### Selection of Nanomaterials for Energy Harvesting and Storage Applications Prof. Kaushik Pal Department of Mechanical and Industrial Engineering Indian Institute of Technology, Roorkee

# Lecture – 08 H<sub>2</sub> Production from Electrolysis

Hello my friends, today we are going to discuss about the Hydrogen Production from Electrolysis. So, basically last couple of lecture basically we are discussing about the hydrant productions by different techniques. So, in this particular lecture, we are going to discuss about the hydrogen production from electrolysis process. So, before going to start exactly at what about the hydrolysis process, just let us know that as the world is generating lots of pollutants enough to change adversely the ecosystems.

Yes, because nowadays the main concern is the waste materials and the waste product, because it is creating a lots of problems to the environment in terms of pollutions, in terms of the carbon dioxide or maybe the carbon monoxide emissions which is a harmful element for our human beings.

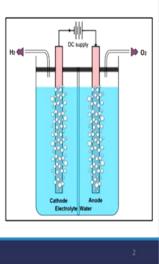
So, basically this ecosystems need certain kind of a change because certain kind of techniques or may be the technology by which we can generate the future fuel, but not creating any kind of problems to the environment itself that means, I am talking about the clean energy generations.

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#### **Introduction:**

- As the world is generating lots of pollutants enough to change adversely the ecosystem, there is a need of clean energy which is not harmful to the environment.
- Hydrogen is not found in appreciable or exploitable concentrations freely on Earth and instead must be produced from other compounds.
- Hydrogen may also be produced via electrolysis of water. In this process electricity (electro-) is used to break down (-lysis) water (H<sub>2</sub>O) into its component parts of oxygen and hydrogen with no harmful or polluting side-products

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So, hydrogen is not found in appreciable or exploitable concentrations freely on earth and instead must be produced from other compounds. Yes, because hydrogen is available onto the earth, but that is also very limited, so that is why the scientist are working on different techniques just to produce the hydrogen, so that it can be stored and it can be utilized for future applications.

So, in terms of that the first and foremost thing is coming is the water, because that is H 2 O. So, hydrogen and oxygen atoms are there. So, if we able to break that hydrogen and oxygen, then automatically that hydrogen we can capture and we can utilized for future applications. Because nowadays that is also the another concern is that every time we are talking about the saves water, do not waste the water. So, in that particular case, what is happening that water we are wasting or maybe we are not conserving that water up to that much level. Say suppose nowadays people are very much concerned about the rainwater harvesting.

So, if in future we are able to store this waste water or maybe that rainwater, and then after that by electrolysis process, if we are able to split that water into the hydrogen and oxygen and that will be the wonderful things. Because at that time of production of the hydrogen, it will not create any kind of polluted gas or maybe any kind of toxic gas which can be harmful to the environment itself that is why the scientist are tending towards this particular technology.

So, electrolysis process, so basically it is having two terms, one is called the electro, another one is called the lysis. So, electro has come from the electricity. So, basically we are giving certain kind of potential difference in between the two electrodes that is why electro word has come. And lysis means the breakdown, so that means, here we are doing the breakdown of the water into hydrogen and oxygen that is why we are talking it as a electrolysis process.

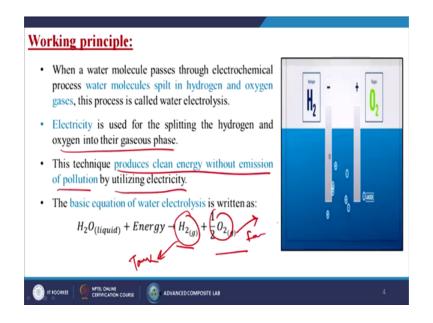
So, by this particular process, simple, we are applying the electrode, we are giving the potential difference by which we are breaking the hydrogen and oxygen, and then that hydrogen we are capturing into the tank, and oxygen directly it is coming to the environment. So, the both way one way is that we are storing the hydrogen as well as we are giving the oxygen to the environment, so that is why it is the most clean technology till today.

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Year	Inventor	Invention	
1789	Jan Rudolph Deiman Adriaan Paets van Troostwijk	First demonstrated water electrolysis using an electrostatic generator.	
1800	J.W. Ritter	Exploited Volta's battery technology and allowed separation o the product gases.	
1888	Dmitry Lachinov	Developed a method of industrial synthesis of hydrogen & oxygen via electrolysis.	
1890	Charles Renard	Constructed a water electrolysis unit to generate hydrogen fo use in airships.	
Mid 1960s	General Electric	Developed proton exchange membrane for producing electricit for Gemini space program, and later adapted for electrolysis.	

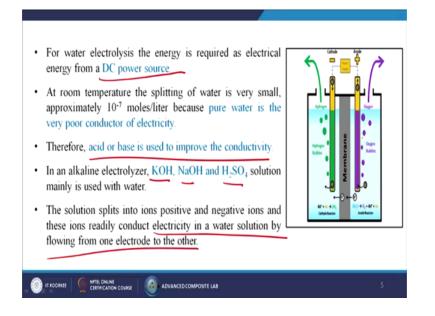
So, now, if we talk about the history, it has been started in the year of 1789 by Jan Rudolph Deiman Adriaan Paets van Troostwijk, first demonstrate the water electrolysis using an electrostatic generator. So, they have started this particular technology. But that time they have not knowing that in future this hydrogen storage or maybe the capture will be the great importance because we can use it for the future fuel. Then slowly, slowly, we have come down and we have come down to mid 1960s, where the GE that is the General Electric, they have developed the proton exchange membrane for producing the electricity for their Gemini space program, and later adapt it for electrolysis technique.

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So, what is the working principle of this electrolysis technique? So, basically as I told already it is a simple, one I am having a container in which I am putting the water, then I am having two electrodes, I am dipping those electrodes into the systems. I am giving the potential difference in between that by which the water molecule is breaking into the hydrogen gas and the oxygen gas. So, simple we are doing the splitting of that water, sometimes we are calling it is a water splitting technology also or maybe the techniques also.

So, in this case, electricity is used for the splitting the hydrogen and oxygen into their gaseous phase. This technique produces clean energy without emission of pollutions by utilizing the electricity. The basic equations as I told you already H 2 O, it is into the liquid form, we are giving the energy in terms of the electricity. And then it is producing the hydrogen gas and the half oxygen over there. So, automatically this hydrogen gas we are storing into the tank itself and then this half O 2, it is directly coming to the environment. So, like this way we can store the hydrogen, and we can produce the oxygen towards the environment.



So, for water electrolysis the energy is required as electrical energy from a dc power source. At room temperature the splitting of water is very small approximately 10 to the power minus 7 moles per liter, because as we know that water is the very poor conductor of electricity. So, in this case what is the next plan, next plan is that either I have to make it the some alkaline medium or maybe some kind of basic medium, so that the current easily passes through the water and it can breaks.

Therefore, acid or base is used to improve the conductivity. In an alkaline electrolyzer, basically potassium hydroxide, sodium hydroxide, sulfuric acid solutions mainly is used with water, either it will be acidic or maybe it will be basic. The solution splits into ions positive and negative ions and these ions readily conduct electricity in a water solution by flowing from one electrode to the another.

So, from this image you can understand that is basically we are dipping two electrodes over there. In this case, we have added another one membrane. In this case, I am having two electrodes. And I am putting some kind of sulfuric acids or may be potassium hydroxide or sodium hydroxide into the water. So, what is happening? So, sodium hydroxide is breaking into the sodium ion and the OH minus, so that sodium plus will help to break the water into the H plus and the OH minus. So, automatically what will happen, in this particular case the hydrogen gas will come out in this particular case the

oxygen will be coming out, so that means, the membrane is acting as a separator in between these two electrodes.

 Classification of water electrolysis technologies:

 • Water electrolysis technology can de divides into three main classifications on the basis of electrolyte used in the electrolysis cell.

 • Water electrolysis

 • Water electrolysis

 • Alkaline electrolysis

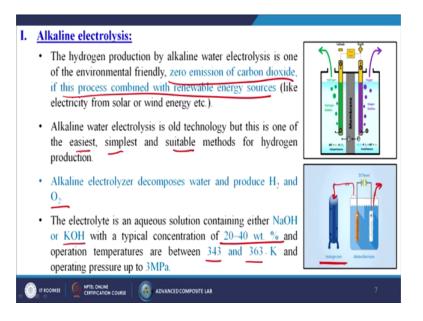
 • Polymer/proton electrolysis

 • Steam electrolysis

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So, classification of water electrolysis technologies. So, basically water electrolysis technology can be divides into three main classifications on the basis of electrolyte used in the electrolysis cell. What are those first? One is called the alkaline electrolysis, polymer or proton electrolyte membrane electrolysis, and the last one is called the steam electrolysis.

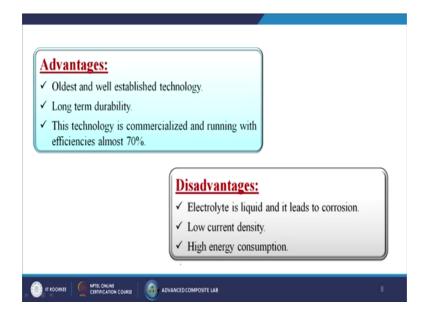
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So, what is alkaline electrolysis? The hydrogen production by alkaline water electrolysis is one of the environmental friendly, zero emission of carbon dioxide, if this process combined with renewable energy source like electricity from solar or wind energy. That means, whatever the potential difference or maybe the electricity we are producing we are giving to the systems if we do not take it directly from the any kind of electricity whatever we are using like ac or dc. If we are able to produce that electricity also from the tidal energy or maybe the solar energy, then the whole system will be best on the renewable source as well as the hydrogen production.

So, alkaline water electrolysis is old technology, but this is one of the easiest, simplest and suitable methods for hydrogen production. Alkaline electrolyzer decomposes water and produces the hydrogen and oxygen. So, in this particular case, you can see. Directly we have put the hydrogen tank over there through which the through this pipe the hydrogen is coming and restoring into the systems, and through these the oxygen is coming directly to the environment itself. So, the electrolyte is an aqueous solution containing either sodium hydroxide or may be the potassium hydroxide as I already told you with a typical concentration of 20 to 40 weight percent, and operation temperatures are between 343 to 363 Kelvin and operating pressure up to 3 Mega Pascal.

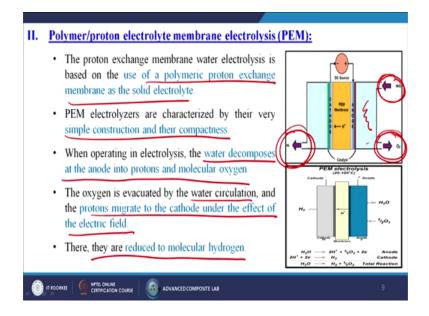
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Now, what is the advantages? So, this is as I told already this is the oldest and well established technology, long term durability. This technology is commercialized and

running with efficiencies almost 70 percent. Of course, there are certain disadvantages electrolyte is liquid and it leads to corrosion; low current density and high energy consumption. So, these all are the disadvantages for this particular technology.

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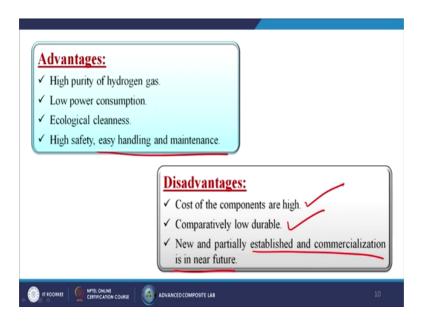


Now, we are moving to the second one that is called the polymer or maybe proton electrolyte membrane electrolysis in short basically we are calling it as a PEM. The proton exchange membrane water electrolysis is based on the use of a polymeric proton exchange membrane as the solid electrolyte. So, this is the yellow in colour is the solid one. It is made by some kind of polymer which can sustain that particular temperature as well as which can sustain inside that water for a long time without swelling, so that is a prime considerations over there.

So, basically the PEM electrolyzers are characterized by their very simple construction and their compactness. When operating in electrolysis, the water decomposes at the anode into protons and molecular oxygen. The oxygen is evacuated by the water circulations, and the protons migrate to the cathode under the effect of the electric field. There they are reduced to molecular hydrogen. So, from H plus they are converting into the hydrogen gas, and then it is coming out from the system. So, from here it is coming out.

So, in this case what happened in the anode side, so basically we are flowing the water. So, this water is going to inside, which is breaking into the H plus ion and the OH minus or half oxygen, and then that half oxygen is coming out from here. So, basically the continuous water is coming inside the system, it is breaking H plus is going to the cathode side which we are taking it as a hydrogen gas, and the rest oxygen gas is coming out. So, that is the main concept of this polymer or maybe the proton exchange membrane electrolysis technique.

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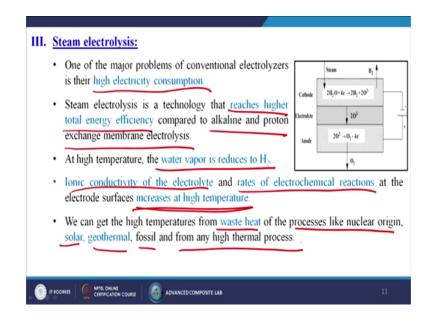


So, now what are the advantages? So, high purity of hydrogen gas, low power consumption, ecological cleanness, high safety and easy handling and the maintenance of this particular technology. Of course, there are certain disadvantages. Cost of the components are high, comparatively low durable as I told already because there is a chance of the swelling of that polymer membrane. New and partially established and commercialization is in near future, and not only that when the water is splitting it is generating certain kind of temperature also, so that material should have that capability it can withstand that particular temperature.

Till now people are working with the nafion, basically nafion polymer with some kind of titanium dioxide or maybe the silicon dioxide. Nowadays, people have started working with the peek that is polyether ether ketone polymer sometimes you are doing the sulfonations of that peek also, sometimes you are calling it is a s peek with titanium dioxide or may be the silicon dioxide or maybe sometimes we are doing the coating of the titanium dioxide or silicon dioxide with some ceramic materials or maybe doping, so

that it can withstand certain temperature or maybe it can work at the higher temperature, and also it cannot change its shape and size with water or may be the electrolyte for a longer time.

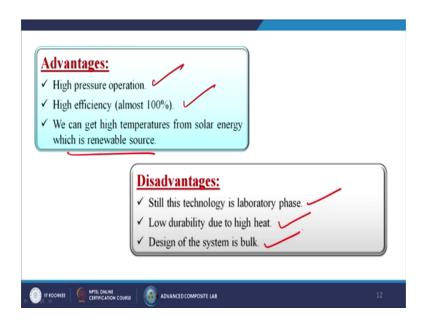
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Now, the third one is called the steam electrolysis. So, one of the major problems of conventional electrolyzers is their high electricity consumption. Steam electrolysis is the technology that reaches higher total energy efficiency compared to alkaline and proton exchange membrane electrolysis. At high temperature, the water vapor is reduces to hydrogen. Ionic conductivity of the electrolyte and rates of electrochemical reactions at the electrode surface increases at high temperature, so that means, we are injecting the water, then we are giving a tremendous heat by which the water is converting into the steam and then from that particular steam at particular temperature we are taking out the hydrogen gas.

Now, we can get the high temperatures from waste heat of the processes like nuclear origin, solar, geothermal, fossil fuels and from any high thermal process. So, basically whatever the waste heat, we are not utilizing that heat maybe we can use for this particular technology, so that no new heat generations is required, that means, no electricity or maybe no other energy is required. Simple from that particular waste heat we can converted into the hydrogen gas production.

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What are the advantages? It is having high pressure operations; high efficiency almost 100 percent; we can get high temperatures from solar energy which is the renewable source. Of course, there are certain disadvantages, still this technology is laboratory phase, low durability due to high heat, design of the system is quite bulk, that means, the design or maybe that equipment is little bit bigger.

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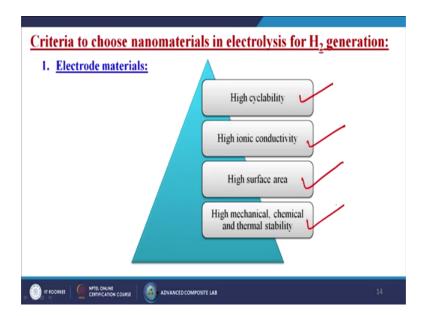
lifferent types of water electrolysis techniques:						
Electrolysis technology	Alkaline Electrolysis	Membrane Electrolysis	High Temperature Electrolysis			
Anode Reaction Oxygen Evolution Reaction (OER)	$20H^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	$H_2 O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	$0^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$			
Cathode Reaction Hydrogen Evolution Reaction (HER)	$H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2 0 + 2e^- \rightarrow H_2 + 0^{2-}$			
Charge carrier	ОН-)	(#*)	02-			
Operating Temperature Range	40 – 90 °C	20 – 100 °C	700 – 1000 °C			

Now, this is the overall comparison in between this particular three techniques that is called alkaline electrolysis, membrane electrolysis and high temperature electrolysis. So,

if I talk about the anode reactions, so this is the basically reactions is happening at the anode. And from there simple we are getting the oxygen gas. Cathode reactions sometimes you are calling it as the HER – H E R, because this is called the hydrogen evolution reactions from which we are getting the hydrogen gas.

So, basically these reactions are taking place at three different cathode positions. Charge carrier say suppose for alkaline electrolysis it is the hydroxyl ion. Membrane electrolysis it is the h plus and high temperature electrolysis that is the oxygen 2 minus ion. Operating temperature generally alkaline electrolysis works in between 40 to 90 degree centigrade. Membrane electrolysis it can goes up to 20 to 100 degree centigrades, and high temperature electrolysis it can go from 700 to 1000 degree centigrade, so that is the basic comparison in between these three techniques.

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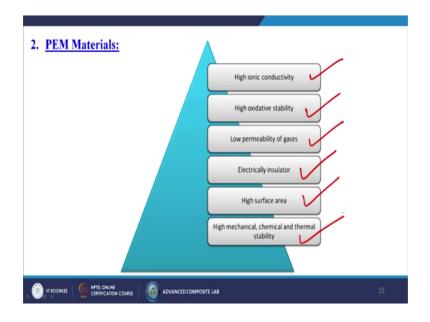


Now, let us discuss about the criteria to choose the nano materials in electrolysis for hydrogen generations. If I talk about the electrode materials, till now we talking about electrode materials and electrolyte, but what should be the input parameters or maybe the primary considerations for choosing any kind of electrode material. It should have high cyclability, high ionic conductivity, high surface area, high mechanical chemical and thermal stability.

Also another important parameter is that it should be highly against or maybe anti corrosiveness should be there; otherwise what will happen the material will degrade. Not

only that it should have to withstand with the high temperature. And of course, it should have high cyclability means I can use that electrode for several times then only the dissolution will be taking place, and then after that we are going to change the new electrode materials. High ionic conductivity, so it should generate the high ions or maybe higher rate of ions inside the system for breaking the water. High surface area means it will cover or maybe within short time, it can be able to produce the hydrogen gas and the oxygen gas. So, these all are the prime considerations for choosing any kind of electrode materials.

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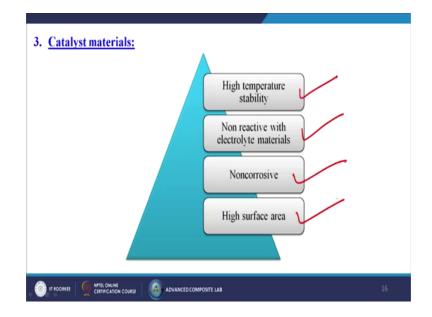


Now, come to the PEM materials. So, polymer electrolyte membrane materials, it should have high ionic conductivity, high oxidative stability, low permeability of the gases, electrically insulator, high surface area high mechanical chemical and the thermal stability. So, this should be the prime considerations for choosing any kind of polymer electrolyte materials.

Now, one thing I am going to tell you or maybe I am going to share with you that a single material cannot produce all these properties at a time, so that is why nowadays people are introducing different types of nanofillers into the polymer and making it as a composite materials, and then they are trying to use it for the polymer electrolyte. membrane Otherwise, what will happen, that polymer maybe virgin polymer cannot give this kind of properties all together. So, people are doing the engineering over there. And

from that particular results or maybe from that particular research results, now they are adding the different nanofillers at different ratio or maybe the weight percent, and now they are adding it and to make that polymer electrolyte membrane, so that it can fulfill all this requirements together.

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Then third one is called the catalyst materials. So, it should have high temperature stability, non-reactive with electrolyte materials, non-corrosives and the high surface area. So, these four are the prime consideration for choosing the catalyst materials. Sometimes, it may happen that when you are giving the electricity to those electrodes, maybe it is not possible to break the water. So, easily or maybe it is some alkaline or basic medium are there, but still it is not possible. So, that time we have to add any kind of third party material which can increase the rate of reactions, so that the hydrogen and oxygen can break so easily or maybe within some certain temperature or maybe certain pressure.

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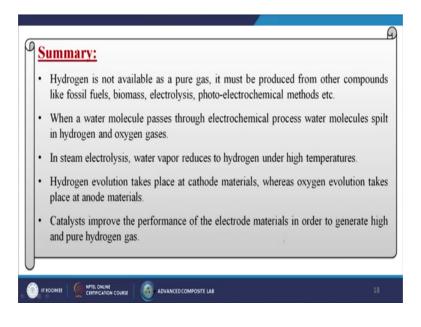
Electrolysis technology	Alkaline	PEM	Solid Oxide
Anode materials	Ni and its alloys etc.	IrO <sub>2</sub> , Ir-Sn oxide, Rh, RhO <sub>2</sub> etc.	Ni, Li-Ni, Co-Ni etc.
Cathode materials	Cd, Pb, Cu, Ag, Pt, Pd etc.	Pt, Pt/Activated Carbon etc.	Monel wire [Nickel 400] etc.
Electrolyte materials	KOH, NaOH & H <sub>2</sub> SO <sub>4</sub> etc.	PEM membrane: Nafion, Flemion etc.	ZrO <sub>2</sub> stabilized by Y <sub>2</sub> O <sub>3</sub> , MgO or CaO etc
Catalyst materials	Ni-Zn, Ni-Co-Zn, RuO <sub>2</sub> , LaCoO3 etc.	Ti coated IrO <sub>2</sub> , MoS <sub>2</sub> with graphite, WO <sub>3</sub> nanorods, Pd/CNTs etc.	

Next, what are the different materials used in electrolysis of hydrogen generations. So, as I told already in anode materials basically for the alkaline case people are using the nickel and its alloy. For polymer electrolyte membrane, people are using the iridium oxides, iridium tin oxides, all this kind of things. Solid oxides like nickel, lithium-nickel composites, cobalt-nickel compositions basically they are using. For cathode materials they are using like cadmium, lead, copper, silver, etcetera. For polymer electrolyte membrane basically they are using platinum or maybe the platinum activated carbon materials. Solid oxide like monel wire like nickel 400 etcetera basically they are using.

For electrolyte materials, they are basically using the potassium hydroxide, sodium hydroxide and the sulfuric acid for the alkaline case. For polymer electrolyte membrane basically as I told already they are using the nafion membrane or maybe flemion membrane. And for solid oxide basically they are using the zirconia oxide stabilized by yttrium oxide, magnesium oxide or maybe the calcium oxides. For catalyst materials, basically they are using nickel zinc combinations or may be the nickel cobalt zinc combinations, or may be the ruthenium oxides or may be the lanthanum cobalt oxides etcetera. And for polymer electrolyte membrane, basically people are using the titanium coated iridium oxides, Mo S 2 molybdenum disulfide with graphite, tungsten oxides nanorods or maybe the palladium carbon nanotubes combinations. And not only that people are using so many as I told already they are using the titanium dioxide coated by zirconia oxides, or may be the silicon dioxides coated by some kind of ceramic materials.

So, basically nowadays peoples are tending towards the composite materials for the better efficiency.

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Now, we have come to the last slide of this particular lecture. So, in this particular lecture, we have discussed about that hydrogen is not available as a pure gas as I told already it must be produced from other compounds like fossil fuels, biomass, electrolysis, photo-electrochemical methods etcetera.

When a water molecule passes through electrochemical process water molecules split in hydrogen and the oxygen gases. In steam electrolysis, water vapor reduces to hydrogen under high temperatures. Hydrogen evolution takes place at cathode materials, where oxygen evolution takes place at anode materials. Catalysts improve the performance of the electrode materials in order to generate high and pure hydrogen gas. So, these all of the things we have covered in this particular lecture.

Thank you.