Physics of Renewable Energy Systems
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Lecture 35
Effect of Temperature on Supercapacitor Performance

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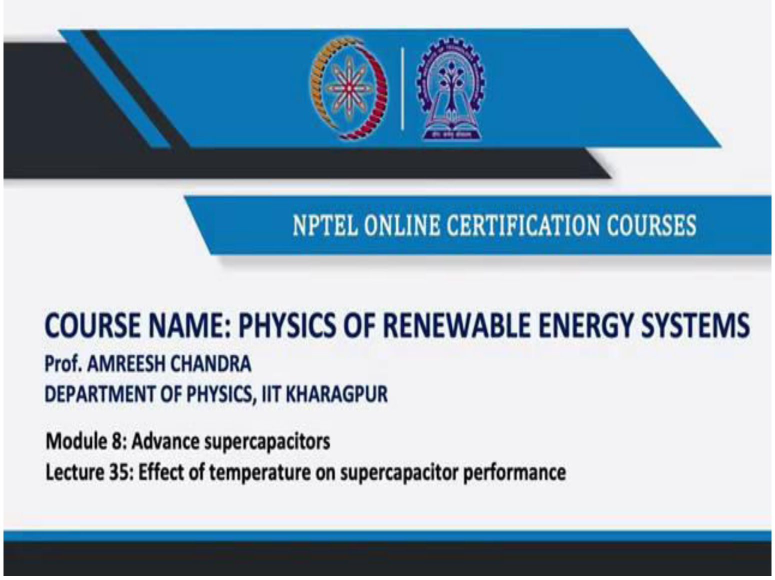

NPTEL ONLINE CERTIFICATION COURSES

COURSE NAME: PHYSICS OF RENEWABLE ENERGY SYSTEMS
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Module 8: Advance supercapacitors
Lecture 35: Effect of temperature on supercapacitor performance

Welcome back let us continue our discussion on supercapacitors. And till now we have seen what are EDLC, we have also seen what are zero capacitors and how do we actually fabricate a device. Now, once I have a device what am I going to do about it? We are going to apply the device, or use the device somewhere.

Now, the moment I take the device out of the lamp, to the real-world situation, then there are other factors which come into play, which you could have controlled in the lab. These factors include varying temperatures, varying moisture, varying pressures, varying electric field, varying magnetic field, varying vibrations and so on so forth. But these factors have not been considered till now in any of the lectures.

So, when we take the device out of the lab and to the real application, then we must consider the real-world scenario. And in the next two lectures, that is the one I am going to give now, and the next lecture you will see that these factors can influence the performance of energy storage devices.

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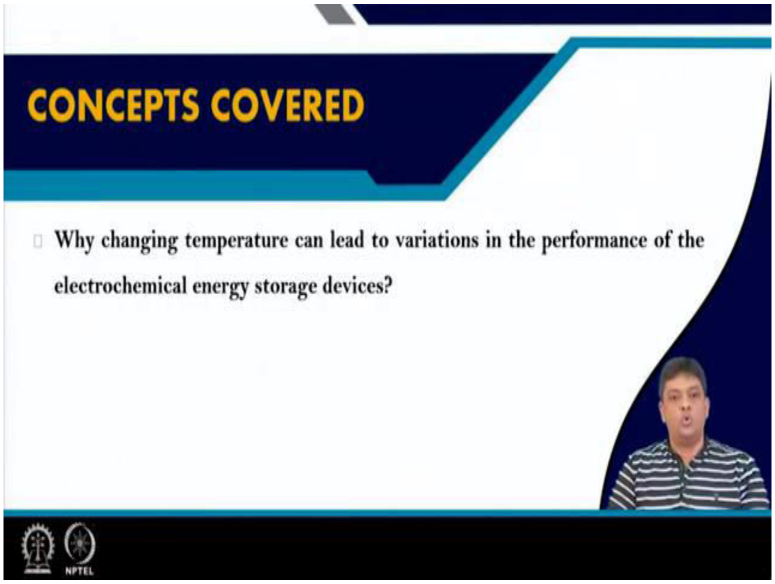

CONCEPTS COVERED

- Why changing temperature can lead to variations in the performance of the electrochemical energy storage devices?

You will be able to see today that, one of the most common factors, which can modulate the performance of energy storage devices is temperature. If you look around and see the temperature range in which your energy storage device will be lithium and battery, or supercapacitor are being used, they range from minus, let us say 30 degrees to around plus 70, or plus 80 degrees.

So, you are looking at in a temperature range of 100 degrees plus minus, and if you want to have a device, then it should be stable in this temperature range, else the device rating must be such that it clearly specifies the temperature range in which the device, which you have fabricated can be utilized. Otherwise, it will lead to failures, failure in the performance.

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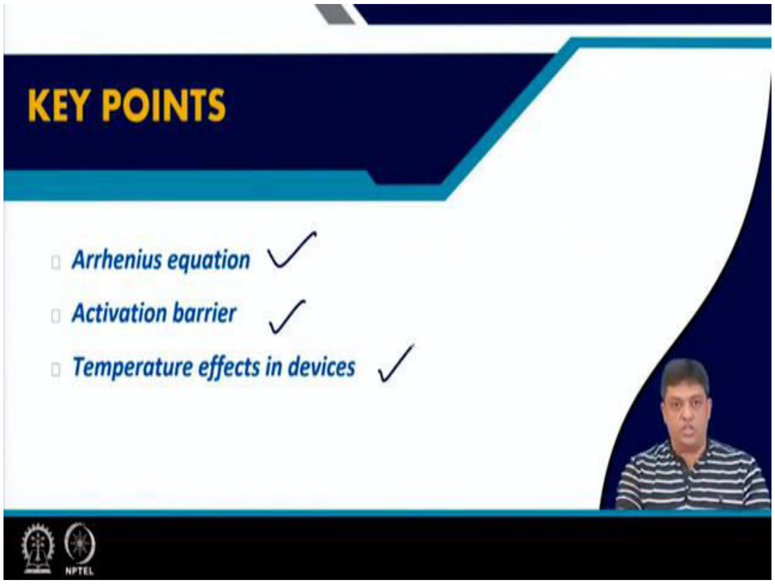

KEY POINTS

- *Arrhenius equation* ✓
- *Activation barrier* ✓
- *Temperature effects in devices* ✓

So, there are mathematical formulations and equations, which are used to explain the changes as a function of temperature, or external factors. And there is an underlying physics, which can be used to explain the variations in these devices as a function of temperature. So, you must understand by the time we end this lecture, the concept of Arrhenius equation. What do we understand by activation barrier? What is getting activated and which barrier are we talking about? And finally, you will be able to appreciate the difficulties of making devices, which can be used over a large temperature range.

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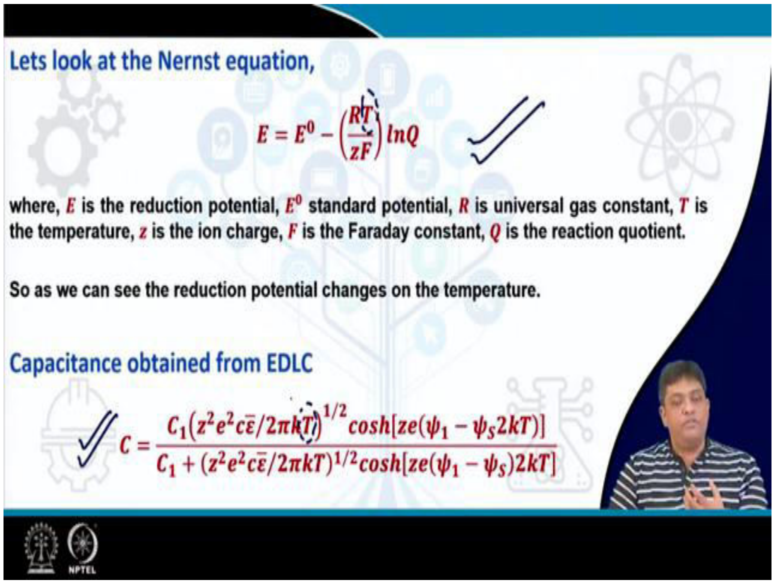

Lets look at the Nernst equation,

$$E = E^0 - \left(\frac{RT}{zF}\right) lnQ$$ ✓

where, E is the reduction potential, E^0 standard potential, R is universal gas constant, T is the temperature, z is the ion charge, F is the Faraday constant, Q is the reaction quotient.

So as we can see the reduction potential changes on the temperature.

Capacitance obtained from EDLC

✓ $$C = \frac{C_1(z^2e^2c\bar{\varepsilon}/2\pi kT)^{1/2} cosh[ze(\psi_1 - \psi_S 2kT)]}{C_1 + (z^2e^2c\bar{\varepsilon}/2\pi kT)^{1/2} cosh[ze(\psi_1 - \psi_S)2kT]}$$

What have we seen till now? We have seen in the Nernst equation, that the reduction potential is related with the standard potential and there is a factor T, which is involved and rest of the other factors are mostly constant, mostly constant R is a constant, F is a constant. But the reaction quotient and the ion charge, which you are considering may be varying, but the changes would be minimal, it is the factor T, which is going to change the reduction potential, this is what you can infer by looking at this equation.

We have seen in the lecture, where we were talking about the capacitance obtained in electric double layer capacitors is given by the equation at the bottom of this slide. Again, what do you see? You see the change in the dielectric constant, or the average dielectric constant, as well as the temperature, which is going to change the value of C, when you are talking about electric double layer capacitors. But have we actually considered the variation in temperature till now, we were taking the measurements and characterizing the devices at room temperature, or STP.

Let us say the room temperature was 25 degrees. So, we were discussing everything at 25 degrees and we were estimating the performance at this temperature. But if you see around, if you see your own country, you if you are in the northern part of the country, then you look around from January to July to October, you have a wide variation in the temperature.

So, you can go from minus 10 degrees, minus 15 degrees to plus 50 degrees, not only as a function of month, but also if you are moving, let us say from Rajasthan to West Bengal, then also as a function of distance, even in the same month you can see variations in the temperature. So, you have to consider the variation of temperature.

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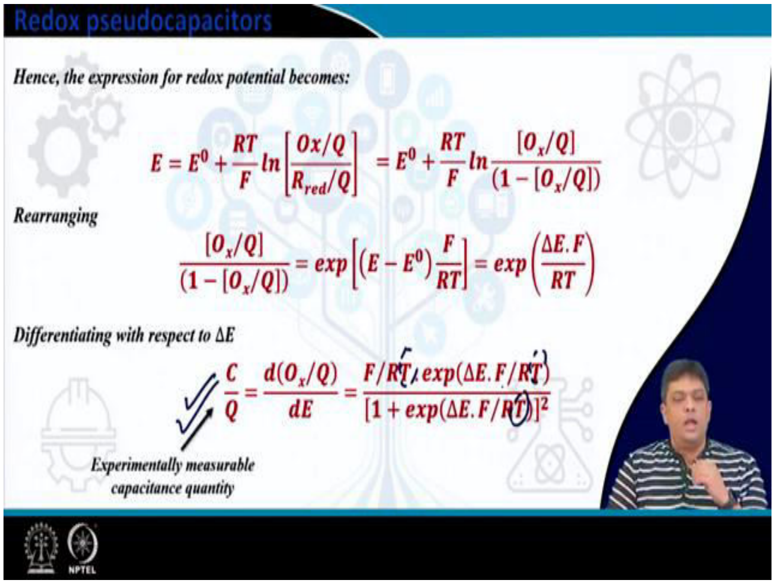

Redox pseudocapacitors

Hence, the expression for redox potential becomes:

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

Rearranging

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

Differentiating with respect to ΔE

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

Experimentally measurable capacitance quantity

What have we seen in the redox pseudo-based type pseudo capacitors? We again considered the redox potentials, the standard potentials and finally we derived the equation of C by Q. And then we if we know the charge, then we could estimate the value of C. And in this equation again you have the contribution of temperature.

And till now we have not considered the variation in this, but with the discussions in the previous three slides, you would be now realizing that, yes you change the temperature the performance will change, or at least if I change the temperature in which, or the temperature around the device, then the performance of the device may actually change, because the mathematical formulations are clearly indicating towards that direction.

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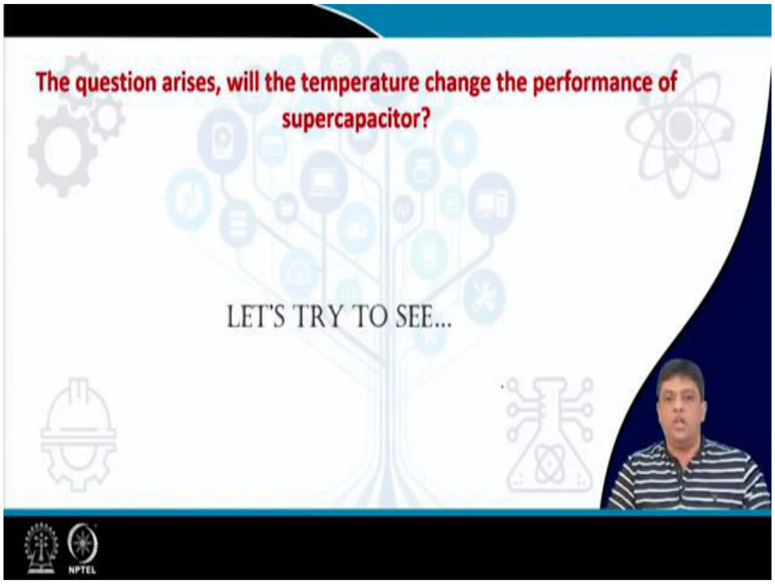

The question arises, will the temperature change the performance of supercapacitor?

LET'S TRY TO SEE...

So, what are we doing? We have to take the device and see its performance by changing the temperature around it, let the device equilibrate that means, you give the device enough time to reach to the same temperature of that of its surrounding. And then you perform the measurement. So, that is important, because you may take a device out of the lab, that is at 25 degrees take it outside the lab, where it is 50 degrees, but you do not give the device time to actually equilibrate with the temperature outside and bring the device back inside the lab.

So, the performance may not be as different as what you may have seen in the lab, but you must give time for the equilibration process to take place and then only you should perform the measurements.

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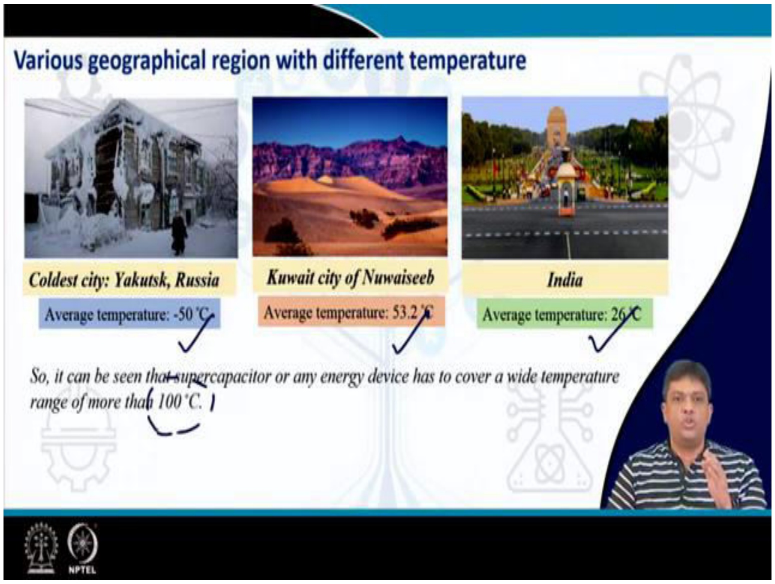

Various geographical region with different temperature

Coldest city: Yakutsk, Russia

Average temperature: -50 °C

Kuwait city of Nuwaiseeb

Average temperature: 53.2 °C

India

Average temperature: 26 °C

So, it can be seen that supercapacitor or any energy device has to cover a wide temperature range of more than 100 °C.

So, you can go from very cold temperatures, to high temperatures, or you can also see moderate temperatures, if you average out throughout the year. So, as it was said that, you are looking at capacitors and batteries, which should be stable over a wide temperature range.

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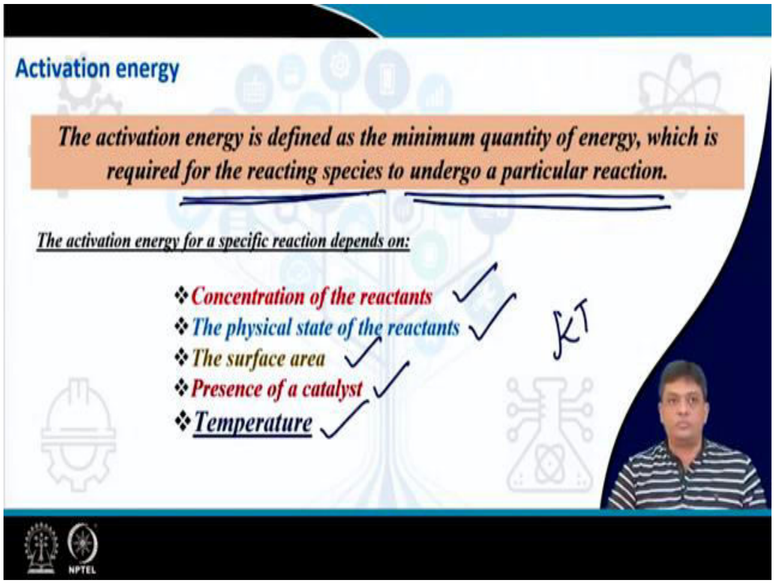

Activation energy

The activation energy is defined as the minimum quantity of energy, which is required for the reacting species to undergo a particular reaction.

The activation energy for a specific reaction depends on:

- *Concentration of the reactants* ✓
- *The physical state of the reactants* ✓
- *The surface area* ✓
- *Presence of a catalyst* ✓
- *Temperature* ✓

So, one was coming from the mathematical formulation. It was clear that there can be certain modulations in the performance. Next thing what we have seen is, what we saw that, you were using aqueous liquid, or aqueous electrolytes and these aqueous electrolytes had these solvated ions and these ions were randomly moving, they were moving, because of what because of the thermal energy K T.

And the motion was random means you were talking about Brownian motion, this is what we have seen earlier. When you applied charge on the field, then what was happening you were seeing the formation of double layer at the solid electrolyte interface. Now, you say that this Brownian motion is driven by what, is driven by the thermal energy K T, again K T, I say that please estimate the thermal energy, let us say at minus 100 degrees, that is 173 K. And then estimate the thermal energy at plus 100 degrees, that is 373 K.

So, clearly you will believe, as if we are just talking about something, which is very evident, that there will be change in the thermal energy and because of this the motion of the ions, or the solvated ions would also be different, because in the first case where we had gone to lower temperatures, the energy would be less and the motion would be slightly suppressed. Then what we see at a higher temperature.

And so, there is one thing which is very clear, the temperature will also affect the motion of the solvated ions and as that happens you will also see the changes at the double layer. And the third thing which comes into picture is the activation energy. What is activation energy? This is the energy defined as the minimum quantity of energy, which is required for the reacting species to undergo a particular reaction. If there has to be, let us say a reaction, which is of redox type either reduction, or oxidation, which is taking place.

Then this will take place only, when the reacting species have the minimum energy associated, or available. The activation energy for a specific reaction also depends on the concentration of the reactants, the physical state of the reaction, the surface area of the particles, or the reactants. If you use catalyst, then the activation energy can be changed, or you can control the reaction rates. And finally, you have the contribution from temperature.

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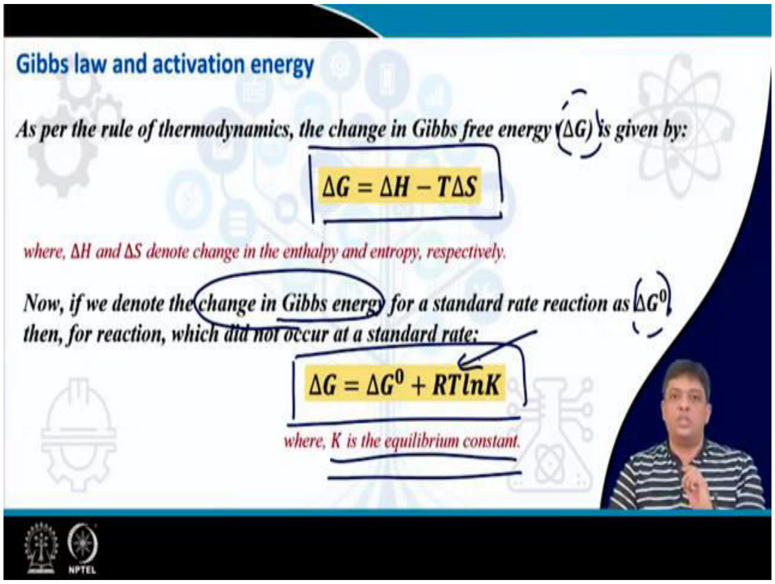

Gibbs law and activation energy

As per the rule of thermodynamics, the change in Gibbs free energy (ΔG) is given by:

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH and ΔS denote change in the enthalpy and entropy, respectively.

Now, if we denote the change in Gibbs energy for a standard rate reaction as ΔG^0 then, for reaction, which did not occur at a standard rate:

$$\Delta G = \Delta G^0 + RT\ln K$$

where, K is the equilibrium constant.

If you go back to thermodynamics, then the change in the Gibbs free energy, delta G is given by what, delta G is equal to delta H, minus T delta S. What is H and S? S is the entropy, H is the enthalpy. So, the change in Gibbs free energy is given by the change in enthalpy minus T times the change in entropy.

Now, suppose we denote the change in Gibbs free energy, for a standard rate reaction as delta G^0, then for a reaction which did not occur at a standard rate, then there change in delta G is given by the relation delta G is equal to delta G^0 plus RT ln k, where k is the equilibrium constant. Again, what are we seeing? We are clearly seeing temperature effects are there.

So, if I increase the temperature, then change in Gibbs free energy would be different, if I decrease the temperature change in energy would be different. And if the change in Gibbs free energy is different, what is the state in which the system would like to stabilize, would be the state in which it is in the minimum energy state. So, by changing the temperature, again you are changing the reaction kinetics.

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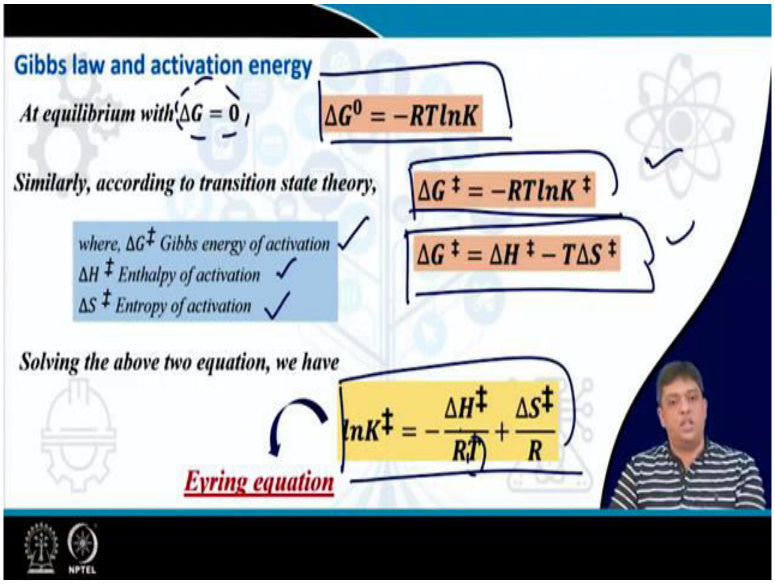

Gibbs law and activation energy

At equilibrium with $\Delta G = 0$, $\Delta G^0 = -RT\ln K$

Similarly, according to transition state theory, $\Delta G^{\ddagger} = -RT\ln K^{\ddagger}$ ✓

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ ✓

where, $\Delta G^{\ddagger}$ Gibbs energy of activation ✓
$\Delta H^{\ddagger}$ Enthalpy of activation ✓
$\Delta S^{\ddagger}$ Entropy of activation ✓

Solving the above two equation, we have

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}$$

Eyring equation

At equilibrium what happens? Delta G is equal to 0, this is the condition of equilibrium. So, what you get delta G^0 is actually equal to minus RT ln k. Similarly, according to the transition state theory, what have we seen that, delta G double plus is equal to minus RT ln k double plus, and delta G double plus can also be written as delta H double plus minus T delta S double plus, where the delta G double plus is the Gibbs energy of activation, delta H double plus is the enthalpy of activation, and delta S is the entropy of activation.

So, activation something which becomes active, so you are making some parameter to start becoming active, or you are ensuring that there is some change in the parameter. So, you are activating certain phenomena, or modulations in a parameter. Let us solve these two equations which are given and then you can get ln k double plus is equal to minus delta H double plus by RT plus delta S double plus by R. This is the Eyring equation.

Now, from here you can again see, that even the change in the equilibrium constants are related to temperature. So, from whichever angle you look at a system, temperature will affect the chemical reactions. And so, if you are making a device, where the activity, or the electrochemical reactions are taking place, then by changing the temperature, there will be appreciable change in the performance should be clear from the discussion.

So, you come from minimization of Gibbs free energy, or you talk in terms of the Brownian motion, any or you talk in terms of the EDLC equations, or the pseudo capacitor equations, everywhere it is clear, that temperature will play an important role. What do you actually want out of a device? You want out of a device, that even if I change the temperature, the performance should not change significantly.

So, if I go into a place, where the temperature is much higher, then also battery, or the supercapacitors must have the similar output, just like the one which I see if I go to a place, where there is snow outside and I am standing outside. Then also the performance should be similar, that is what we are seeing and that is what is done in the thermal management system of the overall device.

So, you try to ensure that the device is actually seeing a moderate temperature throughout, if it is too cold then you are ensuring that, the system is heated and the temperature around the device is moderate, and if it is too hot outside, or in the periphery of the device, then you are actually ensuring that the cooling mechanism comes in and maintains a moderate temperature, that is what is done in the thermal management side of the whole system.

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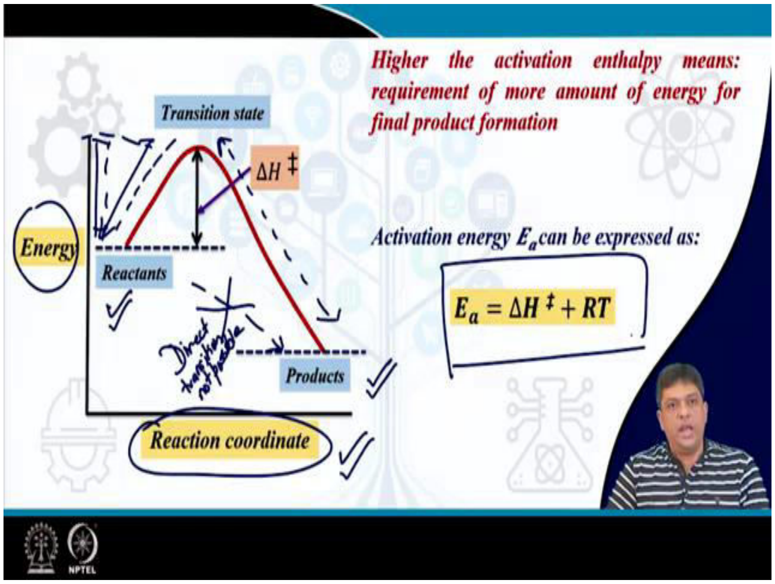

Higher the activation enthalpy means: requirement of more amount of energy for final product formation

Activation energy E_a can be expressed as:

$$E_a = \Delta H^{\ddagger} + RT$$

So, this is what your activation energy curve actually looks. So, you have energy versus reaction coordinate, reaction coordinate you can talk in terms of any of the parameters you choose. So, you can use any of these reaction coordinates, which you are actually going to monitor. Now, so you have the reactants, when you give them energy, then the reactants finally have to go to the product form. But the transition is not direct, the reactants have to overcome a barrier and beyond that barrier, the system starts minimizing its Gibbs free energy, and then only you reach to the products.

So, this is the activation barrier, which you are talking about. So, the system has to obtain extra energy, then only it will transform to the other side of this barrier, and you will obtain the final product. So, direct transition not possible, so direct transition not possible, it is only when the reaction coordinate has overcome this barrier, which is called as the activation barrier. And the associated activation energy can be written as delta H double plus, plus RT.

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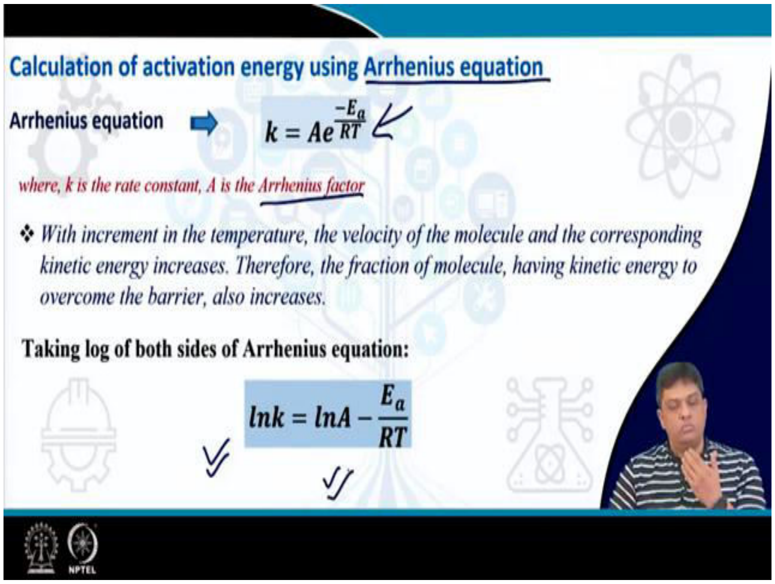

Calculation of activation energy using Arrhenius equation

Arrhenius equation ➡ $k = Ae^{\frac{-E_a}{RT}}$

where, k is the rate constant, A is the Arrhenius factor

- *With increment in the temperature, the velocity of the molecule and the corresponding kinetic energy increases. Therefore, the fraction of molecule, having kinetic energy to overcome the barrier, also increases.*

Taking log of both sides of Arrhenius equation:

$$lnk = lnA - \frac{E_a}{RT}$$

The activation energy can be calculated using the Arrhenius equation, which is of the form of A e raise the power of minus E a by RT and k is the rate constant, and A is the Arrhenius factor. Taking log of both the sides what you get? You get ln k is equal to ln A minus E a by RT. So, you solve this.

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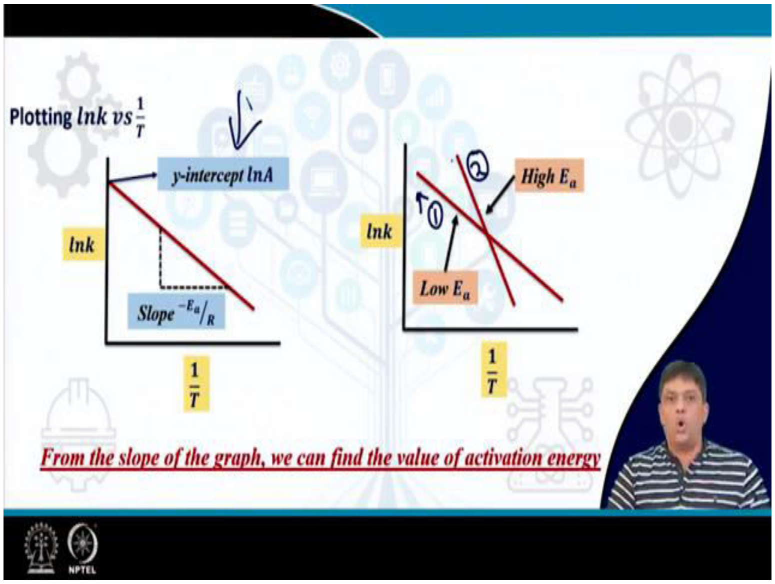

Plotting $\ln k$ vs $\frac{1}{T}$

From the slope of the graph, we can find the value of activation energy

Then you plot ln k versus 1 by T and the y intercept will give you the value of ln A, and slope will give you minus E a by R, and hence you can get the value of E a quite easily. So, if you have low activation energy, or you have E a, which is low, then you get a curve which is given here, let us say curve number 1. And if you have high E a, then you get a much different slope, and this looks something like this, which is given in curve2.

So, it is clear that you change the temperature, then your activation barriers change, the height of the barrier change, and hence the reaction changes, and you can therefore expect change in the reaction coordinates.

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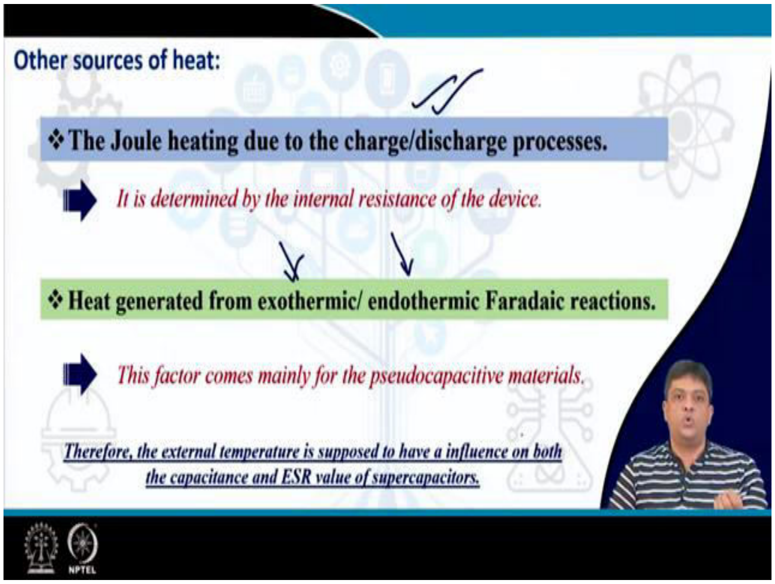

Other sources of heat:

- **The Joule heating due to the charge/discharge processes.**
  - *It is determined by the internal resistance of the device.*
- **Heat generated from exothermic/ endothermic Faradaic reactions.**
  - *This factor comes mainly for the pseudocapacitive materials.*

Therefore, the external temperature is supposed to have a influence on both the capacitance and ESR value of supercapacitors.

So, then there are other factors, which can lead to changes in the temperature, these can be Joule heating, coming in from the internal resistance of the device, and this becomes prominent during the charge discharge processes, or if you have Faradaic reactions in pseudo capacitors, which are exothermic, or endothermic, then they can also lead to exothermic heat, or endothermic heat.

So, it is about change in the temperature, if you give heat, or you take heat, then you are going to change the temperature. And the device may actually see a different operating temperature than what you are expecting. Hence, it must be very clear, that there are various factors and the real device actually sees change of temperature, because of these factors and we must therefore see whether there is actually a change in the performance.

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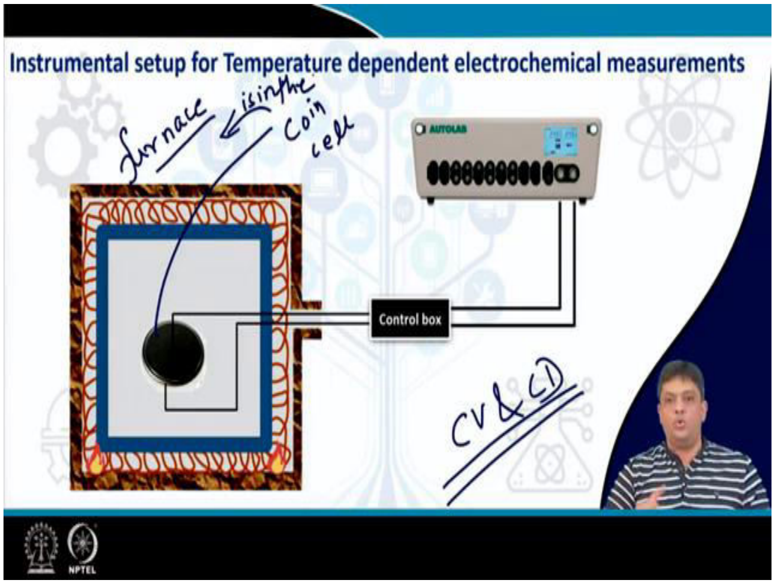

Instrumental setup for Temperature dependent electrochemical measurements

The measurements are done in a very simple way, even you before you take the device to real world, you must already anticipate and find out what is the change, which can take place. So, you perform the CV and CD measurements. Let us say the electrochemical measurements, which we discussed earlier this week, but you perform in a condition, where the cell, coin cell is in the furnace.

So, you take the coin cell, put that coin cell in a furnace. So, you can heat the furnace and then after equilibrating, you can perform the CV, CD measurements and then recalculate your capacitance values and see what those values are in comparison to the values you got at the room temperature.

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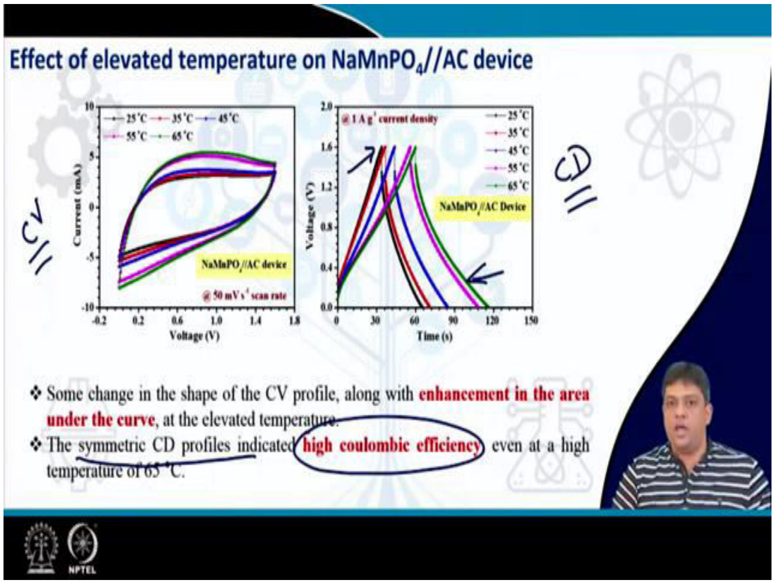

Effect of elevated temperature on $NaMnPO_4//AC$ device

- Some change in the shape of the CV profile, along with **enhancement in the area under the curve**, at the elevated temperature.
- The symmetric CD profiles indicated **high coulombic efficiency** even at a high temperature of 65 °C.

And we have just taken this example from sodium-based supercapacitors, because sodium-based batteries and supercapacitors are becoming very important for India, because India wants to move away from lithium-based systems owing to geopolitical issues and high cost, and limited reserves and deposits of lithium. So, we would like to move towards sodium.

So, just for an example I took this sodium, manganese, phosphate, and activated carbon-based asymmetric supercapacitor cell, and you can clearly see that even in the CV curve, or the CD curve, if you see the scans, it is clear that the nature of the curve is changing as a function of temperature.

So, we started with the black curve, which was representing the measurement at 25-degree C, and when you have reached 65-degree C, you find that the curve is very different, along with that you see enhancement in the area under the curve at elevated temperatures. But in this sample, or the device based on sodium manganese phosphate and activated carbon-based electrodes, you see that the CD profiles are quite symmetric.

So, the nature of the CD profiles, or the CV profiles do not change, hence they have high coulombic efficiencies, even at higher temperatures.

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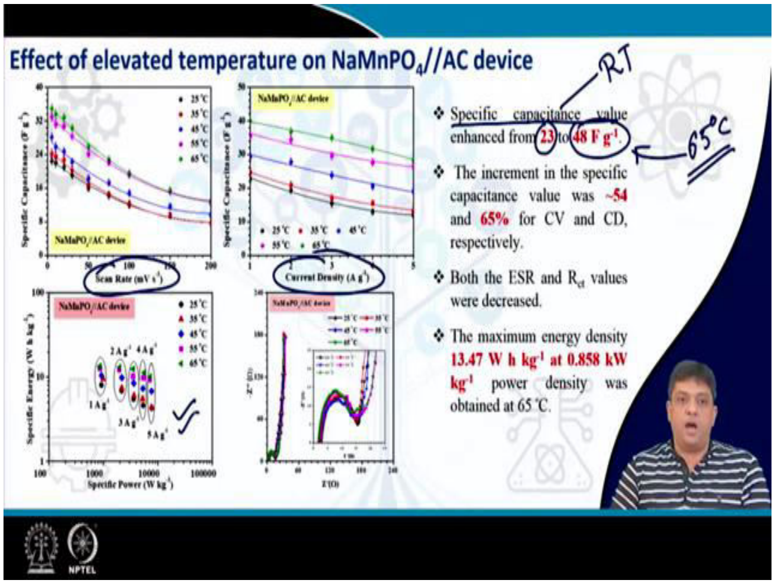

Effect of elevated temperature on $NaMnPO_4$//AC device

RT

- Specific capacitance value enhanced from 23 to 48 F g^{-1}.

65°C

- The increment in the specific capacitance value was ~54 and 65% for CV and CD, respectively.
- Both the ESR and R_{ct} values were decreased.
- The maximum energy density 13.47 W h kg^{-1} at 0.858 kW kg^{-1} power density was obtained at 65 °C.

They are quite stable to cycling also, and you can see, that the nature of curve also, or variation as a function of scan rate, or current densities remain similar. So, it is not as if the device is performing in a way, which is very different from the room temperature, it is only the magnitude which is changing.

Magnitude of what? You are seeing change in the magnitude of the specific capacitance for example, if this is the value at room temperature, which was observed, if you recalculate from the data you will find, that the value shoots up to 48, 48 farads per gram. So, there is a significant increase in the specific capacitance. And what could be the reasons, you could see the same effect in the specific energy as well as specific power curves.

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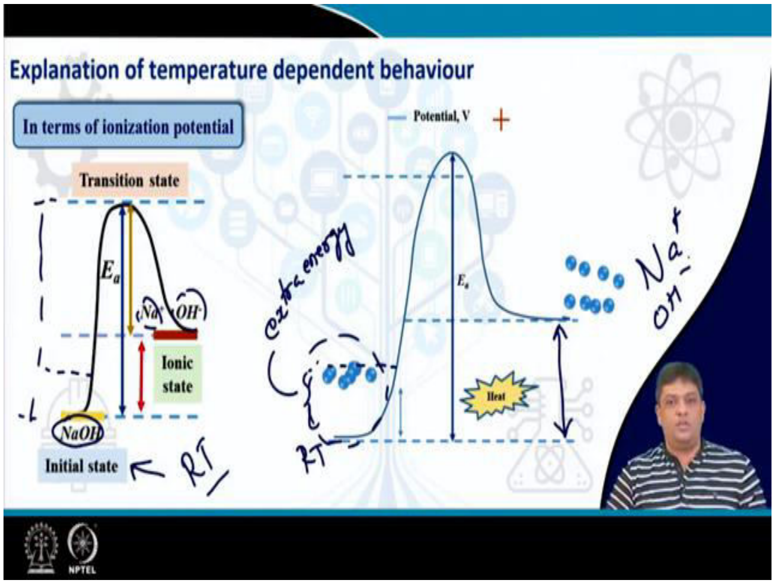

Explanation of temperature dependent behaviour

In terms of ionization potential

Transition state

E_a

Na

OH^-

Ionic state

NaOH

Initial state

RT

Potential, V

+

extra energy

RT

E_a

Heat

Na^+

OH^-

So, what can happen, the reason is actually coming in terms of the ionization potential. So, what was the electrolyte used? It was sodium hydroxide. So, to go to an ionic state, where you have sodium and OH minus, you have to go to the activation barrier and cross the activation barrier and then only you get an ionic state.

So, if you are at in the initial case. which was the room temperature case. but in the second case what was happening, you were already at 65 degrees. So, you had systems, which were already at a height, which is more than the height which you were seeing at room temperature. So, you already had extra energy. If you had extra energy, then the effective barrier height came down.

So, you had extra energy, so with the probability that you will be able to cross the barrier would was increasing, and hence you would find that system would be able to cross the barrier, and you will get the ionic states and you will get Na plus and OH minus, and you will have the electrolyte ions, which would then take part in the formation of the double layer, or the pseudo capacitive effects.

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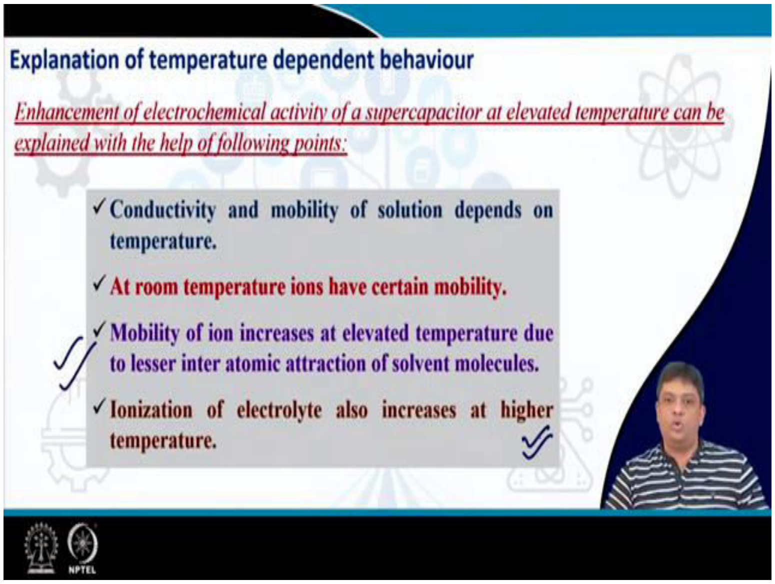

Explanation of temperature dependent behaviour

Enhancement of electrochemical activity of a supercapacitor at elevated temperature can be explained with the help of following points:

- ✓ Conductivity and mobility of solution depends on temperature.
- ✓ At room temperature ions have certain mobility.
- ✓ Mobility of ion increases at elevated temperature due to lesser inter atomic attraction of solvent molecules.
- ✓ Ionization of electrolyte also increases at higher temperature.

Therefore, the temperature dependent behavior can also be explained in terms of changing mobility of solution, you will see that at room temperatures, I have certain mobility and the mobility of the ions increase at elevated temperature. So, effectively you are see having the reduction in the barrier height.

Ionization of the electrolyte also increases at higher temperatures, and more ionized species are obtained and hence the performance is expected to increase, because then you have more ions to contribute in the double layer, or pseudo capacitive behavior of the device.

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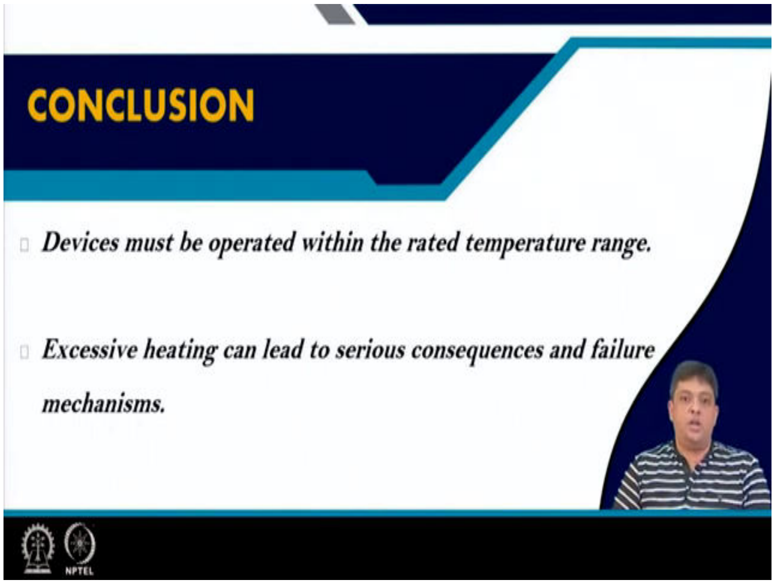

CONCLUSION

☐ *Devices must be operated within the rated temperature range.*

☐ *Excessive heating can lead to serious consequences and failure mechanisms.*

What we discussed today it must be very clear to you now, that the devices must be operated within the rated temperature range. Otherwise, there are various failure mechanisms, which will set in. And excessive heating can lead to serious consequences and failure mechanisms, which can destroy your device quite quickly, and you may end up getting performances, which are very different from what is expected out of these devices.

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These are the references from which the details were obtained. And I thank you for attending today's lecture.