Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture – 09
Photo-electrochemical Production of Hydrogen Using solar Energy

Hello my friends, now we are going to discuss on Photo-electrochemical Productions of Hydrogen Using the Solar Energy. So, as I told already in our last lecture that the production of the hydrogen by so many means. So, in this particular lecture, we are going to discuss about the using the solar energy by photo electrochemical productions of the hydrogen process.

So, basically, the hydrogen is widely considered to be the fuel in the powering of non-polluting vehicles, domestic heating's and the aircrafts. Yes, because hydrogen will become the future fuel for the globe, because after certain time maybe the fossil fuels or maybe the petroleum products is going to be finished. So, automatically that gap will be taken care by the hydrogen itself.

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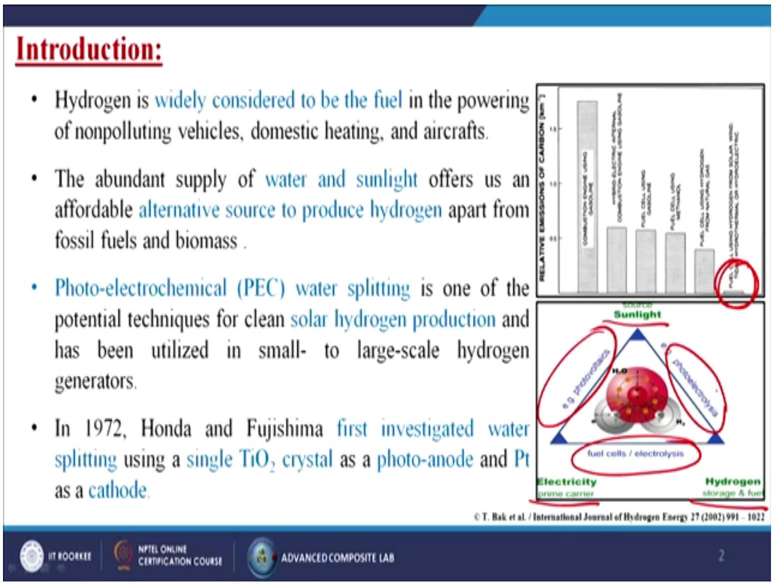

So, now the abandoned supply of water and sunlight offers us an affordable alternative source to produce hydrogen apart from fossil fuels and the biomass. Till now, we are discussing about that only we are going to produce the hydrogen from the biomass or maybe the fossil fuels, but there are some other techniques also by which we can produce the hydrogen gas itself. So, that one of the technique is called the photo electrochemical water splitting, is one of the potential techniques for clean solar hydrogen productions and has been utilized in small to large scale hydrogen generators.

In the year of 1972, Honda and Fujishima first investigated water splitting using a single titanium dioxide crystal, as a photo anode and platinum as a cathode itself. So, now, from the right-hand side image you can see that how in the y axis it is there that relative emissions of the carbon. So, if we talk about the combustion of engine by using gasoline it is too high, but same times if we talked about the hybrid electric internal combustion engine using gasoline. So, that time it is little bit reduced.

But now you come to the last part, this is the most important part because where we are using the fuel cell using the hydrogen from solar wind, then title hydrothermal or maybe the hydroelectric case. So, in this case you see the emissions is very very less, so that is why the people or maybe the scientist are nowadays tending to the hydrogen productions and the hydrogen storage for the future fuel because first of all it will fill the gap of the scarcity of the fossil fuels and the petroleum products as well as it will reduce the pollutions to the environment. And then from the bottom we can see that now, that is a very good triangle basically, the triangle consists of the source or which is nothing but the sunlight, then electricity which is nothing but the prime career and the hydrogen is storage and fuel.

Now, if we convert from sunlight to electricity we are doing basically by the photovoltaics cell itself. Now, if we talk about from electricity to the hydrogen then basically, we are talking about the fuel cells and maybe the electrolysis techniques. And when directly we are taking the sunlight to the hydrogen storage or maybe the productions then basically, we are doing the photo electrolysis kind of things. So, that is the beautiful image by which we can understand that if we convert one energy or maybe the sunlight to the hydrogen storage or maybe the electricity, what we need to do.

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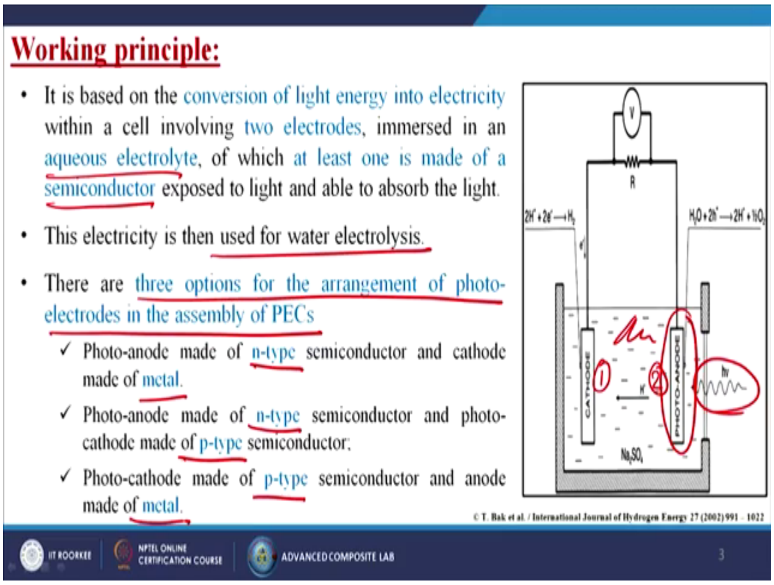

Now, what is the working principle? Basically, it is best on the conversion of the light energy into electricity within a cell involving two electrodes. So, you can see that that is the number 1 electrode which is acting as a cathode and another one is acting as a anode. So, basically, two electrodes we are using over here, immersed in an aqueous electrolyte.

So, this basically, the aqueous electrolyte over there of which at least one is made of a semiconductor exposed to light and able to absorb the light; that means, in between these two electrode one electrode should be the photo-electrode. Means when the direct sunlight will come on to that electrode it should react. So, that is the case, so that is why in this particular case we are using the photo anode where the sunlight or maybe the frequency of the light is coming and heating. This electricity is then used for water electrolysis.

Now, there are three options for the arrangement of photo-electrodes in the assembly of PECs. Photo-anode made of n-type semiconductor and cathode made of metal. Photo-anode made of n-type semiconductor and photo cathode made of p-type semiconductor. Photo-cathode made of p-type semiconductor and anode made of metal, so that is a combinations. Either one may be the semiconductor one may be the metal or maybe it can be the opposite. So, it depends upon whether that material or maybe the semiconducting material is the n-type or maybe the p-type.

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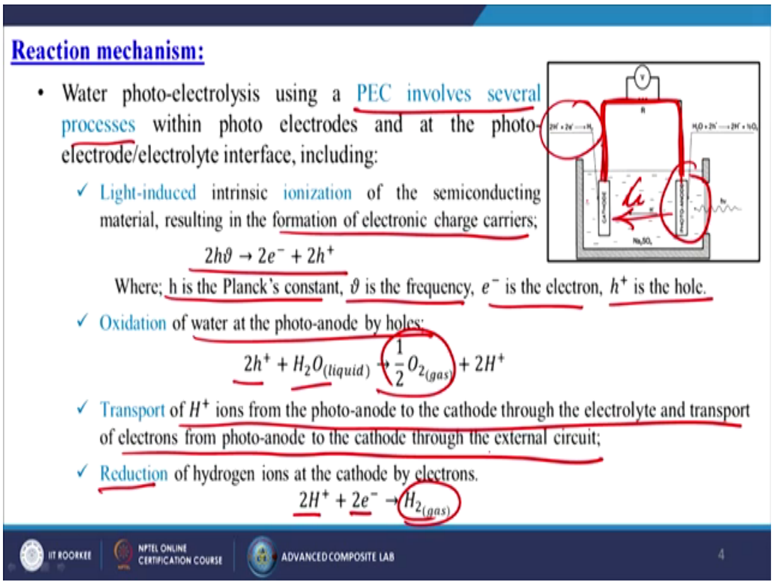

Then what is the reaction mechanism? So, what are photo electrolysis using a PEC involves several processes within photo-electrodes and at the photo-electrode or maybe the electrolyte interface including light induced intrinsic ionization of the semiconducting material resulting in the formation of electronic charge carriers which is happening in this particular case itself, when the sunlight or maybe the light is directly coming to the photo-electrode itself.

What is happening? The happening is taking place this one. Then 2h nu is tends to 2 electron it is giving and plus 2 hole pair basically it is giving. So, now, where h is the Planck's constant, nu is the frequency, e is the e minus is the electron and h plus is nothing, but the hole. So, that means, it is generating two hole and two electron simultaneously.

Now, oxidation state. Oxidation of the water at the photo anode by the holes itself 2h plus H 2 because now, in this particular case we are having that water also water contain. So, that basically, producing the oxygen gas plus 2H plus ion. So, now, transport of H plus ions from the photo anode to the cathode through the electrolyte and transport of electrons from photo anode to the cathode through the external circuit. Now, the circuit actually coming into the picture by which this H plus ion is directly going through here. And now, what is happening? Reduction is taking place of the hydrogen ion that is 2 plus

H plus 2e minus which is producing the hydrogen gas. So, basically, the hydrogen gas is taking place into the cathode.

Now, what are the extra electron will go? So, now, we have connected this two by which the electron is flowing and from there basically, we are capturing the electron itself or maybe the vice versa things then electron basically, it is passing through over here then electron is coming to the cathode 2H H plus ion is coming over here and then 2H plus 2e it is creating the hydrogen gas in this particular zone. So, basically, we are doing the short circuiting kind of things by which the electron is coming to the cathode and H plus ion is coming by the transport, and then H plus ion and e and then it is producing the hydrogen gas over there.

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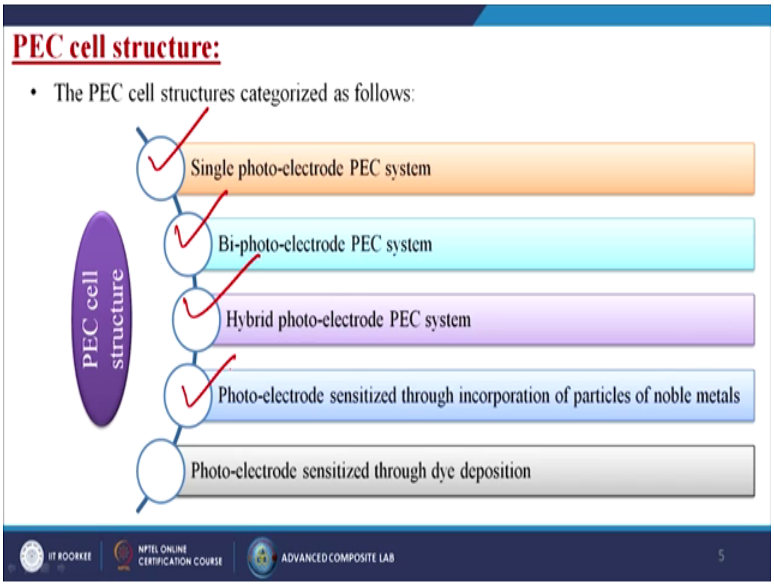

Now, what is the PEC cells structure? The PEC cell structure categorized as follows like single photo-electrode PEC system, bi-photo-electrode PEC system, hybrid photo-electrode PEC system, photo-electrode sensitized through incorporation of particles of noble metals, photo-electrode sensitized through dye depositions. So, basically, this is talking about the PEC cell structure.

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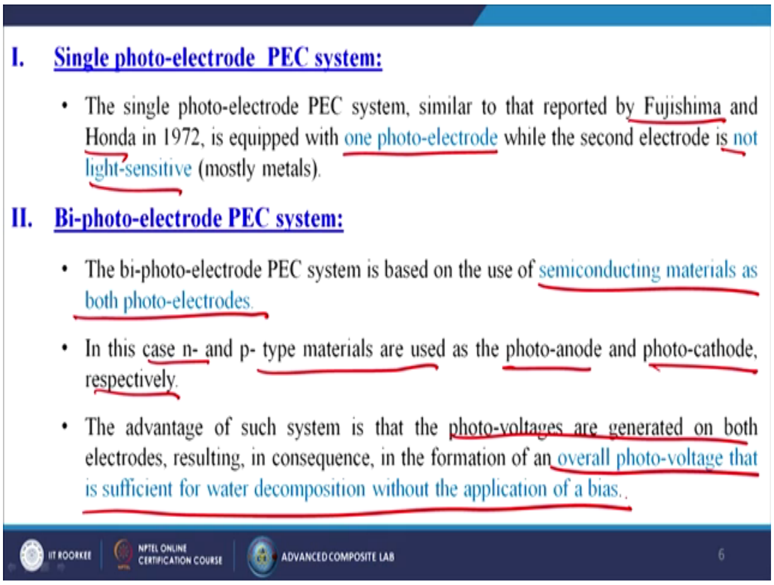

Now, we are going to discuss one by one. So, fast is called the single photo-electrode PEC system. The single photo-electrode PEC system similar to that reported by Fujishima and Honda in 1972, is equipped with one photo-electrode while the second electrode is not the light sensitive or maybe the mostly metals. So, how we are coming to the latest? So, this is the first primary studies has been done by some scientist where they have used one photo-electrode and the other is also not the photo-electrode, maybe that is some kind of other metals itself.

Next on is called the bi photo-electrode PEC systems. In the bi photo-electrode PEC system is based on the use of semiconducting materials as both photo-electrodes. Now, anode and cathode both are the same materials. In this case n and p-type materials are used as the photo anode and photo cathode respectively. So, one should be the n-type another should be the p-type semiconductor materials. The advantage of such system is that photo voltage are generated on both electrodes, resulting in consequence in the formation of an overall photo voltage that is sufficient for water decomposition without the applications of a bias voltage.

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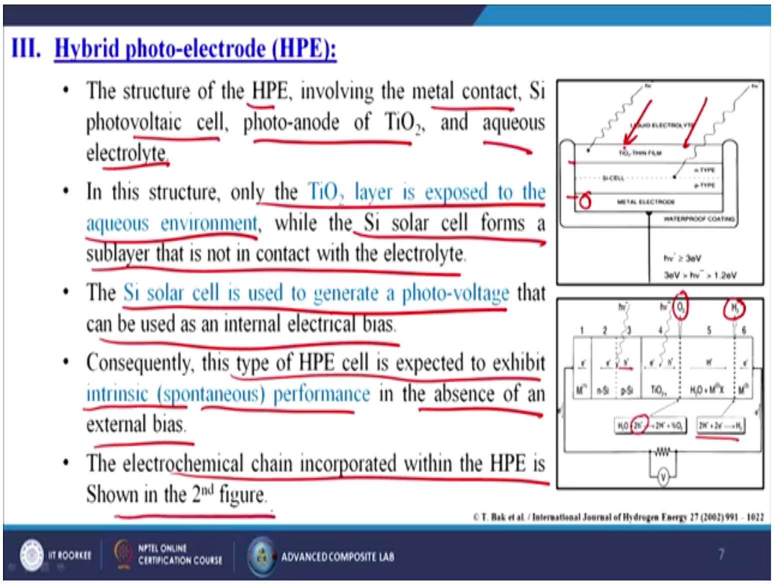

Next is called the Hybrid Photo-Electrode HPE. So, the structure of the HPE involving the metal contact that is silicon photovoltaic cell, photo anode of titanium dioxide and aqueous electrolyte. So, in this particular case we can see that is the number 1 electrode over here which is acting as a metal materials, so metal electrode it is known as. Outside is the waterproof coating basically, we are using. Now, we are using the silicon of two type, one is the n-type silicon another one is called the p-type silicon. And then top of that we are using another titanium dioxide thin film and the whole thing is immersed into the liquid electrolyte itself.

Now, what is happening? The light is coming into the titanium dioxide, light is coming to the interface in between the n-type and p-type semiconductor. So, what is happening? In this structure only the TiO 2 layer is exposed to the aqueous environment. Now, see, only the liquid is acting in this particular, liquid is unable to go inside it. While the silicon solar cell forms a sub layer that is not in contact with the electrolyte. So, this is under the electrolyte, means it is not touching with the liquid electrolyte itself.

The silicon solar cell is used to generate a photo voltage that can be caused as an internal electrical bias. Consequently, this type of HPE cell is expected to exhibit intrinsic, intrinsic means the spontaneous emissions. So, basically, the spontaneous performance in the absence of an external bias. So, in this case what happened? The electrochemical cells what we are putting over there now, this is the whole structure over there. So, I am having that metal electrode, then n-types silicon, then p-type silicon, then I am having the titanium dioxide, then I am having that liquid electrolyte over there. So, in these particular case what happened? Water plus 2h plus ion, so it is it is forming 2H plus plus half oxygen. So, it is generating the oxygen in this particular case which that is why the oxygen is coming out from the system itself.

In this particular point what is happening? 2H plus again it is taking 2 electron and then it is forming the hydrogen gas and it is coming out from the system itself. So, in this particular case the h means the hole basically, this is the hole 2h prime means nothing, but the two hole. So, basically, the hole movement is taking place and electron movement is taking place in to the opposite directions that is the basic semiconductor theory. So, if the electron will move into one directions, the opposite directions the hole will be moving. So, the electrochemical chain incorporated with the hep shown in the second figure itself.

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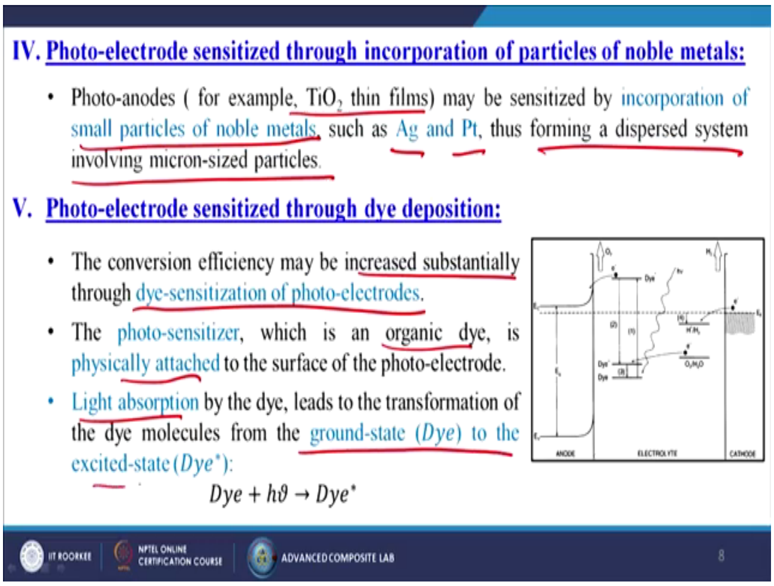

Next the fourth one is called the photo-electrode sensitized through incorporation of particles of noble metals. Photo-anodes for example, titanium dioxide thin films maybe sensitized by incorporation of small particles of the noble metals, such as silver or maybe the platinum or may be sometimes the both thus forming a disperse system involving micron sized particles. Now, the nanotechnology has come into the picture. So, people are trying to incorporate some kind of nano label fillers into the system, so that we can get the better efficiency from it.

Then the fifth one is called the photo-electrodes sensitized through dye depositions. The conversion efficiency may be increased substantially through dye sensitization of photo-electrodes. The photo-sensitizer, which is an organic dye, is physically attached to the surface of the photo-electrode. So, now, we are introducing another materials to the photo-electrodes.

Simple some dye sensitized materials we are going to do either we are going to deposit or maybe we are going to do the some kind of wrapping or maybe coating on to the photo-electrode itself. So, light absorption by the dye leads to the transformation of the dye molecules from the ground state to the excited state; that means, also it is creating certain kind of hole over there. So, now dye when it is getting the frequency light frequency, so automatically it is become the dye prime.

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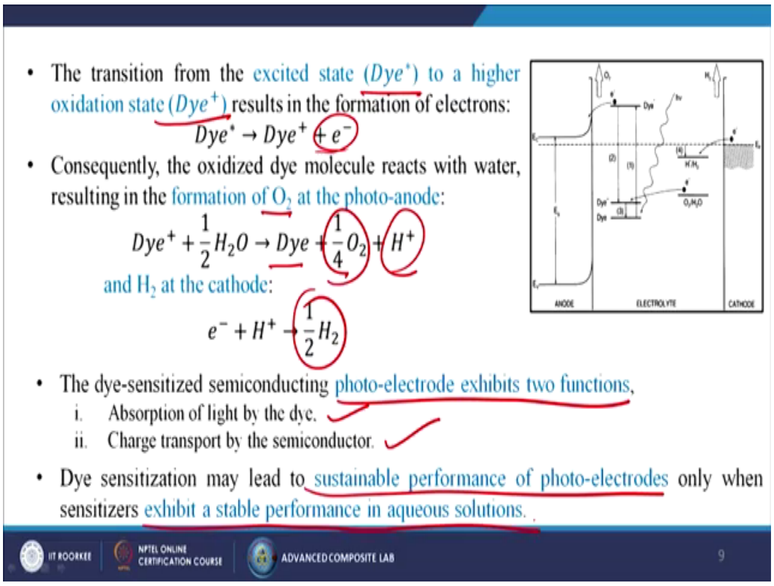

The transition from the excited state to a higher oxidation state; that means, dye prime to dye plus results in the formations of the electrons; that means, it is releasing one electrons over there. Consequently, the oxidized dye molecules react with water resulting the formation of O 2 at the photo anode. So, dye plus plus half H 2 O, so dye plus one-fourth O oxygen plus H plus ion it is giving and at H 2 at the cathode same thing; same thing like the previous one. Then the electron is coming over there, H plus ion is coming over there and they are mixing together and they are forming the hydrogen gas which is taking place at the cathode.

So, the dye sensitized semiconducting photo-electrode exhibits two functions basically, one is called the absorption of light by the dye and the charge transport by the semiconductor itself. Dye sensitization may lead to sustainable performance of photo-electrodes only when sensitizers exhibit a stable performance in aqueous solutions. Yes, because whatever the dye we are going to use that should be stable in the aquatic solutions or maybe the aqueous solutions. It should not be degrade or maybe it should not be dissolved.

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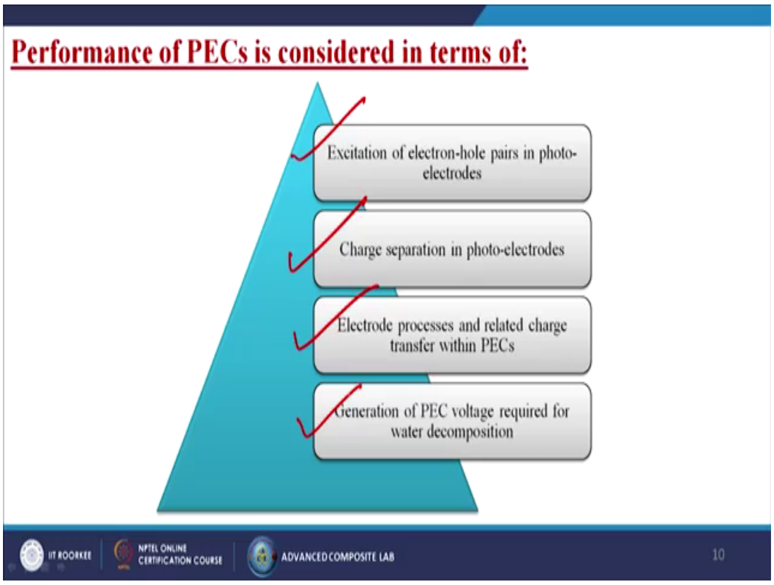

Now, what is the performance of PECs is considered in terms of excitations of electrons hole pairs in photo-electrodes, charge separation in photo-electrodes, electrode process and related charge transfer within PECs, and generation of PEC voltage required for the water decompositions. So, these all are the 4 different performance by which the total efficiency of this particular systems can exist.

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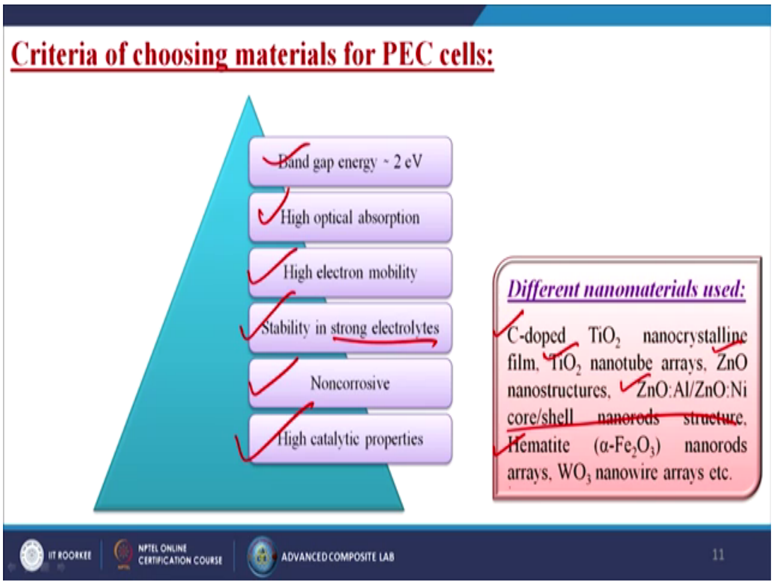

Criteria for choosing materials of the PEC cell. Basically, the material which have the band gap energy more than or maybe equivalent 2 volt. It should have high optical absorption properties. It should have high electron mobility. Stability in strong electrolytes because otherwise maybe we are using some kind of salts or maybe some kind of acids it should not react with the electrolytes itself. It should be non-corrosive; that means, after reacting or maybe after dissolutions it should not create any corrosiveness to the electrodes or maybe to the container itself. And it should have high catalytic properties.

Now, what kind of materials nowadays the scientists are using? Basically, they are using the carbon doped titanium dioxide nanocrystalline film, titanium dioxide nanotube arrays, zinc oxide nanostructures, zinc oxide combinations of the composites like aluminum, zinc oxide with nickel core shell nanorods structure. So, it is a one kind of hybrid structure. Hematite nanorods arrays, then tungsten oxide nanowire arrays.

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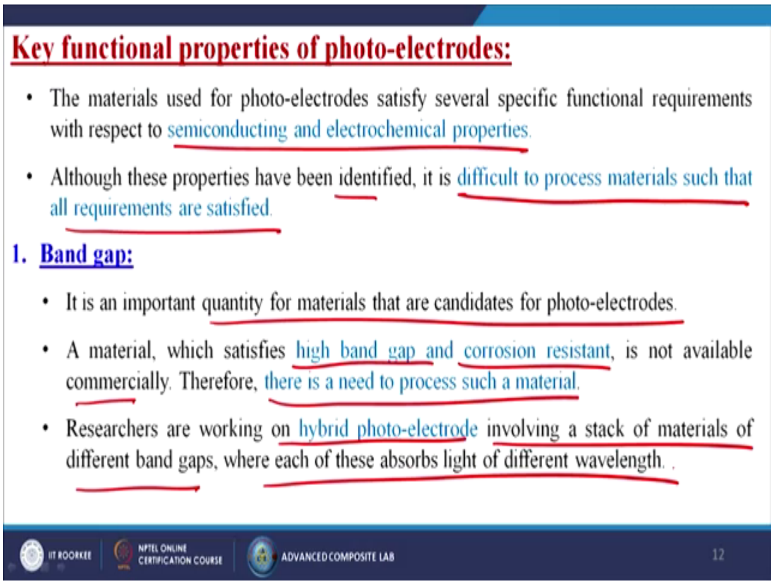

So, what is the key functional properties of the photo-electrodes? The material used for photo-electrode satisfy several specific functional requirements with respect to semiconducting and the electrochemical properties. Although, these properties have been identified it is difficult to process materials such that all requirements are satisfied. Yes of course, because when you are going to introduce a new materials, so of course, it is going to increase certain properties, but simultaneously it is going to decrease certain properties also. So, all together, all property will increase by a particular material it is really difficult to prepare.

Now, the first one is called the band gap. It is an important quantity of for material that are candidates for photo-electrodes. As I told already the band gap should be equivalent to the 2 volt. A material which satisfies high band gap and corrosion resistance is not available commercially therefore, there is need to process such a material. Researchers are working on hybrid photo-electrode involving a stack of materials of different band gaps where each of these absorbs light of different wavelength. So; that means, automatically we can get the equivalent of the 2 volt over there as a band gap.

Then the second one is called the Schottky Barrier. Schottky Barrier is very famous phenomenon because the our scientist who has invented this one is name was the Schottky. So, basically, by his name this is known as the Schottky Barrier basically, this is taking place at the metal and the semiconductor interface itself. So, this phenomena is taking place.

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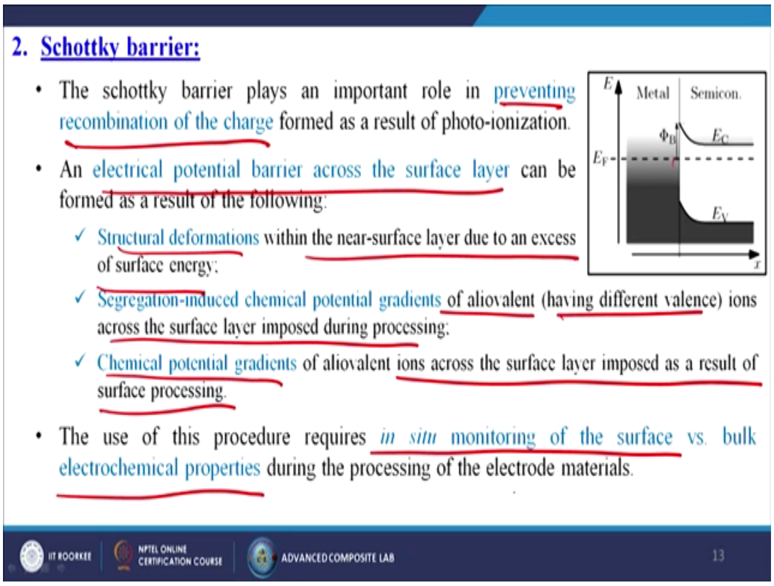

The Schottky Barrier plays an important role in preventing recombinations of the charge formed as a result of photo ionization. An electrical potential barrier across the surfer layer can be formed as a result of the following. Structural deformations within the near surface layer due to an excess of surface energy. So, basically, it is taking place in this particular zone itself. Segregation induced chemical potential gradients of aliovalent having different valance ions across the surface layer imposed during processing.

Chemical potential gradients of aliovalent ions across the surface layer imposed as a result of surface processing. So, basically, this is a one kind of phenomena is basically, happening in this particular junction case where the metal and semiconductor are coming into the contact. The use of this procedure requires in situ monitoring of the surface versus bulk electrochemical properties during the processing of the electrode materials.

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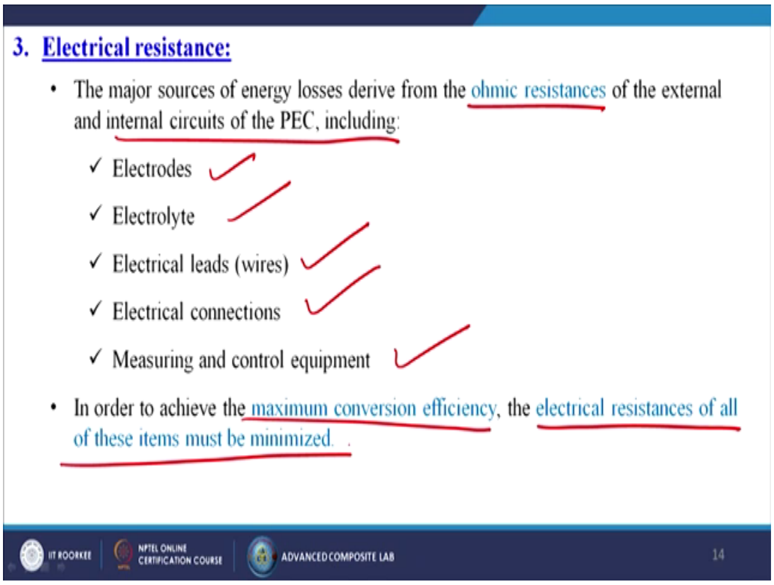

Next one is called the electrical resistance. The major source of energy losses derive from the ohmic resistance of the external and internal circuits of the PEC including electrodes, electrolyte, electrical leads or maybe the wires, electrical connections measuring and control equipment. In order to achieve the maximum conversion efficiency the electrical resistances of all of these item must be minimized. So, that is the prime considerations over here.

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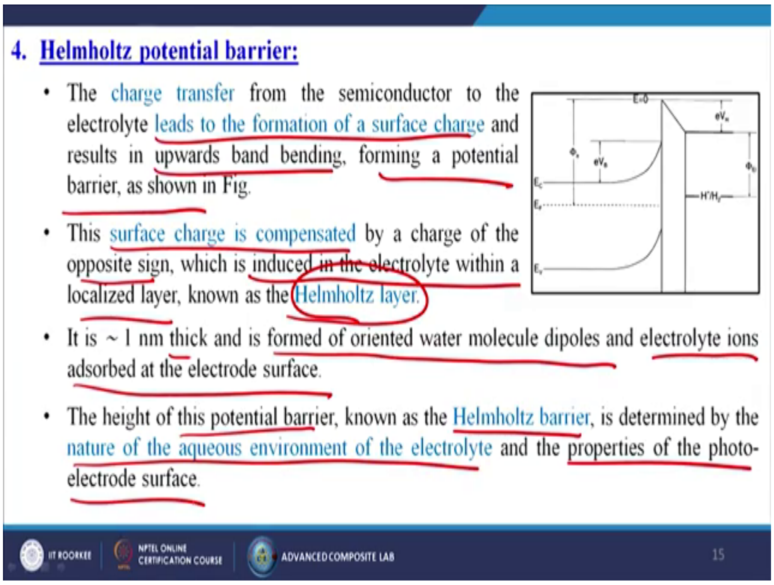

Next the fourth one is called the Helmholtz potential barrier. The charge transfer from the semiconductor to the electrolyte leads to the formation of a surface charge and results in upwards band bending forming a potential barrier as shown in this particular image. This surface charge is compensated by a charge of the opposite sign, which is induced in the electrolyte within a localized layer known as the Helmholtz layer basically.

So, in this particular case what is happening? As I told already the surface charge is compensated by a charge of the opposite sign. So, if one should be the minus, so same equivalent the plus will be there, which is induced in the electrolyte within a localized layer. So, in this particular case you can see, so layer formations is taking place in the electrolyte known as the Helmholtz layer.

It is almost equivalent to the 1 nanometer thick and is formed of oriented water molecules dipoles and electrolyte ions absorbed at the electrode surface. So, basically, when you are using the 2 electrode some water molecule can stick on to the electrode itself.

The height of this potential barrier known as Helmholtz barrier is determined by the nature of the aqueous environment of the electrolyte and the properties of the photo-electrode surface. So, that is the case over here.

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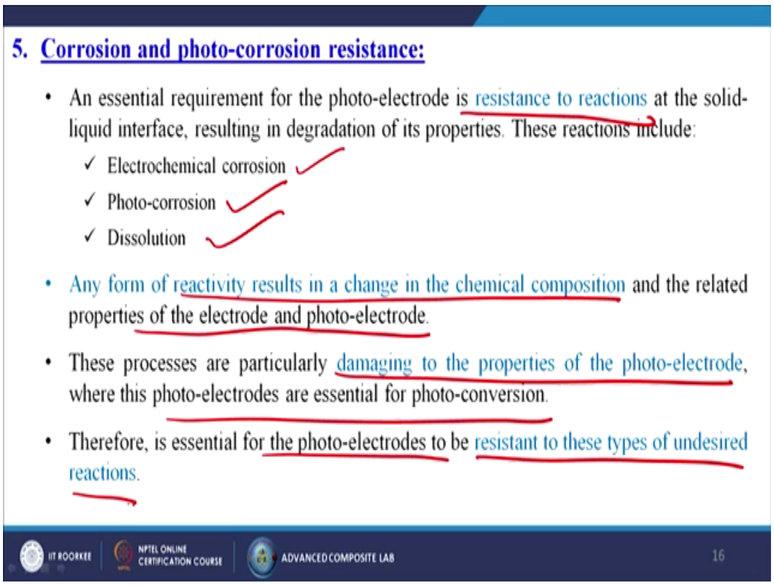

Next the 5th one is called the corrosion and photo corrosion resistance. An essential requirement for the photo-electrode is resistance to reactions at the solid liquid interface resulting in degradation of its properties. These reactions includes, electrochemical corrosion, photo corrosion and the dissolution. Any form of reactivity results in a change in the electrical compositions and the related properties of the electrode and photo-electrode. This processes are particularly damaging to the properties of the photo-electrode, where this photo-electrodes are essential for photo conversion. Therefore, is essential for the photo-electrodes to be resistant to this types of undesired reactions.

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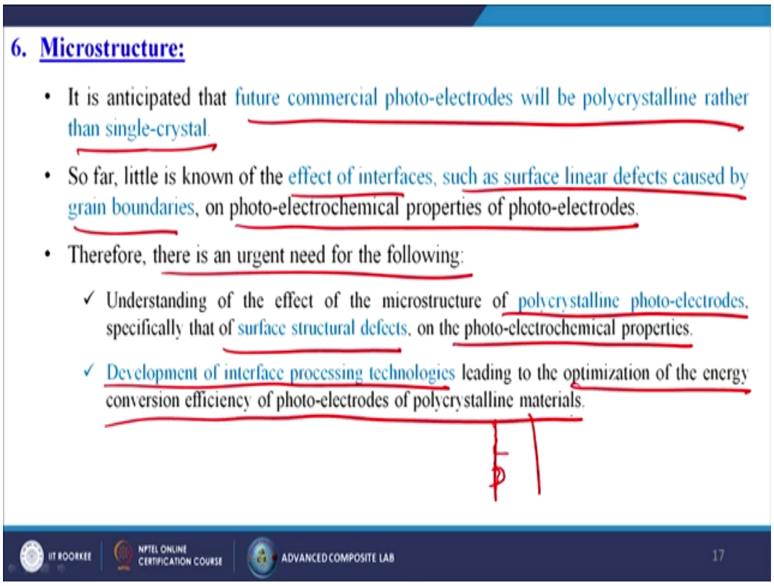

Then the 6th one is called the microstructure. It is anticipated that future commercial photo electrons will be polycrystalline rather than the single crystal. So far this is little known of the effect of interfaces such as surface linear defects caused by the grain boundaries on photo electrochemical properties of the photo-electrodes because when you are preparing the photo-electrodes at the surface if it is not so smooth or maybe some cracks or maybe some pores are present, so that time it creates little bit of the problem. So, that we have to minimize.

Therefore, there is an urgent need for the following. Understanding of the effect of the microstructure of polycrystalline photo-electrodes, specially that of the surface structural defects on the photo electrochemical properties. Development of interface processing technologies leading to the optimizations of the energy conversion efficiency of photo-electrodes of polycrystalline materials. So, this is the another conditions.

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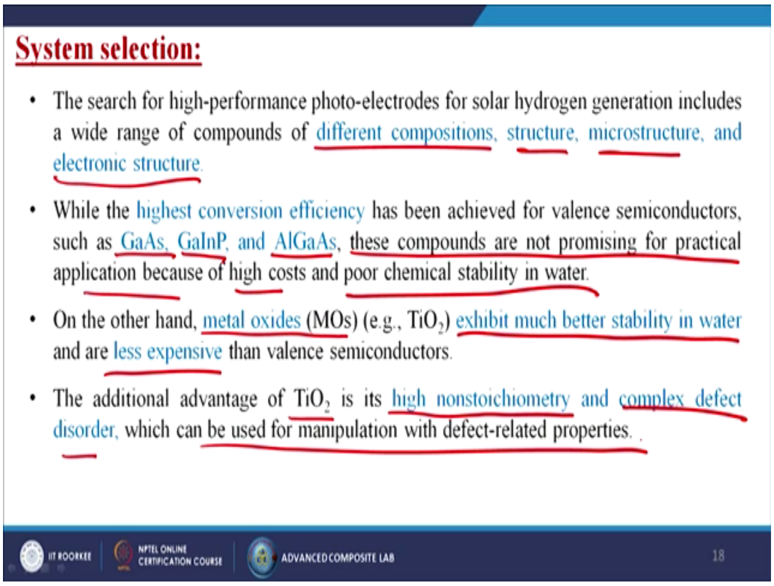

Now, how you are going to choose the system? The search for high performance photo-electrodes for solar hydrogen generation includes a wide range of compounds of different compositions, structure, microstructure and electronic structure. While the highest conversion efficiency has been achieved for valence semiconductors such as gallium arsenide, gallium indium phosphorus, aluminium gallium arsenide, these compounds are not promising for practical application because of high costs and poor chemical stability in water itself.

On the other hand, metal oxides like titanium oxide exhibit much better stability in water and are less expensive than the valence semiconductors. The additional advantage of titanium dioxide is its high nonstoichiometry and complex defect disorder which can be used for manipulation with defect related properties itself.

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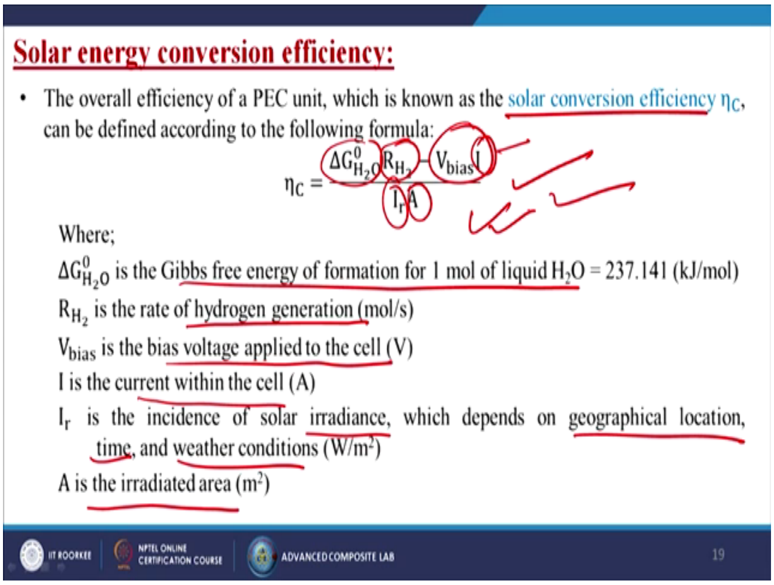

Now, what is the solar energy conversion efficiency? The overall efficiency of a PEC unit which is known as the solar conversion efficiency that is the sigma C basically, can be defined according to the following formula. So, this is the basically, the formula, where del G prime H 2 O is the Gibbs free energy of formation for 1 mole of liquid water that is equal to 237.141 kilo Joule per mole 237.141 kilo Joule per mole. So, this is the thing.

Next R H 2 is the rate of hydrogen generations that is mole per second. So, this is the second one. Then V bias is the bias voltage applied to the cell that is also in volt , so this is the case. And of course, I here, the I is called the current within the cell that is in ampere. I r is this one, is the incidence of solar irradiance which depends on geographical locations, time and weather conditions that is watt per meter square. And capital A is the irradiated area that is into the meter square. So, by this equations basically, we can get the solar conversion efficiency of the PEC unit.

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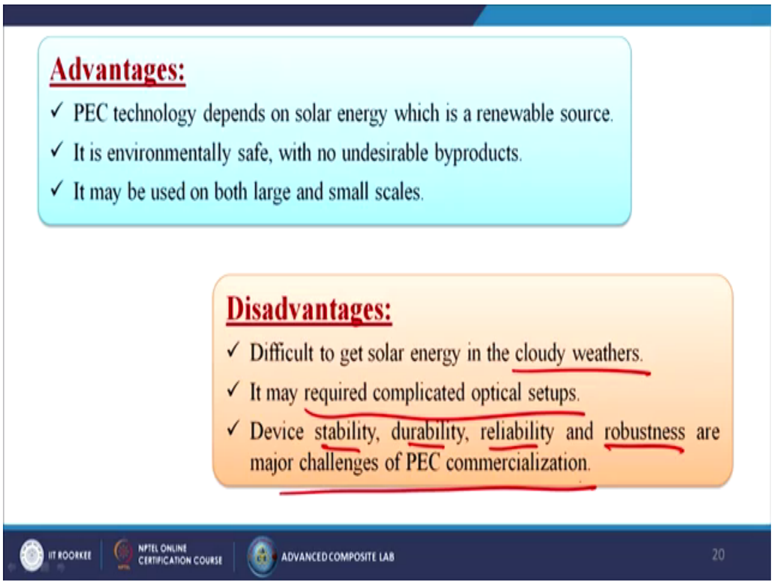

Now, what are the advantages? PEC technology depends on solar energy which is renewable source. It is environmentally safe with no undesirable by products. It may be used on both large and small scales and of course, there are certain disadvantages too. Difficult to get solar energy in the cloudy weathers, that is there. It may required complicated optical setups. Device stability, durability, reliability and robustness are major challenges of PEC commercialization's that is true.

That is why the people have still trying to work on it, so that it can be more durable, it can be more reliable or maybe it can be very rigid or maybe the robust, so that in outside any environment whether it is a hot or cold or maybe the rainy season it can withstand the temperature differences with the environment itself. So, still the scientists are working on this particular area.

Now, we have come to the last slide of this particular lecture. So, in summary we can say that photo-electrochemical water splitting is one of the potential technique for clean solar hydrogen productions and has been utilized in small to large scale hydrogen generators. Second, water photo electrolysis using a PEC involves ionizations, oxidations, transport and reduction process within photo-electrodes and at the photo-electrode electrolyte interfaces.

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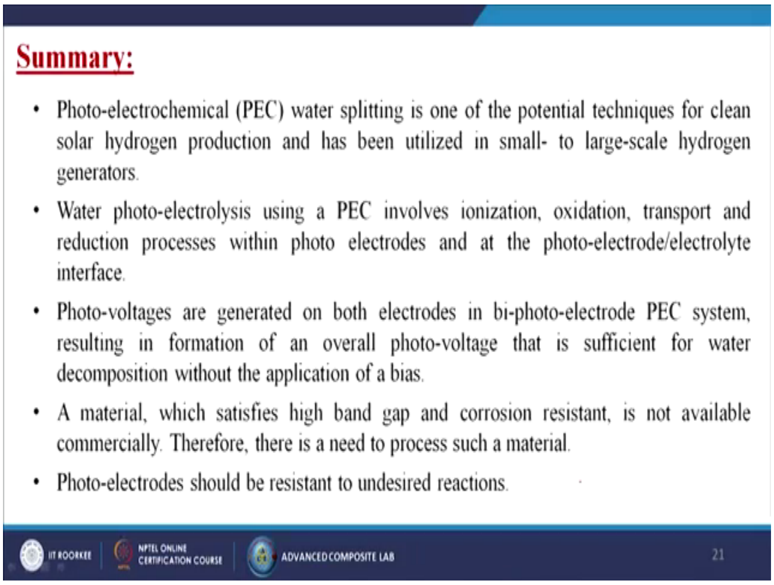

Photo-voltages are generated on both electrodes in bi-photo-electrode PEC system resulting in formation of an overall photo voltage that is sufficient for water decompositions without the applications of a bias. A material which satisfies high band gap and corrosion resistance is not available commercially. Therefore, there is a need to process such a material. Photo-electrode should be resistance to undesired reactions itself. So, this is all about the photo electrochemical water splitting by sunlight itself.

Thank you.