

Physics of Renewable Energy Systems
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Lecture 36
Effect of External Magnetic Field and Frequency on Supercapacitors

Hello let us start the final lecture of this week. In the previous lecture, I gave you an overview about the changes, which can occur in energy storage devices, such as lithium ion batteries, or supercapacitors as a function of varying temperatures.

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The slide features a blue header with two circular logos. Below the header is a blue banner with the text "NPTEL ONLINE CERTIFICATION COURSES". The main content area is white and contains the following text:

COURSE NAME: PHYSICS OF RENEWABLE ENERGY SYSTEMS
Prof. AMREESH CHANDRA
DEPARTMENT OF PHYSICS, IIT KHARAGPUR

Module 8: Advance supercapacitors
Lecture 36: Effect of external magnetic field and frequency on supercapacitors

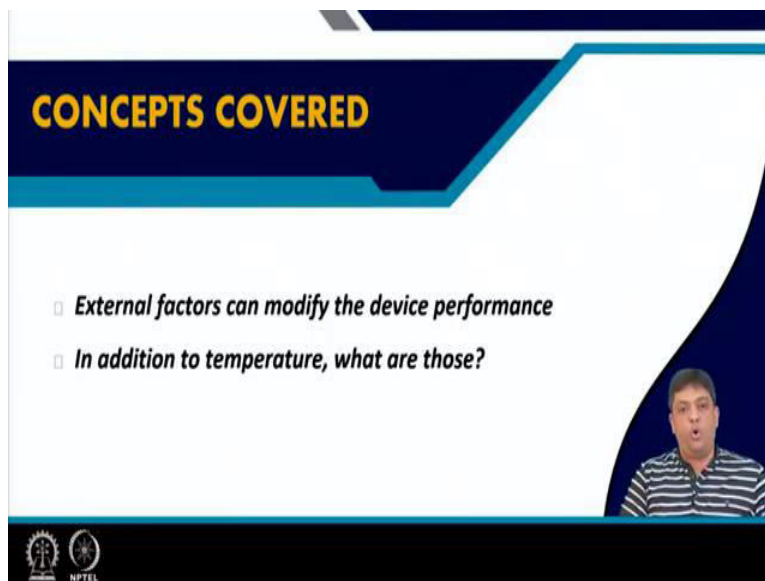
There are other factors, which can also come into picture and they can also modulate the behavior of these devices. And these factors can be vibration, external vibration. So, if I am taking a mobile and I am walking on a road, then the mobile is continuously shaking as my, you can see if I keep my mobile in my hand and then the hand is moving, that means the mobile is continuously having vibrations. And these are driven by external factors.

So, the battery will also experience the vibrations, or the supercapacitors, which are integrated in today's mobile, because they are used to deliver power to the flash in these mobiles, just to extend the life of the battery.

So, when you switch on the flash, or use flash, then the power is not extracted immediately out of the battery, the battery has already charged the capacitor and then the capacitor is able to deliver that extra power in a, to these flash. So, that you can save the batteries.

So, your supercapacitors as well as batteries are going to experience vibrations. So, what will happen? You can have magnetic field variations, you can take it near a place where our devices, or high current is flowing and then you have induced feeble, but weak magnetic field may be present, then will you see effect in these devices. And these are other factors, which are also there that can affect the performance of a device and that is what we are going to start today.

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The slide features a dark blue header with the text "CONCEPTS COVERED" in yellow. Below the header, there are two bullet points in a light blue font: "External factors can modify the device performance" and "In addition to temperature, what are those?". In the bottom right corner, there is a small video inset showing a man in a striped shirt speaking. At the bottom left, there are logos for NPTEL and other institutions.

In today's lecture you will see, that in addition to temperature, there are additional factors, which can appreciably modulate, or modify the performance of energy storage devices. And these kind of factors are mostly ignored in most of the literature, or published reports. There are recent reports, which are coming in and dealing with these effects, although many a times the industrial aspect, or the industry knows these details, but they are hidden from the general public, or the end user, because of IPR issues.

So, there are factors and ways to protect the device from these external factors and they are quite simple and you if you are able to understand, you will be easily able to contribute in developing newer strategies to protect the device from variations, be it be temperature, be it be pressure, be it be humidity, or factors like external vibration, or magnetic, or electric field.

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KEY POINTS

**Commercializing a device takes time
because a lot of factors have to be considered,
while developing the final product.**

You may have just realized, that I was giving the concept slide and I took a minute, or two, because there are so many factors, which are involved before I can even think of taking a device to real world application. You have seen right from materials choice, to fabrication, before that you have seen the time required to characterize the material, then to use that material in a device, characterize the device, and that to adjust the laboratory scale.

Before you can go to industrial level you must know, what are the complex situations that can arrive, if you scale up something, if you start producing. Let us say copper oxide in few grams and then in few kgs, can you do it. Then there are lot of additional factors coming to a picture, or any other electrode be it be carbon, be it be any other electrode material, which you can talk, we have talked about cobalt oxide.

So, there are problems associated with scale up and once you have scaled up, then again you have to make devices and you have to make devices in batches. Then do you get the same performance batch after batch, or there are variations from one batch to the other. So, there are large number of factors, which have to be controlled before a material goes into a device, device goes to scale up, and then the device can then reach the real world application. I hope you will be able to further appreciate this point. And you will see that commercializing a device takes time, because of various factors, which are involved during the development stage of the same.

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The slide features a central graphic of a tree where the branches are composed of various icons related to technology and science, such as gears, a lightbulb, a battery, a smartphone, a microscope, and a circuit board. The text on the slide reads: *Today, let us focus on two more factors (extrinsic), which can change the performance of batteries and supercapacitors...* In the bottom right corner, there is a small video inset of a man in a striped shirt. The bottom of the slide contains logos for NPTEL and a university emblem.

So, in today's lecture let us see, what are the other two common factors, which can modulate the performance of batteries and supercapacitors, and after hearing this lecture, I hope you will make sure that, when you are using your mobile phones, or you are using lithium ion batteries, or battery super cap based device, then you do not put it under direct sun, you do not overheat the device, or you do not keep it near to magnetic field, or you do not induce appreciable vibrations in and around the place, where this device is actually being utilized.

So, you try to protect the device in a better manner. So, that the life span of the storage device improves and if that does improve your overall phone will see improvement in its lifetime.

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❖ An electric field \vec{E} generates because of the charge particle and the force \vec{F} on any other charge q can be expressed as:

$$\vec{F} = q\vec{E}$$

❖ Hence, the electric field at a point in space by a stationary charge (Q) can be expressed as:

$$\vec{E} = \frac{Q}{4\pi\epsilon_0 r^2} \hat{r}$$

where, r is the distance between the charge and the point where the electric field is to be measured.



What have we seen till now? We have seen, that an electric field E is generated, because of the charge particle and the force F on any other charge q , can be expressed by force is equal to q dot E , or q into E . And the electric field at a point in space by a stationary charge Q , can be written as Q by, Q by 4π epsilon naught r square vector r , is equal to E . This is what we have seen.

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Gouy-Chapman Model


Solving the Boltzmann distribution of the ions using Poisson's electrostatic law and associated boundary conditions, the capacitance value for the diffuse layer could be expressed as:

$$C_D = \left(\frac{2Z^2 e^2 C_0 \epsilon_r \epsilon_0}{k_B T} \right)^{1/2} \cosh\left(\frac{ZeV}{2k_B T}\right)$$

where, Z , e , C_0 , k_B , T and V denote ionic charge, electronic charge, bulk concentration of ionic species, Boltzmann constant, temperature, and the applied potential, respectively.

Disadvantages:

- This model also considered the charge as point charges.
- Overestimated the ionic concentration close to the charge surface.
- Failed in the case of multivalent ions to explain the charge concentration.



In the Gouy- Chapman model, we have seen that, using the Boltzmann distribution and the Poisson's electrostatic law, we have seen the way you can calculate the capacitance value in the diffuse layer. So, we have seen in the Gouy-Chapman model, this formula was derived and you

could see, that you have a formula for determining the capacitance, very good and we have also discussed the effect of temperature on these EDLC in the previous lecture.

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Redox pseudocapacitors

Hence, the expression for redox potential becomes:

$$E = E^0 + \frac{RT}{F} \ln \left[\frac{O_x/Q}{R_{red}/Q} \right] = E^0 + \frac{RT}{F} \ln \frac{[O_x/Q]}{(1 - [O_x/Q])}$$

Rearranging

$$\frac{[O_x/Q]}{(1 - [O_x/Q])} = \exp \left[(E - E^0) \frac{F}{RT} \right] = \exp \left(\frac{\Delta E \cdot F}{RT} \right)$$

Differentiating with respect to ΔE

$$\frac{C}{Q} = \frac{d(O_x/Q)}{dE} = \frac{F/RT \cdot \exp(\Delta E \cdot F/RT)}{[1 + \exp(\Delta E \cdot F/RT)]^2}$$

Experimentally measurable capacitance quantity

Same thing we have also seen in the redox capacitors, that you can derive the relation for C by Q, and you have the variation E, which is taken into consideration. Now, one thing which you should realize that all the theories, which we were using till now, only considered one factor that is the electric field, or the associated force, which is experienced by a charge, because of the other charge.

So, what is the force acting on a charge, because of a charged particle and that too we were expressing in terms of E, the electric field.







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Supercapacitor







Only deals with the electrical force $F = q \cdot E$
No incorporation of the magnetic term.

Positive electrode
Negative electrode
Electrolyte
Separator
Load resistance
Electric field
Schematic of a supercapacitor.

The question arises that what happens when a magnetic field is appearing near the supercapacitor?



If magnetic field changes?



But if you introduce the magnetic field, then what happens? If I take this supercapacitor device and keep it near a magnetic field, then what will happen?

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Lorentz force

$$F_L = q\vec{E} + q(\vec{v} \times \vec{B})$$

where, q , E , v and B represent charge, electric field applied, velocity of the charge and magnetic field, respectively.

This force is applied to the electrons or charges that flow perpendicular to the electric field.

The law is first appeared in the work of James Clerk Maxwell, published in 1865.
Hendrik Lorentz arrived at a complete derivation in 1895, and so the law was named after him.

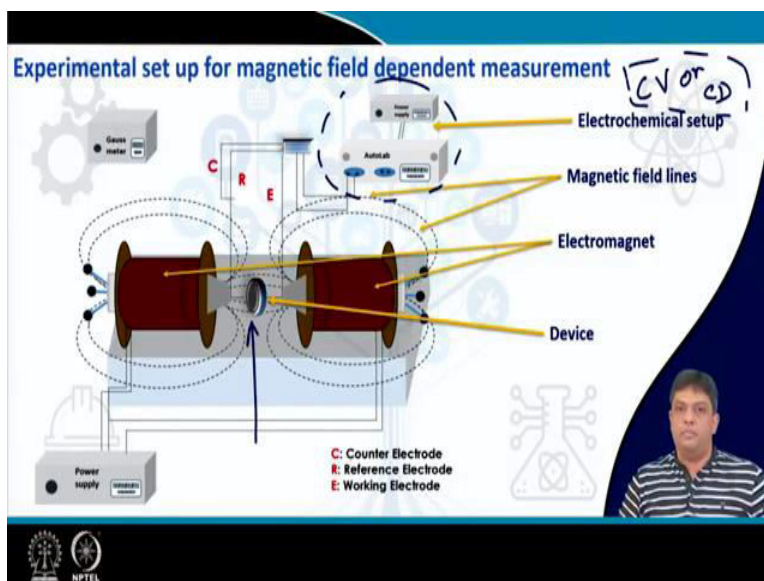
The slide includes a diagram showing a charge q moving with velocity v to the right. A magnetic field B is directed into the page (indicated by a dot in a circle). Three paths are shown for different charge signs: $q < 0$ curves upwards, $q = 0$ is a straight line, and $q > 0$ curves downwards. The slide also features a small video inset of a man in a striped shirt and the NPTEL logo at the bottom.

If I consider the appearance of a magnetic field, then immediately you have an additional term, which is coming into picture earlier, we were talking about the force, which was just equal to $q \cdot E$. But now we are talking about an additional term and the total force now is given by the Lorentz force, that is $q \cdot E$ plus $q \cdot v \times B$.

Now, you have an additional term, therefore what is it indicating, the force is actually increased in its magnitude, or you have seen some change in the force, which will be acting on the charges. And if that is happening, what will happen to the double layer formation, the solvated ion motion, the pseudo capacitive effects.

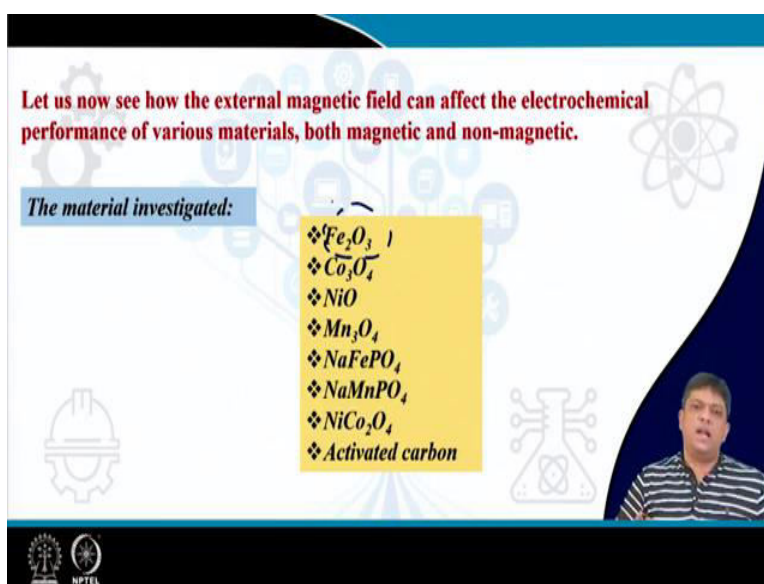
Because, now the magnitude of force, which we were thinking is driving many of the factors, which we considered while deriving the theory of pseudo capacitors, or EDLC has changed. And it does not change, because of intrinsic factor, but an extrinsic factor, that is magnetic field. So, what will happen and will there be change in that

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So, this is the way you can see the effect, so you can keep the coin cell between the poles of the electromagnet. And very slowly you can increase the field and then carry out the CV, CD measurements, CV, or CD measurements, which were discussed earlier. So, we are going to determine this specific capacitance using the cyclic voltometry, or the charge discharge measurements.

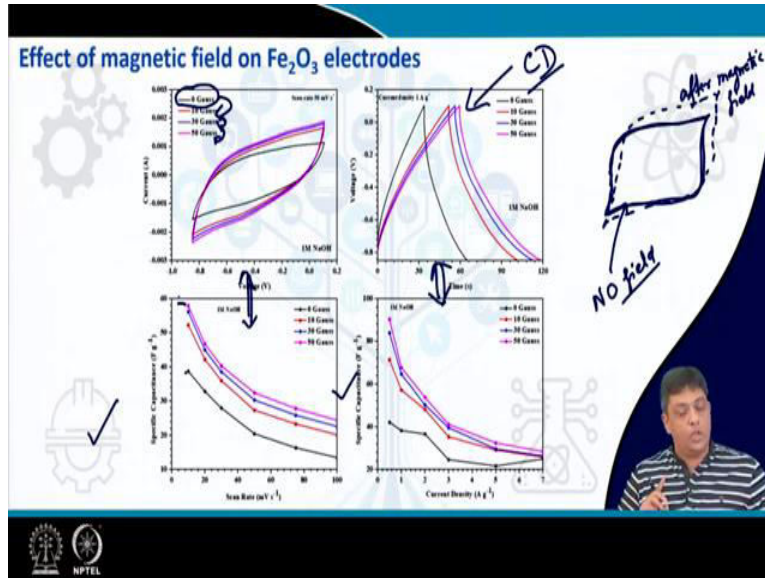
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To start we have discussed various materials, but let us take a simple case, a case where we are talking and using a material, which is ferromagnetic, that means it has iron in it. So, if there is

change in magnetic field, then it will be most felt by iron based materials. So, that is why let us start with iron oxide.

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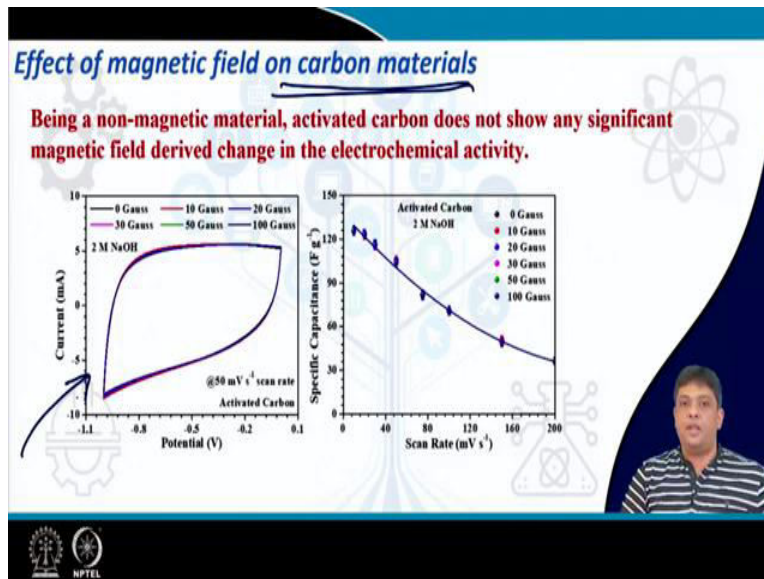
And the measurements are performed, what you are doing, you start with 0 Gauss, then go to 10 Gauss, then to 30 Gauss, and then to 50 Gauss. What did you expect? You thought that, you will put the supercapacitor in a magnetic field and nothing will happen and the cyclic curve, which will be there will be just retracing its path.

So, you will see the retracing of the path, even if you were changing the magnetic field. But you do not see that, what you actually see is, that the the cyclic curve is changing its nature and what you are seeing is maybe an increased area. So, this is what you are seeing, this is after magnetic field and the solid line 0 gauss, so 0 field, or no field.

Why is this happening? Same thing is clear, in the charge discharge measurements, obviously when you are increasing the magnetic field, the indication is such that the overall storage capacity of the device is increasing.

And you can clearly see from the specific capacitance calculations, using the corresponding data, that you from 0 gauss. Let us say it is 38 farads per gram, you have jumped to something like 58 farads per gram. And that is significant nearly 75 percent increase, in terms of percent you are seeing an increase of nearly 75 percent, or more. And if that is happening what is the reason? So, now there is an additional factor, which can modulate the performance, that is magnetic field.

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But if you do the same measurements using carbon based materials, or carbon as the electrode, that you make a symmetric electrode using carbon, you do not see the change in the specific capacitance under magnetic field. So, if you analyze, what we have seen till now, what is the major inference you will draw? The major inference is, if you use a magnetic oxide, or a magnetic material to make the electrode of an energy storage device, then the device must be protected suitably, if it is to be operated near the magnetic field. Otherwise, there would be changes, which will be observed in its specified parameters, because of the changing magnetic field.

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Effect of magnetic field on metal oxide based devices

The diagram illustrates the effect of a magnetic field on metal oxide based devices. It shows four states: (a) Equilibrium state without magnetic field, (b) Equilibrium state with magnetic field, (c) Polarization state without magnetic field, and (d) Polarization state with magnetic field. A central diagram shows magnetic field lines (incoming, inside cell, outgoing) and a small inset shows a cross-section of a device with electrodes and electrolyte.

Effect of magnetic field on metal oxide based devices

❖ One of the reasons behind the increase in capacitance response in magnetic field is magneto hydrodynamic (MHD) effect.

What is MHD?
MHD is a physical phenomenon which can explain the influence of an external magnetic field on the motion of a conducting fluid. It is basically the study of the dynamics of electrically conducting fluids.

❖ This increases the magnetic current in the system because of the feedback mechanism and increase in vigorous hydrodynamic stirring.

❖ The suppressed magnetic field dependence can be easily explained if we examine the expected valence state of the elements in the material.

The diagram illustrates the MHD effect. It shows a cross-section of a device with electrodes and electrolyte, with magnetic field lines (B) and current (I) flowing through it. The diagram shows the interaction between the magnetic field and the current, leading to the MHD effect.

And these can happen, because of various reasons and the main reason, which is given is something like this, if you have the electrolyte and the electrode. Then as a function of applied field, what you see? You see the force, which is higher coming in because of the Lorentz force.

So, you have increased the force and therefore the velocity, by which the ions will move inside, or intercalate would be higher and you would be able to utilize much more higher area than the earlier case.

And the second effect is called the magneto hydrodynamic effect, this effect is actually the effect which influences the motion of a conducting fluid. So, when you apply field, then the conductive

fluid experiences, modulations in the motion of the charges, and because of the modulation in the flow of the conducting charges, you will see that the layered structures, which you get, or the layers you get at the interfaces would be very different.

And hence you have change in the specific capacitance as a function of changing magnetic field. This magneto hydrodynamic effect increases the magnetic current in the system, because of the feedback mechanism and increase in the hydrodynamic stirring. The suppressed magnetic field dependence can be also easily explained, if we examine the expected valence state of the elements of the material.

So, if you go from one material to the other and if you change the nature. So, if you go from let us say iron to carbon based material, one is magnetic, other is not, then this kind of changes are mostly observed in magnetic materials and not the non magnetic materials.

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The slide is titled "Theoretical interpretation of magnetic results". It contains the following text:

As already discussed in the previous lectures, the charge storage mechanism of a supercapacitor can be explained by the following well-established theoretical models

- ❖ Helmholtz Model
- ❖ Gouy-Chapman Model
- ❖ Stern Model

But, none of them can explained the behaviour of magnetic supercapacitor, as they don't contain any magnetic field related terms.

Hence, a modified theoretical model is necessary to explain magnetic field dependent performance alteration of a supercapacitor

The slide also features a small video inset of a man in a striped shirt in the bottom right corner and the NPTEL logo in the bottom left corner.

As stated all the theories till now they were utilizing the variation of electric field concept only.

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Theoretical interpretation of magnetic results

The magnetic field dependent behaviour of supercapacitor can be explained with some modification of Fick's law

$$J = -D \frac{\partial C}{\partial x} + \frac{n F}{R T} D C v B$$

Modified Fick's law introducing a convection term, which arises due to the magnetic field

In presence of magnetic field, the modified flux current pertains the change in concentration C with time as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \frac{n F D v B}{R T} \frac{\partial C}{\partial x}$$

Controls the corresponding concentration of the charges C_0 and C_R

$$E_0 = E'_0 + \frac{R T}{n F} \ln \frac{C_0}{C_R}$$

(Nernst's equation) links the surface electrode potential with the concentration of the ions

So, to explain the changes in the magnetic field one has to use a modified Fick's law for diffusion, because that is changing as a function of applied magnetic field. So, you to the Fick's law you have to introduce a convection term, which is given by $\frac{n F}{R T} D C v B$, and this convection term drives the changes in the specific concentrations. So, as a function of changing concentration, you will see the changes in the double layer performance.

So, you can see that the changes in the concentration, controls the concentration of charges C_0 and C_R , and hence you will get the changes in the Nernst equation, where you are taking into consideration C_0 and C_R . And hence if E_0 is changing your double layer formation would change and the magnitude will be very different.

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Substituting the values of C_0 and C_R obtained from modified diffusion equation using Laplace transformation method in the Nernst's equation, we get:

Charging Time step $\rightarrow t < t_c$ [$i(t) = i$]

$$E = E_0 - \frac{RT}{2nF} \ln \frac{D_0}{D_R} - \frac{RT}{nF} i \alpha t^{0.5} - \frac{RT}{nF} i^2 \alpha^2 t$$

where, constant $\alpha = \frac{2}{nFD^{0.5}C_0}$

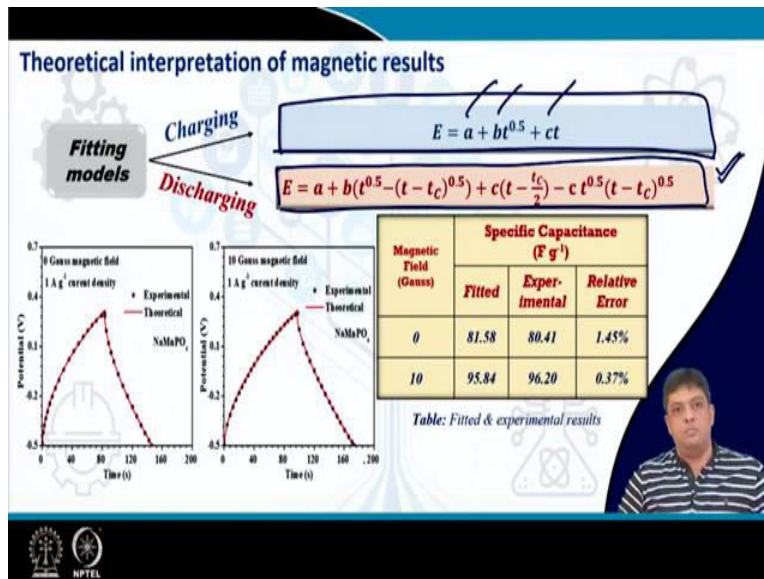
Discharging Time step $\rightarrow t > t_c$ [$i(t) = -i$]

$$E = E_0 - \frac{RT}{2nF} \ln \frac{D_0}{D_R} - \frac{RT}{nF} i \alpha (t^{0.5} - (t - t_c)^{0.5}) - \frac{RT}{nF} i^2 \alpha^2 (t - \frac{t_c}{2}) + \frac{RT}{nF} i^2 \alpha^2 t^{0.5} (t - t_c)^{0.5}$$

Now, we have already obtained a model, where we see that your field is actually going to change, because of the external magnetic field. So, substituting the values of C_0 and C_R , which are obtained from modified diffusion equation and using the Laplace transformation method in the Nernst equation we get, the term for the operating voltage window E , where we have used the term α is equal to 2 by $n F D$ raise to power 0.5 by C_0 .

And you have two conditions charging and discharging, for these two conditions you take the two regions. So, you take two regions, one below this, and the other above the maximum. So, you can obtain the two relations, for charging and discharging cycles.

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Once you have obtained this model, you can use the constants a b and c, and rewrite the equation and you will get again two equations, one for discharging and one for charging. You have the equation you plot the value of E, as a function of time, you will get the red curve, which is drawn in the graph. And you can clearly see, that the curve is actually fitting the magnetic field dependent variation in specific capacitance, that is the CV, or the CD curves can be easily fitted using this modified theoretical model, which takes into consideration, an additional convection term, which is there in the Fick's law, where which is driving the diffusion of ion in the solution the electrolyte, or the diffusion of the electrolyte ion within the materials, that are used.

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As we seen earlier: external magnetic field can affect the capacitor performance.

What is next?
External vibration

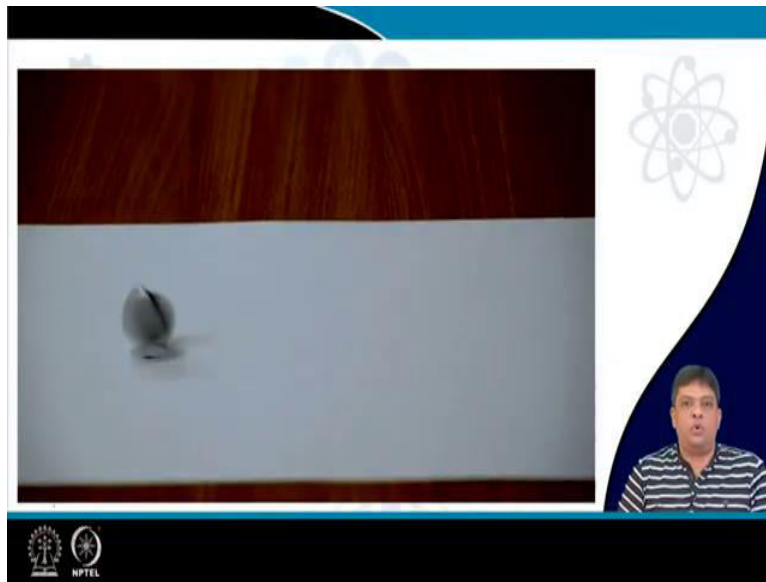
The slide features a yellow text box with the main text. The background is white with various icons: gears, a tree of nodes, an atom, a hard hat, and a circuit board. A small video inset of a man in a striped shirt is in the bottom right corner. The NPTEL logo is at the bottom left.

So, till now what have we seen? We have seen one factor which is very evident, that is temperature can affect the performance of the energy storage device. The next factor that was magnetic field, it was non trivial, but you would have realized that it can also change.

And finally the factor, which is there which can change the performance significantly is the external vibration, as I described in the beginning of this lecture, if your device is continuously vibrating, then what happens to the performance of the storage device.

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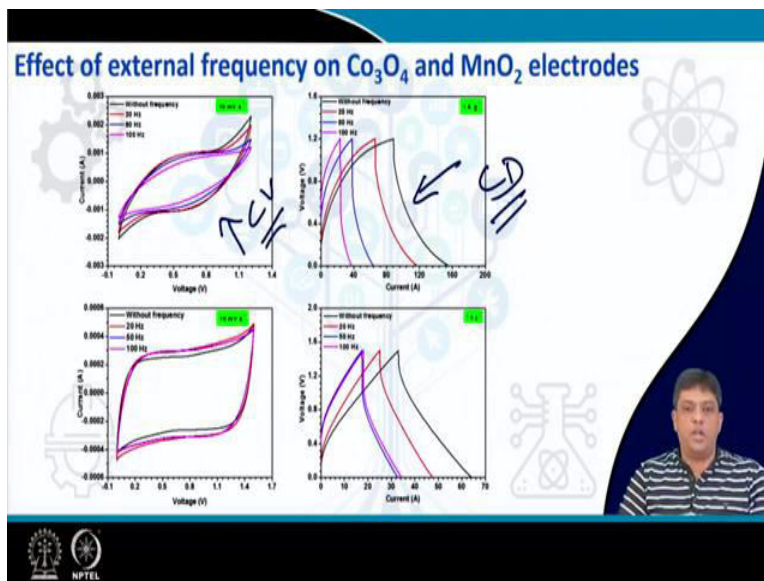
The slide shows a video of a small, dark, cylindrical object on a wooden surface. The video is paused. The background is white with an atom icon. A small video inset of a man in a striped shirt is in the bottom right corner. The NPTEL logo is at the bottom left.



So, let us take the example of the coin cell, which we have been discussing. So, what are we saying that, you have a coin cell and let it, it falls down, then what will happen? No then there is a battery, where people are throwing, or then there is something, where you have seen that the battery is falling on the ground and then it has suffered vibration effect.

So, you have gone from static condition, which you are seeing now on the screen and just before that the battery had seen significant variations coming in because of vibrational effects.

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So, will the performance change? If you perform this experiment you will see, that similar to what we saw in the magnetic field dependent variations, again there is appreciable change in the CD, or CV curves, which indicate modulation in the specific capacitance. The details of the theory, which is used to explain these kind of features are beyond the scope of this course, because the explanation lies in understanding, the theory of ultrasonic.


And this is slightly beyond the scope of this course, but if you are interested, then you will have to read through the published literature and then they will be describing these things in detail, using the theory of ultrasonic's, or you can contact me and we will be sending you the relevant publications in this area.

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Cavitation effect in the electrode with the presence of the external vibration




A high-speed video frame showing a dark, irregularly shaped cavitation bubble on a light-colored electrode. The bubble is suspended by two thin wires. The background is a light gray.




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Cavitation effect in the electrode with the presence of the external vibration

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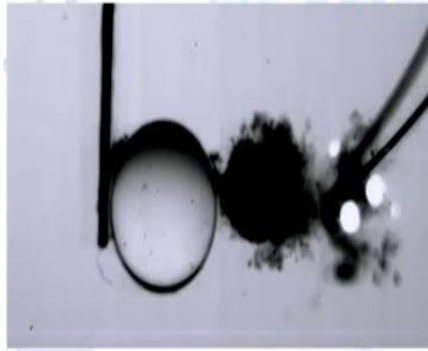


A high-speed video frame showing a dark, irregularly shaped cavitation bubble on a light-colored electrode. The bubble is suspended by two thin wires. The background is a light gray.



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Cavitation effect in the electrode with the presence of the external vibration



Cavitation effect in the electrode with the presence of the external vibration

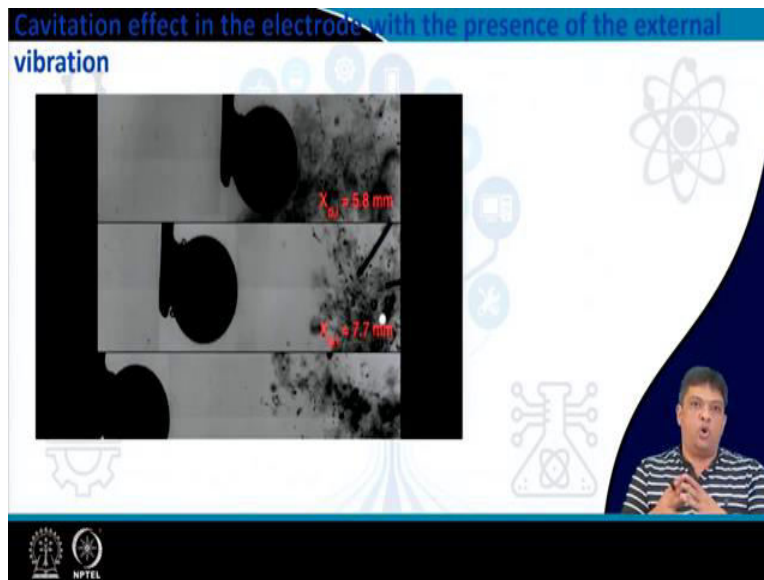


Cavitation effect in the electrode with the presence of the external vibration



Cavitation effect in the electrode with the presence of the external vibration





But there is additional effect, which one can visualize and then you will be able to understand, why this changes can happen and that is called the cavitation effect. What is cavitation effect? The cavitation effect is that, you have appearance of a bubble, because of changes in the potential, or the field around, or this bubble and because of this vibration after a certain time the bubble becomes too big, and it explodes and because of this explosion at the nano scale the local temperature around this explosion of the bubble can be quite significant.

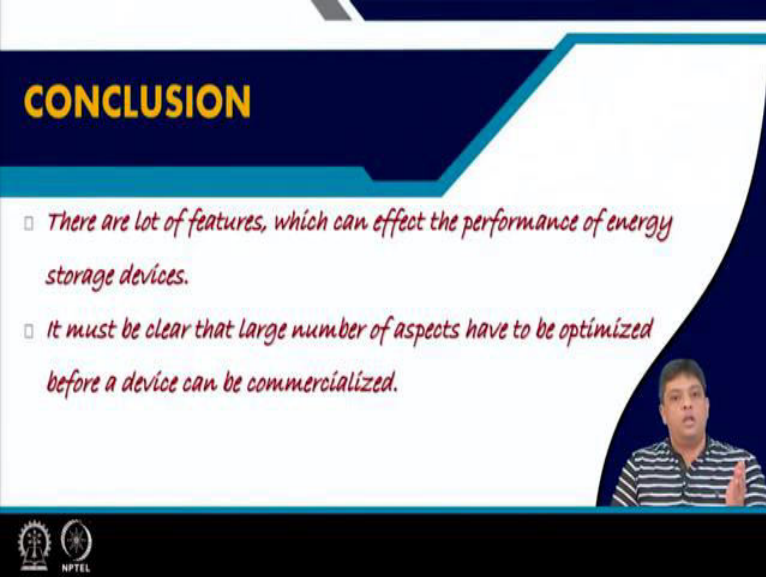
And because of the change in the temperature, what will happen? The double layer, which is forming at the interface will feel this change in the temperature and the device will have a different performance all together. So, you can see this effect and that is observed in this curve. So, this is what a cavitation experiment looks like.

So, you are having a liquid, which is monitored and then what you are seeing you will see that, if there is a bubble which is formed, then because of this electric field, or field induced there is an explosion in this bubble. And because of this there is appreciable change, or increase in the temperature near the field, or the electrodes.

And you can clearly see that, even if this is at very, very small level you can still see the nature of the explosion. And hence you can imagine the modulations, which would be occurring in the double layer, or the pseudo capacitance, or the redox induced pseudo capacitance, which you are estimating.

Hence, you can expect changes as a function of external vibrations. And therefore I hope now you will understand, why it is said that try to avoid your mobile phones, or your laptops from very heavy external vibrational conditions, because then your energy storage devices itself is going to deteriorate in performance and that would affect the, the life span of the device.

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CONCLUSION

- *There are lot of features, which can effect the performance of energy storage devices.*
- *It must be clear that large number of aspects have to be optimized before a device can be commercialized.*

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Today I discussed two parameters, which can affect the performance of the device. In the earlier lecture, I had discussed temperature effect and I have still not discussed many other factors, be it be changing electric field, be it be changing pressures, or any other factors, which you can think is changing around the device.

So, there are lot of features, which can affect the performance of an energy storage device, this sentence must be clear to you. And before I go to the next module, I will once again reiterate this point, that there are large number of aspects, that have to optimized before the energy storage device, such as supercapacitor, or a device like lithium ion battery, or sodium ion battery can actually be commercialized. And therefore it takes time to take a product from lab to market

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These are the major references, which were used for preparing this, and the previous lecture. And I thank you for attending this module on supercapacitor and from next lecture, we will move to fuel cell. Thank you very much.