Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 26
Different Types of Electrolyzer Technologies

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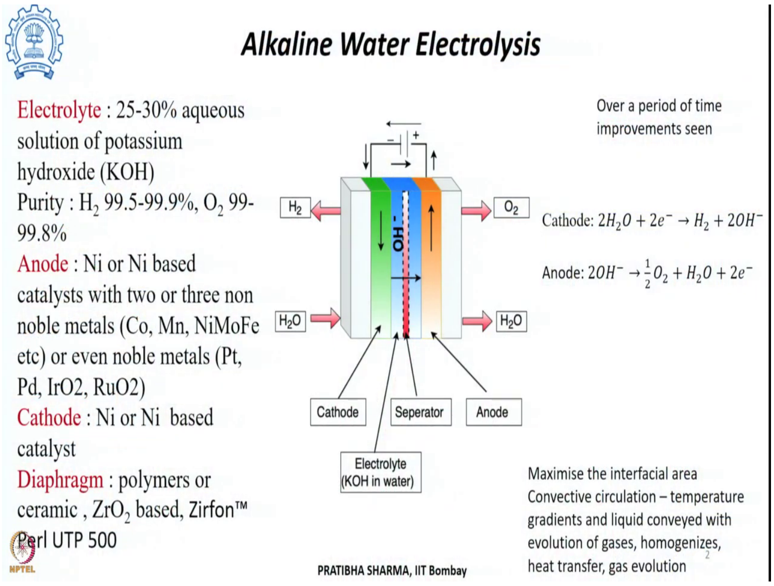

In this class we will see the four different electrolysis technologies. So, the first one is alkaline water electrolys.is this alkaline water electrolysis is a mature technology and it is most widely used global technology for producing hydrogen by means of electrolysis. This is a safe method, this is reliable and it is less expensive compared to the acidic electrolysis, it involves lower cost materials components as compared to the PEM electrolysis.

Now, this alkaline water electrolysis this was used as early as 1920s and at that time this was the technique to produce hydrogen in various chemical and fertilizer industries. There were several plants of capacity as high as 165 megawatt at that time and these plants were located close to the hydroelectric power plants to supply the required electrical energy for the process.

These plants were located in India, Canada, Norway then Egypt and there were several other countries when such large scale electrolysis units were commissioned. But these all got like the interest went away or and these were decommissioned in 1970, when the more efficient, more cost effective method steam methane reforming that came into picture.

So, the first method of electrolysis or the first technology for water electrolysis that we will study is the alkaline water electrolyzer, this electrolysis has seen large advancements, several advancements, several improvements over a period of time. And these improvements have been like in terms of increased current density which reduces the CAPEX the capital expenditure.

And then it has also seen like improvement in terms of the efficiency which results into like the reduction in the operating expenditure so OPEX price. There have been improvement in terms of the materials, the diaphragm material, the electro catalyst which have been used, the cell configuration which has been used.

So, as such the process is where we have an electrochemical cell and an alkaline electrolyte. Now, if you look at the cell there are two electrodes a separator and then current collectors. So, water is fed onto the cathode side, where it forms hydrogen, the hydrogen gas is evolved and hydroxyl ions are produced on the cathode side.

Now, these hydroxyl ions which are produced onto the cathode side, they migrate through the separator or diaphragm and then they reach on to the anode side. Now, at the anode side these hydroxyl ions recombine to produce oxygen, water and two electrons are liberated. So, this oxygen is evolved in the process, the two electrons which are liberated pass through the external circuit making the electrical circuit complete and this is how the alkaline water electrolysis reaction takes place.

Now, the electrolyte used in the electrolysis is 25 to 30 percent of aqueous solution of potassium hydroxide and the purity of hydrogen which we can achieve in the process is 99.5 percent to 99.9 percent. The oxygen purity which we can achieve is 99 percent to 99.8 percent. In the alkaline water electrolysis since the electrolyte which is used it is less corrosive, than the acidic electrolysis therefore we can use non noble metals.

So, the anode is typically nickel or nickel based material with electro catalyst, this could be 2 or 3 non noble metals. It could be cobalt manganese, nickel, molybdenum, iron or even noble metals can also be used like platinum, palladium, iridium oxide, ruthenium oxide. The cathode side is having nickel or nickel based catalyst and the separator or the diaphragm this is generally Zirfon, ZrO2 based, Zirfon Perl UTP 500. It can also be polymer or ceramic based as well.

Now, in this process, since the electrochemical reactions are taking place at the interface as such, the interfacial area between the electrode and electrolyte needs to be maximized and this can be maximized by having a like increased surface area and as such porous electrodes with several perforations are being used in the electrolysis process.

A convective circulation is established in the process and this arises because of the temperature gradient and the liquid which is conveyed with the evolution of the gases. So, as the gases are evolved because of the convection in the liquid, this is a liquid electrolyte that is used in the process.

So, this results into many benefits, this convective circulation. However, this is natural circulation it is dominant at the lower current density. This advantage of this convective circulation is that, it not only homogenizes the electro active species, the reactants, the products being formed are evolved out. So, it helps in evaluation of the gases, it helps in better heat transfer in the process.

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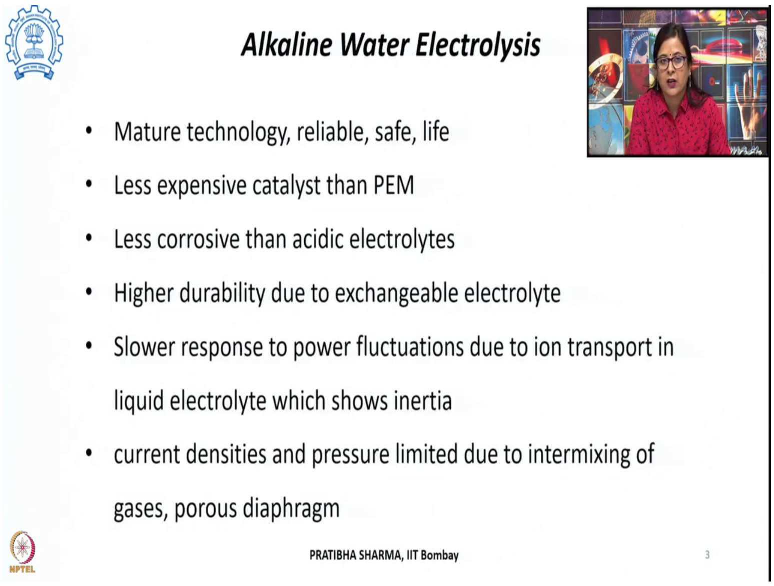

Now, if we look at the alkaline water electrolysis, this is as I mentioned that it is a mature technology, it is quite reliable and safe it is having a high life. So, the recently reported one it is like it can be of 30 years as well.

Since the electrolyte used is less corrosive than the acidic electrolyte, we can use less expensive catalyst in the process of alkaline water electrolysis as compared to the polymer electrolyte membrane electrolysis. Since, it is a liquid electrolyte it could be exchangeable as such the durability of the electrolyte of the process of the cell is higher.

But since the in the process hydroxyl ions are transported across the separator, the process has a slower response towards the power fluctuations. This is because the ion transport occurs in a liquid electrolyte and these ions they show a little inertia and as such as the power fluctuates the response change in the electrochemical reaction is comparatively slower. And the current densities and pressure, these are here limited due to the inter mixing of gases.

So, there is a porous diaphragm in the process, as such it cannot operate at a higher current densities or a higher pressure. Because at those conditions there will be an intermixing of the gas, resulting into the crossover of the gaseous products.

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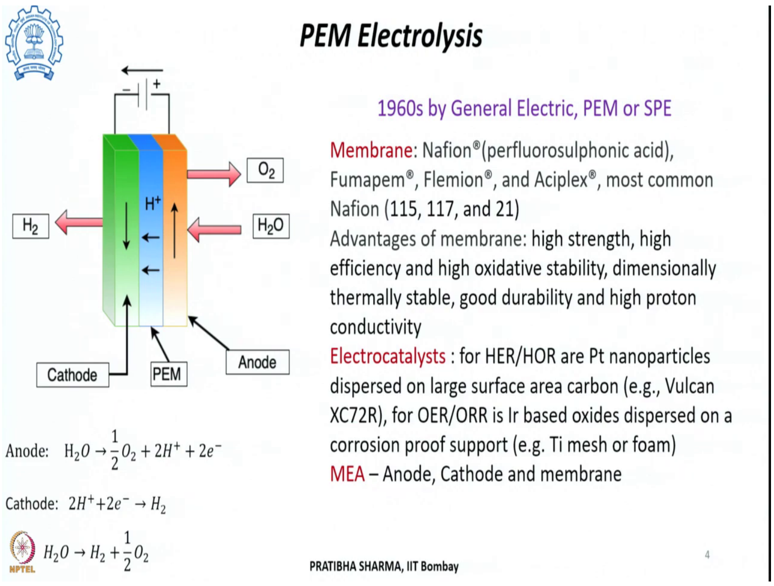

Now, the second electrolysis technology is the polymer electrolyte membrane or proton exchange membrane or solid polymer electrolysis process. This technique for water electrolysis, this was first commissioned by general electric in 1960s, although the membrane based technology were used earlier in 1950s as well, but for first electrolysis process was demonstrated by general electric.

Now, the process is we have a membrane, which is polymeric membrane and it allows selectively ions to flow through it. On the anode side the reaction is that it produces 1/2 O_2 + 2 H^+ + $2e^-$. So, the oxygen gas is evolved on the anode side, there are hydrated protons ions which are produced on the anode side and two electrons these are liberated.

So, the electrons follow the external circuit and ions they permeate through membrane, when they reach on to the cathode side the proton they undergo a reduction and reduce hydrogen. So, on the cathode side hydrogen gas is evolved. The overall reaction that takes place is water splitting into hydrogen and oxygen the component gases.

In a typical polymer electrolyte membrane the most commonly used membrane is Nafion, which is a perfluorosulphonic acid membrane. The other options are Fumapem, Flemion, Aciplex, but the most commonly used one is the Nafion membrane and this particular membrane has several advantages.

These advantages are it has a high strength, it has high efficiency, it results into high oxidative stability, it is thermally stable, good durability, it has a higher proton conductivity. Now, on to both the sides of the membrane, there are electro catalysts present for the hydrogen evaluation reaction and the oxygen evaluation reaction. So, the electro catalysts which are used for hydrogen evaluation reaction or hydrogen oxidation reaction onto the cathode side, these are platinum nanoparticles or platinum which is dispersed on large surface area carbon.

Example like the carbon is Vulcan XC72R, on the other side the anode side for the oxygen evaluation reaction or the oxygen reduction reaction, the electro catalyst is Iridium based. So, the Iridium based oxides are dispersed onto a corrosion proof support which is generally titanium mesh or foam.

Since the medium of the electrolysis is acidic in nature as such, there is a demand in terms of materials. The materials which are used are either titanium based or noble metals. So, this method of electrolysis is more expensive compared to the alkaline water electrolysis. This anode, cathode and membrane they are integrated together to form a unit which is known as membrane electrode assembly.

So, all the three, anode, cathode and membrane they make together the unit which is known as membrane electrode assembly.

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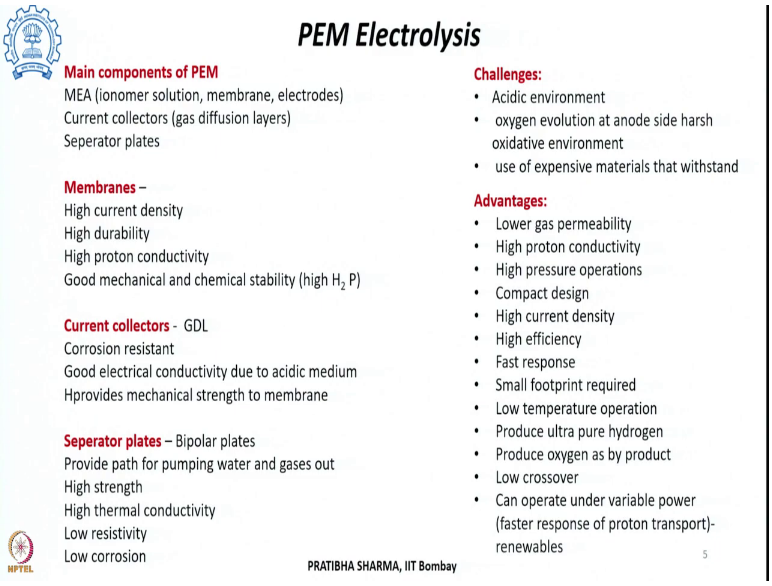

Now, the major components of the PEM electrolysis, Polymer Electrolyte Membrane electrolysis are: this membrane electrode assembly which is the ionomer solution membrane and the two electrodes, the current collectors which is the GDL, Gas Diffusion Layer and the separator plates are the bipolar plates.

Now, the membranes are such that they have high current density, they have high durability, good proton conductivity, they should be mechanically and chemically stable. And this is because of the component membrane electrode assembly and its structural integrity, mechanical stability that the two compartments, the hydrogen evolution side or the cathode side and anode side they can work at differential pressures.

So, the hydrogen has evolved at a higher pressure. This could be 70 bar or 80 bar as against the oxygen evolution side or the anode side, where the oxygen is at the ambient pressure. So, high differential pressure could be achieved at the same time because of the mechanical integrity, the chemical stability, crossover is less intermixing of the product gases is much less in case of PEM electrolysis.

The another component is current collector or the gas diffusion layer, this gas diffusion layer need to be corrosion resistant, it should have good electrical conductivity and this is because of the acidic media also it is having a good electrical conductivity. It should provide high mechanical strength to the membrane.

There are separator plates or the bipolar plates and these bipolar plates provide path for pumping water as well as the gases to come out from the electrolytic cell. It should have a high strength, high thermal conductivity, low resistivity and low levels of corrosion. So, these are the requirement or expectations from the bipolar plate.

Now, in PEM electrolysis, although there are several advantages, but there are several challenges also. Since the electrolyte involved is acidic and the electrolysis is carried out in an acidic media, there is a harsh environment that the materials have to face.

So, the materials requirement is they should be able to withstand these harsh oxidative environment, acidic environment and as such more expensive materials are required for the electrolysis to be carried out. As against that there are certain advantages also of the process, it has a low gas permeability.

So, less crossover, it has a high proton conductivity. We can get high pressure hydrogen from it, so it can enable high pressure operations because of the stability of the MEA, there it can operate at a differential pressure. And as such these type of electrolyzer can be used at places, where they can give hydrogen at a higher pressure and the additional compression unit for compressing can be avoided at places like it can be used at a refuelling station, it can be used for at places where high purity hydrogen is required, but at a higher pressure as well.

These units are more compact, they can provide high current density, PEM has a high efficiency at the same time it has a faster response. So, any power fluctuations, the response to the power fluctuations is very fast because the transport of charge carriers is much faster. It has a smaller footprint requirement, it has a low temperature operation, the hydrogen produced is ultra-pure in this case 99.999 percent purity of hydrogen we can get. At the same time we are getting oxygen as a by product, which can be used for various medicinal applications.

There is a low crossover which is observed and it can operate under variable power requirement. So, as if there is a power fluctuation, then the response to the proton transport is much faster, the proton transport we know that it is 3 times faster than the hydroxyl ion transport, as such it can operate under variable power. And as such this has the favourable characteristic to be integrated with the renewables, where the renewables intermittency can be matched using the PEM electrolysis unit.

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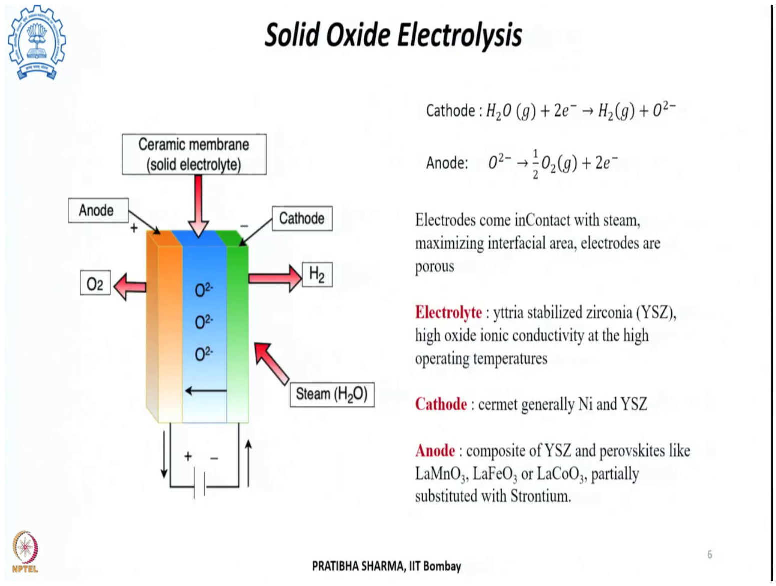

The third technology for electrolysis is solid oxide electrolysis, this is an advanced electrolysis technique which is steam electrolysis where in the electrochemical reaction takes place at a higher temperature. So, it could be 700 to 1000 degree centigrade and the water is in its vapor form. So, it steam electrolysis and the energy which is required to produce steam or to take water from the liquid state to vapor state can be supplied by means of either a waste heat or by means of nuclear or by means of a solar thermal plant.

Now, the basic reactions that occurs in a solid oxide electrolysis are, on the cathode side the steam undergoes reaction such that it produces hydrogen and hydrogen gas is evolved onto the cathode side, with oxide ions produced which migrate across the solid electrolyte. So, as the name itself suggests, the solid oxide electrolysis the electrolyte used is a solid oxide or an oxygen permeable membrane which allows the oxide ions to flow from the cathode side to the anode side.

Now, as these oxide ions migrate from the cathode towards anode, they recombine to form oxygen. So, the oxygen is evolved onto the anode side and producing or liberating two electrons. These electrons again flow through the external circuit and ions they flow through the internal inside the electrolytic cell.

Now, these electrodes since they come in contact with steam, it has to be a reaction such that the electrochemical reaction needs to be faster and that can be done by maximizing the inter facial area between the electrode and the electrolyte. The electrodes, these electrodes which are used these are porous so as to have a higher interfacial area. The electrolyte generally used is yttria stabilized zirconia and this is a high oxide ionic conductivity at higher operating temperatures, which are there in the solid oxide electrolysis.

The cathode used is a cermet generally nickel and yttria stabilized zirconia. The anode used is a composite of yttria stabilize zirconia and perovskites, various perovskites like LaMnO3, LaFeO3 or LaCoO3 and these could be partially substituted with strontium.

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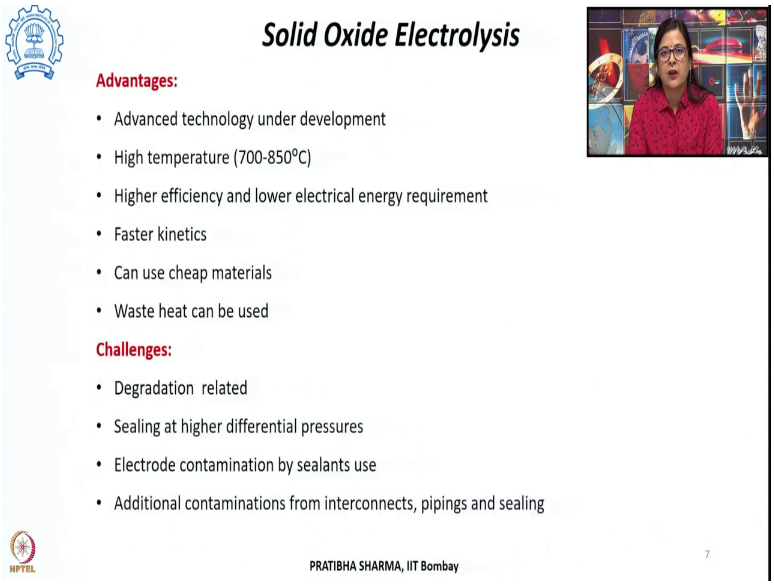

So, the solid oxide electrolysis this is a high temperature electrolysis or a steam electrolysis which takes place at a higher temperature, this is an advanced technology still under development. So, very small capacity demonstrations have been there, it is having a high efficiency. The reason being the required temperature, as we have seen in the earlier classes that total required energy for the electrolysis to take place can come from electrical energy and from thermal energy input.

If the energy which is provided by means of thermal energy input, it increases the required electrical energy input reduces, as such the efficiency of the process is higher with a lower electrical energy requirement. Since the temperature of operations are higher as such the reaction kinetics are much faster under these operating set of conditions.

The medium here is not very corrosive as such we can use cheap materials, non noble metals and even the required temperature can be provided by means of waste heat through different processes. But the major challenges which are faced in solid oxide electrolysis is at such high temperature there are degradation related issues, they are issues related with the sealing at higher differential pressure, there are problems associated with the contamination from the sealant at such high temperature, there are additional contamination issues that arises from the interconnects, from the piping from the sealing.

So, there are these challenges needs to be addressed so that this can be taken up to the commercial scale. Now, a more recent, the latest technology of electrolysis is anion exchange membrane electrolysis, this is a technique which uses the advantages of both PEM as well as alkaline water electrolysis.

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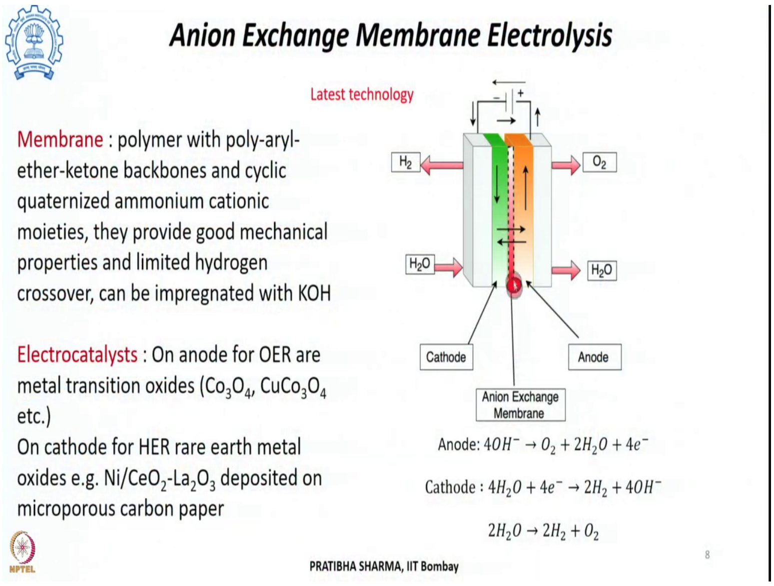

And in the process of this electrolysis, again this is a membrane based method, but it allows anion exchange across the membrane.

So, the reaction that takes place, on the cathode side water is being fed such that it forms hydrogen and hydroxyl ions in this case. So, this membrane is permeable towards hydroxyl ions, on the cathode side the hydrogen is being evolved and the hydroxyl ion which are produced they migrate through anion exchange membrane onto the anode side.

On the anode side these hydroxyl ions combine together to form oxygen which is evolved producing water and electron. So, this electron they again pass through the external circuit.

So, these are the reactions taking place on the anode and cathode side and the overall reaction is water splitting into hydrogen and oxygen its constituents.

This membrane which is anion exchange membrane, allowing hydroxyl ions to pass through it, this is usually a polymer with poly aryl ether ketone backbone and cyclic quaternized ammonium cationic moieties. This type of membrane it provides good mechanical properties and limited hydrogen crossover. There is a problem associated with the ionic conductivity; however, that can be improved by impregnation with KOH, but that also affects its durability.

The various electro catalysts which can be used for an anion exchange membrane electrolysis, like on the anode side for the oxygen evaluation reaction these are transition metal oxide, like CO3O4, CuCo3O4. On the cathode side, for the hydrogen evaluation reaction rare earth metals could be used, their oxides can be used like nickel, cerium oxide, lanthanum oxide deposited on a microporous carbon paper.

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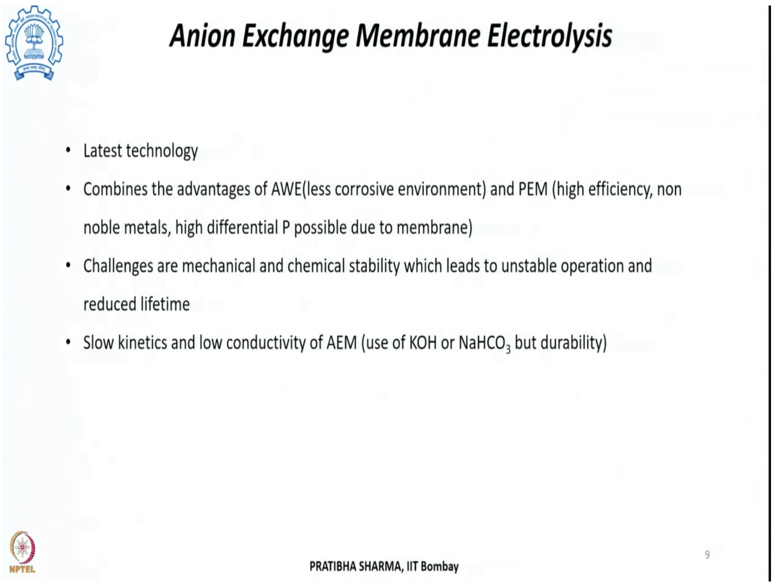

Now, this is the most recent technology, the latest technology and as I mentioned it combines the advantages of both alkaline water electrolysis, the advantage that it has a less corrosive environment.

Wherein the electrolyte used or the membrane used is a hydroxyl ion permeable membrane, the environment used is less corrosive compared to the PEM and it has combined advantage of PEM of having high efficiency, use of non noble metals because of the less corrosive environment. Because of the use of membrane even we can achieve high differential pressures. So, high hydrogen pressure as against the ambient oxygen pressure.

But then there are challenges towards its commercialization, these challenges are in terms of the mechanical and chemical stability, which can lead to unstable operation and reduced lifetime. At the same time there is a problem associated with the slow kinetics and low conductivity of the anion exchange membrane and this the low conductivity can be considered by adding KOH or $NaHCO_3$, but then that affects its durability.

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Comparison of different electrolyser technologies

Sr. No.	Characteristics	Alkaline electrolyser	PEM electrolyser	SOEC electrolyser
1.	Electrical efficiency (% LHV)	63 – 70	56 – 60	74 – 81
2.	Operating pressure (bar)	1 – 30	30 – 80	1
3.	Operating temperature (°C)	60 – 80	50 – 80	650 – 1000
4.	Stack lifetime (operating hours)	60,000 – 90,000	30,000 – 90,000	10,000 – 30,000
5.	Load range (%, relative to nominal load)	10 – 110	0 – 160	20 – 100
6.	Plant footprint (m^2/kWe)	0.095	0.048	-
7.	CAPEX (USD/kWe)	500 – 1,400	1,100 – 1,800	2,800 – 5,600

Ref. : IEA report, 2019

Now, to compare all the three major technologies, alkaline water electrolysis, PEM electrolysis and solid oxide electrolysis in terms of the various parameters we can see that the electrical efficiency in terms of the percentage lower heating value for alkaline water electrolysis, this lies in the range of 63 to 70. For PEM this is 56 to 60; however, for solid oxide electrolysis this is higher because this is a high temperature electrolysis and a part of the required energy come from the thermal energy input. So, the efficiency is 74 to 81 percent.

The operating pressure which can be achieved in an alkaline electrolyzer is 1 to 30 bar; however, it is much higher in PEM electrolyzer, which is 30 to 80 bar and this is because of the compact MEA being present which allows high differential pressure or hydrogen pressure; however, in SOEC this is 1 bar.

The operating temperature for alkaline water electrolysis is between 60 to 80, for PEM it is 50 to 80; however, solid oxide electrolysis occurs at a higher temperature 650 degree to 1000 degree centigrade. The stack lifetime or the number of operating hours for alkaline water electrolysis this is higher, 60000 to 90000 hours of operation. For PEM this is 30000 to 90000 hours. For solid oxide because of the materials degradation, this is somewhere between 10000 to 30000 hours.

The load range in which it can be operated, that the percentage relative to the nominal load. So, it can operate at a lower load, at the same time higher load. So, 10 to 110 percent. However, PEM electrolysers they have a broad range, wherein they can operate between 0 to 160 percent of the load. They are faster in response, they can be easily integrated with the renewables, they can adapt with the load variations.

For SOEC, this lies in the range of 20 percent to 100 percent, the plant footprint which is required in meter square per kilowatt of electric is 0.095 for alkaline, but it is smaller for PEM because these are compact. So, it is 0.048 for PEM electrolysis. So, the CAPEX cost this we will see in more detail in the later classes.

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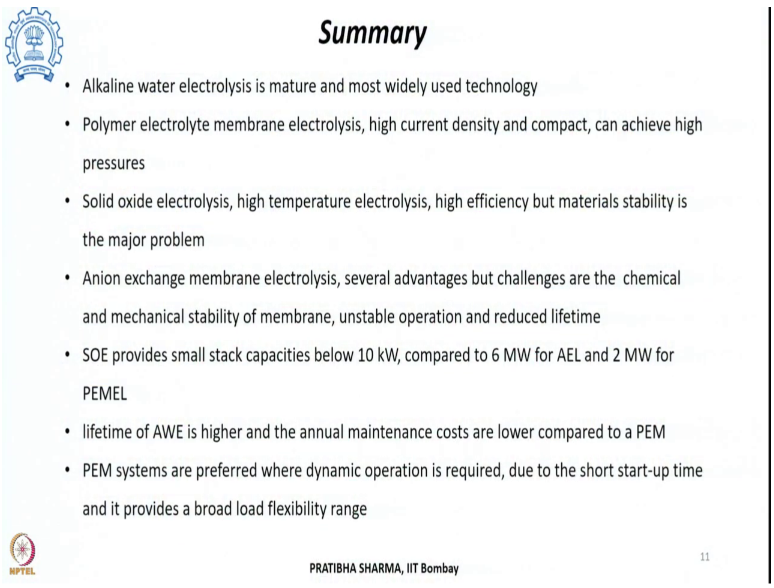

To summarize this part, we have seen the various electrolysis technologies which are there. Among them the alkaline water electrolysis is the most widely used and mature technology, the polymer electrolyte membrane electrolysis it provides high current density it is compact and we can achieve higher pressures with polymer electrolyte membrane based technology.

With solid oxide electrolysis, this is a high temperature electrolysis this provides higher efficiency, but then there are issues related to the material stability at that high temperatures.

There is a recent technology which is anion exchange membrane electrolysis, this has several advantages, but then at the same time there are challenges associated with it which are in terms of chemical and mechanical stability of membrane, unstable operation and reduced lifetime.

Now, the stack capacities for SOE, which has been demonstrated is about 10 kilowatt compared to about 6 megawatts for alkaline electrolysis, 2 megawatt for PEM electrolysis. The lifetime of alkaline water electrolysis is higher and it has an annual maintenance cost which is much lower compared to the PEM electrolysis.

The conditions inside alkaline water electrolysis being non corrosive and there are less expensive materials being used. So, it is alkaline water electrolysis is less expensive compared to the PEM electrolysis. The PEM electrolysis; however, these systems are preferred when the requirement is that of a dynamic operation.

So, they change or they adapt to the load variation very fast. So, where there is a dynamic operation required, we can use PEM electrolysis systems. Where there is a short start-up time at that point, it can provide a broad load flexibility. So, there the PEM electrolysis setups will be more suitable.

Thank you.