Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 24

Fundamental of Electrolysis of Water

In this class we will see the different components involved in electrochemical cell and what are the different barriers to the electrochemical reaction which occurs in the electrolysis process. What are the different components, their requirements and how do they impact.

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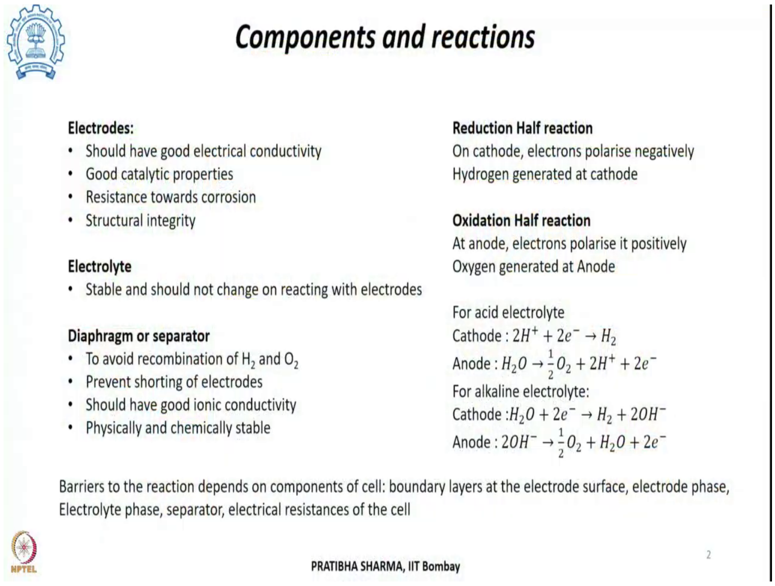

Components and reactions

Electrodes:

- Should have good electrical conductivity
- Good catalytic properties
- Resistance towards corrosion
- Structural integrity

Electrolyte

- Stable and should not change on reacting with electrodes

Diaphragm or separator

- To avoid recombination of H_2 and O_2
- Prevent shorting of electrodes
- Should have good ionic conductivity
- Physically and chemically stable

Reduction Half reaction

On cathode, electrons polarise negatively
Hydrogen generated at cathode

Oxidation Half reaction

At anode, electrons polarise it positively
Oxygen generated at Anode

For acid electrolyte
Cathode : $2H^+ + 2e^- \rightarrow H_2$
Anode : $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
For alkaline electrolyte:
Cathode : $H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Anode : $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Barriers to the reaction depends on components of cell: boundary layers at the electrode surface, electrode phase, Electrolyte phase, separator, electrical resistances of the cell

So, if we look at the different components then there is an electrode, electrolyte and diaphragm and they need to satisfy certain requirements in the electrolytic cell. If you look at the barriers to the reaction which occurs in the electrolytic cell, that all depends upon the different components of the cell. Now these barriers could be, there could be boundary layers being formed at the electrode surface, then the electrode phase, its characteristics, the characteristics of the electrolyte involved.

What kind of separator is being used, what are the different electrical resistances involved in the process. And, all these determine the behavior of current, I-V, efficiency and the amount of hydrogen being produced from a particular electrolytic cell.

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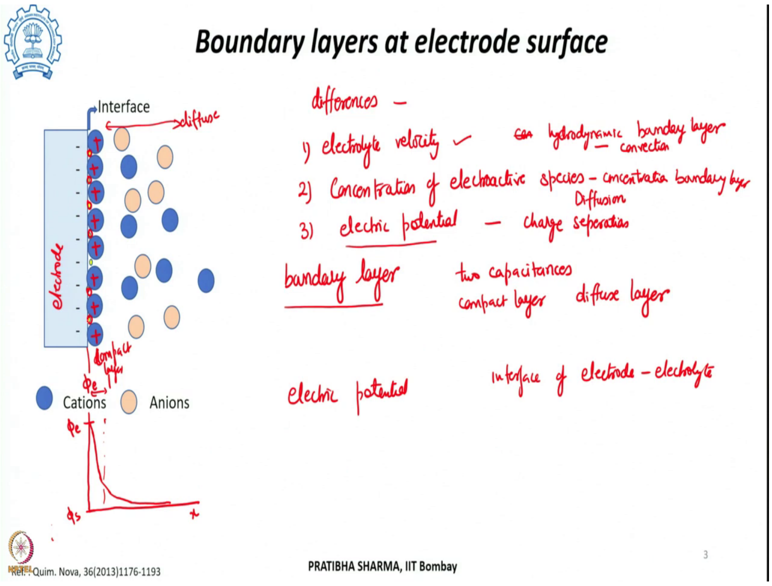

Boundary layers at electrode surface

differences –

1) electrolyte velocity ✓ ~~can~~ hydrodynamic boundary layer – convection
2) Concentration of electroactive species – concentration boundary layer Diffusion
3) electric potential – charge seperation

boundary layer two capacitances compact layer diffuse layer

electric potential interface of electrode – electrolyte

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Let us look at one by one each of these. Now, when we look at the electrode and an electrolyte interface so, this is the interface. At this interface there are differences occurring due to the surfaces. One is a solid surface, the another may be a liquid or a solid surface. There are differences in terms of the electrolyte velocity. There are difference because of the concentration of the active, electro active species. And, there are differences which are arising because of the electric potential from the surface of electrode to a certain distance from the electrode.

Now, each of these differences they give rise to a boundary layer at the interface. For example, let us consider the difference in the electric potential at this interface. Now, if we try to plot this as a model wherein we can see that if this is a negative electrode on the surface of it there are positive ions, they form a sort of compact layer. Let us say if at the surface the potential is ϕ_e, the electrode surface. This is a compact layer which is being formed.

And, the remaining there is a diffuse layer. So, which has ions distributed more than that in the electrolyte close to the electrode. So, because of that there is a variation in the potential. So, at the surface if it is ϕ_e and at the electrode surface in the solution if it is ϕ_s. So, in this compact layer it varies linearly and thereafter in the diffuse layer it varies exponentially. Because of the presence of this boundary layer, it acts as if there are two capacitances operating; one which is because of the compact layer and because of the diffuse layer.

And, similar to this boundary layer which is occurring because of the electric potential changes at the interface of electrode and electrolyte. Similarly, there are changes which are because of the electrolyte velocity, concentration boundary layer. Because, of the change in the concentration of electro active species or it could be because of the change in the velocity of electrolyte in the vicinity of the electrode surface and that could give rise to a hydrodynamic boundary layer.

Now, this concentration boundary layer, here the driving force is the diffusion. While, in case of electrolyte velocity, the charge separation is the driving force for the difference in the electric potential that occurs at the interface. However, when it is electrolyte velocity different giving rise to hydrodynamic boundary layer, the difference or the driving force is the convection in the process.

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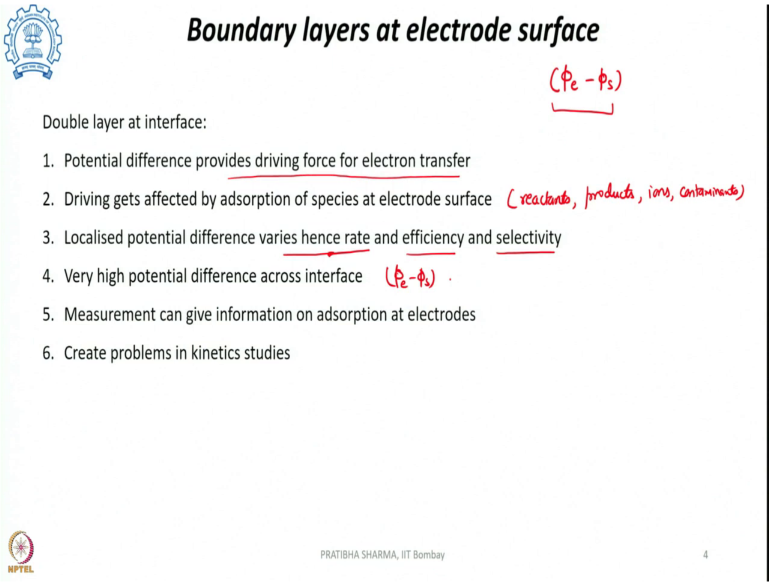

Boundary layers at electrode surface

$\underbrace{(\phi_e - \phi_s)}$

Double layer at interface:

1. Potential difference provides driving force for electron transfer
2. Driving gets affected by adsorption of species at electrode surface (reactants, products, ions, contaminants)
3. Localised potential difference varies hence rate and efficiency and selectivity
4. Very high potential difference across interface $(\phi_e - \phi_s)$.
5. Measurement can give information on adsorption at electrodes
6. Create problems in kinetics studies

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Now, when this difference in the potential ϕ_e minus ϕ_s is existing, that double layer at interface has several consequences. Now, this potential difference which is arising ϕ_e minus ϕ_s that provides the required driving force for the electron to transfer across the electrodes. And that driving force; however, gets affected because of the adsorption of different species at the electrode surface. Now these could be the reactants, these could be products, these could be the different ions, these could be contaminants involved in the process.

Like in the earlier figure we have shown that these are the solvent molecules which get adsorbed onto the electrode surface and that changes this potential difference in the process.

There could be, localized variations which occur because of the potential difference and that in fact, influences the rate of the reaction, the efficiency of the process as well as the selectivity towards hydrogen being produced.

At the same time this potential difference which is arising across the interface that can be very high. Like for example, if ϕ_e minus ϕ_s is equal to 2 volt over 0.2 nanometer, the potential gradient will be 10^{10} volt per meter. Such a high and localized driving force enables energetically difficult processes to be carried out electro chemically. The double layer capacitance measurement can provide information on adsorption at electrodes.

However, it tends to create problem in kinetic studies. Particularly, where high surface area electrodes are involved and when there is rapid potential changes with time due to charging currents.

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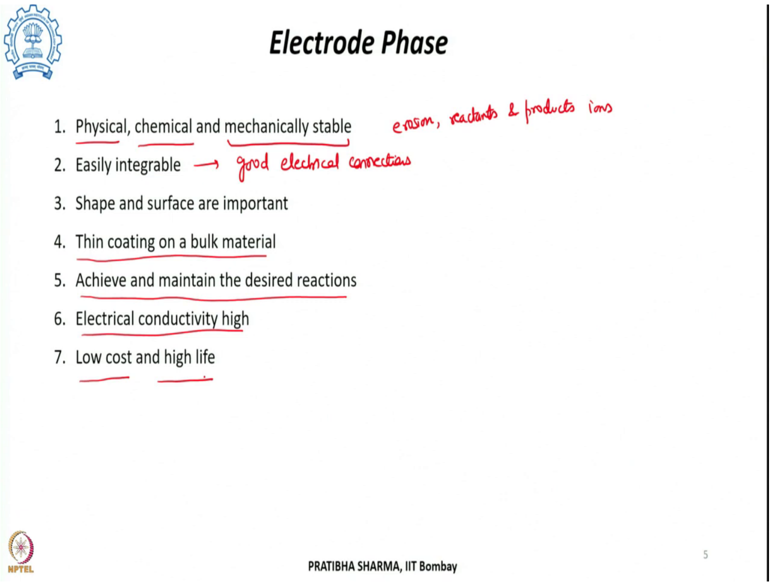

Electrode Phase

1. Physical, chemical and mechanically stable erosion, reactants & products ions
2. Easily integrable → good electrical connections
3. Shape and surface are important
4. Thin coating on a bulk material
5. Achieve and maintain the desired reactions
6. Electrical conductivity high
7. Low cost and high life

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Now, let us look at the electrode phase. Now the electrode phase, the requirement for electrode phase is that it should be mechanically stable. Mechanically stable, it should not undergo erosion when it is acted upon by different reactants, by different products, in the presence of different ions. So, there should not be any loss of electrode when it is subjected to different species.

At the same time, it should remain physically and chemically intact. These electrodes which is being used, it should be easily integrable. By easily integrable we mean, in an electrolytic cell this can be easily connected giving rise to good electrical connections. And, when required can be taken out for inspection or for maintenance. The shape and surface of the electrode phase that also is very important, in the sense that this is the place where the various electrochemical reaction occurs.

So, our phase should be such that it should allow the reactants to get reacted and the products formed to be removed in the process. Now, what happens in this electrodes is usually a very thin coating is considered on a bulk material. The electrodes should be such that the desired reaction should be achieved, desired reactions which leads to the formation of the gaseous product.

However, certain unwanted chemical reactions can be avoided. And, these desired reactions should occur with a high rate of reaction and as such that will define the efficiency of the process, the current density involved in the process. The electrode should have good electrical conductivity and it should definitely have a low cost and high life.

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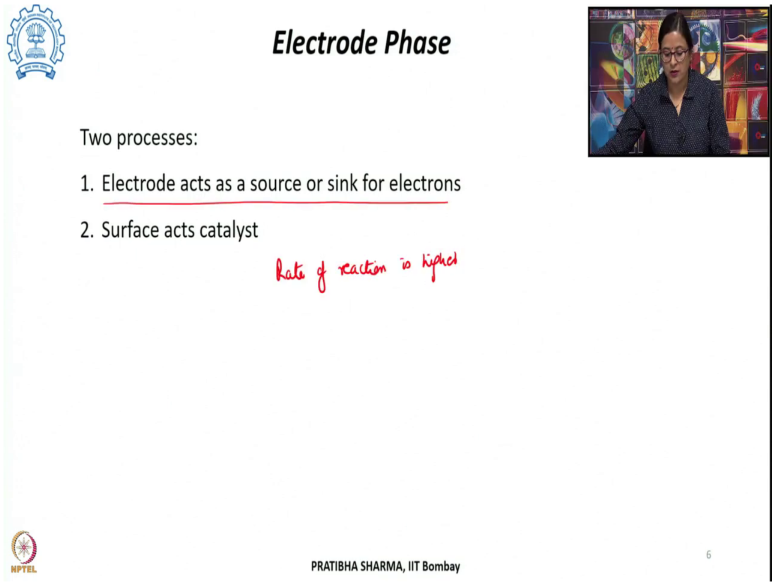

Electrode Phase

Two processes:

1. Electrode acts as a source or sink for electrons
2. Surface acts catalyst

Rate of reaction is higher

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Now, when we look at the processes involved on the electrode surface, then there are two types of electrode processes. One is where it acts as electron source or sink and reaction kinetics are sort of independent of electrode material. Second, electrode surface acts as catalysts and the type as well as rate of reaction depends on interactions between the electrode and electrolyte species.

Thus, a rough surface can provide a high and active electrode area to increase the electro catalytic effect. In water electrolyzers, an electro catalytic electrode surface is required to promote a hydrogen and oxygen evolution at high rate and at low over voltage.

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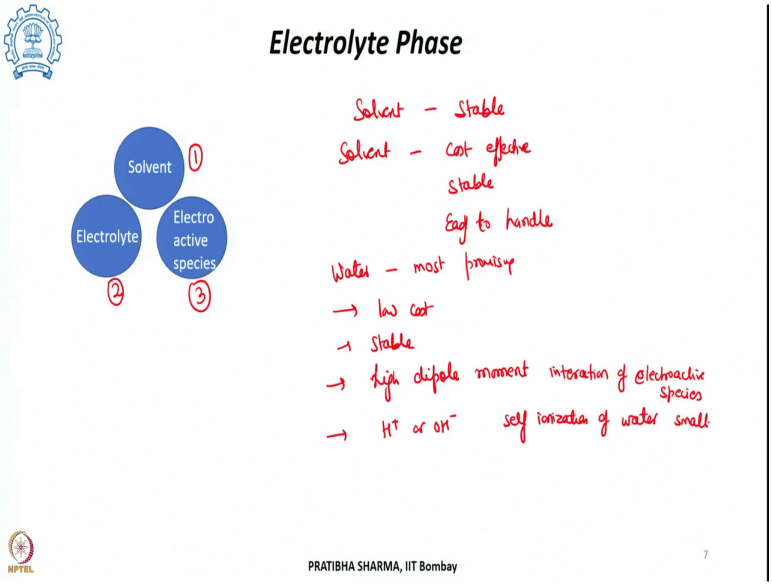

Electrolyte Phase

Solvent – Stable

Solvent – Cost effective
Stable
Easy to handle

Water – most promising
→ low cost
→ Stable
→ high dipole moment interaction of electroactive species
→ H^+ or OH^- self ionization of water small.

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Similarly, if we consider the electrolyte phase, then there are 3 components of it. A solvent which is required which should remain stable under the reaction conditions, an electrolyte and the electro active species. And, these electro active species are nothing, but the reactants. So, now, when we look at the electrolyte, the solvent should be such that it should be cost effective, it should be stable, it should be easy to handle; that means, its disposal as well as handling should be safe and recycling of that should be safe.

So, as such if we look at these solvent then water is the most promising solvent. And, the reason for water being used as a solvent is that it is not only the low cost, stable, the same requirements, it forms an oligomer. So, it has a high dipole moment and this high dipole moment allows the interaction of the electro active species. At the same time, the splitting up of or the ionization of water is very small into H^+ or OH^-. So, it remains stable under the operating conditions. So, as such it is an ideal solvent. So, self ionization of water is relatively very small.

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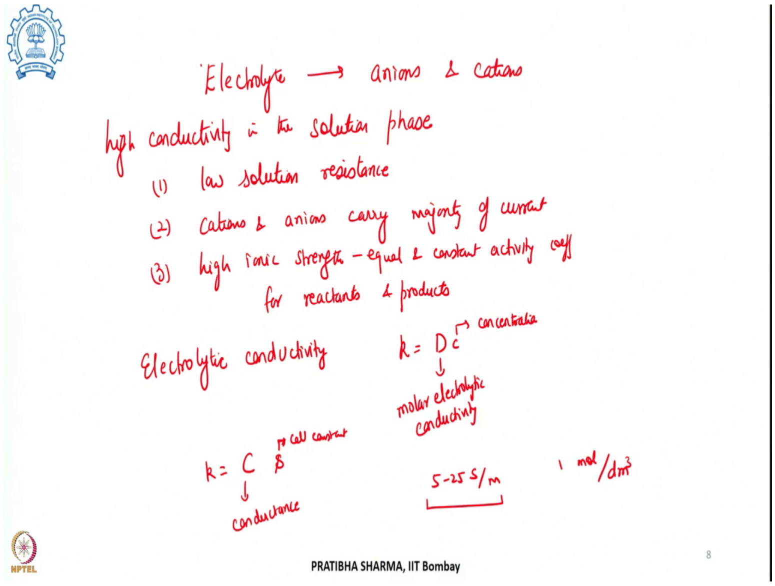

Electrolyte → anions & cations

high conductivity in the solution phase

(1) law solution resistance

(2) cations & anions carry majority of current

(3) high ionic strength – equal & constant activity coeff for reactants & products

Electrolytic conductivity

$$k = \underset{\substack{\downarrow \\ \text{molar electrolytic conductivity}}}{D}\,\overset{\to \text{ concentration}}{c}$$

$$k = \underset{\substack{\downarrow \\ \text{conductance}}}{C}\,\overset{\to \text{ cell constant}}{\beta}$$

$$\underbrace{5\text{-}25\ S/m} \qquad 1\ \text{mol}/dm^3$$

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If you look at the electrolytes, then the high conductivity in the solution phase is the requirement. And that electrolyte that has to disintegrate or dissociate to form anions and cations. What is required is that it should have a high conductivity in the solution phase and this high conductivity will lead to definitely the low resistance. It will result in anions and cations which will basically carry the current. And, it will have a high ionic strength and that results into equal and constant activity coefficient for the reactants and products.

So, if you look at the electrolytic conductivity, this is represented by either the molar electrolytic conductivity times the electrolyte concentration and, it can also be written as conductance times the cell constant and usually for typical cases this electrolytic conductivity it lies in the range of 5 to 25 siemens per meter. And, this is when the typical concentration is of the order of say 1 mole per decimeter cube. So, this is usually the electrolytic conductivity being observed. Another important component of an electrolytic cell is a separator.

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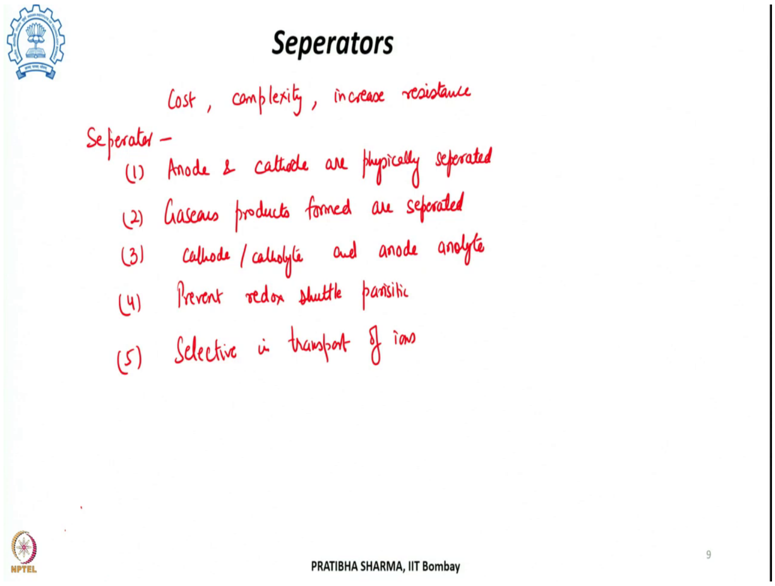

Seperators

Cost, complexity, increase resistance

Seperator –

(1) Anode & cathode are physically seperated

(2) Gaseaus products formed are seperated

(3) Cathode / catholyte and anode anolyte

(4) Prevent redox shuttle parsitic

(5) Selective in transport of ions

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Now, separator although if it is present it has several advantages. But, the presence of separator also leads to disadvantages that like it will add on to the cost, it will add on to the complexity of the system and also it will increase the resistance to the flow of ions. However, separator also plays certain important role like in the presence of separator the two electrodes, they are physically separated and that prevents shorting.

The gaseous products which are released formed in the electrochemical reactions, they are separately produced. So, their intermixing is prevented. At the same time, we can use independent cathode, catholyte and anode, anolyte in the presence of a separator. It can also prevent the redox shuttle which is in fact, parasitic in nature.

So, parasitic redox shuttle which is when the species can undergo reduction at one electrode and it can undergo re-oxidation at the another electrode and that can be avoided. At the same time, the separator can be selective towards one ion and it can selectively allow that particular ion in transport of ions. There are different types of separators which are available.

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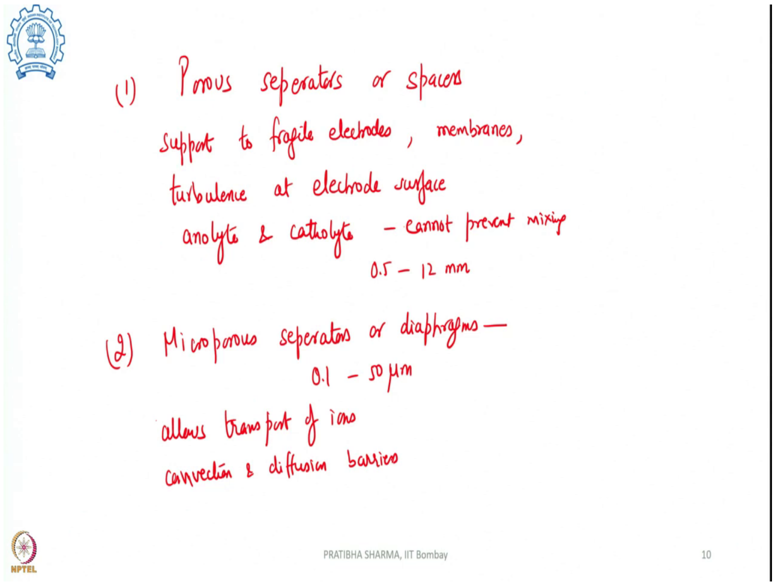

(1) Porous seperators or spacers

support to fragile electrodes , membranes,

turbulence at electrode surface

anolyte & catholyte - cannot prevent mixing

0.5 – 12 mm

(2) Microporous seperators or diaphragms —

0.1 – 50 μm

allows transport of ions

convection & diffusion barriers

These can be either porous separators or these are also called spacers. Now, these porous separators they are such that they can sort of provide support to fragile electrodes. They can even provide support to membranes being used and they can promote a sort of turbulence at the electrode surface. However, they cannot prevent the movement of solvent. They cannot prevent mixing of anolyte and catholyte. Now, usually the pore size which is of these separators that lie in the range of 0.5 to 12 mm.

Another category of separators which can be used are micro porous, where in the pore size is in micron dimensions. Micro porous separators or diaphragms and for them the pore size lies in the range of 0.1 to 50 micron. And, they allow the transport of solvent solute and ions through it by means of hydraulic permeability. However, there are barriers which are because of the presence of these type of separators. The convection and diffusion type of barriers exist when these type of separators are being used.

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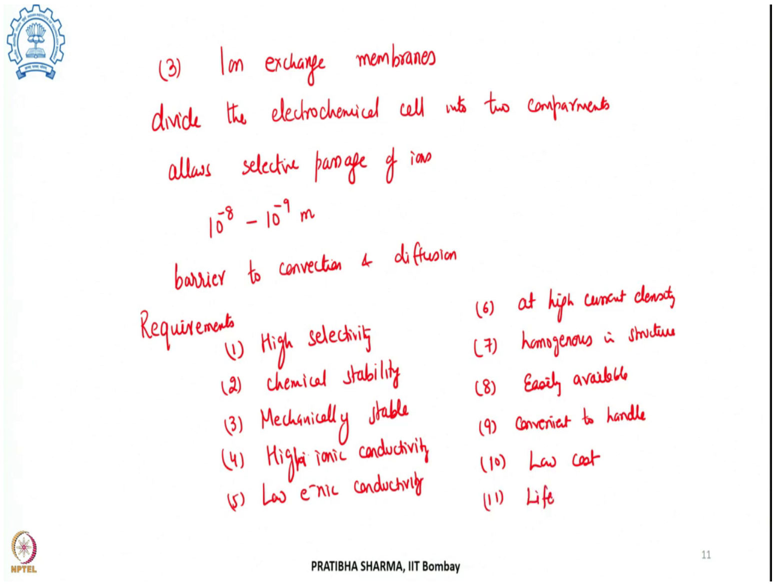

(3) Ion exchange membranes

divide the electrochemical cell into two compartments

allows selective passage of ions

$10^{-8} - 10^{-9}$ m

barrier to convection & diffusion

Requirements

(1) High selectivity
(2) chemical stability
(3) Mechanically stable
(4) High ionic conductivity
(5) Low e^-nic conductivity
(6) at high current density
(7) homogenous in structure
(8) Easily available
(9) Convenient to handle
(10) Low cost
(11) Life

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Or there can be another separator which are ion exchange type which selectively allow a particular type of ions to flow through them. These are ion exchange membrane type of separators which can be used. And these in fact, they divide the electrochemical cell into two compartments.

And, in that case we can use separate anode analyte or separate catholyte we can use. However, they allows selective passage of ions. In the process they have a pore size which is small 10^{-8} to 10^{-9} meters. And, they also function in such a way that they are barrier to convection and diffusion.

But, there are several requirements when it comes to membranes being used in an electrolyzer. These membranes should have very high selectivity and they should be able to permeate only a particular type of ions and not the neutral molecules. They should have high chemical stability under the reaction conditions, when it is subjected to different reactants, products and different ions. These should be mechanically stable.

So, they should be stable, at the same time they should provide strength and flexibility. They should have high ionic conductivity, but a lower electronic conductivity. They should be such that they should operate under variable current densities, can be able to operate at high current density when it is operating under full operation or it should be also be able to operate under lower current densities.

And, at the same time they should be homogeneous in structure. So, that they should not be local variations, it should have throughout the same uniform current densities. It should be easily available, convenient to handle and economical. So, low cost and high life of these membranes which can be used in a electrolyzer.

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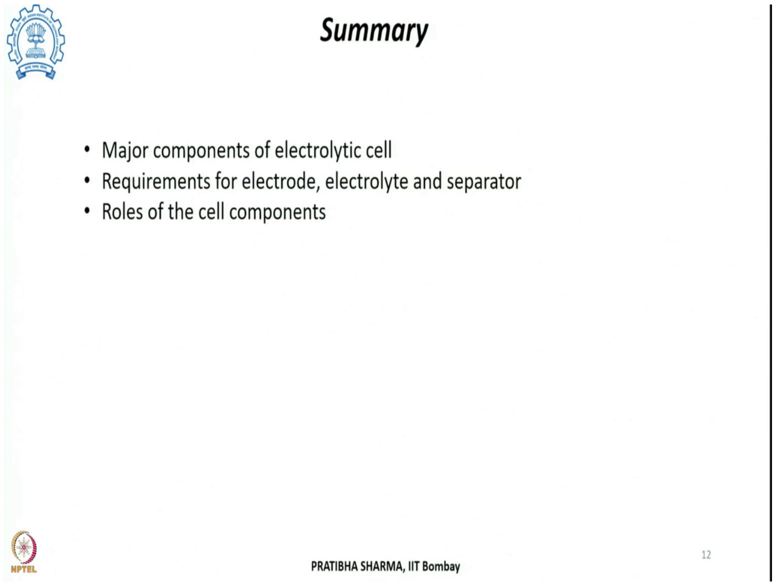

Summary

- Major components of electrolytic cell
- Requirements for electrode, electrolyte and separator
- Roles of the cell components

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To summarize this portion, we have seen the different components involved in the electrolytic cell, what are the different requirements for electrode, electrolyte and separator and how these components, what kind of roles they play in an electrolyzer. So, in the next class, we will see the kinetics involved in the process and how to find out the efficiency of an electrolyzer.

Thank you.