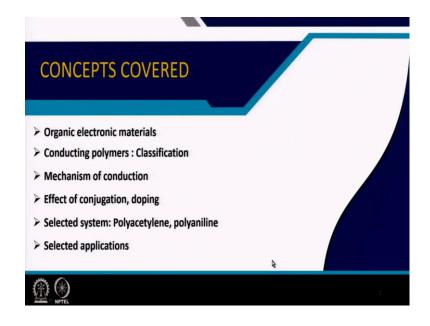
Non - Metallic Materials Prof. Subhasish Basu Majumder Department of Materials Science Centre Indian Institute of Technology, Kharagpur

Module - 08 Thin film growth and fabrication of devices Lecture - 44 Organic electronic materials: conducting polymers, Semi – conducting organic materials, applications

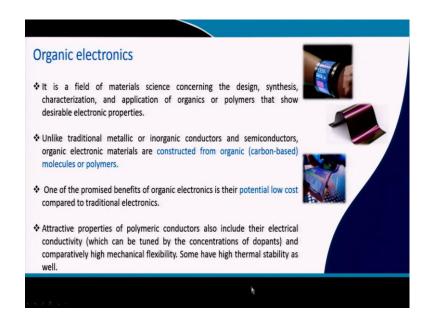
Welcome to my course Non-Metallic Materials. And today, we are in module number 8, Thin Film Growth and Fabrication of Devices. And this is lecture number 44, where I will be talking about Organic electronic materials that will include mostly conducting polymers, which are semiconducting organic materials before doping and some of their relevant applications.

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Now, first I will introduce this organic electronic materials, then we will classify the conducting polymers, then we will highlight the mechanism of conduction and in particular effect of conjugation, doping effect, those things will be covered. And for some of the selected polymer system particularly polyacetylene and polyaniline, we will talk how this conductivity is originated in this polymers and some of the selected applications will be covered.

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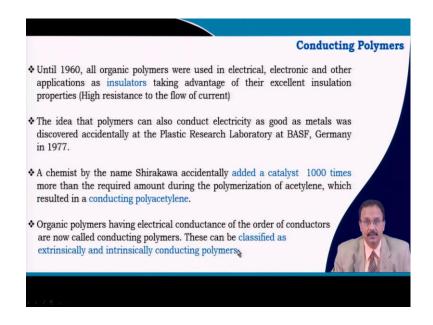
So, you know in the field of material science when we consider particularly designing of the device organic polymers that plays a major role, if you can tune its electrical properties. Now, traditional metallic or inorganic conductors including semiconductors, this organic electronic materials they are basically as the name suggests they are basically organic material that is carbon based.

And mostly the polymer material we will be considering. So, one of the benefits that this materials they are having that is suddenly it is having lower cost as compared to the traditional electro ceramic material or traditional semiconducting based electronic materials.

And also, their electrical conductivity for example, can be tuned by addition of dopants and mostly by the addition of the dopants. And they have flexibility. So, they are flexible. So, lot of flexible electronic devices. Some of them they are already in the market. So, this kind of flexible electronic material can be fabricated by this polymer conducting polymer based materials.

And many of these polymers they have thermal stability as well. So, I mean with mechanical flexibility, this thermal stability is also one of the important aspects to be considered while designing this types of devices.

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So, some 40-50 years back we used to know that the polymers are electrically insulating in nature. So, they were considered to be an insulator and they were used based on their insulating property. So, nowadays you know that German company like BASF, the plastic research laboratory of BASF they have proved that some of the polymers they have metal like conductivity.

And it started from late 70s and now this is one of the most important fields in the material science history. So, accidentally it was discovered, a chemist his name was Shirakawa, he added catalyst you know that for polymerization catalysts are used. So, by chance by mistake he added 1000 times more catalyst than required for the polymerization of acetylene and that resulted this conducting polyacetylene.

So, by mistake it was discovered. And they have now the electrical conductance mostly in the order of the material semiconducting material, but with dopants it can have metal like conductivity. And in principle you can divide this types of conducting polymer either extrinsic or intrinsic conducting polymer.

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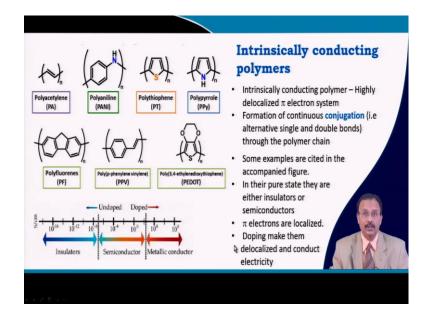


Extrinsic polymer that as the name suggests they are basically a mixture. So, you know that for some of the applications I introduced in this course you can mix the polymer and the active material and some kind of conducting agent to make the whole composite conducting in nature.

So, usually metal fibers can be used, carbon black can be used with insulating polymers. So, this insulating polymers form a continuous kind of phase and the fillers they are basically conducting in nature. So, the composite constitutes extrinsically conducting polymers. But some of the polymers are intrinsically conducting. So, the conductivity for this intrinsic polymer they arise due to the chemical structure change of the organic polymer themselves.

And they conduct electricity when doped either with an oxidizing or a reducing agent or sometimes protonic acids are used as dopant and they exhibit conductivity in this, otherwise insulating polymer.

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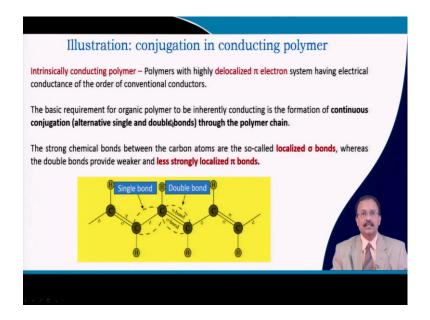


So, some of the examples I have cited that you can see polyacetylene is one of them, then polyaniline and other polymers. So, they are all they can be made intrinsically conducting polymer. So, one thing that you can notice that they have all of them, they have highly delocalized pi electron.

So, these all these polymers are pi electron system. So, that is one thing and they have continuous conjugation; that means, alternate single and double bonds for all these polymers you can have throughout the polymer chain. So, in their pure state, they are either insulator or semiconductor.

So, pi electrons as you know that they are initially localized, but if you dope it, then it can be delocalized and they start to conduct electricity. So, the conductivity initially is in the range, the range of semiconductor, but once they you start doping it, then they can have this metal like conductivity.

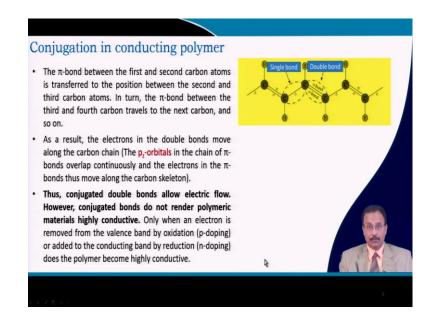
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So, intrinsically conducting polymer, as I said that they have highly delocalized pi electrons and having electrical conductance, it can be in the order of conventional conductors. So, the basic requirement of this organic polymer to be intrinsically conducting is the formation of a continuous conjugation; that means, this alternate single and double bond throughout the polymer chain that is required.

So, you know that the strong chemical bond that exists between the carbon atoms. So, that is the localized sigma bond. And in case of pi bonds the double bonds provide usually weaker and less strongly localized pi bonds.

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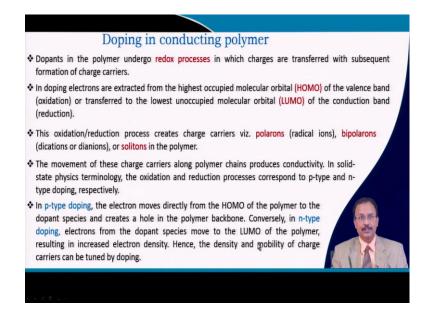
So, the pi bonds between the first and the second carbon atom is transferred to the position between the second and third carbon atom as far as this figure. So, in turn this pi bonds between the third and fourth carbon atoms, they also travel to the next carbon and so on.

So, as a result of this kind of situation, the electrons in the double bond they move along the carbon chain. So, usually p z orbitals in the chain of the pi bonds, they overlap continuously and the electrons that is there in the pi bonds they start moving along the carbon skeleton.

So, the conjugated double bonds allow the electricity, the electric current to flow. But usually this conjugated bonds do not render this polymer to be highly conducting in nature. So, only when an electron is removed either from the valence band we call it oxidation.

So, this is nothing but p-type of doping or added in the conducting bands by reduction, so that is called n-type doping. Then, this polymer become highly conducting in nature.

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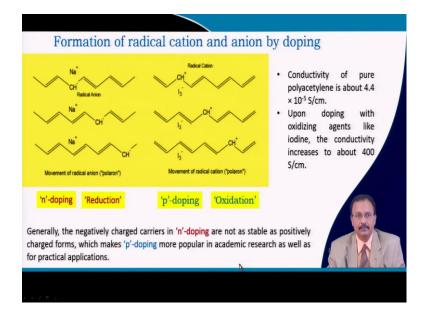
So, dopants that is used in this polymer they undergo a redox process. So, in this redox process, the charge basically is transferred and subsequently the charge carrier forms. So, when you dope this kind of polymer. So, electrons are extracted from the highest occupied molecular orbital we called is a HOMO band.

So, that HOMO band of the valence band we call this is oxidation. And transferred to the lowest unoccupied molecular orbital that is abbreviated as LUMO of the conduction band. So, that happens because of the doping. So, this oxidation and reduction process as I will explain later, on that creates a charge carriers and that could be polarons we call its radical ions, bipolarons also created that could be either dications or dianions, that is termed as solitons that is created in the polymer.

So, movement of this charge carrier along this polymer chains that produces the conductivity. So, the oxidation and reduction process that just I explain that corresponds to the so called p-type or n-type doping which you are familiar with when you study the semiconducting material.

So, in case of the p-type doping, usually electron moves directly from the HOMO band of the polymer to the dopant species. So, that creates a hole, I will explain it in the later slide in the polymer backbone. And if we are talking about the n-type doping electrons from the dopant spaces that move to the LUMO band of the polymer and that results the increase of the electron density. So, the density and the mobility of the charge carriers that can be tuned by different types of dopants added in the polymer.

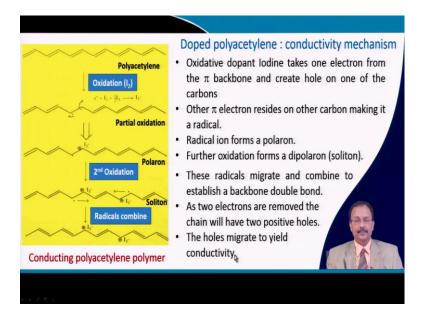
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So, here we can see the n-type doping which is the so called reduction that is taking place. So, here sodium ions that is added and in case of p-type doping iodine is added as the dopants. So, once the otherwise insulating polyacetylin is used if you measure its conductivity that is about 4.4 into 10 raised to minus 5 Semen per centimeter.

So, once it is doped with say iodine, then the conductivity increases about many fold you can see 400 Semen per centimeter that is one can achieve. So, either you can do n-type of doping or p-type of doping. But usually n-type doping is not very stable as positive p-type doping. So, therefore, p-type dopants are more popular both in terms of academic research purpose as well as for its viability for practical application. So, we will concentrate mostly on p-type dopants.

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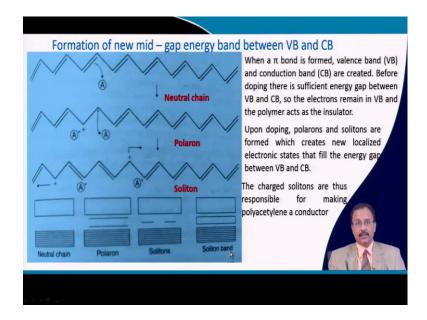
Now, what is happening? A oxidative dopant in the form of iodine that you can add in this polyacetylene at a polymer which is having this kind of alternate single and double bonds. So, this oxidative dopants that iodine that is basically dissolved in a solvent and carbon tetrachloride is used as a solvent.

So, that takes one electron from the pi backbone of the polyacetylene, and eventually it creates a hole on the carbon. So, in this double bond for example, one of them that is taken by the iodine and it creates a hole here. So, other pi electron which is resides on the carbon that forms a radical. So, this one forms a radical, this is a positive ion and this radical forms basically after this partial oxidation it forms a polaron. So, this radical ion and this positive charge they forms a polaron.

Then further oxidation takes place. So, second oxidation again it takes place and again this iodine takes one of the electron and then another polarons is created and this radical also is created. So, this radicals basically migrate, and then they combine and establish another double bond. So, number of double bond increases. So, in fact, the double bond transfers in this polymer chain.

So, this two electrons are removed from the chain and it will have two positive holes. And this holes basically migrate to give the p-type conductivity in this polymer. So, that is the brief mechanism of the conductivity how it generates conductivity in this polymer chain.

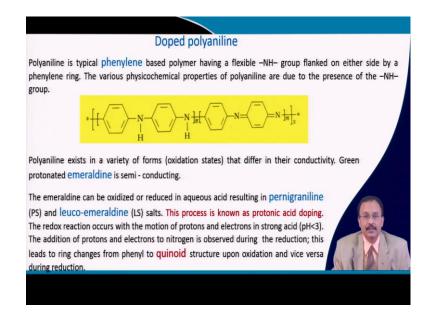
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So, when a pi bond is formed, this valence band and conduction band is created. So, this is basically a valance and conduction band creation before the doping. And there is a sufficient energy gap between this valence and conduction band. So, the electron they basically resides in the valance band and the polymer acts as an insulating material.

So, when you dope it with an acceptor ions like iodine this polaron and this double polaron, basically the solitons they form which creates new localized bands. So, it is in case of polarons and in case of solitons, they create localized electronic state between this original valence and conduction band gap. So, the charge solitons, they are responsible in making this polyacetylin as a conductor.

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So, another example can be cited at doped polyaniline. So, this is I think we described it in one of my earlier lectures that this is a phenylene based polymer. So, they have a flexible N H group that is flanked either side by this phenylene ring.

So, various physiochemical properties of polyaniline that is basically due to the presence of this N H group. So, that polyaniline that exist in a variety of form, so that means, in variety of oxidation state and differ in their conductivity. So, green protonated emeraldine that is a semiconducting. So, this emeraldine can also be oxidized or reduced by aqueous acid.

So, that will result this pernigraniline this is abbreviated as PS or leuco-emeraldine, so this type of salt that is abbreviated as LS salts. So, the process that is known as protonic acid doping. So, the redox reaction that occurs with the motion of the protons and electrons in a strong acid which is having a pH less than 3.

So, the addition of this proton and electron to the nitrogen is observed during the reduction. And this basically leads to the ring changes from phenyl to quinoid structure upon oxidation and vice versa during reduction.

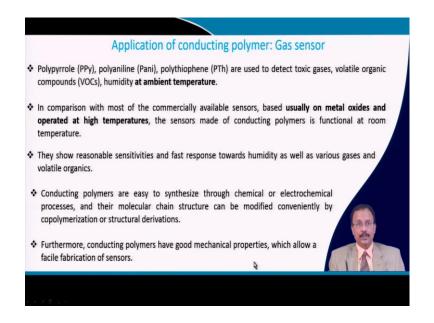
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Formation of pernigraniline (PS) and	leuco – emeraldine (LS)
H ⁺ O ⁺ 	The generation of these charged carriers is responsible for the conductivity of the polymer. Protonated polyaniline converts into a non-conducting blue emeraldine base when treated with a base.
$\begin{array}{c} C^{i'} \\ \hline \\ \hline \\ H^{i'} + B^{i'} \\ \hline \\ H^{i'} + B^{i'} \\ \hline \\ H^{i'} - B^{i'} \\ \hline \\ H^{i'} - B^{i'} \\ \hline \\ \end{array}$	Different oxidation states of polyaniline can be generated by doping with oxidants such as iodine. The conductivity of the resulting form of
	polyaniline is however, lower that obtained by protonic acid doping.
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So, the generation of this charge carrier is responsible for the conductivity into this polymer and protonated polyanile aniline is converted into a non-conducting which is a blue emeraldine base when it is treated instead of a acid, but it is treated with a base. So, different oxidation states of polyaniline can be generated by the doping of oxidants like iodine also can be used.

The conductivity is resulting from the its resulting from polyaniline, but that is usually lower than that of that is obtained by protonic acid doping. So, iodine doping they do not lead to higher conductivity as it is observed in case of protonic acid doping.

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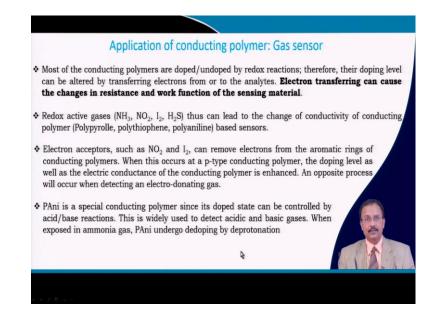


So, this types of conducting polymer they can be used for different applications. So, one such application is the gas sensor, I have already introduced for semiconducting metal oxide type of gas sensors. But this all conducting polymers including polyaniline or you can take polypyrrole they can be used to detect the toxic gases, various types of toxic gases, volatile organic materials, humidity.

And the good part is that they can detect it at ambient temperature. Unlike the semiconducting oxides this polymer can detect this gases at room temperature. So, this show reasonable sensitivity and fast response towards, for example, humidity as well as various gases and volatile organic compounds.

They are easy to synthesize and their conductivity can be changed by the during the gas sensing. So, conducting polymer they have good mechanical property. So, one can it is relatively easy for one to make a polymer based sensors.

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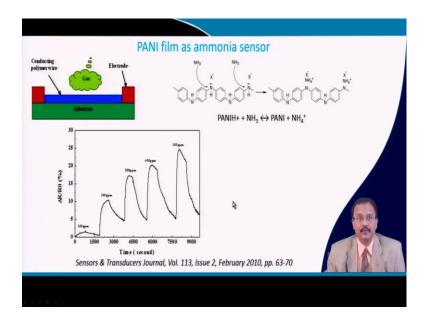


So, most of this conducting polymers, they are doped or by redox reactions, and this electron transfer can cause the change in resistance either in the resistance or the walk function of the sensing material. So, this gas here is acting as a dopant. So, the redox active gases like one can use ammonia, then NO 2, iodine, H 2 S, they can lead to the change in the conductivity of this conducting polymer.

So, as you know NO 2 and iodine they are electron acceptors, they can remove electrons from the aroma aromatic rings of the conducting polymer. So, when this occurs a p-type conducting polymer the doping level as well as the electrical conductance of the conducting polymer they are enhanced and opposite process will occur when they can detect an electron electro donating gases.

So, PANI is considered a special conducting polymer since its doping state can be controlled by the so called acid base reaction. And usually PANI is widely used to detect acidic or basic gases, when exposed for example, to ammonia gas PANI undergo deprotonation, so that is dedoping.

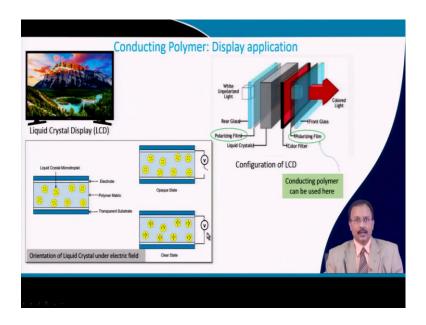
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So, this is the mechanism to detect gas like ammonia. So, a tentative reaction that is taking place is something like this a forming an ammonium ions. And as a result the resistance changes. So, the resistance increases as long as the gas is there. So, it is shown that it can detect ammonia at different concentration.

And then the change the detection the monitoring of the gas that is basically detected by the change in the polymer resistance, and once the gas is flushes out by passing say air, then again it regains its original conductivities. The base level conductivity is regained. So, therefore, it can be used to detect gas at room temperature unlike the normal semiconducting oxides.

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Conducting polymer they can also be used for display applications and usually now ITO is used. So, this is the configuration of a LCD monitor. So, a liquid crystal that is embedded in two electrode. So, you need a transparent electrode material here. So, the conducting polymer can be used that can replace this ITO indium thin oxide type of electrode which are both conducting as well as transparent in nature.

And you know that in case of liquid crystal, when I was talking about the specialty glass it is something similar to this. When you apply a voltage then it can transfer from an opaque state to a clear state and you need a conducting electrode. So, this types of polymer can be used which can replace the otherwise used ITO.

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So, conducting polymer you can coat on transparent non-conducting glass substrate to make the display. And the optimization is required between the transparency and sheet resistance that is important for preparation of this kind of electrode. So, they are light weight, low cost, they are flexible in nature.

So, flexible kind of display that will come in the market very soon. They are also this flexible polymer conducting polymer can be used. So, with further improvement of the properties desired transparency level, enhanced conductivity, adhesion with the substrate, those things are important to develop this technology further.

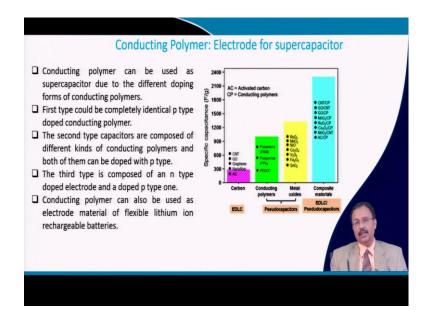
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Parameters t	hat influence the condu	ctivity of conducting polymer
1. Conformat	tion	
2. Solvent us	ed	
3. Type of su	bstrate (hydrophilic/ hyd	drophobic)
	of the polymer	
5. Stability of	f layer to harsh weather	ring conditions and/or elevated thermal.
Materials	Optimum Conductivity	As ITO is a visid and britsle metasial is is not
PANI	~ 800 S/cm	As ITO is a rigid and brittle material, it is not suitable for the development of many
РРҮ	~ 200 S/cm	next-generation display technologies. Therefore,
PEDOT	~ 3000 S/ cm	the quest for alternative electrode materials is
ITO	~ 3500 S/cm	necessary.
		2

So, some of the parameters that influence the conductivity of the conducting polymer that is the conformation. So, sometimes when it is stretched then the conductivity changes. The solvent that is used that is also important a non-toxic solvent should be used. Type of substrate, that will decide for a hydrophilic nature is required for a good kind of coating. Adhesion of the polymer is important, because it should adhere to the substrate well. And finally, the stability is important.

So, ITO you know that they are brittle material. So, if it is replaced by this conducting polymers then one can make flexible display devices. So, if you see the comparison of the conductivity of Pan, PPY, so they do not have conductivity in the level of ITO, but this polymer PEDOT, this is having a very close electronic conductivity very close to ITO and this polymer might have a bright future for flexible electrode.

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Finally, this conducting polymer can also be used. So, I have just cited couple of examples, 3, 4, examples that there may be other important applications area, but this field is growing. So, many more application will come in your future. But this is another thing which is important, unlike you know the super capacitor I have described.

So, mostly EDLC type super capacitor that is the porous carbon if you compare, it is just in between the metal oxide and this EDLC type super capacitor as far as the specific capacitance is considered. So, usually the p-type conductors they are used.

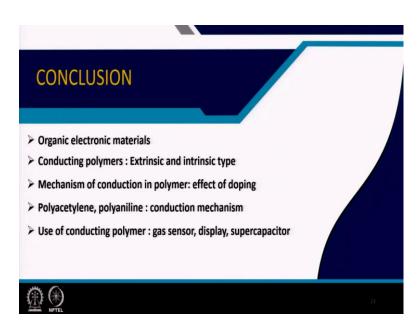
So, various types of polymers that are being used for this super capacitive applications, and finally, conducting polymer people are also trying to use as electrode material for flexible, lithium ion battery, which is also covered in one of my earlier classes the basics of lithium ion battery. So, as an electrode material this conducting polymers they can also be used to make flexible power source.

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So, the reading material for this particular lecture is taken by taken from this book and chapter number 13. And this book also this is the edited version of nanostructured conducting polymers. They are also quite useful as a reference material.

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So, in this particular lecture, we talked about organic electronic materials, conducting polymer, particularly extrinsic and intrinsic type has been described. So, the mechanism of the conduction in polymer, effect of doping in particular p-type doping that has been described.

Mostly, I have described the polyacetylene and polyaniline, the mechanism conduction, conduction mechanism of this two types of polymer. And use of conducting polymer, there may be multiple uses, but out of that the gas sensor, display and super capacitor has been described.

Thank you for your attention.