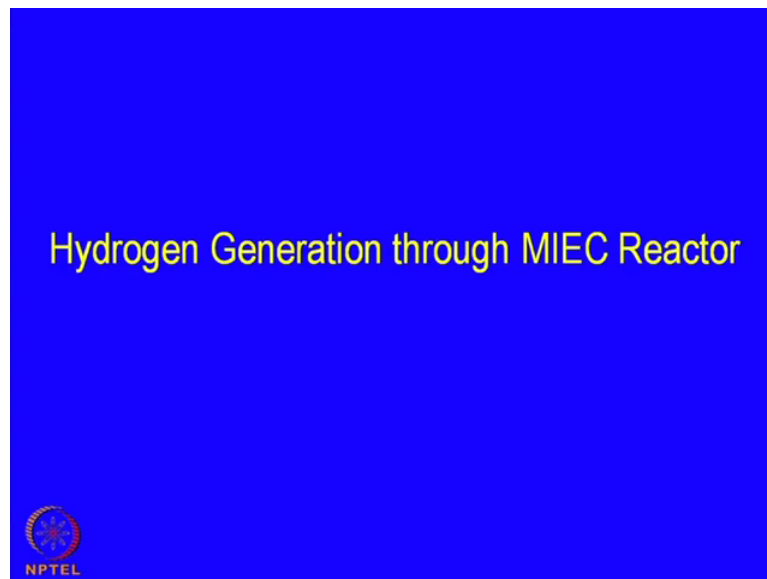


**Advanced Ceramics for Strategic Applications**  
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**Lecture - 31**  
**Hydrogen Generation through MIEC Reactor**

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In this lecture, we discuss the possibility of generating hydrogen with the help of some of the advanced materials some of which we have discussed earlier. So, the title of this lecture is Hydrogen Generation through MIEC reactor. MIEC is nothing but a mixed ionic and electronic conductivity in oxides, MIEC is conduction, actually mixed ionic and electronic conduction in oxides and we make reactors out of that material.

Let us discuss how exactly one can make hydrogen, a separate hydrogen I mean gas mixture using some of these oxides. Earlier, we have discussed the conductivity or electrical conduction process in oxides under different conditions partial pressure or different composition. And we have encountered or we have come across some of them are purely ionic conductors, some of them are purely electronic conductor either n-type semiconductor or a p-type semiconductor. And then, there is a group of oxides where this mixed oxides mixed conductive is available that means partly it is ionic, and partly it is electronic. And this oxides have every useful role in generation of separation of hydrogen from a mixture of gas mixtures.

Now, why hydrogen? We are talking about the energy sector and hydrogen is used one of the very useful one can say energy carrier and it has a very high calorific value and as well as it can be combined with oxygen to form water and therefore, it can release lot of energy so before we come to the actual discussion of how one can generate hydrogen using some of these mixed stock sites let me have a look at or discuss.

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The basically the energy sector what is the problem of the energy sector and why we are so much interest at in hydrogen or generating hydrogen earlier? We have discussed about the fuel cells that is one of the most efficient devices for converting hydrogen into electricity unfortunately hydrogen is not available in nature. The available in the combined form as water we have a huge resources water huge quantity of water available in this on this earth surface of the earth but we do not have hydrogen. On the other hand, hydrogen is a good energy carrier. It can once available it can be used as a very good fuel however the question is how to get hydrogen? So, it is completely related to energy and environment our interest how hydrogen is primarily from the environmental point of view. At the same time, it is a store house of energy and that is why if you can use the hydrogen as a source of energy then at a one go two of the things can be addressed or solved. One is the energy crisis and the other is the environmental problems or the environmental issues because so far the fuels we use most of the fuels use for energy generation is fossil fuels and once you burn the fossil fuels you generate carbon dioxide

we are invariably getting carbon dioxide these are one of the products and that carbon dioxide is polluting the environment.

We have it is a very important greenhouse gas and so global warming all these things are happening primarily because we are burning. So, much of hydro carbons and carbon dioxide is getting generated the percentage of carbon dioxide in the environment in the outside atmosphere is increasing day by day. So, we have to go high from the carbon cycle or the generation of carbon dioxide has to be minimize as much as possible so the whole sector is called the energy and environment sector and what are the different strategies if you want to maintain our environment and at the side energy without energy we cannot leave we need energy without energy the man cant cannot continue the human race cannot continue like this.

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**Long Term Strategy**


**Complete change over**

from Carbon Economy ( $C + O_2 \Rightarrow CO_2 + CO$ )

to Hydrogen Economy ( $H_2 + O_2 \Rightarrow H_2O$ )

**Success would however depend on**

- 1) Economic production of Hydrogen
- 2) Efficient conversion of hydrogen to different forms of power.

 **OR FULL DEPENDENCE ON RENEWABLE ENERGY**

Therefore, we need to generate energy, but at the same time we have to keep our environment clean so what would the different strategies general strategies are like this. We have do a long term strategy there are long term strategy as well as short term strategy in the sense long term because we do not have the technology. We would not have the right kind of the technology we may have some ideas, but we do not have the technology to repulsed or to recommence in a commercial scale and therefore, one is long term strategy and other will be short term strategy. In the long term strategy, what we are doing is trying to do complete change over from the carbon economy to the hydrogen

economy that is the terminology normally used that means basically from carbon cycle to hydrogen cycle.

In carbon cycle, we are binding carbon or combining carbon in the oxygen and producing carbon dioxide and carbon monoxide both of which are pollutants so where the environment is concern. So, if you can avoid that and still generate power or energy the other alternative may be go to the hydrogen economy, so that we have a store house of hydrogen and generate hydrogen and then combine with the oxygen to make it to H<sub>2</sub>O so the product of combustion is H<sub>2</sub>O which is a nonpolluting gas and the nonpolluting species. Therefore, the ideal situation is can you completely get rid of carbon and go to hydrogen that is but the question is how it can be economic because hydrogen is not available as such. So, one is to generate hydrogen and that generation of hydrogen also needs certain energy.

Can you generate hydrogen without using any energy? It is not possible. So, you have to basically generate hydrogen with some energy and then there is a products where how exactly it can be done even if the technology is available they may not be commercially feasible. The success would however depend, if you want to completely change over to hydrogen; one depend on the economic production of hydrogen or the efficient conversion of hydrogen to different forms of power and it is not all its actually both. So, first of all, you have to generate hydrogen and then that hydrogen has to be converted to either electricity or some other motive powers in a much more efficient manner.

Then, you can conserve hydrogen also to conserve the fuel so this is a long term strategy and people are working on various aspects of it, but the solutions are far away still long time will take before we can solve these problems. Or of course, the other alternative is already on that is full dependence on renewable energy like solar energy wind energy wave energy and so on. So, go to the renewable energy and how ever you do not have to combine bond within you are not producing any producing any gaseous products either carbon dioxide, carbon monoxide or hydrogen or moisture nothing is been produced. So, directly you are getting the energy from the solar or wind.

However, once again there are still quite costly and although that technology is available and the technology is slowly being propagated and being used in more and more or extensive manner.

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## Short Term Strategy

### Reduce Green House Gas emission by

- a) Reduction in consumption of fossil fuel  
( More efficient Energy Conversion Devices)
- b) Use fossil fuel to generate SYNGAS  
( mixtures of  $H_2$ , CO,  $CO_2$  etc)  
followed by efficient separation of  $H_2$  and sequestration  
of  $CO_2$ .



So, in the short range time or till we get a complete solution of hydrogen energy, we can have a short run short range strategy or short term strategy that is reduce greenhouse gas emission by reducing reduction in the consumption of the fossil fuel; that means you can you consume less fossil fuel to generate the said amount of energy. So, that you need more efficient energy conversion devices compared to thermal plants you should have much better efficient systems, so that we generate the same amount of power, but consuming less fuel. So, that is another strategy lot of work lot of technological advancement of taking place in those areas or the use of fossil fuel generate synthetic gas which is basically a mixture of hydrogen carbon monoxide and carbon dioxide followed by an efficient separation of hydrogen and sequestration of carbon dioxide.

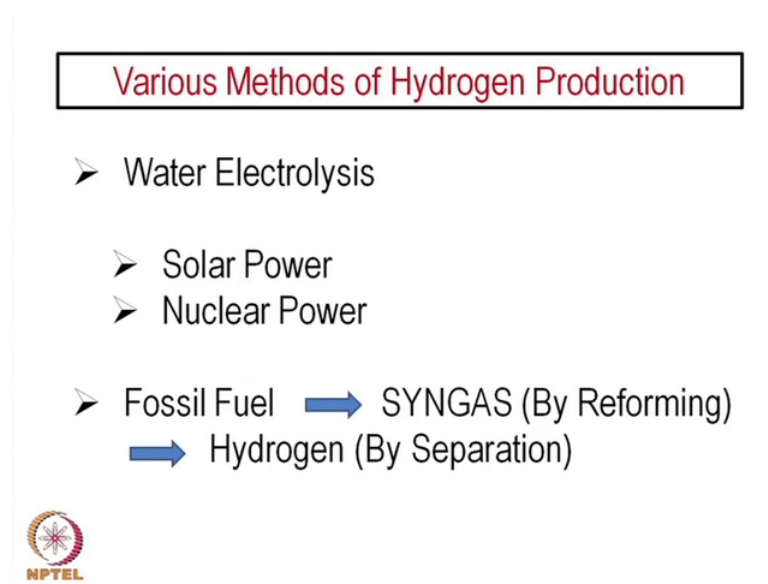
That means, you can still use the fossil fuels which has still some reserve in this world and from that we convert or convert that basically carbon hydrocarbons to a mixture of hydrogen carbon monoxide and carbon dioxide and then separate out these three gases. Because two of them hydrogen and carbon monoxide are combustible gases one can generate power out of that electrical power and carbon dioxide can be sequester that means you do not allow this carbon dioxide to environment you can convert into various ways. There are many different techniques now available or sequester some means to separate carbon dioxide and make it in the converting in the solid form and put it in the in the earth or inside the earth, so that it does not go in to the environment and pollute the

environment. These are different strategies being followed and extensively such work is going on different aspects of what we discussed right now.

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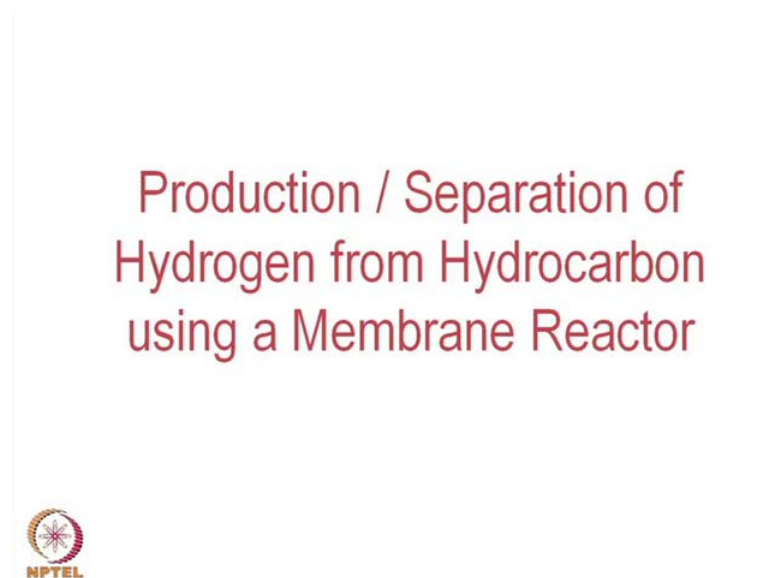
So, under this situation hydrogen generation or hydrogen production is certainly a very important issue. How to get hydrogen by different techniques; so that we can slowly move towards hydrogen economy these are the different techniques by which one can make hydrogen. Simplest way every one can think of very simple way to think that the water can be electrolyzed water electrolysis is the best most simplest way to get

hydrogen although, it is not still an economical we actually need power to water electrolyze water than to generate power out of the hydrogen to produce.

So, that there is a problem at this point of time, but if you can get power electrical power from different sources like solar power is a renewable power. So, you are not producing any carbon are either are not producing any environmental pollution and therefore, you can generate although it may not be very efficient process. But at least, you can get hydrogen using solar still it is not an economic proposition or you can use nuclear power to electrolyze water there are many different techniques, different methodology of water electrolysis and one can have more efficient water electrolysis not at room temperature may be at higher temperature.

First different kind of systems possibilities still use fossil fuel as I have mentioned earlier to prepare syngas synthetic gas a mixture of different gases including hydrogen this is basically on can do the, so called a reforming reaction and then separate out hydrogen. So, our interest is in the last one if we have a syngas as generates syngas and then separate out hydrogen and the they are sound the advance ceramic oxide acts will can be of help to us.

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So, the topic now will be the production and separation of hydrogen from hydrocarbon using a membrane reactor, membrane reactor made off oxides basically membrane is nothing but a semi permeable barrier through which a selective species can move

through and others are retained in the other side. So, that is the basic definition of membrane so its calls sometimes, the semi permeable membranes, but the membrane structures maybe different. The simplest way to imagine an membrane as having some porous structure so there may be pores of different sizes. So, depending on the size of the species some of the species can go through and the others can be retained just like a printer paper, but much finer scale. So, this is basically a membrane or semi permeable membrane so one can think of some porous membranes with controlled pore size with redesigned pore size, but what will be discussing today is not the porous membranes basically a nonporous membranes.

So, but even than one can and will drive through drive through some of the species through this dense structure as we have done in case of fuel cell. Fuel cell is a again a electrolyte is basically a dense membrane through which an oxygen can pass through, but no other gas can pass through. So, if you have an oxygen and conductor as in case of a zirconium it is stabilized zirconia and oxygen can pass through the material so itself is a kind of membrane through which only oxygen particular species live oxygen and pass through no other gas no other species can pass through. So, it is also a membrane definite, but it is a dense membrane not a porous membrane. So, it is not a molecular diffusion not the molecular diffusion its ionic transport so a membrane having ionic transport property are basically a dense membrane. So, we will be discussing that and how such membranes can be used for the generation of hydrogen.

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### Production of Hydrogen from a hydrocarbon feedstock

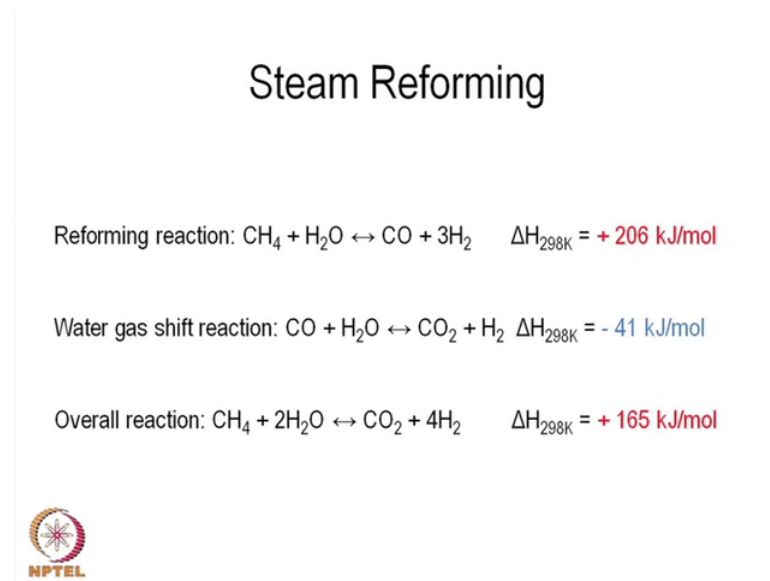
- Steam Reforming
- Partial Oxidation
- Auto-thermal Reforming





Now, before that before we come to be actually membrane or there characteristics and their properties let us look at how one can get hydrogen from hydrocarbon. There are various techniques basically it is called the reformation, reforming techniques we are reforming the actions. There are three kinds of reactions by which a hydrogen can be generated from hydrocarbon one is called the steam reforming other is partial oxidation and third one is called auto thermal reforming what of those characteristics are these details of these reactions.

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This is what we call steam reforming reaction, is basically taking methane is on the examples of hydrocarbon  $\text{CH}_4$  plus  $\text{H}_2\text{O}$   $\text{CO}$  plus  $\text{H}_2$  and this is a exothermic reaction. So, just by reaction with of course, you need some catalysts and so on when discussing that at this point of time, but is a methane and hydra  $\text{H}_2\text{O}$  can generate high carbon dioxide and hydrogen which both of them has a harm combustible gases hundreds of energy associate water gas shift reaction is like this.

Carbon dioxide carbon monoxide and  $\text{H}_2\text{O}$  this carbon monoxide and  $\text{H}_2\text{O}$  can react to give you carbon dioxide and  $\text{H}_2\text{O}$  the overall reaction on these addition to is actually these of course, a endothermic reaction and overall ratio is  $\text{CH}_4$  plus two  $\text{H}_2\text{O}$  is  $\text{CO}_2$  plus four hydrogen. So you are getting hydrogen gas mixture of carbon dioxide and hydrogen from the hydrocarbon and that is what is known as the steam reforming reaction.

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## Partial Oxidation

Partial Oxidation reaction:  $\text{CH}_4 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2$   $\Delta H_{298\text{K}} = +35.7 \text{ kJ/mol}$

Complete combustion:  $\text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$   $\Delta H_{298\text{K}} = +890 \text{ kJ/mol}$



Once again, it is a exothermic reaction in partial oxidation the other type of reaction forming reaction is partial oxidation reaction in CH<sub>4</sub> plus half H<sub>2</sub>O is CO plus 2H<sub>2</sub> and again this is a exothermic reaction and a complete combustion commercial undertaking of a complete combustion. Then of course, is much higher energy can be derived so that with oxygen full oxygen who income cumbersome because here you are generating CO we are generating CO<sub>2</sub> to complete combustion is taking place 2H<sub>2</sub> and you get a lot of energy here.

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## Auto-thermal Reforming

- Combination of both steam reforming and partial oxidation
- Heat generated from partial oxidation is used as an input for the steam reforming reaction




The auto thermal reforming is basically a combination of both steam reforming and partial oxidation which are just discussed so heat generated from the one is exothermic and other endothermic. And therefore, partially generate the heat and that heat can be utilized for the reforming your heat generated from the partial oxidation is used as the input for the steam reforming reaction so partially you are burn it and generates heat and that heat can be used for the conversion of hydrocarbon to the synthetic gas that is  $H_2$  plus  $CO_2$ .

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Typical  $H_2$  Separation Membranes

- Polymer (Organic)
- Ceramic (Inorganic)
- Cermet (Inorganic)



Now, if you have a semi permeable membrane at this stage so we are generating a steam a generating a mixture of gases hydrogen and carbon dioxide and if you have a material through which only hydrogen can pass through. But carbon dioxide is not passing through then that can separate that such a system can separate the hydrogen and one can generate pure hydrogen out of that separated. So, this is the role of semi permeable membranes or the oxides which we are talking of; there can be not only oxide so one can have polymers these are, this can also be used to relative low-temperature. Ceramics inorganic membrane that is will discussing few minutes and then also have some cermets like a ceramic and metal composites so that can also be used for this purpose.

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### Advantages of Membrane reactors over conventional Tubular Reactors

- Reduction in operation cost
- Higher conversion of hydrocarbon achieved
- Simultaneous production and separation of hydrogen



Advantages of membrane reactor over the, conventional well these are reactors, these are relatively new concept of using a reaction chamber and the separation chamber simultaneously. So, that is what the advantage is the reduction in operation cost higher or conversion of hydrocarbon is achieved an simultaneous production and separation of the hydrogen. So, normally under the current situation what happens is a you reforming reaction gas and then take it to another chamber and try to find out use as a either a membrane separation or different other separation techniques to separate the gases. So, the reaction chamber is different and the separation chamber is different, but if you can make a ceramic membrane; ceramic membrane either dense membrane or a porous. And when we are talking here about dense membrane those then membrane can forms the reaction chamber itself because these reaction takes high-temperature.

So, the ceramics, can be used as the reaction chamber and the same ceramics if it is semi permeable membrane the property is there in that is ceramics that can also be used as a separation chamber. But ultimately, at the end of the process get a pure hydrogen after the reaction and separation is complete within the same chamber these are the advantageous you get when compared to the normal tubular reactors which has been standardized over the year or over the decades for reforming reactions.

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## Inorganic Membranes

- High selectivity for separation
- Operate at high temperature range of 500 – 1000 °C
- Resistance to corrosive liquids and gases (Chemical resistance)
- Can withstand high pressure (mechanical strength)



Well, these are some the characteristics of the inorganic membranes we are talking of high selectivity for separation between surface and efficiencies very high, operate at temperatures. Because these are inorganic membranes are ceramic membranes can operate at a temperature of 500 to 1000 degree Celsius which is also own a high-temperature record for the reform. We are reformation reforming reaction, resistance to corrosion liquids and gases there really inert and therefore, there the less corrosive and no corrosion at all, can withstand high pressure will mechanical strength of these membranes compared to... Of course, while we are talking is talking this point is basically are talking about a comparison polymorphs.

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(MIEC)



Mixed Ionic and Electronic Conductor

### Two Different Forms of MIEC

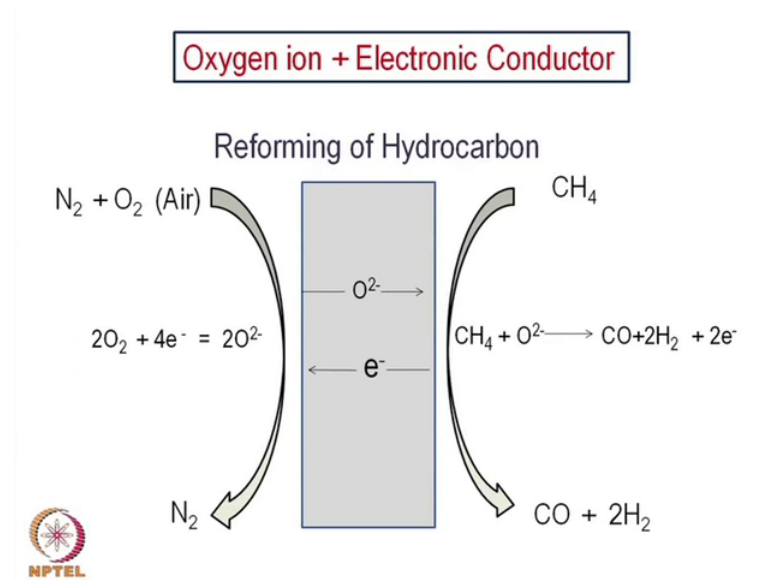
- Oxygen ion + Electronic Conductor
- Proton (Hydrogen ion) + Electronic Conductors



So, this is MIEC in this context, we have importance of the MIEC and that is mixed ionic and electronic conductor. So, this is the basic discussion we are coming to two different forms of MIEC one is types you can say one is oxygen ion plus electronic conductor and the other is proton hydrogen ion conductor and electronic conduct. We have come across oxygen and conductivity in YSZ which is course a pure ionic conductor, there is no electronic conductivity. But there are some other oxides in mixed oxides perovskite base we will see what are those, in which we have oxygen and conductivity mixed and conductivity oxygen and conductivity in addition to electronic conductivity so in the same material we have both.

Similarly, have another group of materials in which not the oxygen, but the hydrogen and is the conductor. We come across earlier in a proton membrane electrolyte or the polymer electrolyte fuel cell, were hydrogen and if the conduct conducting species in a polymer matrix creates the polymer is a hydrogen ion conductor. Similar things can happen in some of the oxides, but is not pure hydrogen ion conduct it is partly hydrogen ion conductivity and partly electronic conductivity so great that can also be used for this kind separation.

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Well first of all, let us take if you have a oxygen ion conductor or a mixed conduct are oxygen plus electronic conductor this as I mention few minutes back that we are talking about a reaction chamber where actually it is membrane and reaction taking place. And

membrane is basically an alliance in species to pass through and allowing reaction to proceed in certain reaction. So, this is an example where oxygen and electron both are the conducting species. So, this is our membrane and the wall of the reactor you can say so you have an oxygen conduction and electronic conduction. So, oxygen ion is moving in this direction and electron will be moving the opposite direction. So, this is the normal situation, ion move in one direction an electron will move the other direction so particularly for the oxygen ion.

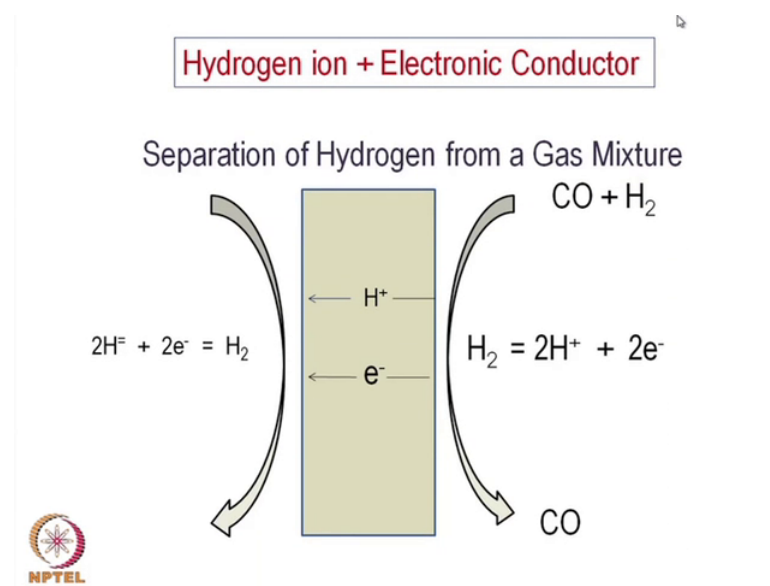
Now, this is a some sort of an electrolytic electrolyte, earlier you have seen a fuel cell where ion is moving oxygen ion moving through the electrolyte and electron is moving in the outer circuit generating the current. And you can draw current because of flow of oxygen ion here there is no question outer circuit, there is no EMF generated were not increasing any voltage also from outside. What we are having is basically a potential difference oxygen potential difference on-site high oxygen potential and on the other side low oxygen potential and that is the driving force which drives oxygen ion to move from one site to the other. But since, oxygen ion is moving so there will be charge accumulation on one side so from one side it goes to the other side, so there will charge accumulation until nonetheless there is a neutralization. So, the electron has to come back in case of fuel cell the electron was moving the outer circuit so you are getting were getting a current in the external circuit. Here, it is basically a kind of short circuiting the electron is moving within the materials itself.

So, this negative charge in the form of sitting overwrought oxygen are this electronic charge moving in this direction, but a corresponding electronic charge has to also move in the form of electronic charge has to also move in the form of electrons. So, this is in the form of ions and this is in the form of electrons and that is how the circuit is completed. So, there is no EMF generated, there is no is a very impressed EMF from outside so on its own the charge is getting transported through the material and the driving force is basically oxygen potential higher oxygen potential on the other side and lower oxygen potential on the other (( )) higher oxygen potential on one side and the lower oxygen potential on the other side. Now, one can imagine, what kind of reforming hydrocarbons can take place once again a taking example of CH<sub>4</sub> in hydro carbon, on this side hydrocarbon is pouring and once in comes in contact with this at the relatively

high-temperature there will be some catalyst may be required for high-temperature there will be some catalyst for its ionization and so on.

So, CH<sub>4</sub> will be reacting with the oxygen ion which is coming from the other side. This oxygen ion come and react this and forming a carbon monoxide and hydrogen. So, it is basically a dissociation of this in the or oxidation of this actually and oxidation of CH<sub>4</sub> conforming CO plus H<sub>2</sub> and releasing two electrons. Now, this electrons we will be transported back to the system t his system this will come to this and then combine with this and the on the other hand beside the reaction will be oxygen which is coming from a here. So, oxygen is flowing and oxygen is getting consumed by this reaction this electrons which is coming from the other side is ionizing this, the gas and becoming an oxygen ion. So, why this process it will continue so on one side is a hydrocarbon and other side there flow of air and automatically the product is a mixture of carbon monoxide and hydrogen. So, this is the reforming reaction, reforming reaction using this kind will mixed ionic electronic conductor.

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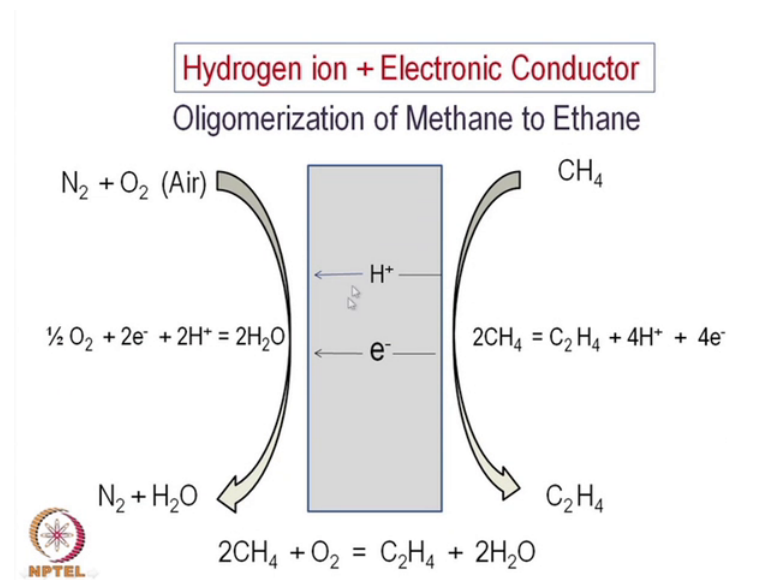
One can also get similar situations; this is a separation are not reforming reaction. In the reforming reaction we have already got the carbon monoxide and hydrogen and in this reactor we are getting separating will have a feat which is carbon monoxide and hydrogen. And then this material is hydrogen ion conductor and together with the electronic conductivity so you have a hydrogen ion conductivity as well as electronic



ion, unlike the previous one is the oxygen ion conductivity and electronic conductivity. Here the material is hydrogen ion conductor together with electronic conductor. So, both of them will move in the same direction because one is positive and the other is negative so both of them will move in the same direction. Here, carbon monoxide hydrogen will be separated out or ionized with H plus and two electron and this hydrogen will move to this.

So, here this electron Hydrogen this will be positive 2H minus but H plus and 2H plus and two electron will make in the hydrogen. (( )). So, 2H plus the two electron that will make H<sub>2</sub> so this hydrogen actually be available on the other side and carbon monoxide will go through. So, it can be we have taken carbon monoxide here but it can be mixture of carbon dioxide and hydrogen as well. So, to maintain the similarity we have kept this carbon monoxide and hydrogen syngas, but it can have carbon dioxide and hydrogen so carbon dioxide will come here and hydrogen will go on the side, so you can get hydrogen on the other side after reforming reaction of the hydrocarbon. So, by the process of 2 things this can be done the same chamber also and if you have reform gas can separated from this using a MIEC membrane the dense so far dense membrane.

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Well, there are using and hydrogen on conductor also one can make some kind of an oxidation reaction like this CH<sub>4</sub> in fact it is a what we call Oligomerization of methane to ethane. So, there taking oxygen on this side one can CH<sub>4</sub>, can be converted to C<sub>2</sub>H<sub>4</sub>

by this reaction the same processes is same CH<sub>4</sub> plus, 2CH<sub>4</sub> becomes C<sub>2</sub>H<sub>4</sub> plus 4 hydrogen and becomes four electrons here. These four electrons goes there and hydrogen also goes the same direction and it combines they are with H<sub>2</sub>O formation with air taking oxygen on the nitrogen and oxygen and ultimately and nitrogen and H<sub>2</sub>O. So, this kind of membrane is our membrane reactors can be used for making different chemical reactions particularly the gases phase. And the both mixed oxides either hydrogen electron or oxygen electron can be used for this kind of carrying out such kind of reactions elevated temperature.

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### Materials for the Oxygen Separation

- Materials of Current Interest :  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$
- New Materials :  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ,  $\text{CeO}_2\text{-LaCrO}_3$ , etc.

**Advantages:**

- High selectivity of oxygen under very low pressure ( $\sim 10^{-3}$  bar), operates under very high partial pressure gradient

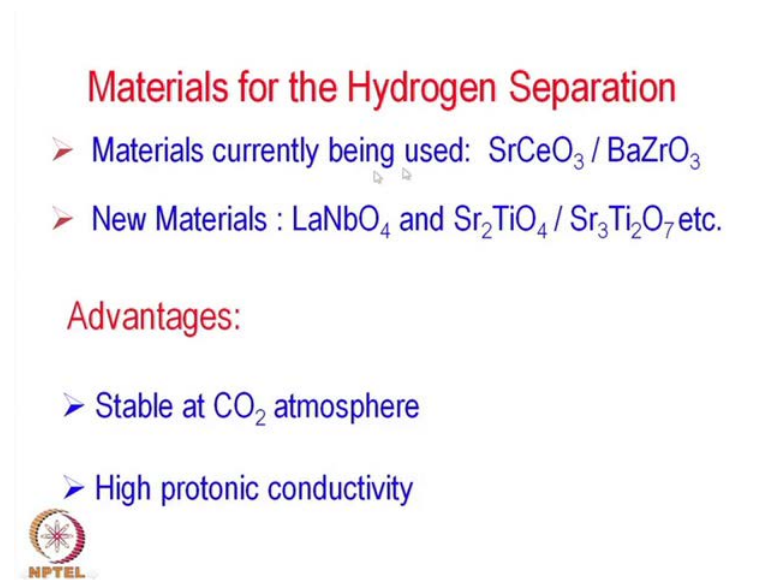
High yield for oxygen collection

The actual materials we have seen that some of them are oxygen ion conduct are together the electron conductor and the others are hydrogen ion conductors together electronic conductor. The materials actual materials which have been found or shown such properties materials of current interest is this one then that few others, but this is one of them important one out of them it is lanthanum strontium iron cobalt, cobalt ferrite actually. So, this is actually a l s c f one can say. Lanthanum strontium, say again it perovskite structure basically distorted kind of perovskite structure and you have a this, compound and this is what you call the oxygen for oxygen separation oxygen ion plus electronic conductivity some the new materials are also being researched on that the lanthanum strontium gallium ferrite cobalt use gallium or even CO<sub>2</sub> lanthanum Chromite. Lanthanum Chromite you have come across as a interconnect material and CO<sub>2</sub> a mixture basically composite of CO<sub>2</sub> and lanthanum chromite, that can also be

used for this purposes. The advantage is of this kind of material a high selectivity of oxygen under very low pressure 10 to the power minus 3 bar.

Basically, it is the partial pressure of oxygen which is the driving force either the partial pressure oxygen or partial pressure hydrogen that is the basic driving force to make the reaction happen in one direction operates under very high partial pressure gradient. So, even under very high, partial pressure gradient they do not change the structure so they do not change their properties also high yield off oxygen collection, so one can and then separate oxygen by this process.

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**Materials for the Hydrogen Separation**

- Materials currently being used:  $\text{SrCeO}_3$  /  $\text{BaZrO}_3$
- New Materials :  $\text{LaNbO}_4$  and  $\text{Sr}_2\text{TiO}_4$  /  $\text{Sr}_3\text{Ti}_2\text{O}_7$  etc.

**Advantages:**

- Stable at  $\text{CO}_2$  atmosphere
- High protonic conductivity



Materials for the hydrogen separation is like this, strontium once again a perovskite compound having proton conductivity. What is called the hydrogen separation basically proton conductor hydrogen ion conductor that was oxygen ion conductor. Barium zirconate another compound and few other related new materials are being researched on is lanthanum magnet strontium titanate and strontium titanium oxide is also another form strontium titanate of different a molecular is here. Advantages again, similar things stable at carbon dioxide atmosphere and high proton conductivity. So, some of the oxides you can see who also have proton conductivity and not only oxygen ion conductivity one can have hydrogen and conductivity in such materials

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### Properties of Selected H<sub>2</sub> Separation membranes

	Membrane Types				
	Dense Polymer	Micro-porous Ceramic	Dense Metallic	Porous Carbon	Dense Ceramics
Temp. Range	< 373 K	473 - 873 K	573 - 873 K	773 - 1173 K	873 - 1173 K
H <sub>2</sub> Selectivity	low	5 - 139	>1000	4 - 20	>1000
Materials	polymers	silica, alumina, zirconia, titania, zeolites	palladium and its alloys	carbon	Proton Conducting ceramics



While these are some of the comparison of some of the membranes hydrogen particularly for hydrogen separation and we have dense polymer membrane that is a proton conductivity. So, we have seen liking these are operated to low-temperature however the selectivity hydrogen and selectivity low and these are polymer materials basically dense polymers micro porous ceramics a these are a well there are will discuss will discuss separately polymer micro porous ceramics and what are the porous membranes, inorganic membranes are ceramic membranes. They have in addition to the gas separation they have many many other applications have different lectures separate lecture from them.

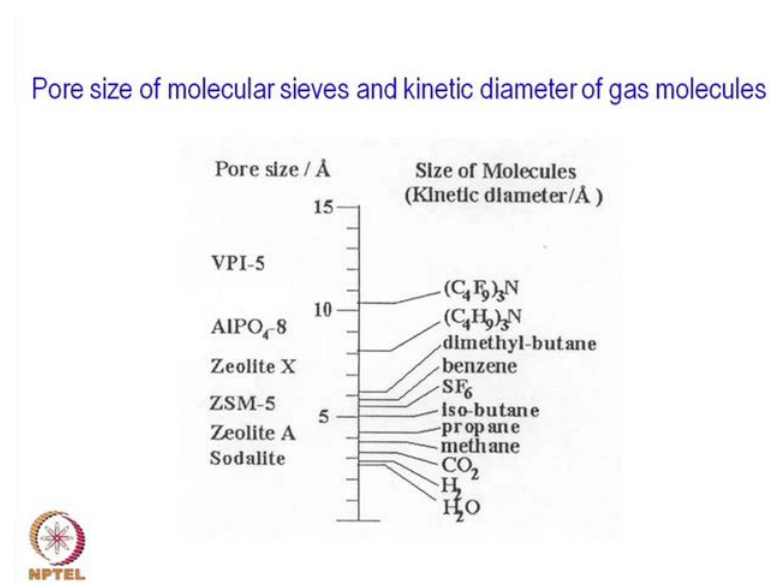
So, micro porous ceramics is another group, then dense metallic material palladium and this is also dense material these can be used for hydrogen separation may be we will discuss separately not they are not start mixed ion conductors. But some of these are palladium and its alloys actually can absorb lot of hydrogen and that is how they can separate hydrogen from a mixture of hydrogen and carbon dioxide, carbon monoxide synthetic gas as so this is a useful material, but the mechanism of separation is a little different and you can see the selectivity is very high more than 1000.

So, the ratio the ratio is more than 1000 how much is retained and how much goes to the other side and porous carbon can also be used were the selectivity is again very low, but it can be used at a very high-temperature. What we have discussed so far is actually the

proton ion conducting ceramics and you can see compared to others are the selectivity of or the separation efficiency is extremely high once again it is comparable to the dense metallic membranes metallic membranes of palladium. As you can see, palladium is quite costly material compared to that these are quite cheaper material and one can have more or less are comparable selectivity in this kind of membranes and they can also operate a fairly high-temperature.

So, these are some the comparisons of membranes particularly for hydrogen separation.

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Well in the last slide in this is that, basically it is not be dense membrane only which can be used for hydrogen separation, but there are a porous membranes. Porous membranes again high-temperature membranes can also be used for hydrogen separation we have in an earlier slide we have talked about the micro porous ceramic membranes here the micro porous these are all dense membrane is made of a polymer made of metal this is porous carbon membrane and this is dense ceramic membrane.

So, we have already discuss them dense membrane are a polymer membrane so discussing other some other context metallic membrane we have not been discussed. We did not discuss what is a is just mentioned that can be used in a different way because palladium has a lot of adsorption property. Now, of towards hydrogen these are to one is porous carbon and micro porous ceramics, can also be used for hydrogen separation and you can see here it is a this zealites, the zealites they are made off for they can be made

of silica alumina zirconium not all for hydrogen separation they can be used for many different other purposes. But particularly, this is zeolites made up zeolites can be used for or hydrogen separation how that is given in the next slide because it controls the pore sizes the molecular sieves and the kinetic diameter of gas molecules that what is compared here are these are the pore sizes dimensions in the pore sizes are in the any in units of angstrom.

So, is 5 angstrom 10 angstrom and 15 angstrom and on this side there are different compounds ceramic compounds and most of them are zeolites not zeolites have basically silicates different kind of silicates and a they are structures is very interesting some kind of a molecular passage molecular hole through which some of these oxides some of these species can pass through. So, these are not a the porous are not made out of the agglomeration of the powders as we know ceramics porous materials are basically prepared from basically powders when these powders gets consolidated you have always some porous generate these are is basically physical force. Now, zeolites also have some pores, but in a different structure different scale they are crystallographic pores in the atoms of these your zeolites or the iron in the zeolites in such a manner that are crystallographic passages crystallographic tunnels.

So, these tunnels a good enough that is through and through trans and so these are generated not because of the agglomeration of the powders or consolidation of the powders, but because of the crystallographic arrangement of the atoms the atoms are arranged in such a way there are some crystal variety and these tunnels sizes you for depending on the particular composition.

So, these are different kind of compositions and the different kind of structure as where the tunnel size is different and it starts from as you can see here about 2.5 angstrom and one can go up to ten angstrom. So, for example, aluminum phosphate as about a very high are more than the close to ten angstrom zeolite x these are some are some standard take some standard compositions which is been a categorized named as zeolite ZSM 5. Zeolite a sodalite all of them are zeolites of different compositions and difference slightly different structures and therefore, they have different pore sizes or crystallographic pore sizes or tunnels sizes. And the on this other side on the right hand side you have the kinetic diameter of some of the gases molecules there are water molecule is here then you have H<sub>2</sub>CO<sub>2</sub>, methane propane isobutene and the SF<sub>6</sub> benzene

and so on depending on that particular composition of these on the particular molecules they have different kind in diameter of molecules so they also carry to some extent.

So, each you have a particular for example, so dealite the sodalite the tunnel size crystallographic tunnel sizes somewhere here in between hydrogen and carbon dioxide just very closely are precisely below are the carbon dioxide and just about the H<sub>2</sub>O. So, if you can make synthesize your zeolite like sodalite, then you can actually detain hydrogen. Because this diameter is more than that of hydrogen so you can pass through hydrogen and retain carbon dioxide.

So, that is also one of the principles by which using the pore size very definite pore size of the crystallographic structure as a one can separate hydrogen from carbon dioxide. So, such membranes are also being developed and it is being tried out in different do a research lab throughout the world that the membranes of this kind the molecular based on molecular sieves. Of course your zeolite have been used as a molecular sieves for a long time for adsorption of different gases and catalysis catalyst carrier since one. So, zeolites being used synthesised many of different kind of zeolites have been used in context of the catalysts that is the reason and they have been given different kind of name's and depending on the particular characteristics.

So, what we are interested here is a find out the pore sizes a particular zeolite whose pore size is slightly larger than carbon larger then hydrogen and smaller than CO<sub>2</sub> or so if one can use them just by a molecular diffusion molecular diffusion not by ionic diffusion. Earlier, what will discuss the ionic diffusion your we are talking about the molecular diffusion by the process one can actually separate out hydrogen and carbon dioxide. So, this is another technique by using porous and this, so we have discussed both the dense membrane is value have mixed ionic an electronic conductivity and then porous membranes by controlling the crystal structure can maintain a particular pore size a very definite pore size which is in between hydrogen and carbon mono carbon dioxide on can the separate them out.

So, first of all you have to have basically and what we are talking about is first to fall to try to get a mixture of gases hydrogen and carbon dioxide from hydrocarbon is available hydrocarbons and then separate hydrogen and carbon dioxide so carbon dioxide. Of course should not be released to the atmosphere so that it does not increase the pollution,

but the hydrogen can be used for as if you fuel to generate electricity or other forms of energy.

So, this is the basic philosophy on which sound the advance ceramic materials are also be used materials are also being used in the area energy technology. So, to conclude we have a earlier discussed the fuel cell in the domain of energy technology were hydrogen is one of the basic fuels but then since hydrogen is not available. Naturally, will have generate hydrogen by some means and one of the ways is to is a source of the hydrocarbon which can be reformed prepared is synthetic gas and then generate hydrogen and other. Of course, is to use renewable energy and electrolytes water, those are almost of these processors still not, commercial being tried out, but experimentally the technologies getting developed.

So, that solve where as the energy technology and the application of advance materials advance are ceramics in the sector of in the energy sector is concerned.