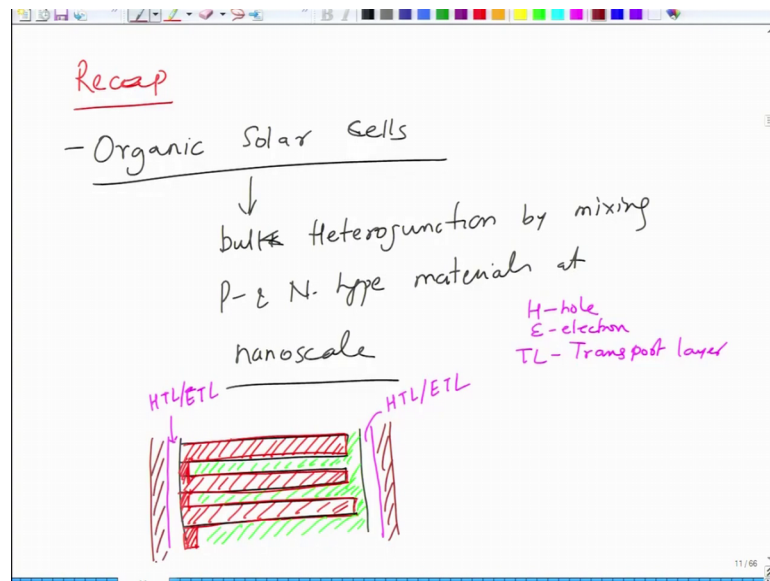


Solar Photovoltaics: Principles, Technologies and Materials
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Lecture - 40
Generation III Technologies: Organic and Dye Sensitized Solar Cells

We begin with a new lecture of this course Solar Photovoltaics.

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So, what we have discussed in the last class was some something on details of Organic Solar Cells. So, we discussed the details of organic solar cells, we looked at why is there a need to increase the thickness of organic solar cells so that we can improve light absorption. This is countered by the fact that exciton have low diffusion length in the organic solar organic semiconductors, but we can make innovative designs such as bulk heterojunction; bulk heterojunction which gives rise to bulk heterojunction which is a nanoscale mixture of by mixing P and N type materials at nanoscale so that you bring the interface closer to exciton than to bring the exciton closer to the interface.

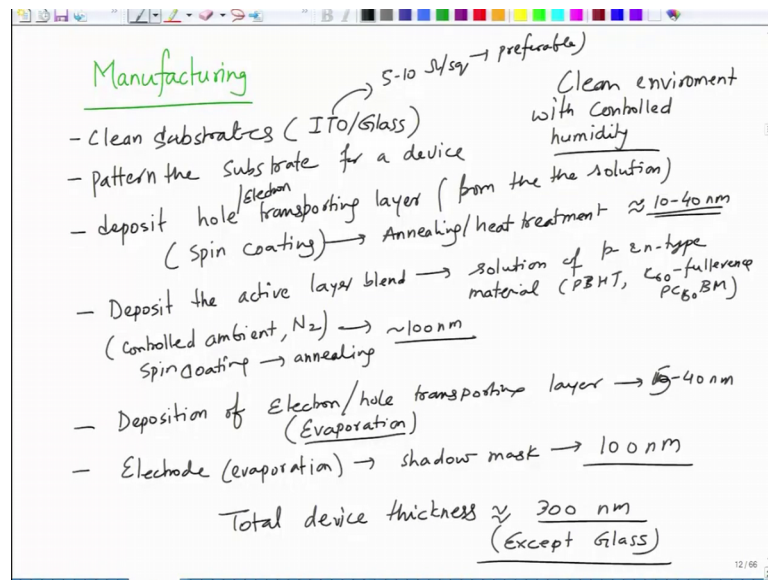
So, interface wherever exciton is formed, it finds a interface in the vicinity and hence, it is able to and then interface provides an electric field to break it up in the carriers and another requirement is that the two phases must make a continuous network inter penetrating network so that carriers are always able to diffuse to respective electrodes. If they are not able to move to different electrodes, then they will again be lost. As a result

it is important that the the network of two phases is continuous even at nano scale it must be continuous.

So, ideally you would like to have a structure like this. So, let us say you have these two electrodes. This is the ideal structure you would like to have inter penetrating network. So, this is one phase and this is the another phase, you can say this green one is the another phase. So, you have one phase making a good contact with cathode and another phase making out contact with the anode. This is a ideal picture, it will not always work like this. But this is what is the desirable aspect and every side on the two sides, we also have carrier selective layers. So, we have we call them as HTL slash ETL electron transport layer or hole transport layer. So, this would be again HTL or ETL electron.

So, H hole; E electron; TL mean transport layer; some people also call them as hole blocking layer or electron blocking layers because they block the other carriers. So, and then we will have electrodes on the two sides these would be the electrodes. So, this is a typical structure that you will typical device structure that you will see. Generally the way these devices are made is very simple.

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So, manufacturing is very very straightforward, but it is done in controlled environment. So, first what you do is that you clean the substrates and substrates are generally ITO coated glass and this ITO has a sheet resistance of 5 to 10 Ohms per square preferable. So, lower sheet resistance is preferable. Clean the substrate, then you pattern the

substrate; pattern the substrate so that the junctions are made at designated places. So, you pattern the substrate to form a device for a given device structure for a given device. Then, we deposit hole transporting layer from the solution of and this is done by spin coating.

Then and deposit spin coating followed by annealing or heat treatment at a given temperature ok. So, what is important at this stage is the spin speed, the spin time the amount of material that you put the time at which you annealed the temperature at which you anneal, time for which you anneal and temperature at which you anneal. This will determine the thickness and microstructure of that. So, this is generally of the order of 10 to 40 nanometers that is the idea depending upon the type of material. Then, you deposit the active layer blend and blend is basically a solution of p and n type materials such as P3HT poly 3 hexylthiophene and C 60 that is fullerene; we call it as PCBM; PC60BM.

Again, you spin coat it at a given spin speed for a given time followed by heat treatment. This is generally done in controlled ambient such as nitrogen ambient and then, anneal it at certain temperature for certain time to get a thickness of the order of about 100 nanometers. So, again same space same method spin coating followed by annealing. Then we deposit what we call as deposition of electron slash hole transporting layer. So, in this case it could be hole slash electron transporting layer.

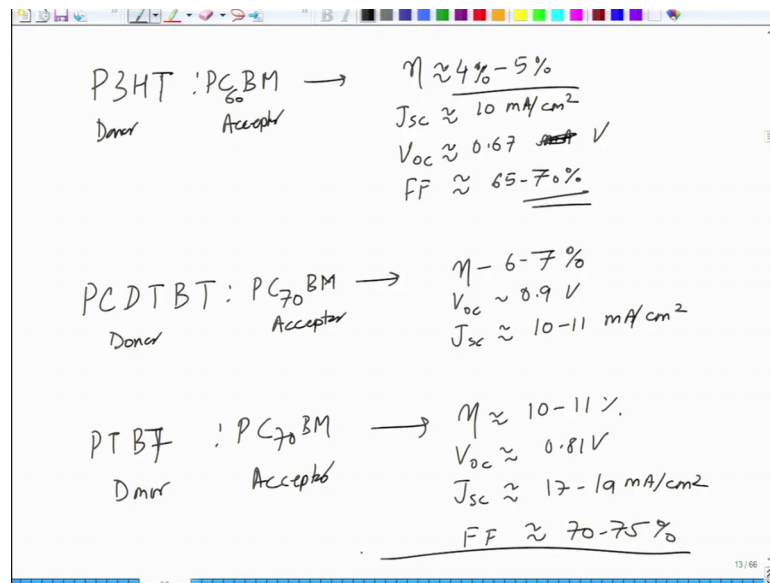
So, if it is hole, then you deposit electron; if it is electron, then you deposit the hole right. And then, we deposit what we call as electrode. This layer is often deposited using evaporation because once you deposit active layer, you do not want to damage it using solvents. So, because solvent can dissolve the active layer as a result we generally deposit is using a process called as evaporation and then, we evaporate electrode through the shadow mask. So, again this layer is about 10 to 40 nanometer thin; it could be 5 also in certain cases and electrode is about 100 nanometer thin.

So, you can see the hole device thickness starting from hole transport layer is of the order of 200 or 250 nanometers. So, very total device thicknesses like if you also include ITO it is about 300 nanometer except glass. So, it is a basically nano structured device. So, as a result the way you manufacture is very important that is why you manufacture these in clean environment, if you have a dust particle, if you have an either second phase present

here whose size is more than the size of the thickness. Then, you kill the device. So, it is very important that manufacturing is done in clean environment with controlled humidity because these polymers are very very susceptible to humidity.

So, there are different hetero structure that are present in the in the literature. So, the one which are based on for example P3HT PCBM.

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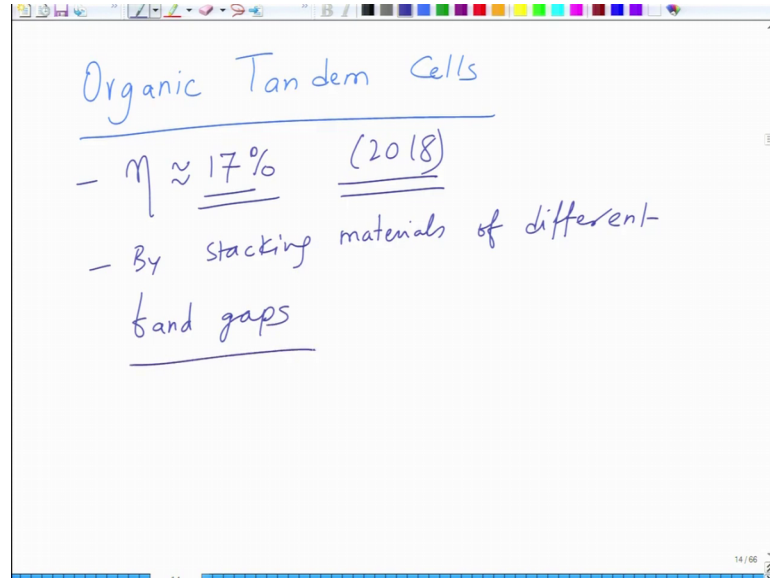
They give you efficiency of the order of 4 percent. The current that we obtain is of the order of J_{sc} is of the order of 10 milliamps per centimeter square. The V_{oc} is of the order of 0.67 milliamps per centimeters sorry volts and the Fill Factor is of the order of 65 to 70 percent in these devices. 4 to you can say 5 percent; the best devices.

The ones which are based on another polymer PCDTBT and in this case we use PC70BM so this is donor, this is acceptor. These hetero junctions give efficiencies of the order of about 6 to 7 percent and V_{oc} of the order of nearly 0.9 Volt and J_{sc} of the order of 10 to 11 milliamps per centimeter square. We have another material which is reset material PTB7; PTB7 based device and they are again with PC70BM.

This is a donor and this is the acceptor. Here also P3HT is a donor and this is a acceptor. These devices give you efficiencies of the order of nearly they give you 10 to 11 percent; V_{oc} is of the order of 0.8 Volt; 0.81 Volt roughly. J_{sc} is of the order of 17 to 19 milliamps

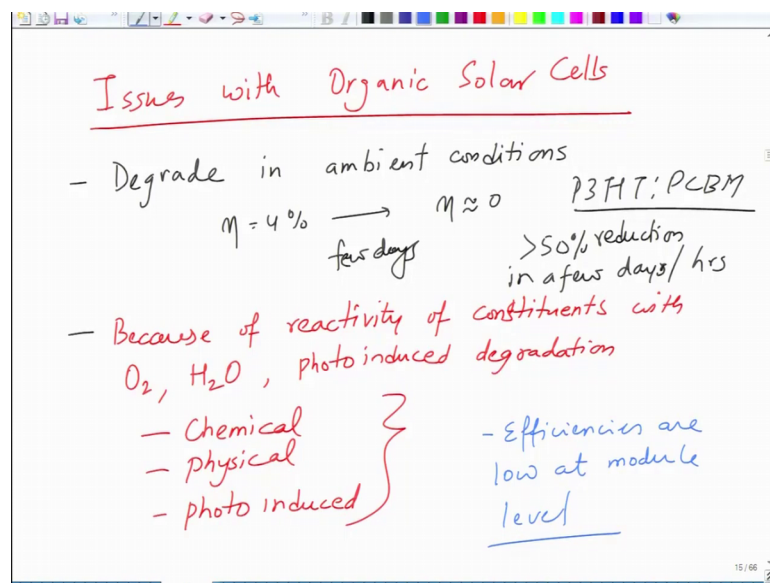
per centimeter square. Fill factor is about 70 to 75 percent. The organic tandem cells where you combine various polymers.

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So, organic tandem cells they give you efficiencies of the order of about. So, right now we have about 17 percent obtained. This is in 2018 reported and they use again the same multi junction concept that by stacking of; by stacking materials of different band gaps ok.

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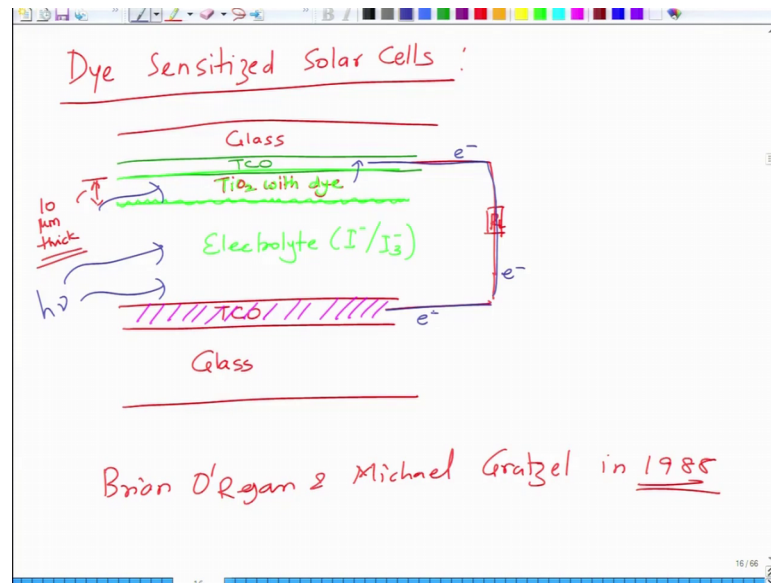
The problems there are how the certain problems with the organic solar cells issues with. The issues are they degrade in ambient conditions. So, efficiency for example, degrades from about 4 percent to nearly 0 in few days for a P3HT PCBM and sometimes. So, and so these degrade very strongly; so, nearly more than 50 percent reduction in a few days, in fact for certain materials in a few hours under ambient conditions. So, what is important is and what have why this happens is that this happens because of reactivity of constituents with oxygen, with moisture and also photo induced degradation. There are multiple degradation mechanisms that are present in the literature; there are a lot of reviews available.

So, degradation could be chemical; it could be physical and it could be photo induced. All these three types of degradations are possible. So, the constituents in such as active layer, hole transporting layer as well electron transporting layer all the electrodes may chemically degrade upon reaction with oxygen and moisture. They may physically damage their morphology will change and the light accelerates the process in many cases. So, these materials are prone to degradation and that is one of the reasons why they have not made it successful commercially. Why they have not they are not successful commercially because of this degradation issues.

Of course, efficiencies are lower; efficiencies are low at a module level; efficiencies are low at module level and poor degradation characteristics. So, these two problems have led to unsuccessful commercialization of these technology. However, lot of efforts are on to improve the degradation characteristics by developing better materials by making better encapsulants which can which can prevent the diffusion of moisture and oxygen into the devices. So, work is still on to improve these devices. So, this is still a technology which is pretty much which is extensively being researched and it is quite promising for future.

So, next we will move on to another promising technology which is third generation technology is Dye Sensitized Solar Cells.

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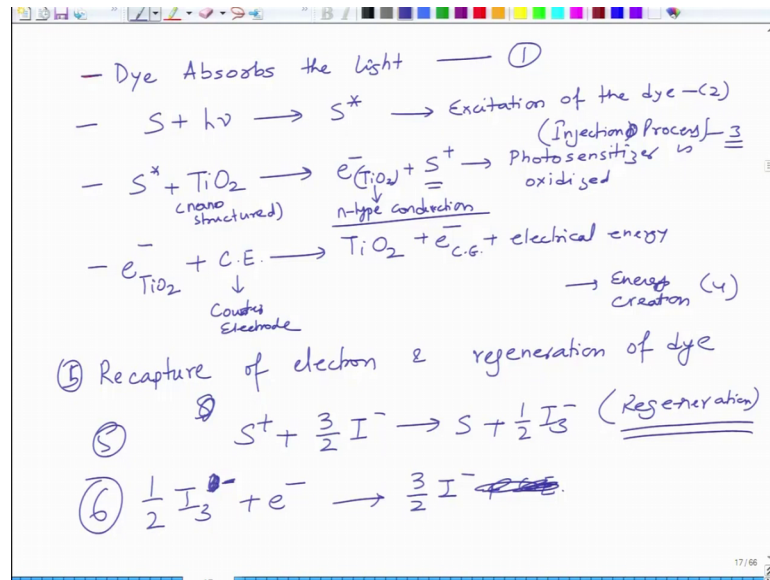
So, these dye sensitized solar cells are different from normal solar cells in the sense that they are also electrochemical solar cells and they use different principles of electricity generation as compared to organic or inorganic other solar cells. So, what you have in these devices is something like this. So, we have a glass substrate on which we have a transparent conducting oxide electrode. So, this is a TCO which is some conducting oxide and then, on top we have what we call as a electrolyte. So, here we have a electrolyte which is normally a iodine conducting electrolytes. So, it has I minus I 3 minus ions and then we have what we call as a Ti O2 nano particles with the light sensitive dye.

So, Ti O2 with dye which makes a sort of nice interface with the so interfacial area is very important between the dye. So, this is you can say Ti O2 with dye and this die is photosensitive; then again we have on top a layer of TCO. So, this is TCO transparent in conducting oxide and then again on top we have a glass layer and when you connect these TCOs we have load and we get the electricity out of it, when we shine light to it. And this layer is about in this case nearly 10 micron thick.

The main Ti O2 layer, this was co invented by Brion O'Regan and so, Brion O'Regan and Michael Gratzel in 1988. So, in that sense its much older than organic solar cells and it is, but it is very promising because of simple nature it uses very simple materials, it uses glass substrate; it is some sort of transparent conducting oxide. It uses electrolyte

which can which has iodine as the principal species and then, it is in contact with the Ti O2 solid network which is impregnated with the dye. So, the way this solar cell works is like this.

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So, what happens is that when the first step is the dye; so you can say the dye absorbs the light that is the step number 1 and then, the dye let us say is designated by S when it captures a photon, it gets excited. So, this is excitation of the dye this is number 2. Then, this excited dye which is in contact with the Ti O2 leads to electron generation. So, this is you can say. So, the sensitizer becomes photo excited photo photosensitizer becomes is oxidized.

So, from excited state this guy becomes oxidized between say electrons has created, this electron then moves through the Ti O 2. So, this is called as injection process; you can say this is injection. So, it has injected a electron this is number 3. This electron then which is going through Ti O 2 goes to the counter electrode which is C is the counter electrode. So, Ti O 2 again goes back to its state, the electron goes to the counter electrode and then, this gives rise to what we call as electrical energy because it is connected to a load. So, this step is called as energy creation process; this is number 4.

So, this electron then goes. So, what happens is that so you have the light has fallen here ok; sorry the light has fallen all over the cell, the dye has gotten excited. The electron goes through Ti O 2. It goes through Ti O 2 to TCO comes through the electrical circuit.

So, electron is going like this, comes back to this; once it comes back through the reverse circuit, then this so what happens is that this. Now, the dye gets regenerated because remembered dye was in s plus a state so it has to get regenerated. So, this dye gets regenerated by. So, this this makes so there are two processes would have which happen. So, once the electron reaches first is a recapture of electron, they happen simultaneously, recapture of electron. So, you can say this is 5 and 5 and 6 and then, we have regeneration of dye.

So, this regeneration of dye happens this S plus reacts with $3 \text{ by } 2 \text{ I minus}$ to give rise to S . So, it comes to normal state $I \text{ 3 minus}$, this is regeneration ok. And then, this $I \text{ 3 minus}$ half $I \text{ 2 3 minus}$ this reacts with the electron that has reached back from the circuit from the other side and this gives rise to $3 \text{ by } 2 \text{ I minus}$ plus what we have is then counter electrode right, electron it its comes from the so, this is electron recapture basically. We don't have to write this. So, this is electron recapture essentially.

So, this is what is the overall principle of operation. So, what is happened is let me now. So, first is light absorption by the dye, then we have excitation which results in the electron production. This electron travels through the Ti O 2 because Ti O 2 is a n type conducting material. So, Ti O 2 is a n type conduction right. So, it is a it happens to a n type conduction through Ti O 2 ; Ti O 2 is the n type conducting material. It is a nanostructure Ti O 2 nanostructure is needed because it has maximum interfacial area with the dye.

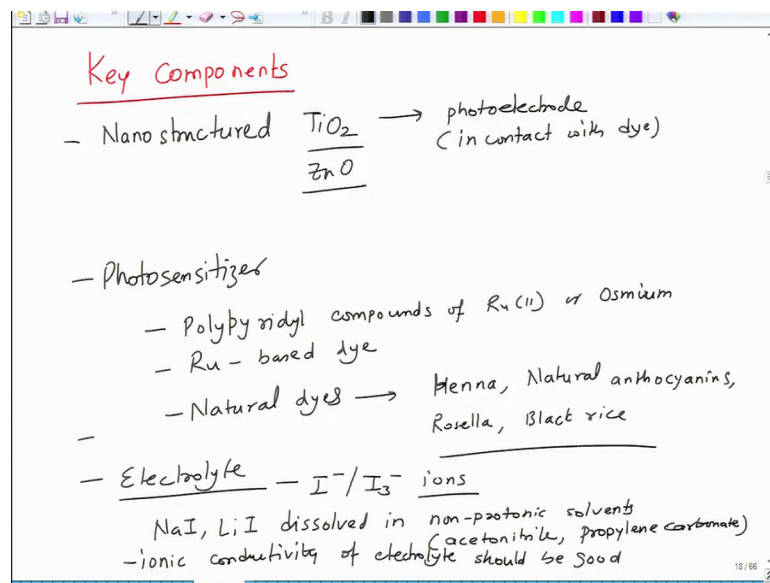
So, it is a nanostructure Ti O 2 , we can say this is nanostructured. The electron then goes through Ti O 2 to the counter electrode and then, it travels from the circuit to the other electrode. On the other electrode, then this electron gets captured. This lets to this leads to formation of this $3 \text{ by } 2 \text{ I minus}$; this $3 \text{ by } 2 \text{ I minus}$; $3 \text{ by } 2 \text{ I minus}$ is basically it reacts with the iodine $I \text{ 3}$ I think it is $I \text{ 3 minus 1 minus}$ yeah. So, it deals with this $I \text{ 3 minus}$ ion gives rise to $3 \text{ by } 2 \text{ I minus}$; this $3 \text{ by } 2 \text{ I minus}$ reacts with the excited dye molecules to convert that back into the normal unexcited that state.

So, in this case what we have is a regeneration of the dye. So, basically the electron which travels back from the circuit, it reacts with the iodine ions to ensure and those iodine ions that then convert it from one state to another which then react to the excited state of dye ions so that you have complete process. So, again we have first is the light

absorption; second is the excitation to result in electron production; third is the diffusion of electrons to the TCO via Ti O₂ nano particles. These electrons then reach the counter electrode and then, this counter because you have a circuit which is connected. So, from the counter electrode they travel through the circuit and then we have a redox reaction, that redox reaction means that you have this you have to convert the excited dye molecule so the normal dye molecules which happens via oxidation of iodine ions and then so oxygen iodine ions. They convert the x they absorb the electron to.

So, first they reduce and then the bigger iodine ion reacts with the excited dye molecule to give you a final state. So, we have redox reaction and then diffusion to the counter electrode where oxidized redox mediator is reduced to I minus ions. So, we have these 5 6 you can say 5 and 6 so this is 5 and this is 6. So, these 6 steps which complete the process of an electricity generation in dye sensitized solar cell.

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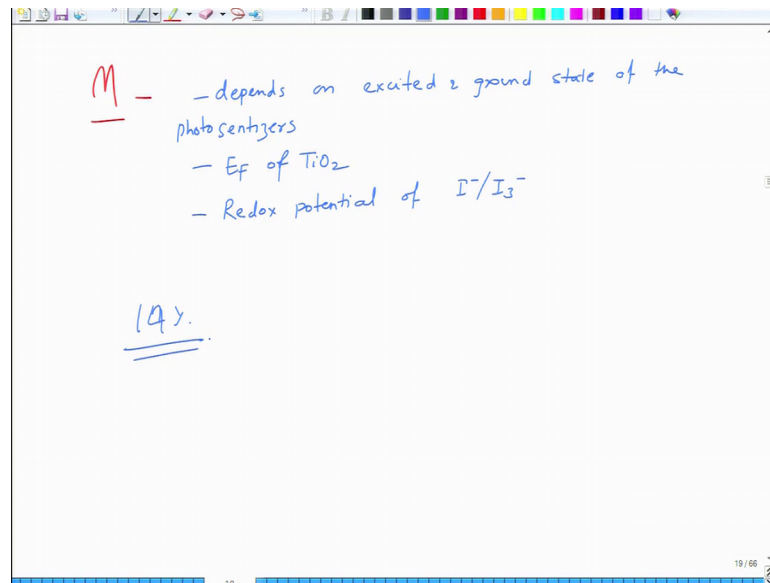
So, what are the key components in there? So, it is a very simple concept. The key components in the solar cell are, the first one is you must have a nano structured Ti O₂ which is also called as a photo electrode in contact with dye. So, you want to maximize the so nanostructure Ti O₂ is there people also use zinc oxide. So, this is a so optimization of this Ti O₂ is extremely important through careful processing. Then we have photo sensitizer; this photo sensitizer is normally for example, it could be poly pyridyl compounds of ruthenium or osmium. So, it is a one of these two materials.

So, basically the dyes are basically the ruthenium based. So, ruthenium based in most cases they are ruthenium based dyes; ruthenium based dyes have good for so photo sensitivity as compared to other dyes. You can also use natural dyes such as if you just want to demonstrate a solar cell in the lab to children, let us say school children then we can use henna for example. Henna is a dye that we know mehendi as we call it and then we have natural antho cyanins, rosella is another dye which is a natural dye and then, we have black rice that is also a natural. So, these dyes can also be used for demonstration of solar cells.

As far as electrolyte is concerned, electrolyte is generally it is a electrolyte contains I minus and I 3 minus ions. So, basically redox ions which are used to regenerate that oxidized dye molecules as we saw earlier how they are regenerated and to complete the electrical circuit by mediating the electrons between nanostructured electrode and the counter electrode. So, these are this is the constituent of electrolyte. Generally, we have things like sodium iodide, lithium iodide etcetera; they are dissolved in non protonic solvents and these solvents are acetonitrile it could be propylene carbonate and so on and so forth and conductivity of ion.

So, in this case the ions have to diffuse in and out right. So, as a result the conductivity of ions is very important. So, ionic conductivity of electrolyte is a important concern; should be good and this is also affected by the viscosity so this interplay between the viscosity and the connectivity.

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So, finally, we will just look at something related to efficiency. So, efficiency in these depends upon the excited state and the ground state of the sensitizer because it depends upon what kind of band gaps it does absorb. So, energy levels within the sensitizer photosensitizer that is then we also have to have Fermi level of TiO_2 appropriately placed so that electrons are able to conduct themselves. And then, we also need to have appropriate redox potential of I^-/I_3^- in the electrolyte ok. These are the factors which affect the efficiency of these solar cell.

So, maximum efficiencies that we have got is about 14 percent right now. So, these are the problem is presence of the dye is liquid which can be controlled to some certain extent using solid dye. So, we will stop here, what we have discussed the dye sensitized solar cell or organic solar cells in this lecture. We will take one more lecture to finish off with the perovskite solar cells.

Thank you.