand about pseudo capacitors, the electric double layer capacitors and then subsequently we will be moving towards our discussion on the requirement and the way we can make hybrid capacitors.

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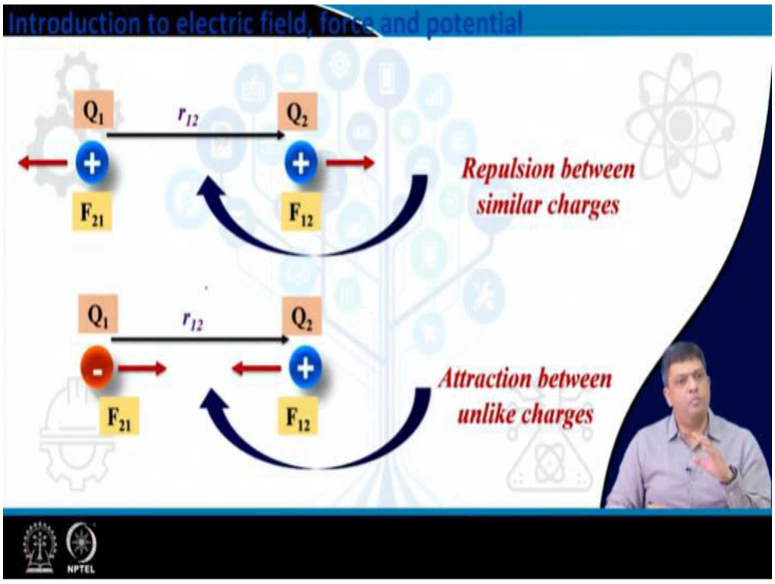

Before we move to supercapacitors it is very important that we understand the difference in charge storage mechanisms between the conventional capacitors and the supercapacitors. So from if you take two charges Q1 and Q2 separated by a distance, then we know like charges repel whereas unlike charges attract.

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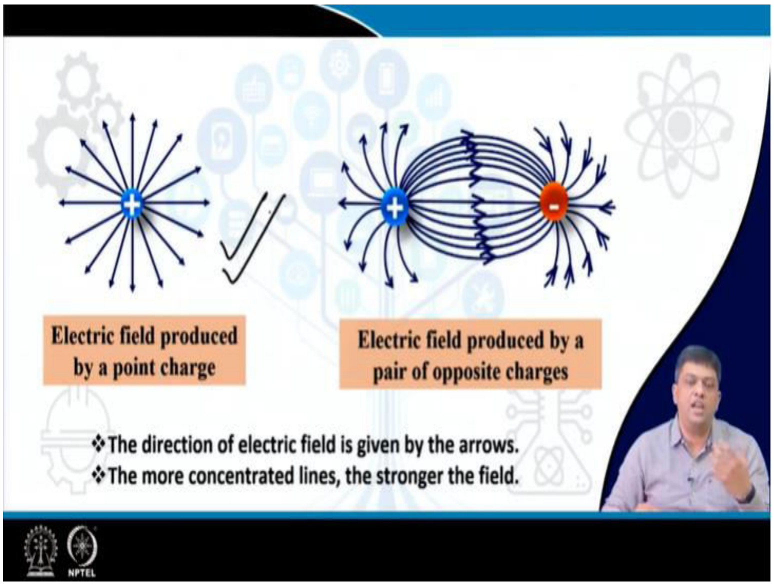

And the law which we had studied in our school days is the Coulomb's law which explains the force generated by one charge on the other. So you can have electric field produced by a point charge and if you have two different types of charges then what happens when they are brought near to each other and what is the nature of electric field that gets generated.

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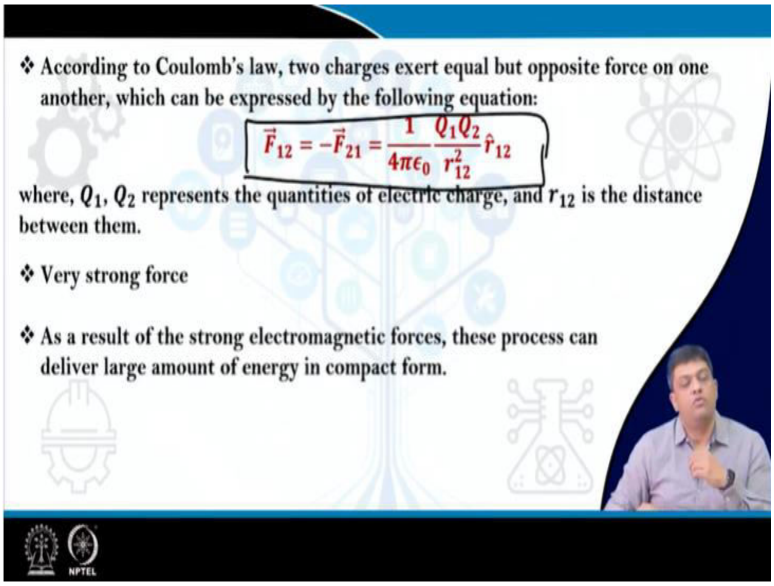

We had seen and from Coulomb's law you know that two charges exert equal and opposite force on one another which can be expressed in terms of, the relation given by force. If you consider from one to two, then the magnitude, if you are looking from two to one would be same, but if you are also considering the vectorial notation then the minus sign comes into the picture. But what you get?

Let us say F12 is equal to 1 by 4 pi epsilon naught Q1 Q2 divided by the distance square and then the direction r12. Now, what does this force actually give? It gives that as a result of this strong electromagnetic force, these processes can deliver large amount of energy in compact form and these kinds of forces are quite strong. So, they are not weak, but strong forces.

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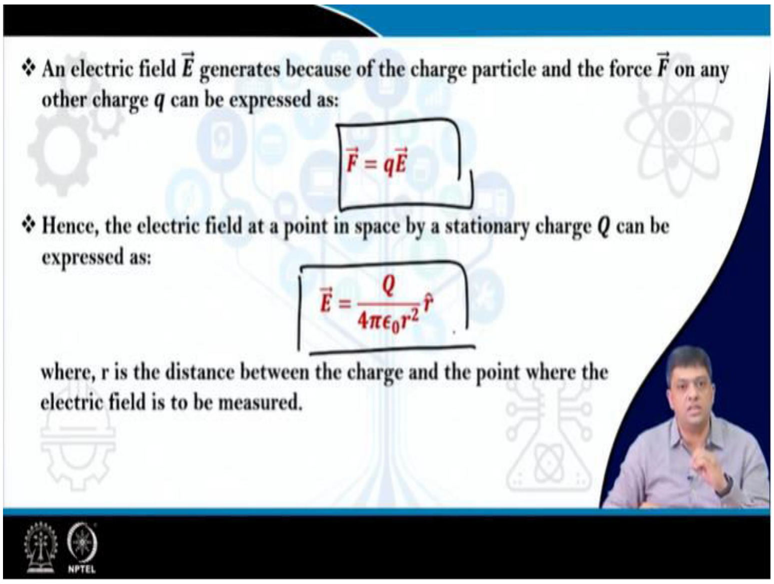

And an electric field generated because of the charge particle and the force on any other particle because of the electric field generated by a charge particle can be expressed as force is equal to q dot E. Hence, the electric field at a point in space by a stationary charge can be expressed as E, vectorial E is equal to Q by four pi epsilon naught r square the unit vector r where r is the distance between the charge in the point.

And where the distance between the charge and the point where the electric field is being measured, so if you measure this charge and then you measure the distance from this charge at different locations then you will get different magnitudes of the electric field.

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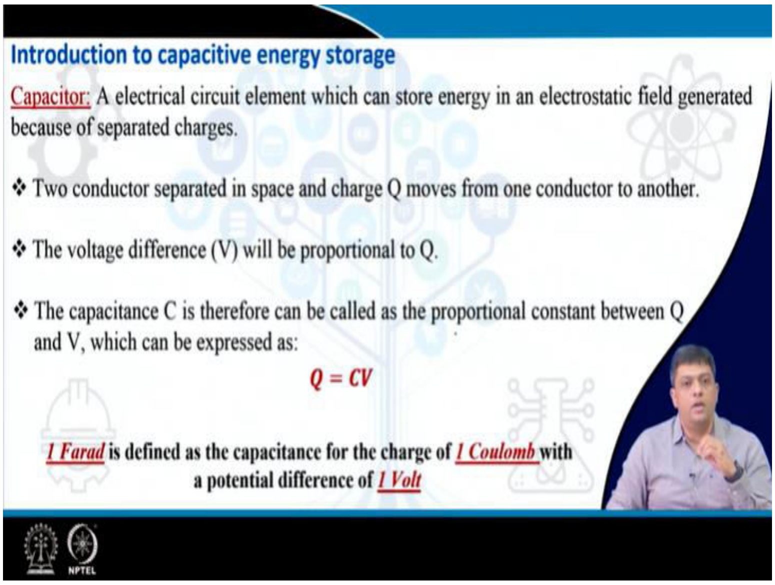

So these were the concepts which we had understood when you were talking about the charges. Then came the device which was actually being used to store these charges and that was called as capacitor. What is a capacitor? I am talking about the conventional capacitor. It is an electrical circuit element which can store energy in an electrostatic field generated because of separated charges.

So you have separation of charge and because of these charges separated from each other there is an appearance of an electrostatic field and that is then expressed in terms of energy. How do you make them? You have two conductors separated by a space and charge Q moves from one conductor to the other and the voltage difference V is proportional to Q.

Q may also be considered as if the charges which are getting deposited on the two conductors. Now, how do you relate V with Q? That is you replace the term proportional that is how you replace proportionality and bring some exactness. And this was explained using the term capacitance C and it is the proportional constant between Q and C, which gave the relation that Q is equal to CV. On where?

When you had two conductors separated by a distance and if you were connecting it to an external source then what was the magnitude or how charges were getting deposited on the two conductors which were separated by a space. And the unit farad is defined as the capacitance for the charge of 1 coulomb with a potential difference of 1 volt that is applied.

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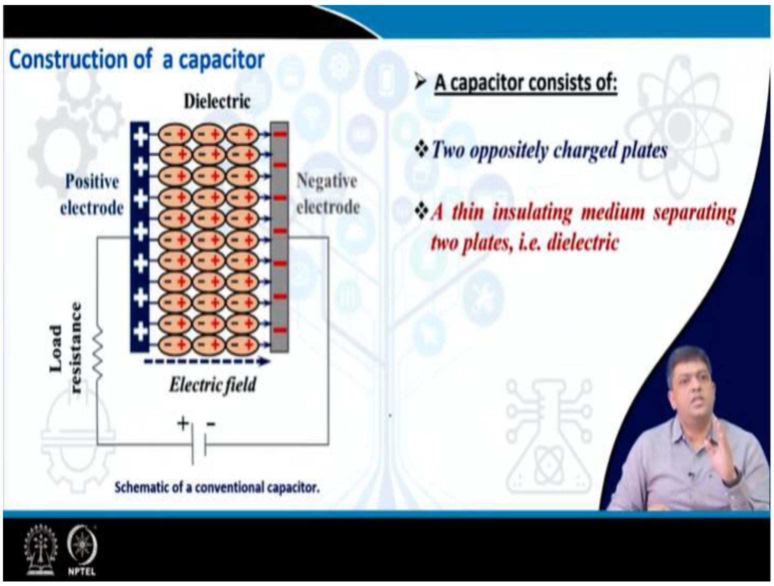

This is the typical figure which we have been seeing right from our school days. You have the conductors, there is a space and this space can be either filled with dielectric or it is an air which also has some dielectric constant value. So, two oppositely charged plates separated by a distance which has a dielectric medium and because of the… What is a dielectric medium?

Which can get polarized, because of the - polarization of this medium you get charges which are forming and you can see if you have a if you consider positive charge the next surface is along forming a negative charge and then you have a positive charge and then the polarization effect drives this stabilization of the negative positive negative positive negative positive directions and that leads to the appearance of the electric field.

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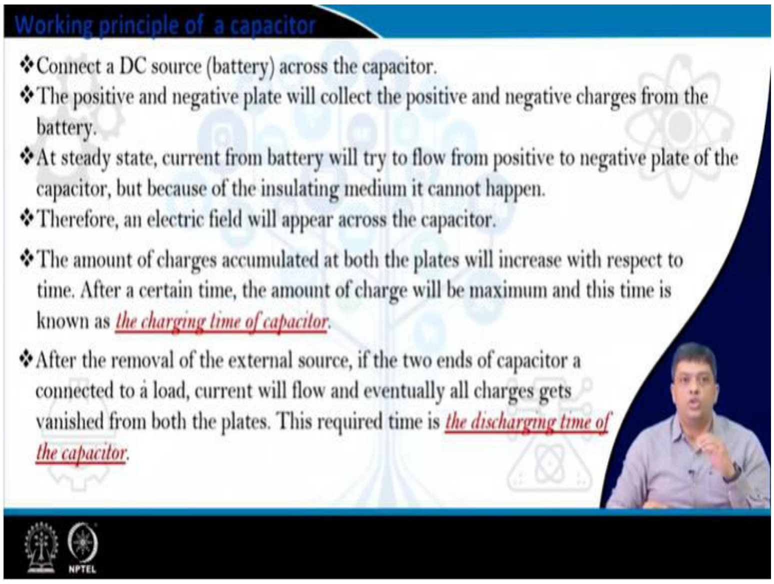

So what we have done? We have connected a DC battery across a capacitor. The charges get collected on the positive and the negative plates and at steady state current from the battery will try to flow from positive to the negative plate of the capacitor but because - of the insulating media that is the dielectric medium it cannot.

Hence, what happens? An electric field appears across the capacitor. While this deposition of charges is taking place you will see that if you allow the time to increase you will have deposition of higher magnitude, so more number of charges will get deposited and then your capacitance will increase, so the electric field will increase.

After a certain time, there will be a maximum which will be obtained and beyond that the capacitor cannot be charged further that means it cannot accumulate or accommodate more charges on its surfaces made up of two conductors and that time is called the charging time of the capacitor.

And once you remove the external source that is the DC source or the battery which we are taking in this case then if the two ends of the capacitor is connected to a load current will flow and eventually all charges will get removed from the plates and this is called the discharging of the capacitor and the time taken to completely discharge the capacitor is a discharging time for the capacitor.

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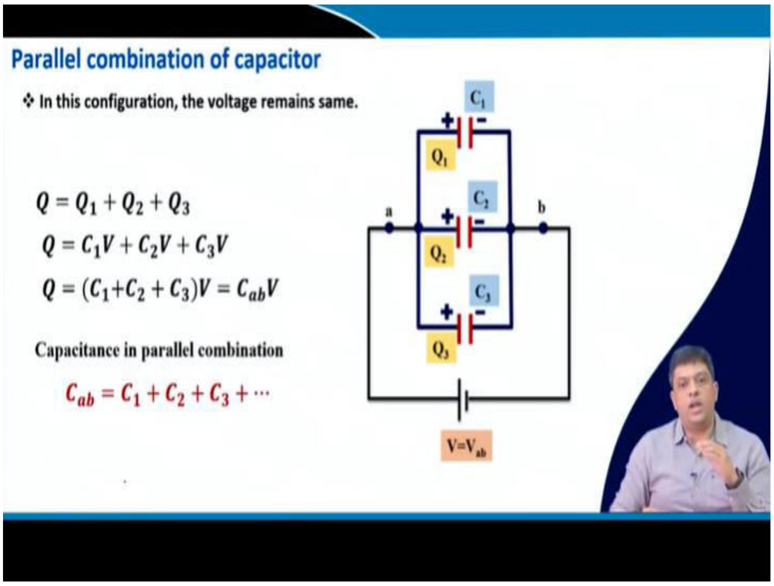

You can combine them in because it is a passive element, so similar to resistance inductors you can have the parallel combination or the series combination. You can see that if you have the parallel combination then the capacitance is additive, the overall capacitance which you will see will be additive.

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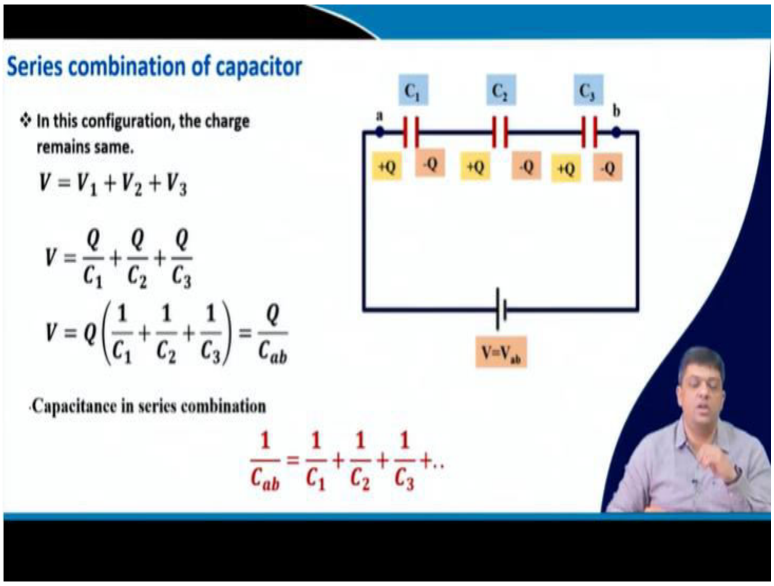

And in the case of series combination, you will get the combination which is the inverse. This is what we have seen from our earlier classes.

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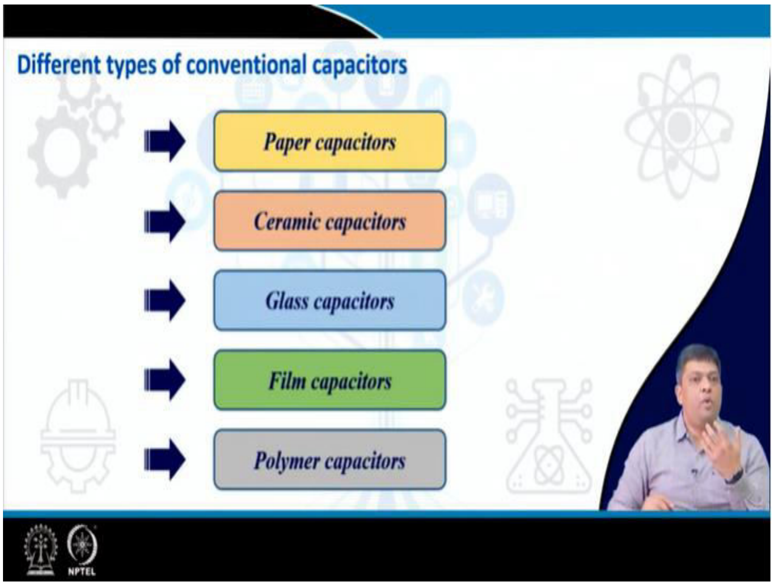

Right from the earlier classes we have been studying that you can have different types of conventional capacitors. There can be Paper capacitors, Ceramic capacitors, Glass capacitors, Film capacitors or Polymer capacitors, in addition to air capacitors or any other capacitors, which is made up of different form of dielectric in the middle.

But if you look into the values, what is the capacitance, which is obtained is mostly in the range of microfarad to millifarads and if you use very high dielectric constant materials based on let us say ferroelectric ceramics then you can increase this capacitance to slightly higher value and maybe you can go to values of 10 raised to power minus 1 to 10 raised to minus 2 farads at most.

But that is not going to serve the purpose when we are talking about storage in renewable base systems where you have to store lot of energy while ensuring that the size consideration is such that you do not increase the size tremendously otherwise you will be ending in different kind of problems. Hence, the only thing was to look for new technologies which could serve our purpose and eliminate the limitations of conventional capacitors.

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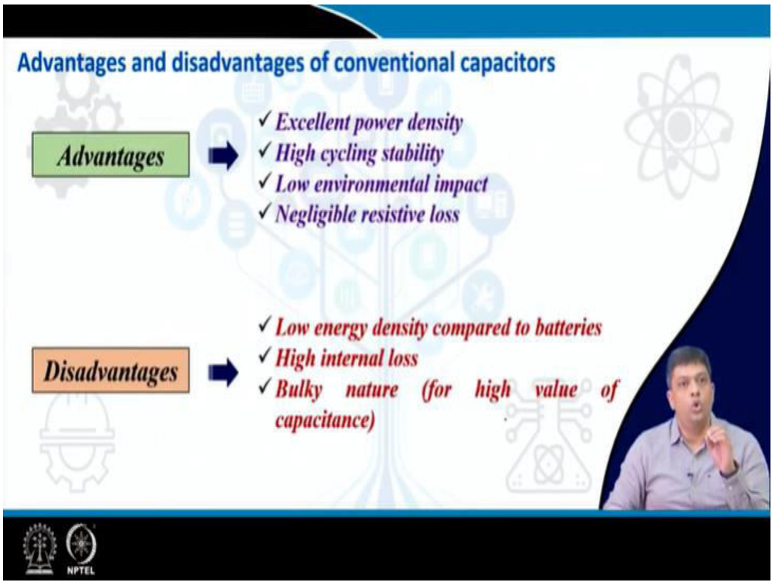

You wanted a system just like conventional capacitor, a system which should have high power density, should have cycling stability, it should have low carbon footprint and as a function of cycling we should have negligible resistive losses.

And you what you want you want to eliminate the disadvantages which are associated with the conventional capacitors that they have low energy densities, high internal loss, if you want to have a system which can store lot of charges then you have to make large size capacitors and then it becomes bulky in size and that is another feature you want to avoid, you do not want to have bulky capacitors or stacks.

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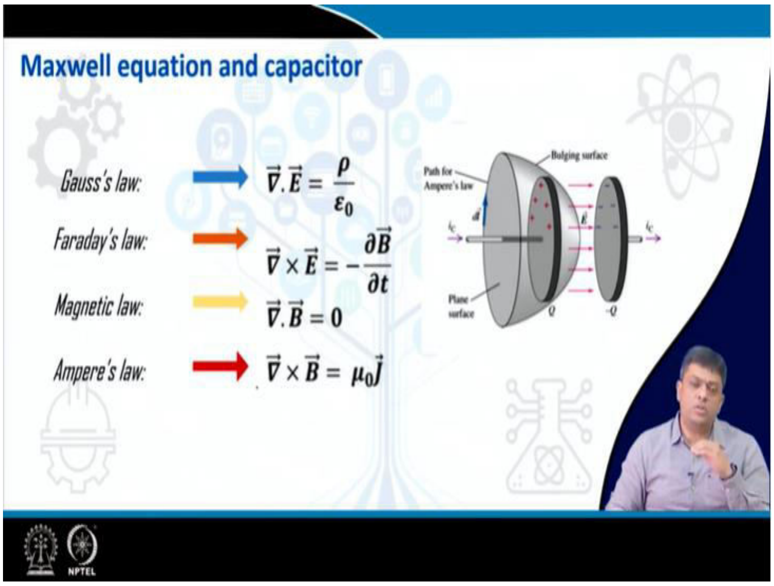

We had also explained the capacitor actions using the Maxwell's equations. So we had seen that Gauss law, Faraday's law and the Ampere's law were able to explain certain features related to the motion of charges.

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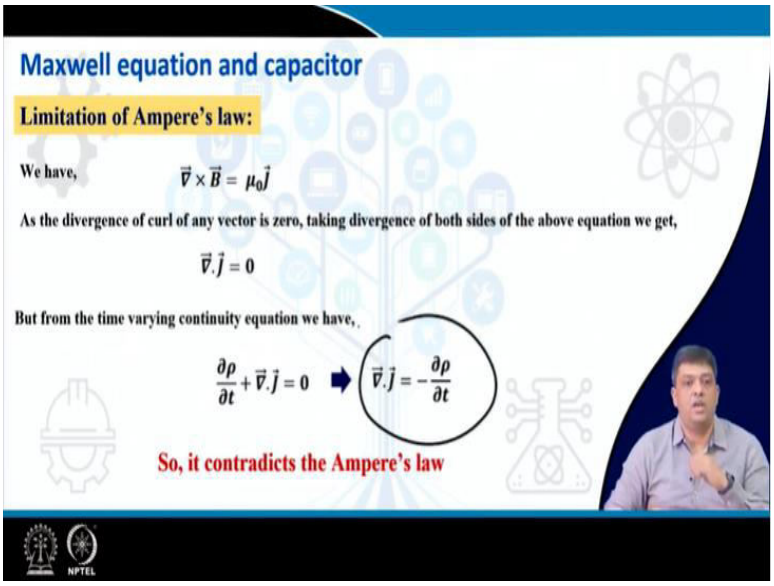

But when you saw Ampere's law, it had some serious limitations where it said that you cannot have the flow of charges if there is a gap but when you saw the capacitor you were actually seeing the appearance of potential, even when there was a gap and effectively there was a current which was getting established in the gap. So you had to modify the Amperes law you have to modify the Ampere's law.

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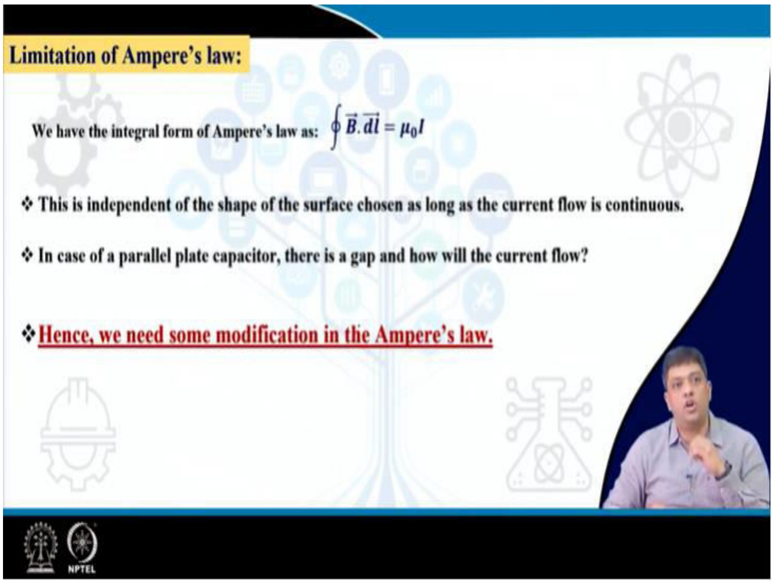

And that is where the contribution of Maxwell's came into the picture and that contribution which now you also understand in terms of displacement current, actually was able to give a suitable explanation as to how in the case of a parallel plate capacitor the current or the electric field gets stabilized.

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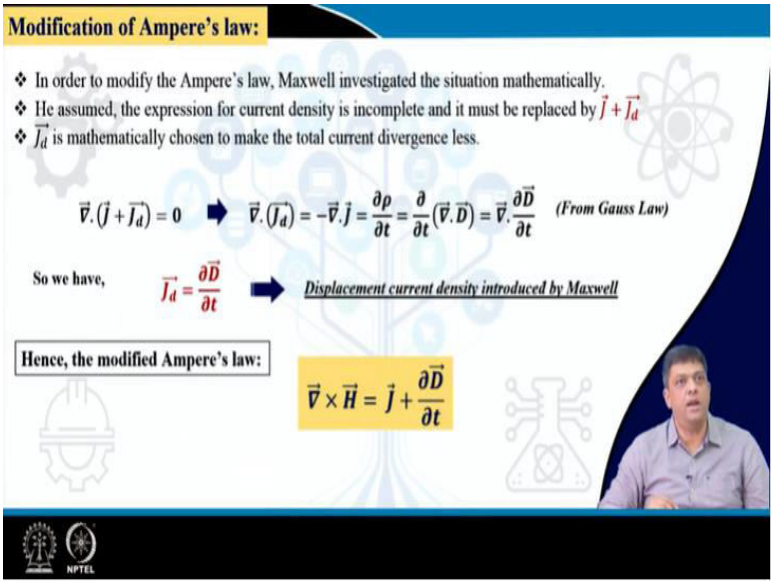

And Maxwell investigated the overall scenario but he investigated mathematically what was the scenario two parallel plates separated by a distance still you had the flow of current and it was indicating as if there was a flow of current in the gap also but how was electron actually flowing when there was no medium in the metal or you had an insulator in the metal.

He assumed that the expression for current density is actually incomplete and it must be replaced by the term j plus j d and j d is mathematically chosen to make the total current divergence, total current divergence less. So it is divergence less.

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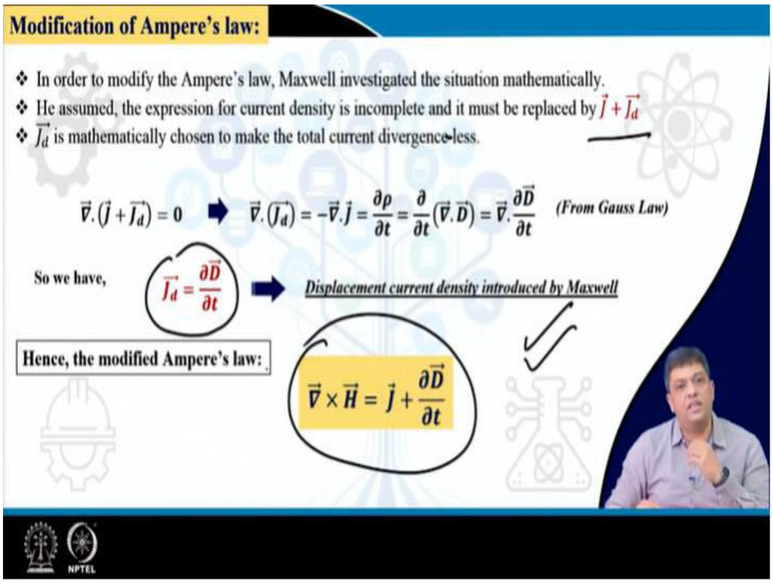

Then if you write the equations, you will get the relation that j d is equal to deba D by deba t and this concept of displacement current density was introduced by Maxwell. And the Ampere's law was then modified and from this you could explain the flow of current in a capacitor and the consequently all the four equations are now known as Maxwell's equations.

Why we are talking about Maxwell's equations, will become clear when we start talking about the theoretical models that are used to explain the supercapacitors and also the way charges accumulate at the two surface of the supercapacitors then these concepts will become very clear and you will understand the relevance of Maxwell's equation much more when we proceed further.

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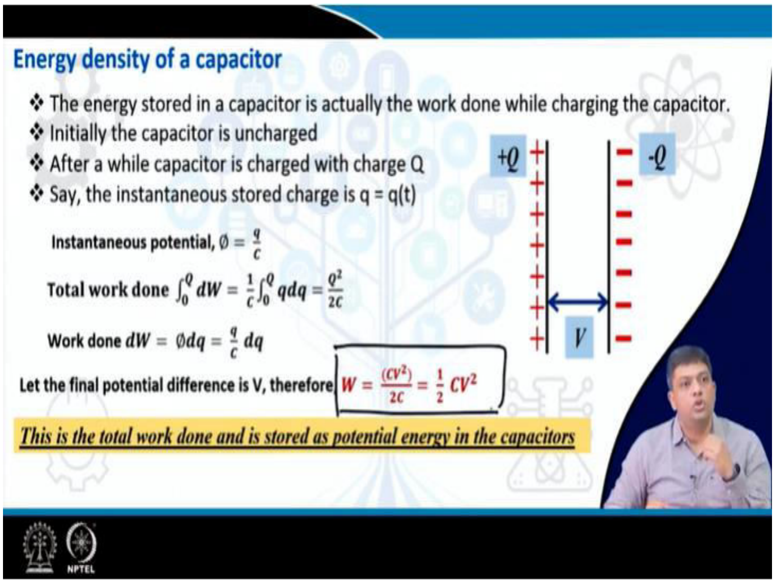

For a conventional capacitor what is the energy density, we already know and I guess there is no need to repeat too much in this lecture or at this moment we can straight away write that the, the final potential difference between the two place is actually given by the total work done and that is the amount of potential energy stored in capacitors.

And this is equal to half CV square. So we calculate the total work done and then we have the, the potential difference calculation and from there we know that it is the potential energy that is step stored on the two surfaces.

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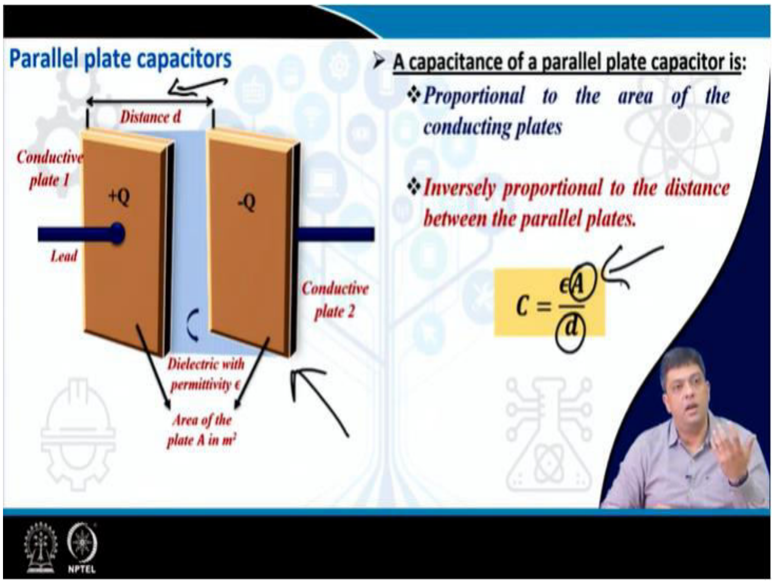

This is the typical parallel plate capacitor construction and you know that when you take into consideration the dielectric constant or the permittivity then if you have the area and distance consideration then capacitance is given by epsilon naught A by d or if you take into the dielectric constant then it is the k epsilon naught A by d, depending upon what condition you are considering.

So you can clearly see that the value of capacitance depends directly on the area so if I want to increase the capacitance value then there are two ways either we decrease the distance between the two plates or we increase the size of the plates. If you decrease the distance then the stability the mechanical stability as well as how do you avoid the short circuiting and other construction or fabrication issues come into picture.

If you increase the area then issues of weight and again issues of fabrication come into picture, therefore what is the way out you have a limited range of changing the values for a and you have a limited range of decreasing the d value and that is the major limitation in increasing the capacitance from conventional capacitors.

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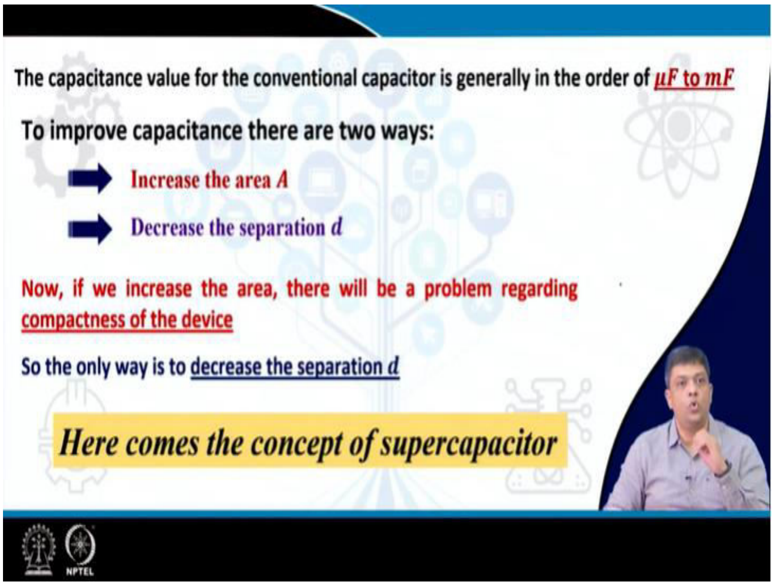

If I now want to increase the capacitance, so what are the two things, either you increase the area or decrease the separation d that is the separation between the two plates. How do you solve this problem and this is where you had the technology which came into the existence and was discovered and that is now known as supercapacitor.

Let us start to understand how these supercapacitors differ from conventional capacitors, how do they actually utilize various types of materials more so nano materials to increase the specific area and how the construction is slightly different from conventional capacitor which leads to the formation of charged layers but with a distance which can be as small as few nanometers or they are in the range of nanometers.

So that led to tremendous increase in the capacitance value and when you saw a colossal increase in the capacitance value in comparison to conventional capacitors the word super was added in front of capacitors, so supercapacitors was the term coined because the capacitance obtained from these kind of capacitors were much much larger than what you get from conventional capacitors. So, I hope now you have understood the coining of the word supercapacitors.

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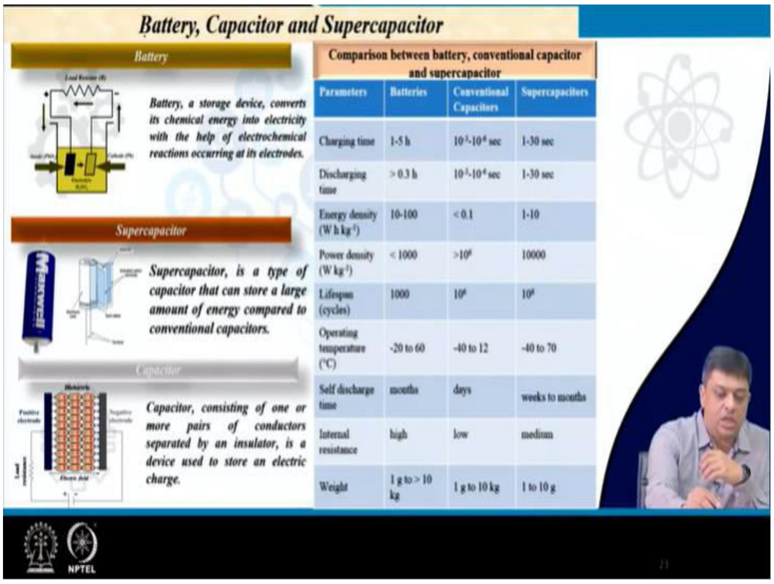

So we have seen the battery, let us say I have drawn the conventional lead acid battery kind of figure. We have understood the capacitors and the technology, which is in the middle now is called the supercapacitor. It is a type of capacitor type of capacitor it actually means it is a capacitor which may be different from conventional capacitor, but has similar physics associated with it.

So it is a type of capacitor. You will understand it is actually an electrochemical capacitor because here the electrochemical reactions play a very important role. So a supercapacitor is a type of capacitor that can store large amount of energy compared to conventional capacitors. And if I have to compare their performances so in terms of charging time you have seen how long does it take to charge your laptop battery.

It takes from an hour to couple of hours or more, in terms of capacitors you can charge them very fast and similarly supercapacitors can also be charged at a much faster rate in few seconds or so, much faster rate in comparison to the batteries, but they can be slightly higher than conventional capacitor. So, there are various parameters which are used to differentiate the battery conventional capacitors and supercapacitors.

You will see those are the charging time, the discharging time, energy density, power density, life span or the cycling stability the range of temperature in which they can work that is the operating temperature, self-discharge time, internal resistance and finally the weight. So, you can see that the weights are different, but if you make stacks of these supercapacitors then their weight also increases much more but then the capacities also shoot up significantly.

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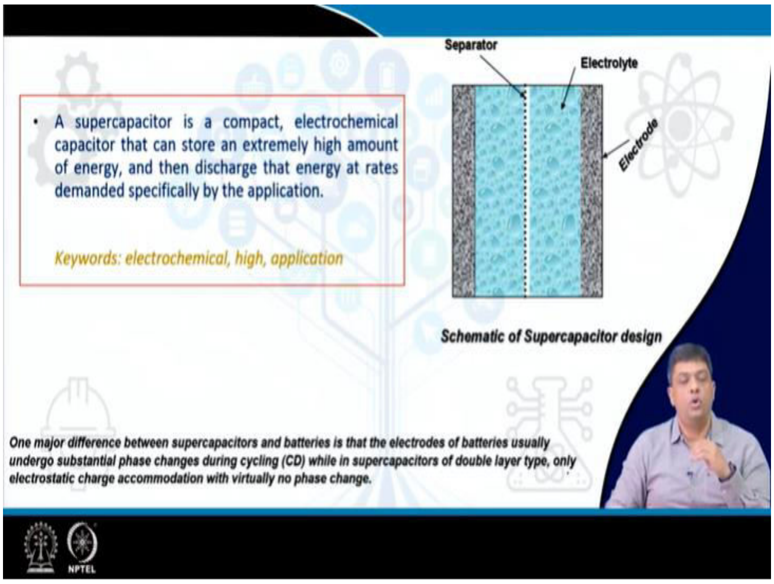

If I have to explain the things which I said in the previous slide then based on those terms and the definitions one can write the definition which is a broad definition for supercapacitor that it is a compact electrochemical capacitor that can store extremely high amount of energy and then discharge that energy at rates demanded specifically by the application.

Compact, why you do not want very large sized capacitors because then the weight will increase and the overall usefulness of the device will go. Electrochemical that means the electrochemical reactions play an important role in these capacitors; it can store energy.

Why? We are talking about energy storage technologies or energy storage devices and capacitor is actually an energy storage devices and then discharge that energy.

Discharge that energy means what, the capacitor can store the energy but that energy will only be useful when it is delivered to an end user or for a particular application. Hence the stored energy has to be delivered to the end user and that is where the terms efficiencies come into picture, what we have been talking you may store lot of energy but if you are unable to deliver the efficiency of the device is very low.

So, if you store lot of energy and deliver all that energy to the end user or the device which is going to utilize that energy, then your efficiencies are very high and there can be various applications for such kind of energy storage systems and for them the requirements may be slightly different. A system may require energy for a longer period of time, but at a slow rate or you can have requirements for higher energy for a shorter period of time.

So, the discharge rates can also vary depending upon the end user demand. Hence, the capacitors should have the capacity to deliver the energy at various rates and supercapacitors can actually deliver the energy at various discharge rates.

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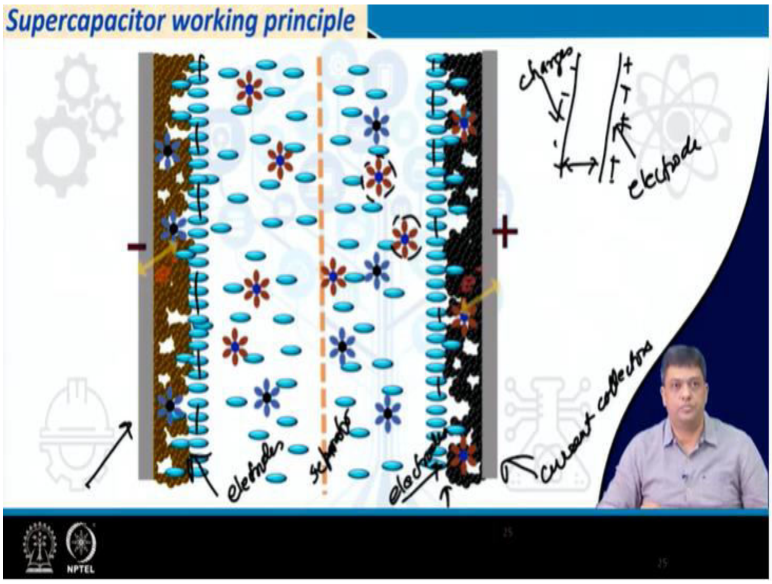

What is the construction? Construction is very simple, you have electrodes and the current collectors, so electrodes and current collectors. I have drawn two different coloured spheres because you can have different types of material. So, if you use same type of materials then they are called as symmetric and if you use two different types of electrode materials and the two plates then they are called as asymmetric capacitors.

Then in the middle you have a separator you have a separator and that is filled or separator is soaked in an electrolyte, where you have the solvated ions formation. So, you have an electrolyte. When you charge these capacitors then some of the electrolyte ions get deposited on the surfaces and that leads to the appearance of the OCV that is the Open Circuit Voltage. Initially, what is the amount of charges which are just getting deposited on the electrodes.

But when you are charging it further then you have the deposition of oppositely polarized charges near the interface and you form a layer. So now if you can see you have a layer then you have a layer coming in from electrode material which you had seen and then there is also a layer of charges this looks very similar to a capacitor.

Yes, there also you had two plates where you had two metallic surfaces on which the charges were getting accumulated and this was separated by a distance and that was called as capacitors. Here also what you have? You have let us say positive charges and then negative charge charges are getting accumulated near the surface and these two charges or charge layers are separated by a distance.

How these distance or this two charge layers are separated? Will become clear as we go more in detail about the supercapacitors and the formation of charged layers, but you can clearly see at this moment that there are two surfaces where opposite charges are getting deposited and they look very similar to capacitors and therefore this whole device can be explained in terms of the physics associated with that of capacitors. So, if you charge, then you can have pseudo capacitors and that things will become clear bit later.

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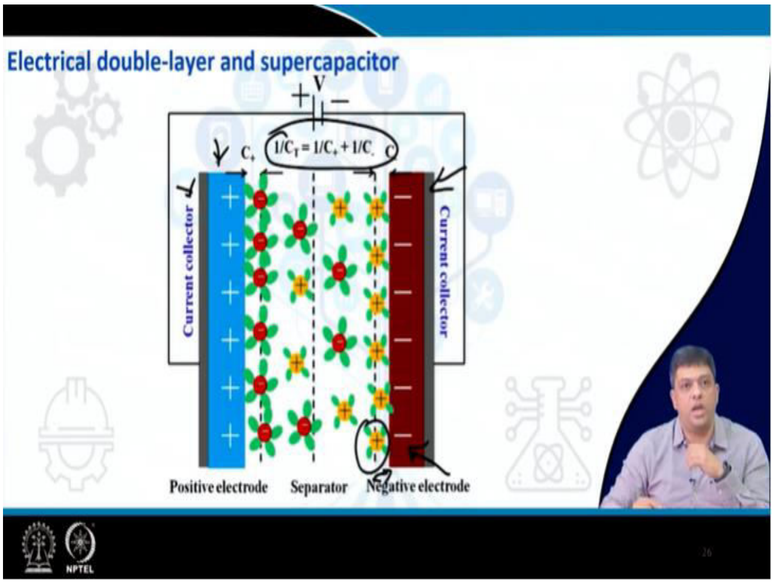

So, if you have capacitors what you are looking at you are looking at the current collectors as I said, the positive electrode, the negative electrode on a current collector. There is the solvated ions which are separated by a distance this distance is extremely small. So, what will be your total capacitance? The total capacitance of this device would be 1 by C T would be equal to 1 plus by C plus 1 by C minus. Why inverse relation?

Because these are series capacitances coming together and if you see the capacitance is now going to be calculated using k epsilon naught A by d and the d value has actually reduced significantly maybe in the range of tens of nanometers or less where in the conventional capacitors you are talking about maybe few micrometers or higher.

So just by decreasing the distance from micro to nano micro ten raised to minus six meters nano ten raised to minus nine meters and how does the capacitance get related. It is k epsilon naught a by d, d is in the denominator, so capacitance will increase by what order if I am decreasing a distance by 10 raised to the power of 3 times, your capacitance will increase by 10 raised power 3 times and that is why the overall capacity increases.

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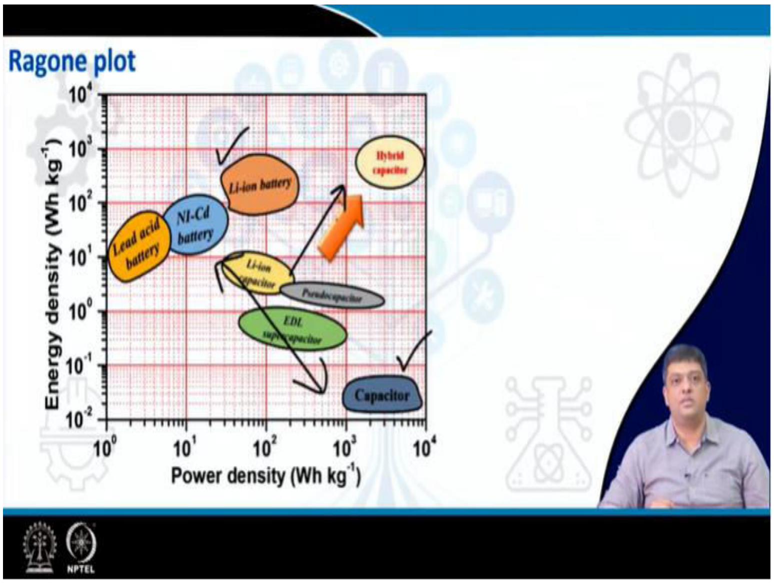

So we started with our discussion that you have conventional capacitors and batteries, so you have batteries and conventional capacitors. There is a gap between the two technologies. To fill this gap there was an advent of new technology that is now known as supercapacitors.

Supercapacitors although looks to be very promising it still has limitations that the energy densities are lower and the power densities are also slightly lower than the conventional capacitors, so you have actually been able to increase the energy densities but you have not reached to the same power densities that are obtained using the conventional capacitors.

So, what is the future? The future is to move in this direction and that is where the hybrid capacitors are important. In the previous slide you may have clearly seen that I had talked to you about electrode materials. I had talked to you materials which were near the positive potential and the ones where you are applying the negative bias.

And hence, it would be clear that materials will once again play a very critical role as they were doing in lithium and batteries. In addition, you will also have the role of electrolyte, the separators and the current collectors, so many things are similar to batteries but lot of things are different from batteries.

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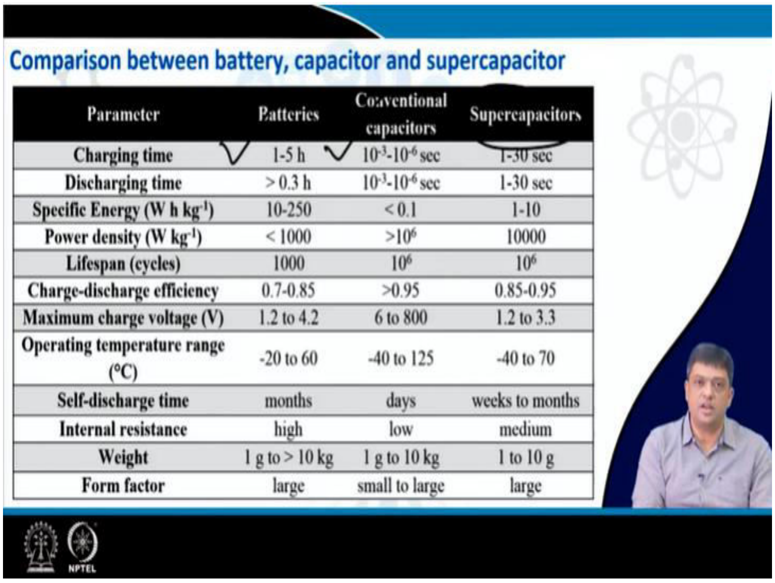

And you can clearly see that was the importance of writing this table. Earlier the supercapacitors have certain advantages of batteries and certain advantages of conventional capacitors and hence they are becoming extremely useful and lot of work is being done in India and the government is also putting in lot of money in this because the range of application for these supercapacitors vary from mobile phones to electric vehicles, from toys to ignition of very large engines, so the range is wide and hence lot of money is being invested to develop new supercapacitors within our country.

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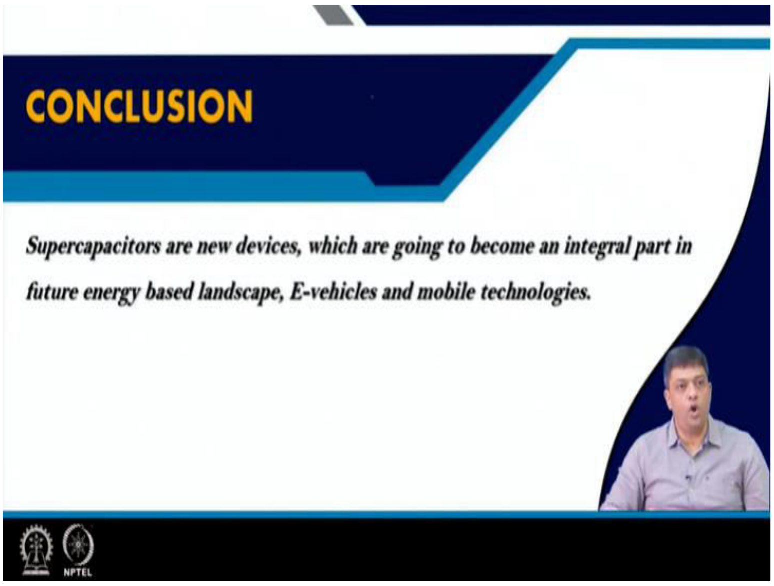

I hope it is clear to you that supercapacitors are new devices, very promising devices and interesting technologies which are going to be an integral part in future energy landscape based on renewables also they are going to be extremely useful in e-vehicles and mobile technologies.

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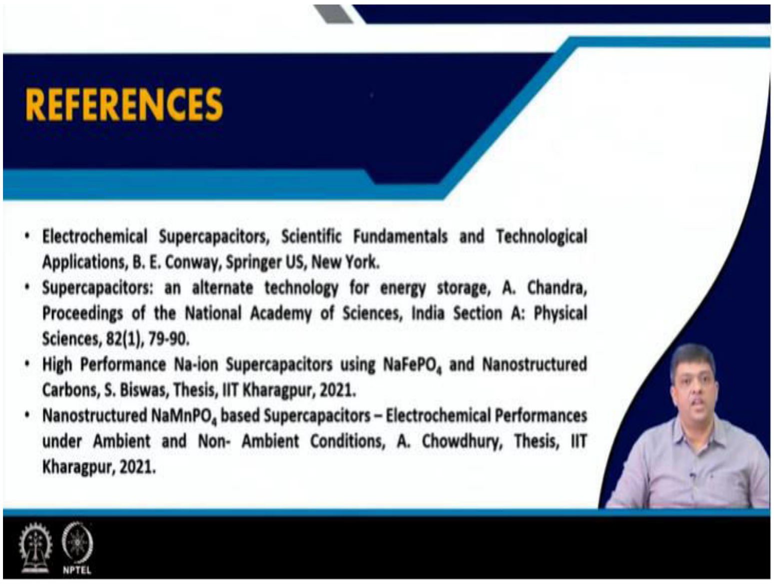

These are the various references that were used to obtain the data and present the results that were discussed today and from next lecture I will move on to the classification of supercapacitors, what are the various types and then one by one we will discuss in detail each one of them. Thank you very much.