Solar Photovoltaics:
Fundamental Technology and Applications
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Lecture-19
Novel Electrolytes for DSSC

Welcome back everyone, in the last lecture we have started talking about the different components of the DSSC devices, what do we have learn that there were 5 important components in a dye sensitized solar cell. The first component is an indium tin oxide glass substrate which is used as a anode material and then the **7** second component is an n-type semiconductor, usually we use titanium dioxide or the different structural form of it.

Third important component is dye or sensitizer molecule and we have seen that there are certain parameters we have to keep in mind while choosing a dye or sensitizer molecule. Like it has to have a very good light absorption properties, it is molar extension coefficient should be very high, it should not aggregate and moreover it is morphology and how it distributed over the semiconducting surface that also place a (()) (01:17).

The fourth important components was the electrolytes, now the electrolyte actually is a major role in the DSSC device. It place the major role because the electrolyte regenerates the whole process. Now when the dye molecule get excited and goes from the ground state to the excited state after sometime it injects this electrons back to the TiO2 conduction band. And that electron using the percolated structure of the titanium dioxide goes to the photo anode and comes back to the outside circuit and complete the load.

But what happens to the dye which has already lost an electron, so it needs an electron or in other way it has to comes back to the ground state. So that it is again in a position of absorbing light again and that work actually is done with the help of the electrolyte. So that is why electrolyte plays a very important role in constructing DSSC device. And we have seen that so whenever we choose an electrolyte so it is viscosity not only matters but also like it energetics also is very very important.

And how much volatile it is or how much corrosive it is that also is a very important parameter. Now today's lecture we will discuss about the different conditions for fabricating the electrolytes and how we choose an optimum electrolytes for a DSSC device. And at the same time what are the electrolytes which have been used in the DSSC device.

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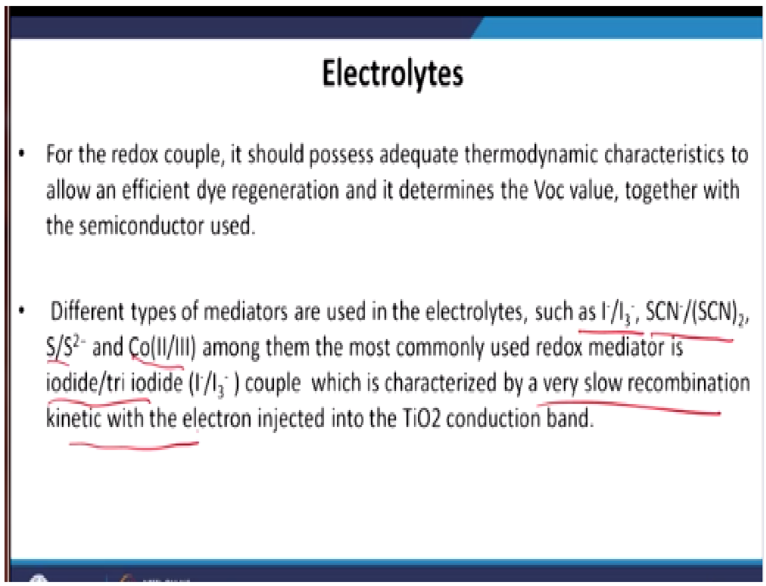

For the redox couple it should possess adequate thermodynamic characteristics to allow an efficient dye regeneration as it determines the Voc values together with the semiconductor used. So basically this electrolyte along with the semiconductor determine the Voc value of the device. So it is very very important to choose what kind of electrolyte we are picking up, different types of mediators are used in the electrolyte such as iodine, tri iodide.

We have used in the last class during the demonstration SCN/(SCN)2 S/S2- and cobalt 2, 3 complex among them most commonly used redox material. Now popularly used redox mediator is iodide/tri iodide, titanium dioxide N3 dye and iodine tri iodide electrolyte that has been well studied and their energetic matches very well. Now the characterizations of these or the good characteristics of this iodine/tri iodide material is that they show a very slow recombination kinetics with the electron injected into the TiO2 conduction band.

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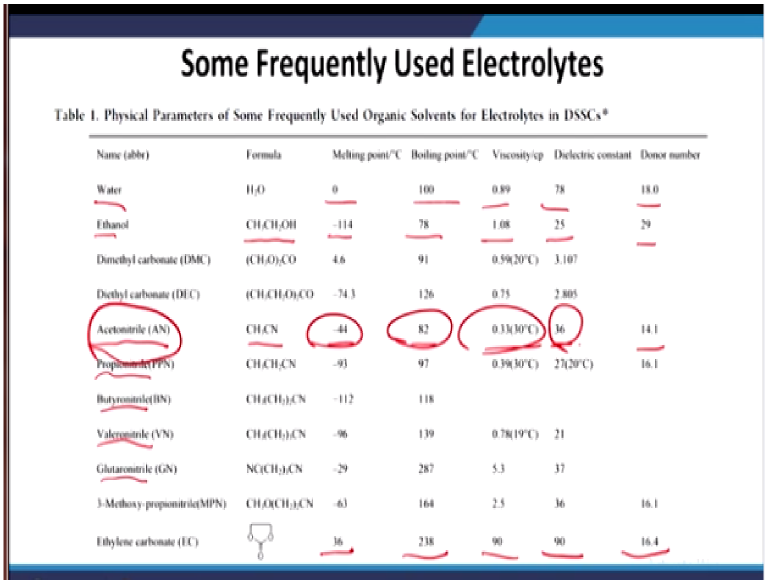

Name (abbr)	Formula	Melting point/°C	Boiling point/°C	Viscosity/cp	Dielectric constant	Donor number
Water	H_2O	0	100	0.89	78	18.0
Ethanol	CH_3CH_2OH	-114	78	1.08	25	29
Dimethyl carbonate (DMC)	$(CH_3O)_2CO$	4.6	91	0.59(20°C)	3.107	
Diethyl carbonate (DEC)	$(CH_3CH_2O)_2CO$	-74.3	126	0.75	2.805	
Acetonitrile (AN)	CH_3CN	-44	82	0.33(30°C)	36	14.1
Propionitrile(PPN)	CH_3CH_2CN	-93	97	0.39(30°C)	27(20°C)	16.1
Butyronitrile(BN)	$CH_3(CH_2)_2CN$	-112	118			
Valeronitrile (VN)	$CH_3(CH_2)_3CN$	-96	139	0.78(19°C)	21	
Glutaronitrile (GN)	$NC(CH_2)_3CN$	-29	287	5.3	37	
3-Methoxy-propionitrile(MPN)	$CH_3O(CH_2)_2CN$	-63	164	2.5	36	16.1
Ethylene carbonate (EC)		36	238	90	90	16.4

Let us take a look about some frequently used electrolytes, for example here we are showing 3, 4 different columns. The first column is the solvent which we use, second column is the formula for that solvent, third is the melting point of that, fourth column is the boiling point, fifth is the viscosity, sixth is the dielectric constant and seventh is the donor number. So physical parameters of some frequently used organic solvents for electrolyte solution.

For example we can take this iodine/tri iodide electrolytes in ethanol we can take in acetonitrile. So, what will be different if I take it in acetonitrile or if I take it in acetone or how do I know in which solvent I will dissolve my iodine/tri iodide electrolytes. So, let us have a look at the properties of the solvent, for example we have an universal solvent water H2O melting point is 0 and you all know that is boiling point is 100 degree Celsius and the viscosity is 0.89, dielectric constant of the water is 78 and donor number is 18.

Then look at the ethanol which has a molecular formula of CH3CH2OH and it has a melting point -114 degree Celsius boiling point 78 degree Celsius and it is viscosity is higher than the water 1.08 and dielectric constant is lower than the water 25. So, that is why it is less polar than the water and donor number is 29. Then another common example we have dimethyl carbonate, we have diethyl carbonate we have acetonitrile which we use very very commonly, acetonitrile is represented by the formula CH3CN

Now it has a melting point -44 degree Celsius, it is boiling point is 82 degree Celsius and it is viscosity is 0.33 or 30 degree Celsius. At 30 degree Celsius is viscosity is 0.33, so you look that it is viscosity is lower than the water, so that is why it is good to make the iodine/tri iodide electrolytes in the acetonitrile solvent and dielectric constant is 36 and it is donor number is 14.1. Similarly you can choose propionitrile PPN, butylnitrile, valeronitrile or glutaronitrile.

So all is changing is the number or the amount of the alkyl group in front of the CN or cyano group, so based on that which change the name propyl, butyl or valero or glutaro. In the case of glutaronitrile we will have NC group also, so there are 2 cyanide group and in between there CH2 3 group is there. And then there are 3 methoxy proponitrile or MPN group and finally ethylene carbonate. Ethylene carbonate has a melting point of 36 and boiling point of 238 quite high and it is viscosity is also very high 90.

So that is why it is not very suitable for making this kind of electrolyte solution in them and dielectric constant is very high 90 and it is donor number is 16.4. So if you look at this chart so some of them has some property is very good and some of them has some other property is very good see if I keep everything as a optimum from this table it looks like acetonitrile plays a role where have a ideal melting point and ideal boiling point viscosity is also very low and the dielectric constant is moderate. So that is why we prefer the acetonitrile as a solvent for dissolving this iodine tri iodide electrolyte.

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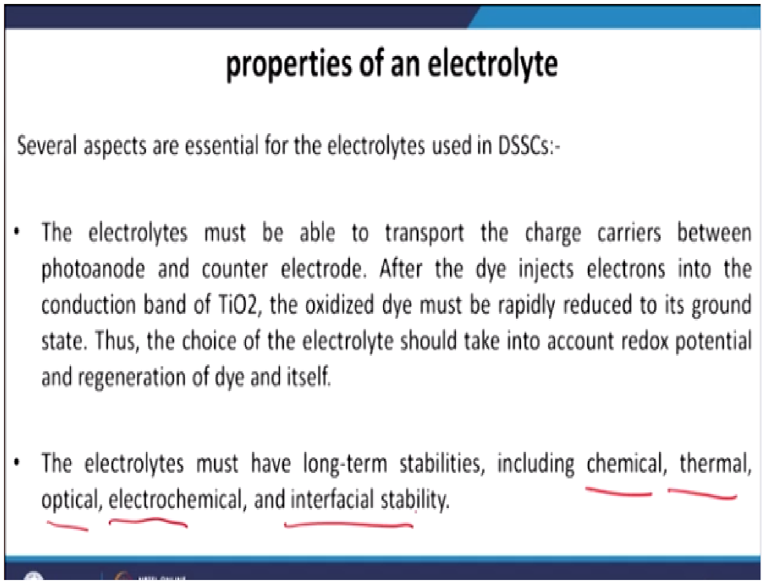

Special aspects are essential for the electrolytes used in DSSC, the electrolytes must be able to transport the charge carriers between photoanode and counter electrode. So it will be able to carry the charge from the photoanode and the counter electrode. After the dye injects electron into the conduction band of the TiO_2, the oxidized dyes must be rapidly reduce to it is ground state. So the role of the electrolyte as you mention is to reduce the dye from it is excited state to the ground state.

Thus the choice of the electrolyte should take into account redox potential and regeneration of the dye and itself. Many times choosing behind that electrolyte molecule depends upon it is cyclic voltammetry base homogeneous level. So, first we need to measure the highest occupied molecular orbital and lowest unoccupied molecular orbital of this redox couple by cyclic voltammetry experiment to see that whether it will be suitable to make the redox couple.

The electrolyte must have long-term stabilities including chemical stability, thermal stability, optical stability, electrochemical stability and interfacial stability. So by chemical stability we mean that this electrolyte solution should not degrade it is constituents atoms or constituents molecules. Thermal stability means if we increase the temperature it should not be very volatile I mean most of the case these are volatiles, so that is one of the disadvantages of the DSSC device.

It is optical property is should be moderate it is electrochemical property should be good, so that the energetics matches well and also the interfacial stability is very very important. Because in most of the cases in the solar cell device interface plays the very important role. Now this electrolytes also are there in the interface of the dimolecule and the counter electrode. So that is why it interfacial stability is also very important while we construct the electrolyte solution.

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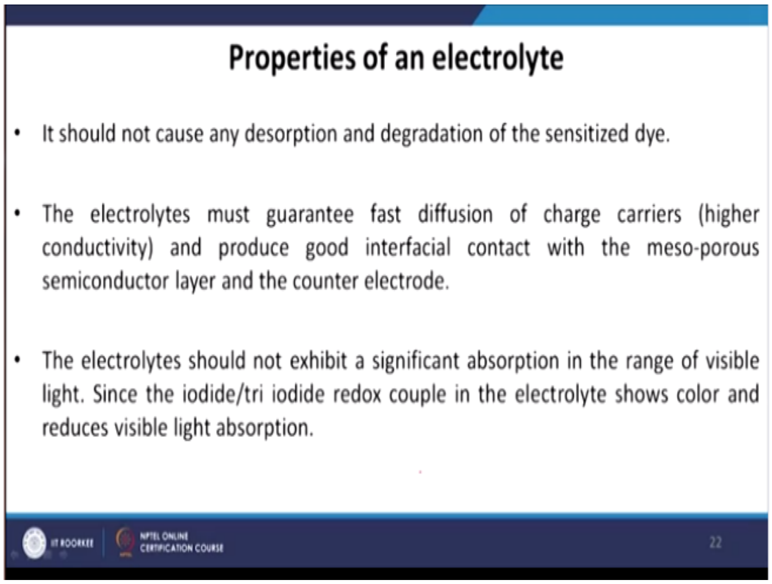

Finally it should not cause any desorption and degradation of the sensitized dyes, obviously we have to very careful that whatever the dye we have chosen and whatever the electrolyte we have chosen this would not interact or chemically react between each other. Otherwise the new complex will be formed and whole things will be changed, the electrolyte must guarantee fast diffusion of the charge carriers for higher conductivity and produce good interfacial contact with the meso-porous semiconductor layer and the counter electrode.

So now this electrolytes are there at the interface of the TiO2 layer and also at the random counter electrode. Now there interfacial stability or the interfacial properties with the TiO2 layer and a random counter electrode should be very good. And at the same time they should express a very fast diffusion of the charge carrier, that means their ionic conductivity should be very high. The electrolytes should not exhibit a significant absorptions in the range of visible light.

Now if the electrolyte absorbs most of the light in the visible line range then it will be problematic for the whole device. Since the iodide/tri iodide redox couple in the electrolyte shows color and reduce visible light absorption that is why it is a preferred choice for making the DSSCs device.

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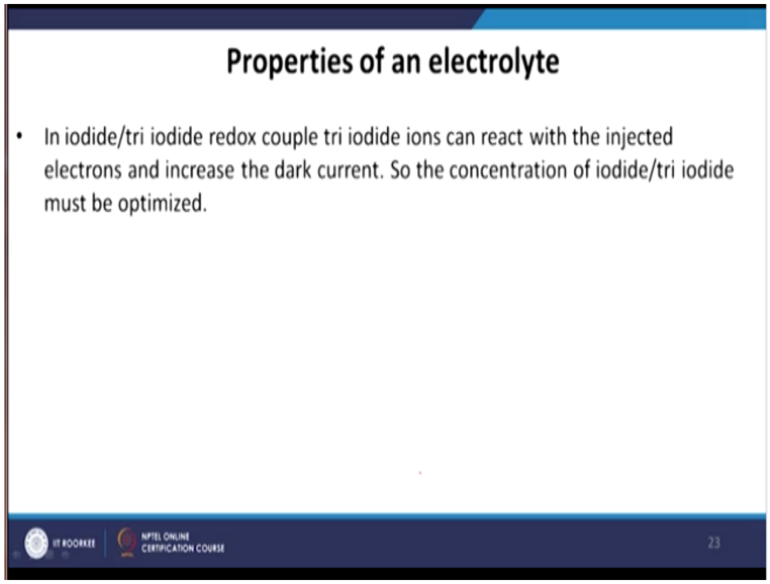

In iodide/tri iodide redox couple tri iodide ions can react with the injected electrons and increase the dark current, so the concentration of iodide/tri iodide must be optimized. Now we can also classify the various kinds of or the various types of the electrolytes in a DSSC device based on their physics state.

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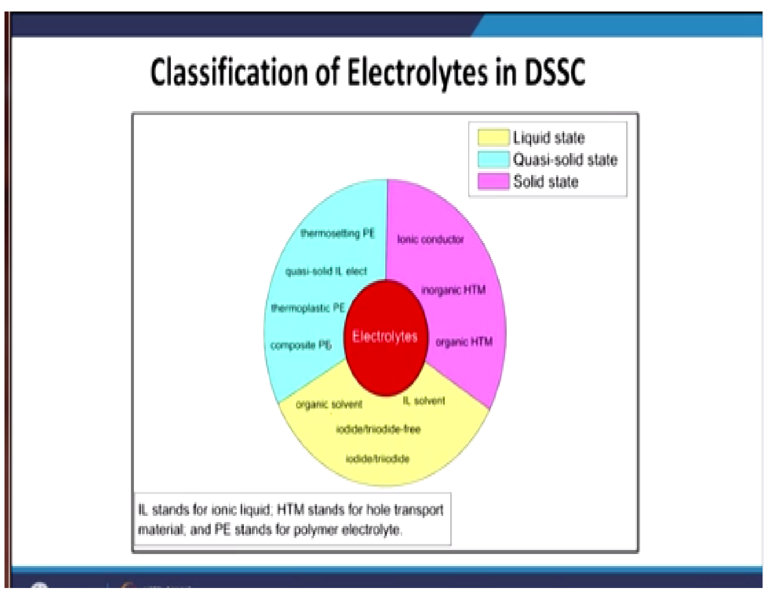

Whether they are liquid state whether they are solid state or whether they are in between liquid and solid that is quasi solid state. So you look this pie chart, so we have this ionic conductor we have inorganic hole transport material we have organic hole transport material in this pink color shaded regions. Then we have organic solvent here, IL stands for the ionic liquid solvent, iodide/tri iodide free and iodide tri iodide.

And here we are showing thermosetting P quasi solid IL, thermoplastic P and composite P. IL stands for ionic liquid, HTL stands for hole transfer material and P stands for polymer electrolytes. So we can use also the polymer as an electrolyte or we can deserve the polymer in a proper solvent to use it as an electrolyte.

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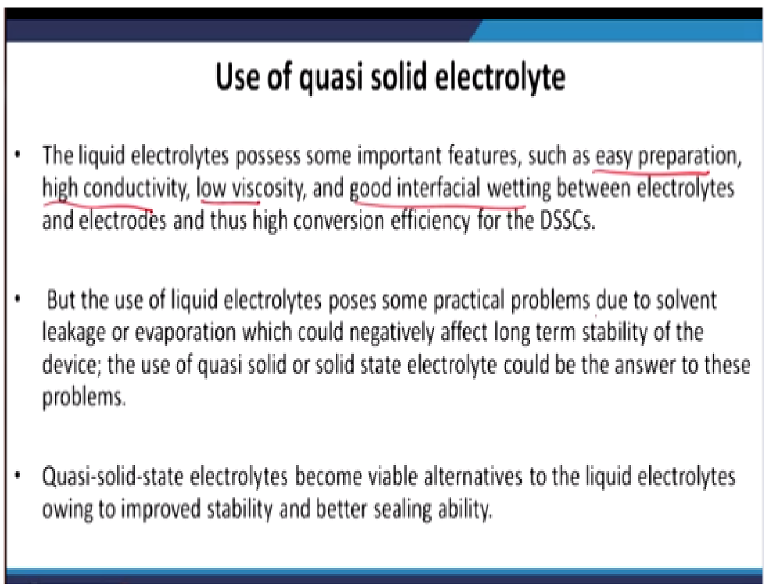

The liquid electrolytes possess some important features, such as easy preparation, high conductivity, low viscosity and good interfacial wetting between electrolytes and electrodes and thus high conversion efficiency for the DSSC. Now these are also the design parameters for the electrolytes, first of all they should be easy to make if we make this thing from the iodine/tri iodide in the acetonitrile, `so the synthesis quite easy.

There should have a high conductivity their viscosity should be low and finally their interfacial wettability with the n-type semiconductor oxide and the platinum counter electrode or whatever electrode you are using that should be very good. Now if all the parameters are optimize then we get a higher efficiency in this DSSC device. But the use of liquid electrolytes poses some practical problems due to solvent leakage or evaporation which could negatively affect the long term stability of the device.

Now this liquid electrolytes they are volatile and corrosives so they evaporate over the time, so if they evaporates so let say I put some drop of electrolyte in my devices. So, if I do not seal it properly after sometime the electrolyte will evaporate. So nothing is left in the devices to regenerate the whole process, now the electrolytes intrinsically shows the properties of the volatility that I cannot get rid of this thing.

So that is one of the major disadvantage of the drawback of the liquid base electrolytes, the use of the quasi-solid or solid state electrolytes could be the answer to this problems. So that is why people have trying to replace the liquid electrolytes with the solid state electrolytes or quasi solid-state electrolytes. Quasi solid state electrolytes become viable alternatives to the liquid electrolytes owing to the improve stability and better sealing ability.

So as I said that the DSSC device has to be sealed properly, otherwise the electrolyte will be volatile it will be evaporated. So now if the (()) (13:03) we can control in the solid state electrolyte then that is advantageous for us, so that is what is done exactly in quasi-solid state electrolyte.

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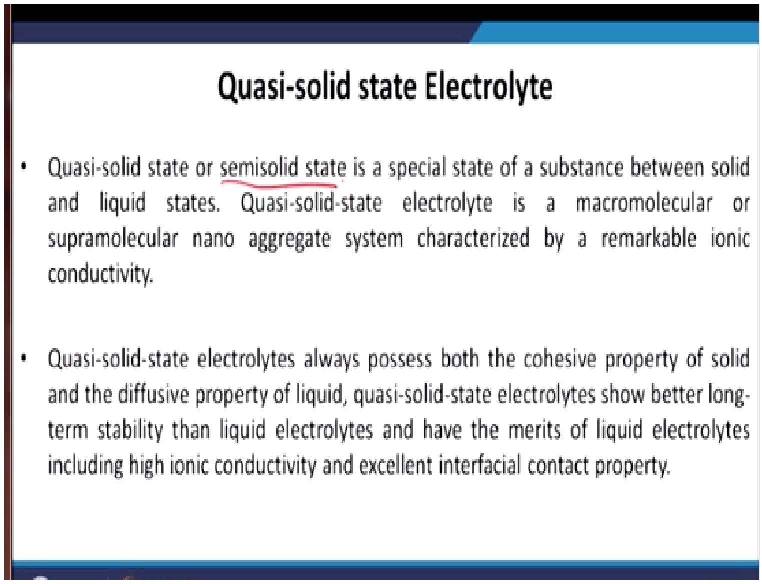

Quasi-solid state electrolytes or semisolid state is a special state of a substance between solid and liquid states. Quasi-solid state electrolyte is a macromolecular or supramolecular nano aggregate system characterized by a remarkable ionic conductivity. So, quasi-solid state electrolytes usually have a very high ionic conductivity value, quasi-solid state electrolytes always possess both the cohesive property of a solid and the diffusive properties of the liquid.

So, they get both the good properties of the solid, so solid so the quasi properties all the molecules in a solids are very tightly bound. And the same times they shows a good properties of the liquid, what is the good properties of the liquid they are taking that the diffusion and quasi-solid state electrolytes show better long-term stability than liquid electrolytes. And have the merits of liquid electrolytes including high ionic conductivity and excellent interfacial contact properties.

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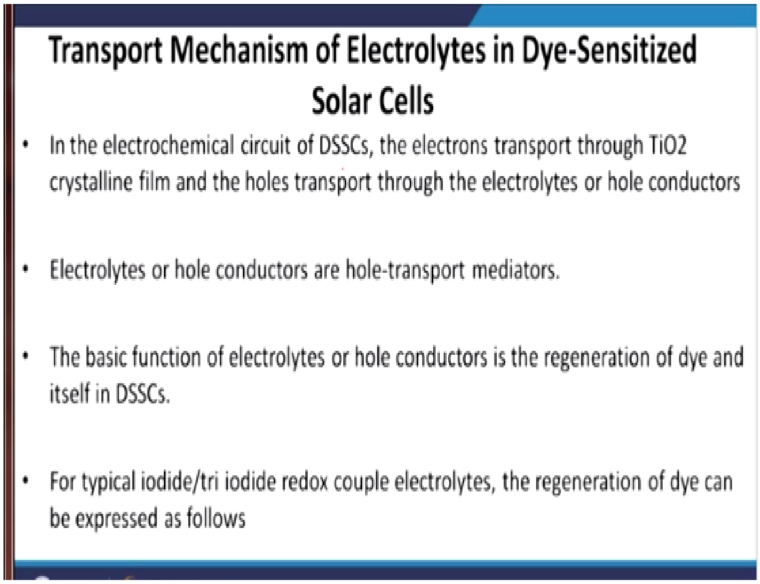

Now let us have a look about the transport mechanism of electrolytes in a DSSC device. In the electrochemical circuit of DSSCs, the electron transport through TiO2 crystalline film and the holes transport through electrolytes or holes conductors. So even if I use a conducting polymer which is a very good which has very good hole conducting properties so that will also act like a good sensitizers as well as a good hole transport material.

So the final objective should be to design a material which can replace by sensitizers and the liquid electrolyte by only one material which can absorb both the light and also can behave as a hole transport material. Electrolytes or hole conductors are hole transport mediators, the basic function of electrolytes so the hole conductors is the regeneration of the dye and itself in DSSC device. For typical iodide/tri iodide redox couple electrolytes the regeneration of the dye can be expressed as the following equations.

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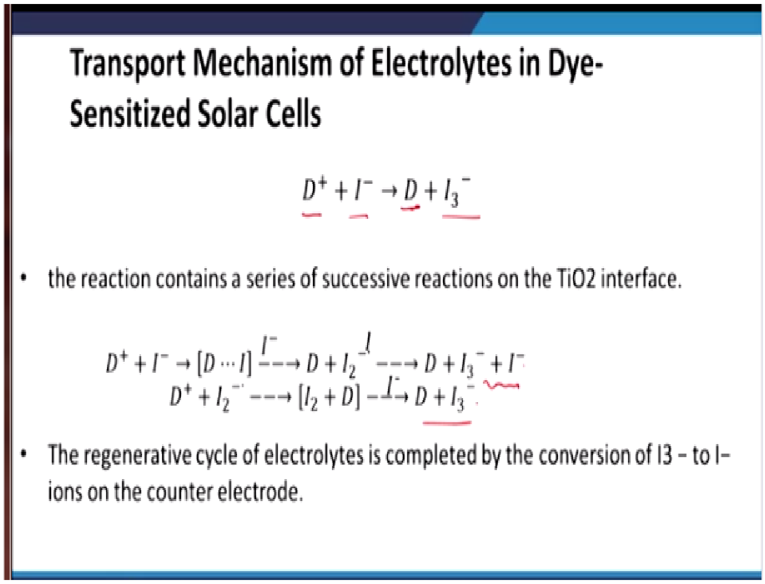

Here you have the dye which is in a excited state, so D+ that is what we mean and then iodine- so the dye in the excited state they grab an electron from this iodine. So it becomes neutralized and it becomes now the only D and the iodine now it has donated it is electron to the dye. So it is becoming more negative, so I3-, the reaction contains a series of successive reactions on the TiO2 interface D+ I- is DI complex, in the presence of more I it will be become D+I2 and finally it will become D+I3-+I-.

So both of them coexist together and this is a dynamic process, so D++I2- =I2+D and finally you get D+I3. The regenerative cycle of electrolytes is completed by the conversion of tri iodide to iodine ions on the counter electrodes. So finally so what happens so iodine has given up it is electron to the dye molecule and dye molecule has been reduce back to it is ground state. Now once the iodine has given it is electron so it has converted to more negatively charge tri iodide.

Now if the regeneration process has to happen again, so not only dye need to be regenerated this electrolytes also needs to be regenerated that means we need to have iodine in the system from the tri iodide. And that job is done at the platinum counter electrode, so where the tri iodide is converted to the iodine and this process cycles. So today we have learnt in details about what are the different varieties of the classes of the electrolytes.

And what are the properties or whatever the design principles for choosing a right electrodes in a DSSC device. Because for optimizing efficiency in a DSSC device choice of electrolytes is also very very important and the final objective should be replace both the sensitizers and the electrolytes with only single material preferably a solid material which can absorb the light in the visible region as well as in the nearer range.

And at the same time and work as an electrolyte material with a very high ionic conductivity and very good wettability at the interface of the semiconductor as well as the counter electrode. Now we have seen that all the there are several choice of the electrolyte steal iodine tri iodide electrolytes is commonly used with the N3 dye, because then make a proper energetics. But the lot of research is ongoing to make new kind of solid state electrolytes.

Because the solid state electrolytes posses the diffusive properties of the liquid and also the quasi properties of the solid and the return all the properties of the liquid state electrolytes like excellent ionic conductivity and good wettability. But at the same time it is not very easy to make a good solid state electrolytes depending upon it is energy level matching and optimizing all the parameters, so there are research are ongoing.

And every day we are coming across with a new materials or new electrolytes but finally the major advantage of the major leap in this technology will only possible if you can make you all solid state devices, then we can seal it properly and we can make roll to roll devices. Now for this particular chapter this based on the dye sensitize solar cells, there are lot of references and lot of research paper are available.

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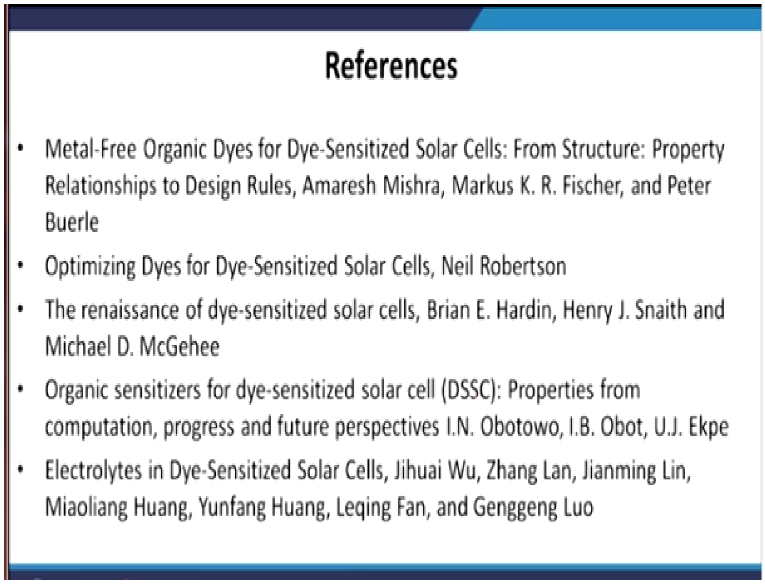

Specially you can look for some of the papers or some of the books like metal-free organic dyes for dye-sensitize solar cells from structure property relationship to design rules by Amarersh Mishra. In this book actually they have talked about like the design synthesis rule for that metal free organic inorganic dyes and there are lot of research papers also available on that. Optimizing dyes for dye-sensitize solar cells by Neil Robertson.

Here they have talked like in a different kinds of dye molecules in the dye sensitize solar cell, the renaissance of dye-sensitize solar cell by Snaith and McGehee. Organic sensitizers for dye-sensitize solar cell DSSC properties from computation, progress and future prospective and electrolytes in DSSC and that was a book by ZhangLan. So, any of the reference will be useful and apart from this books there are lot of research papers and review papers also available which gives in details about the photo physics and working mechanism of a dye-sensitize solar cell.

And how to choose a proper dye and how to choose a new electrolyte material for constructing a DSSC devices. In the next lecture we will talk about the another class of solar cell another class of the third generation solar cell that is the organic solar cells. Dye-sensitize solar cell was an example of a sensitizer base solar cell whether organic solar cell we use conducting polymers as a electron absorbing material.

So not only an electron absorbing material we also will see there the physics will be completely different or the charge carrier dynamics will be completely different from a PN-junction silicon solar cell to an organic solar cell, that will learn in our next class thank you very much.