# Hydrogen Energy: Production, Storage, Transportation and Safety
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## Lecture - 25
## Electrolytic Cell Components and Electrolyzer Stack

Water electrolysis is a non-spontaneous process with the Gibbs free energy change being positive under the practical temperatures and pressure conditions. However, the Gibbs free energy change, it becomes negative at temperatures above 2000 kelvin which are very harsh conditions to operate at.

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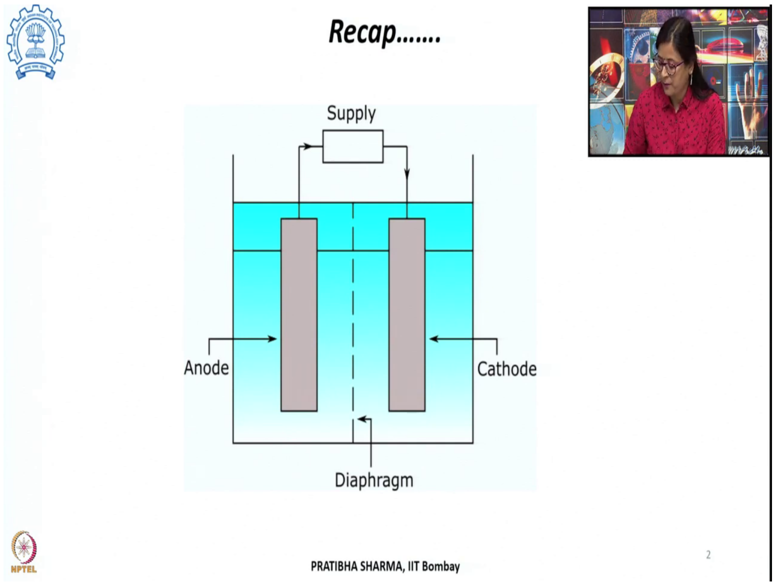

Recap.......

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In the last class, we have seen the major components of the electrolytic cell which is the basic unit of an electrolyzer. And, we have seen that it has two electrodes, an electrolyte and a diaphragm separating the two electrodes. Now, these electrode and electrolyte they have an interface depending upon the cell configuration. And, at these interface the various electrochemical reactions take place.

There is an external supply connected and this is to adjust the Fermi levels of the electrodes so, the redox couple reactions can take place. Now, in this the electrons flow through the external circuit and the ions flow internally into the electrolytic cell. There is a separator and this separator performs two functions. One to physically separate the two electrodes. At the same time the product gases which are released at cathode and anode to prevent the intermixing of these gases. So, that hydrogen from the cathode side can be collected and oxygen from the anode side can be collected separately. So, this is what we have done in the earlier class.

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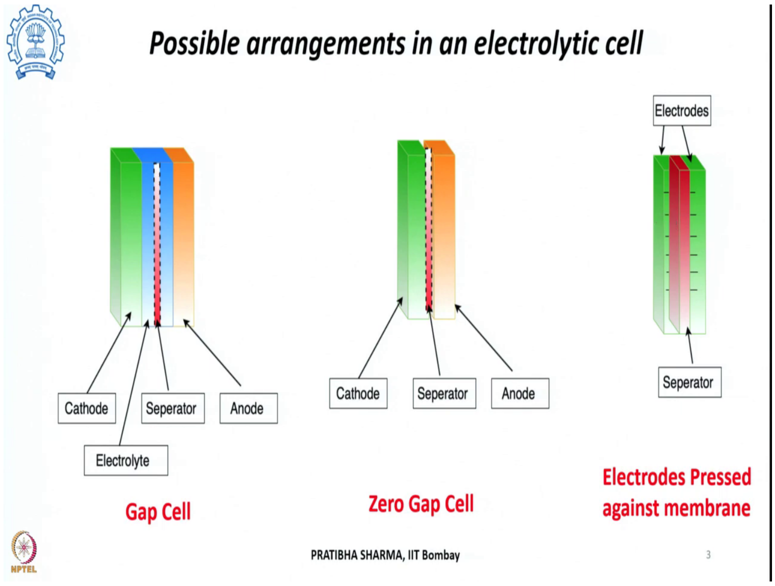

## Possible arrangements in an electrolytic cell

Cathode
Seperator
Anode
Electrolyte
**Gap Cell**

Cathode
Seperator
Anode
**Zero Gap Cell**

Electrodes
Seperator
**Electrodes Pressed against membrane**

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These components can be connected in different possible arrangements. Basically, there are three such concepts which are there of arranging these components in an electrolytic cell. The the first concept is that of a gap cell in which there is a gap between the separator and the two electrodes. Now, this is the simplest and the most conventional type of the arrangement concept, wherein the distance between the electrode and the separator is such that the products or the gases which are formed they are evolved.

And it is low so that the ohmic resistances across the electrolytic cell is lower. Now, in this arrangement the major disadvantage is the products which are coming out or the gas bubbles which are released, they form a sort of thin film onto the surface. And, that is a resistive layer which is formed on the surface. Thereby, it limits the current density which could be achieved in this particular configuration.

The second concept is that of a zero gap cell where the separator is pressed across the two electrodes. The electrodes here are porous with electrolyte present in the inter polar region and this separator has a zero gap with respect to the electrodes. Now, in this particular arrangement the ohmic losses are low compared to the gap cell. And, as such high current densities can be achieved at lower voltages in this particular configuration.

And, this configuration is used for alkaline water electrolysis. There is a third concept which is primarily for the polymer electrolyte membrane based electrolyzers, where the separator is a membrane. And, this membrane selectively allows the ions to pass through. This membrane on both of its surfaces has porous electro catalytic layers and then it is pressed across the current collectors.

Now, in this arrangement we can achieve higher current densities and higher efficiencies. So, these are the three possible arrangements of the various components of an electrolytic cell. Also, we have seen in the last class that the minimum required voltage for the electrolysis to take place which is V reversible is 1.23 volt.

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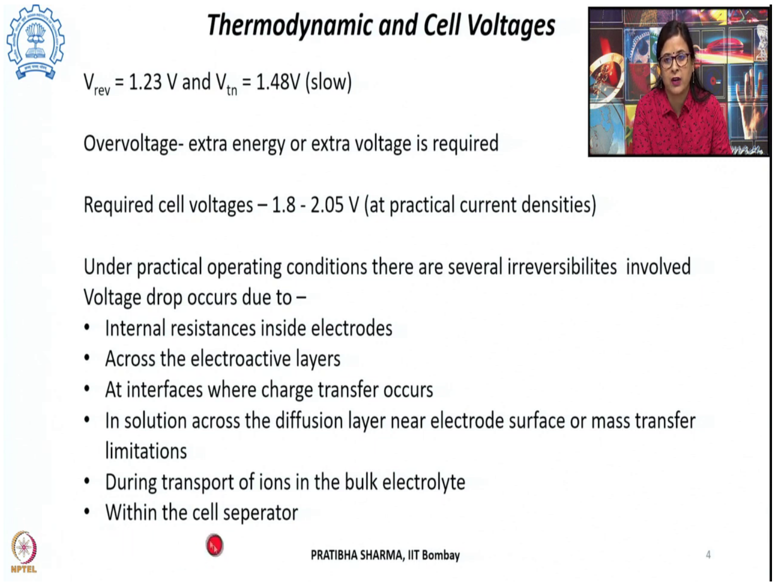

### Thermodynamic and Cell Voltages

$V_{rev}$ = 1.23 V and $V_{tn}$ = 1.48V (slow)

Overvoltage- extra energy or extra voltage is required

Required cell voltages – 1.8 - 2.05 V (at practical current densities)

Under practical operating conditions there are several irreversibilites involved
Voltage drop occurs due to –

- Internal resistances inside electrodes
- Across the electroactive layers
- At interfaces where charge transfer occurs
- In solution across the diffusion layer near electrode surface or mass transfer limitations
- During transport of ions in the bulk electrolyte
- Within the cell seperator

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Now, in this voltage the various components of the reacting species are in the gaseous form. So, water is present in the water vapor form. However, the required energy for converting into water vapour, if that also comes from the electrical energy and the process becomes isothermal.

So, under these conditions when it is the cell is not taking any heat from the surroundings or it is acting in an isothermal condition, then it is known as thermo neutral voltage. And, its value is 1.48 volt which we have seen in the previous class. But, under this voltage, in actual condition the process occurs at a very slow pace.

This can be accelerated by applying an extra energy or an extra voltage. And, this extra energy or extra voltage which is required under practical conditions, under real operating conditions is known as over voltage. Now, there are two reasons for existence of this over voltage. One is because of the low conductivity of water which can be increased by adding salts, acids or bases. And, it is also because of the large activation energy barrier which is for the splitting up of water. And, that can be addressed by appropriate selection of electro catalysts.

Under practical operating conditions, when the current densities are higher for higher hydrogen production; the required cell voltage lies in the range of 1.8 to 2.05 volt. Now, under these conditions there are several irreversibilities involved in the cell. Like there are resistances offered inside the electrolytic cell by the various components. There are resistances towards the charge transfer, towards the charge transport and all those result into voltage drop.

So, these voltage drop can be across the electro active layers present between the various electro active species and the electrode surface. It could be because of internal resistances inside the electrodes. It can occur at the interfaces where the charge transfer occurs. It can be within the solution across the diffusion layer near the electrode surface which is arising because of the mass transfer limitations.

So, in the previous class we have seen that there is a compact layer, then there is a diffuse layer. So, there could be voltage drop occurring because, of the mass transfer limitations. Also, during the transport of ions in the bulk electrolyte there may be an additional resistance which is offered or within the cell separator. Now, all these factors they contribute towards voltage drop within a electrolytic cell under practical operating conditions.

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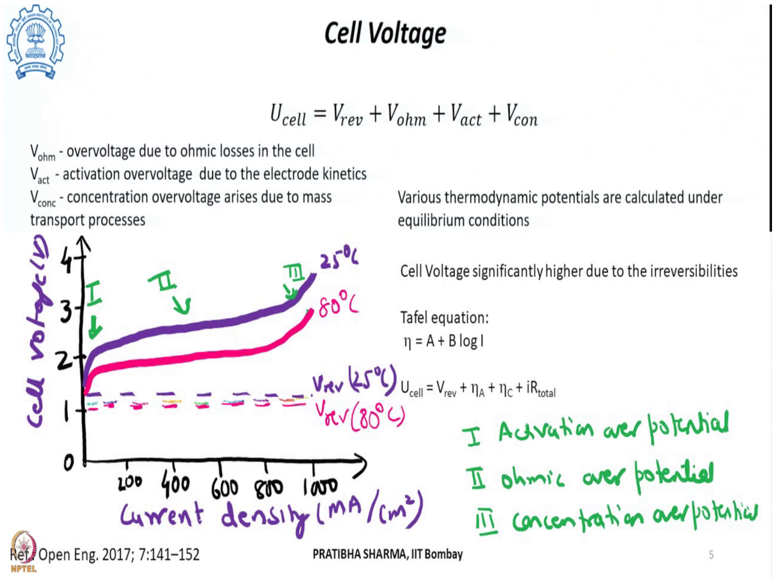

## Cell Voltage

$$U_{cell} = V_{rev} + V_{ohm} + V_{act} + V_{con}$$

$V_{ohm}$ - overvoltage due to ohmic losses in the cell
$V_{act}$ - activation overvoltage due to the electrode kinetics
$V_{conc}$ - concentration overvoltage arises due to mass transport processes

Various thermodynamic potentials are calculated under equilibrium conditions

Cell Voltage significantly higher due to the irreversibilities

Tafel equation:
$\eta = A + B \log I$

$U_{cell} = V_{rev} + \eta_A + \eta_C + iR_{total}$

I Activation over potential
II ohmic over potential
III concentration over potential

Ref: Open Eng. 2017; 7:141–152

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So, under that condition the overall cell voltage is a sum of reversible cell voltage. Another term which is arising because of the ohmic resistance or losses within the cell. Third term which is arising because of the activation over voltage and the last one because of the concentration over voltage. So, the total cell voltage is a sum of all these voltages. First one is the thermodynamic reversible voltage which has a value of 1.23 volt.

Second one which is an ohmic over voltage. This is arising due to the ohmic losses within the cell which is because of the electrical resistance offered by the various components of the cell. These could be electrodes, the interconnections, current collectors. And, this particular part of the voltage over voltage, this is proportional to the current flowing in the electrolytic cell and it is having a linear nature. The third term which is the activation over voltage which is arising because, of the electrode kinetics.

This is the energy barrier which charge carrier has to overcome when it moves from the electro active species like the reactants towards the electrodes and vice versa. So, an extra energy or an extra voltage is required that is to cross this energy barrier by the charge carriers.

And, this comes in the form of activation over voltage and this activation over voltage, has a logarithmic nature. The last component which is the concentration over voltage, this arises because of the mass transport limitations in the electrolytic cell.

Now, the products which are formed if their concentration is higher than the reactants at the interface. So, the products which are formed are not removed at the pace at which; so, that the reactants reach the interface so, that the reaction can take place. In that case there are concentration over voltage is resulting.

Now, if we look at a typical current voltage characteristic, where cell voltage is plotted against the current density; then we can see that there are three regions in the I-V characteristic. So, the first region which is showing a logarithmic nature, this is arising because of the activation over voltage. And, this activation over voltage dominates at the low current densities. And the ohmic over voltage is very less in this particular region, as such it is logarithmic in nature.

And, thereafter there is a linear nature which is observed in the I-V characteristic. So, in this linear region, the activation over voltage potential is less dominated than the ohmic over voltage which is offered by the electrical resistance of the various cell components. Now, in this linear region which is also proportional to the current flowing, this depends upon on the surface area. Like this is much more dominating in the large area industrial scale electrolyzer, this ohmic over potential could be very high in that case.

And, the last region where after this linear region there is a rise that is because of the concentration over voltage or the mass transport limitations in the cell. Now, the various thermodynamic potentials that are calculated which we have seen in the earlier class, these are calculated under equilibrium set of conditions. By equilibrium set of conditions, we mean that there are no irreversibilities involved. But, in actual practice the cell voltage required is sufficiently higher, because of the various irreversibilities in the cell.

These are arising as we have seen because of the resistances of the different components because, of the activation over voltage because of the ohmic over voltage. And, this over voltage can be related with the current density using the Tafel equation. So, the over voltage is given by $(A + B \log I)$, where A and B these are characteristics of anode and cathode and I is the current density offered.

So, in its terms we can write that the cell voltage is equal to the reversible cell voltage plus the over voltage which is the activation over voltage plus the concentration over voltage plus the current flowing through the cell and the total resistance arising, because of the various components of the cell. So, this is how the total cell voltage is related to the various over voltages and the thermodynamic reversible voltage.

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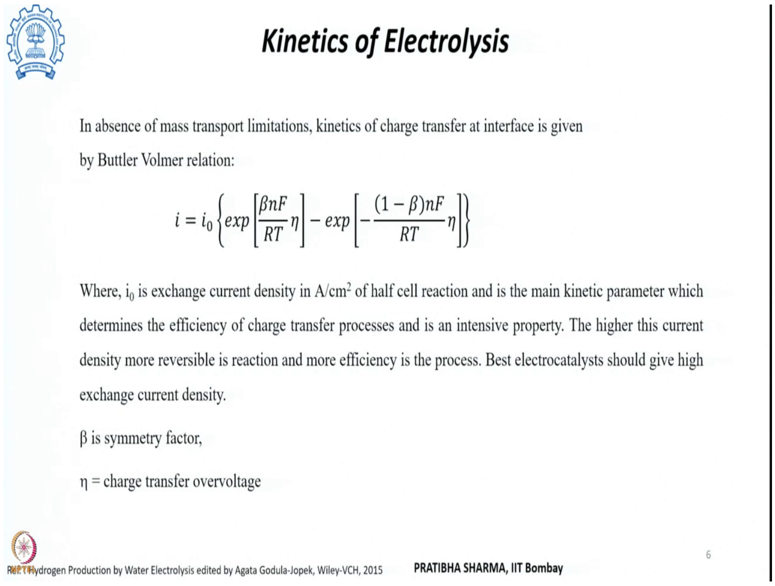

## Kinetics of Electrolysis

In absence of mass transport limitations, kinetics of charge transfer at interface is given by Buttler Volmer relation:

$$i = i_0 \left\{ exp\left[\frac{\beta nF}{RT}\eta\right] - exp\left[-\frac{(1-\beta)nF}{RT}\eta\right]\right\}$$

Where, $i_0$ is exchange current density in A/cm$^2$ of half cell reaction and is the main kinetic parameter which determines the efficiency of charge transfer processes and is an intensive property. The higher this current density more reversible is reaction and more efficiency is the process. Best electrocatalysts should give high exchange current density.

$\beta$ is symmetry factor,

$\eta$ = charge transfer overvoltage

Ref.: Hydrogen Production by Water Electrolysis edited by Agata Godula-Jopek, Wiley-VCH, 2015 **PRATIBHA SHARMA, IIT Bombay**

Now, the kinetics of electrolysis in the absence of any mass transport limitations, the charge transfer kinetics at the interface can be given by the Butler Volmer equation, where the current density is given by the exchange current density times this quantity which is [exponential(($\beta$nF/RT)$\eta$ - exponential(-((1-$\beta$)nF/RT)$\eta$)]. Where, $\beta$ is the symmetry factor, n is the number of electrons exchanged in the process, F is the Faraday's constant, R is gas constant, T is the temperature and $\eta$ is the charge transfer over voltage.

Now, $i_0$ which is the exchange current density which is expressed in ampere per centimeter square for the half cell reaction. This is the major kinetic parameter and this determines the efficiency of the charge transfer process. This is an intensive property. The higher is this current density, the more reversible the reaction will be and the more efficiency of the process will be. So, the best electro catalysts are those which gives high exchange current density.

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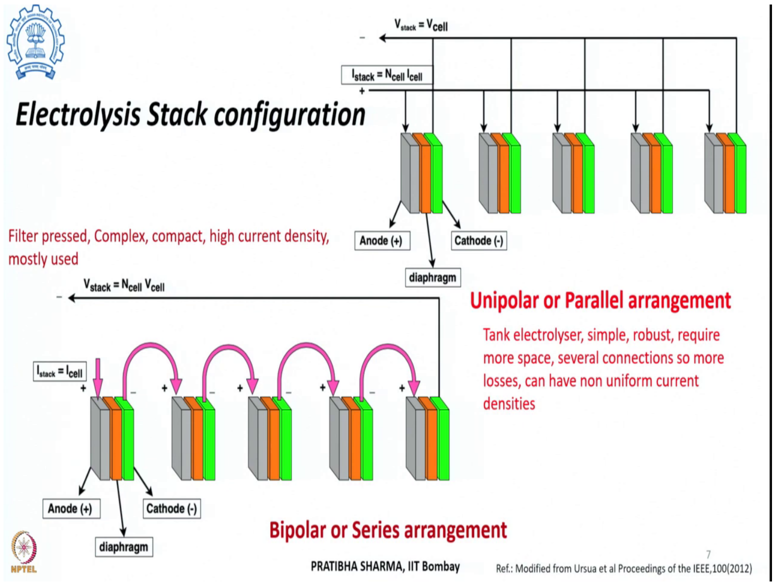

## Electrolysis Stack configuration

Filter pressed, Complex, compact, high current density, mostly used

**Unipolar or Parallel arrangement**

Tank electrolyser, simple, robust, require more space, several connections so more losses, can have non uniform current densities

**Bipolar or Series arrangement**

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Ref.: Modified from Ursua et al Proceedings of the IEEE,100(2012)

Now, till now we have seen the different components of electrolytic cell and then how what are the thermodynamics, what are the kinetics, what are the cell voltages involved in a single electrolytic cell. Now, these hundreds of these electrolytic cell can be combined together to form a electrolysis stack. Now, there are different conformations in which these can be combined. Like there are the two well-known combinations are unipolar or parallel arrangement of the electrolytic cell and the bipolar or series arrangement of the different electrolytic cell.

There is a third combination also possible which is a hybrid one. So, some cells are connected in series, some cells are connected in parallel. However, hybrid combination is not preferred arrangement in an electrolysis stack. Now, let us look at these comparations. The unipolar or the parallel arrangement, wherein each electrode is having a single polarity in each of the electrolytic cell. This is also known as a tank electrolyzer.

So, although there are simplified connections; so, as such it is simple to connect, it is robust, but it requires more of space. Since, there are connections several connections involved. So, there are more of losses involved in the arrangement and it can also result in non-uniform current densities, because the internal resistance of different cells may be different. Now, there is another arrangement where the different electrolytic cells could be connected in series. So, negative of the first connected to the positive of second and same way.

So, the bipolar or series arrangement, it is also known as filter pressed arrangement. This is little complex in terms of the arrangement. However, it is compact and a high current density could be obtained using this particular combination. The most widely used combination is the bipolar or the series arrangement. And, in this the voltage of the stack it depends upon how many number of cells are there in the stack. And, it is number if the each of the cell has V cell voltage, then it is $N_{cell}V_{cell}$.

However, the same current flows through the stack as that of the individual cell. However, here the current obtained in the unipolar or the parallel arrangement is number of cells times the current passing through the individual cell in the unipolar arrangement. So, the most widely used arrangement is that of the series combination or the bipolar arrangement. Now, when we have a stack then the obvious question is how much amount of hydrogen we can produce using that particular electrolysis stack?

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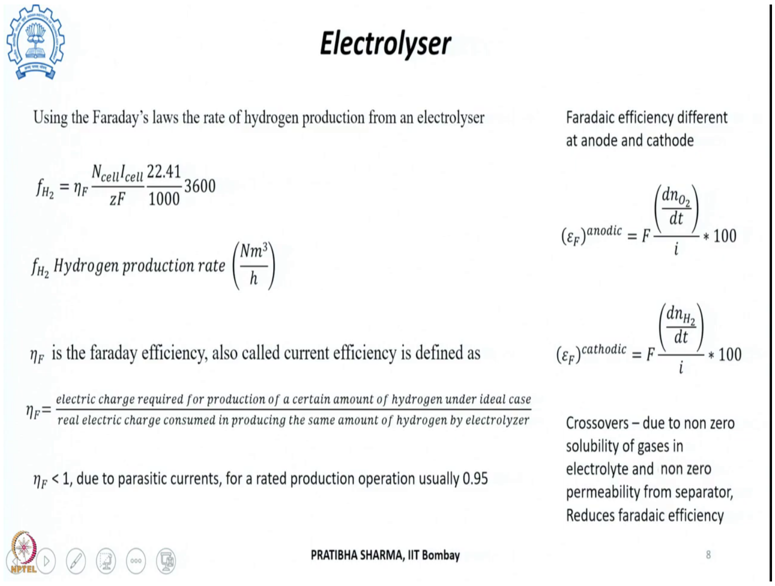

## Electrolyser

Using the Faraday's laws the rate of hydrogen production from an electrolyser

$$f_{H_2} = \eta_F \frac{N_{cell}I_{cell}}{zF}\frac{22.41}{1000}3600$$

$f_{H_2}$ *Hydrogen production rate* $\left(\frac{Nm^3}{h}\right)$

$\eta_F$ is the faraday efficiency, also called current efficiency is defined as

$$\eta_F = \frac{electric\ charge\ required\ for\ production\ of\ a\ certain\ amount\ of\ hydrogen\ under\ ideal\ case}{real\ electric\ charge\ consumed\ in\ producing\ the\ same\ amount\ of\ hydrogen\ by\ electrolyzer}$$

$\eta_F < 1$, due to parasitic currents, for a rated production operation usually 0.95

Faradaic efficiency different at anode and cathode

$$(\varepsilon_F)^{anodic} = F\frac{\left(\frac{dn_{O_2}}{dt}\right)}{i} * 100$$

$$(\varepsilon_F)^{cathodic} = F\frac{\left(\frac{dn_{H_2}}{dt}\right)}{i} * 100$$

Crossovers – due to non zero solubility of gases in electrolyte and non zero permeability from separator, Reduces faradaic efficiency

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The Faraday's laws which relates the amount of hydrogen which can be produced based on the amount of charge being transferred, that could be given by; the rate of hydrogen produced can be given using the Faraday's law as. So, the hydrogen production rate which is in terms of normal meter cube of hydrogen being produced per hour, it is given by the faradaic efficiency $\eta_f$ times $N_{cell}V_{cell}$. So, if there are N number of cells being connected in the stack, each of the cell is having a current flowing of I cell upon zF, where z is the number of electrons being transferred to; in this case F is the Faraday's constant.

And, then there are certain quantities to convert it into normal meter cube per hour. So, this is the amount of hydrogen which can be produced using an electrolyzer. Now, the first term here which is the $\eta_f$, this is the faradaic efficiency. This is also known as the current efficiency and it is defined as the amount of electric charge which is required to produce a certain amount of hydrogen under the ideal conditions.

So, the ideal quantity of the electric charge required to produce a certain quantity of hydrogen under ideal situation to the electric charge which is actually consumed in producing the same amount of hydrogen using an electrolyzer. And, this quantity is usually less than 1. So, its value is less than 1 and the reason for this being less than 1 is as compared to the ideal situation the amount of energy consumed is always higher in case of the actual practice.

This is less than 1 because of the presence of different parasitic currents. These parasitic currents they actually flow through the electrolytic cell, but they do not contribute towards the hydrogen production. And, if they participate or they may participate in the unwanted reactions or if at times certain amount of hydrogen is being produced, that may be lost. It could not be collected in the process.

So, as such if the electrolyzer is operating at a rated production capacity, then usually this value of the faradaic efficiency is less than 1. And, typically maximum it can be even 0.95 or even slightly more than that. Now, this faradaic efficiency or the current efficiency, this is different for the different electrodes.

The anode at which the oxygen evolution occurs or the oxygen reduction reaction occurs, this is always more demanding. Or, the reaction is much slower than the hydrogen evaluation reaction which occurs at the cathode side or the hydrogen oxidation reaction that occurs onto the cathode side.

Now, this can be again represented by on the anodic side, the Faraday's constant and the rate at which the gases are evolved times the actual amount of current being consumed and same it is on to the cathodic side. Now, this it is desired that the gases which are evolved in the process of electrolysis, they should not intermix or there should not be a crossover. Like the hydrogen which is being produced onto the cathode side can go on to the anode side through the separator membrane or diaphragm. And, can either it can combine with oxygen or it can re-oxidize and that is an undesirable phenomenon.

Because, it not only results into loss of the electrical work which we have provided so as to produce hydrogen and oxygen gases. At the same time, it increases the heat dissipation into the cell. And that makes the process inefficient, reduces the efficiency and all this crossover arises because there is a non-zero solubility of these gases, product gases oxygen and hydrogen which are produced in the electrolyte.

At the same time the separator which is being used that also has a non-zero permeability. And, because of this crossover it reduces the faradaic efficiency in the electrochemical cell. Now, how much amount of energy is consumed in an electrolyzer to produce a certain amount of hydrogen is given by the specific energy consumption.

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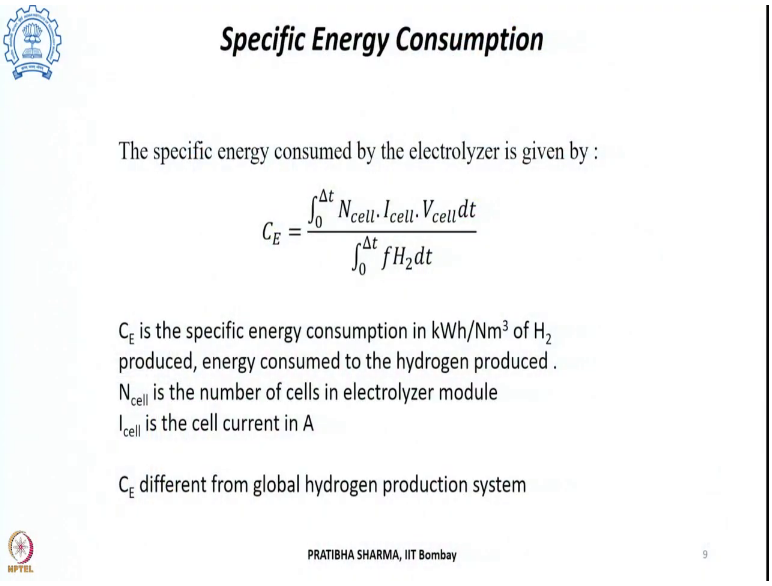

## Specific Energy Consumption

The specific energy consumed by the electrolyzer is given by :

$$C_E = \frac{\int_0^{\Delta t} N_{cell}.I_{cell}.V_{cell}dt}{\int_0^{\Delta t} fH_2dt}$$

$C_E$ is the specific energy consumption in kWh/Nm$^3$ of $H_2$ produced, energy consumed to the hydrogen produced .
$N_{cell}$ is the number of cells in electrolyzer module
$I_{cell}$ is the cell current in A

$C_E$ different from global hydrogen production system

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So, the specific energy consumption which is $C_E$, here it is in kilowatt hour per normal meter cube of hydrogen being produced. And, this is given by the amount of energy consumed to produce hydrogen divided by the amount of hydrogen being produced. So, the amount of hydrogen being produced in the denominator. So, this is an integral over a period of time of a product of Ncell, the number of cells in the electrolysis stack, current flowing through each of the cell and the voltage of the cell, that is being integrated over a period of time, 0 to delta t.

And, in during the same time the amount of hydrogen being produced is there in the denominator. Now, when we consider the electrolysis process the specific energy consumption. However, the under actual conditions there is more energy consumption because of the different auxiliary components in an electrolyzer.

These could be valves, these could be sensors, these could be purification systems which are used, cooling systems which are used. And, then there can be power losses involved in the process. So, the actual amount of energy which is consumed is higher than the in the case of electrolysis in the system, the global hydrogen production system. At the same time the denominator which indicates the amount of hydrogen being produced, that also may have certain losses.

So, the hydrogen which is being produced may undergo losses at the different valves, at different interconnections and all of that may not be collected at the purification system also. So, if we consider all those, the added amount of energy which is required by the auxiliary components and the power losses involved in the numerator.

And, at the same time the various hydrogen losses are included in the denominator. Then, the specific energy consumption will be different from this particular formula. And, then it becomes the specific energy consumption from a global hydrogen production system.

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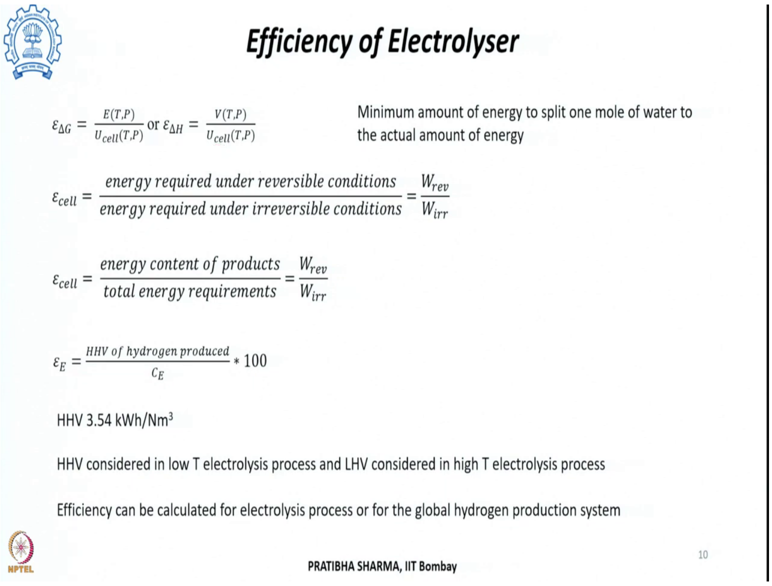

## Efficiency of Electrolyser

$$\varepsilon_{\Delta G} = \frac{E(T,P)}{U_{cell}(T,P)} \text{ or } \varepsilon_{\Delta H} = \frac{V(T,P)}{U_{cell}(T,P)}$$

Minimum amount of energy to split one mole of water to the actual amount of energy

$$\varepsilon_{cell} = \frac{energy\ required\ under\ reversible\ conditions}{energy\ required\ under\ irreversible\ conditions} = \frac{W_{rev}}{W_{irr}}$$

$$\varepsilon_{cell} = \frac{energy\ content\ of\ products}{total\ energy\ requirements} = \frac{W_{rev}}{W_{irr}}$$

$$\varepsilon_E = \frac{HHV\ of\ hydrogen\ produced}{C_E} * 100$$

HHV 3.54 kWh/Nm$^3$

HHV considered in low T electrolysis process and LHV considered in high T electrolysis process

Efficiency can be calculated for electrolysis process or for the global hydrogen production system

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Another important parameter in an electrolyzer is the efficiency of the electrolyzer. Now, if it is an energy efficiency, then it is the minimum amount of energy which is required to split 1 mole of water to the actual total amount of energy required. So, if it is in terms of Gibbs free energy, then the reversible cell voltage upon the actual cell voltage or it could be in terms of the enthalpy, energy efficiency in terms of enthalpy. So, this is the thermoneutral voltage divided by the cell voltage.

So, this is the thermodynamic voltage divided by the actual amount of energy required or the actual cell voltage. Now, in ideal conditions the when we are calculating the various thermodynamic voltages, these are calculated under equilibrium conditions when the system is reversible. So, under equilibrium condition, the energy required under reversible conditions is equal to the energy required under irreversible conditions. And, in that case the energy efficiency of the cell becomes 1.

However, the actual cell efficiency is given by the amount of energy required under reversible conditions divided by the energy required under irreversible conditions. So, the denominator accounts for all the irreversibilities involved in the process. In actual practice always the $W_{reversible}$; so, this is less than the $W_{irreversible}$. The amount of energy required because of the irreversible processes is more.

This is because of the parasitic resistance, the various resistances, electrical resistance involved, the various over voltages that requires additional energy in the process. So, the energy efficiency of the cell is less than 1. It can also be represented in terms of the energy content of the products which are formed to the total amount of energy which is required to produce that product. So, the products formed are here, hydrogen and oxygen. And, the amount of energy which is required to produce these products. This can be given by the higher heating value of hydrogen being produced.

So, the amount of hydrogen which is being produced its higher heating value divided by the specific energy consumption in the process into 100. In higher heating value can be taken as 3.54 kilowatt hour per normal meter cube. But, this higher heating value is taken in low temperature electrolysis process where water is electrolyzed. However, lower heating value has to be taken for high temperature electrolysis process like solid oxide electrolysis, where the water vapor is available for the electrolysis process to take place.

Now, if we consider all the other losses, all the additional energy requirements in the expression; then the efficiency under that conditions is known as the global hydrogen production system efficiency. So, again the energy required including all the peripheral components and the losses, then it becomes the actual efficiency of the electrolyzer.

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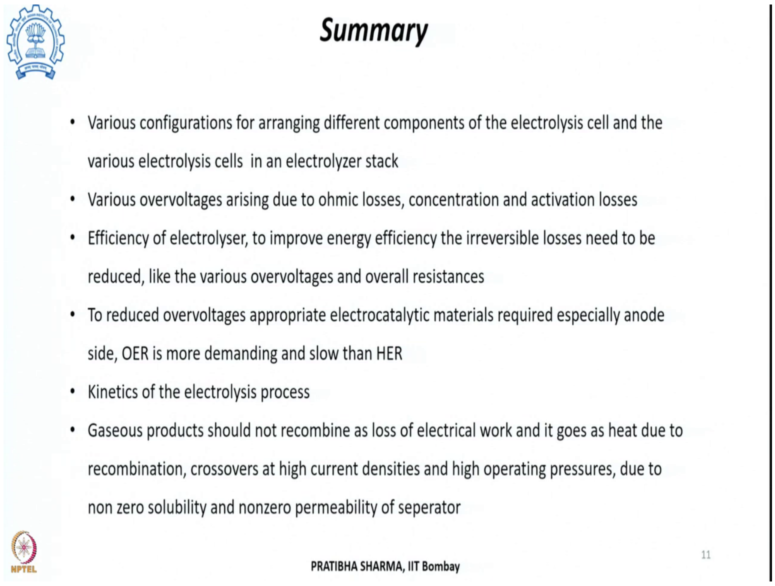

## Summary

- Various configurations for arranging different components of the electrolysis cell and the various electrolysis cells in an electrolyzer stack
- Various overvoltages arising due to ohmic losses, concentration and activation losses
- Efficiency of electrolyser, to improve energy efficiency the irreversible losses need to be reduced, like the various overvoltages and overall resistances
- To reduced overvoltages appropriate electrocatalytic materials required especially anode side, OER is more demanding and slow than HER
- Kinetics of the electrolysis process
- Gaseous products should not recombine as loss of electrical work and it goes as heat due to recombination, crossovers at high current densities and high operating pressures, due to non zero solubility and nonzero permeability of seperator

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To summarize this portion, we have seen the various configurations in which the different components of electrolysis unit can be connected. And, how these electrolysis cell can be integrated together to form an electrolyzer stack. Also we have seen the various over voltages which arises due to the ohmic losses, concentration and activation losses in the process of electrolysis.

We have seen what is the efficiency of an electrolyzer and how we can improve onto the energy efficiency. And, that can be done by reducing the irreversible losses; like the different over voltages and the resistances involved in the process needs to be reduced.

These over voltages can be reduced, if we select an appropriate electrocatalytic material specially on the anode side, because the oxygen evaluation reaction is more demanding and slower compared to the hydrogen evaluation reaction. We have also seen the kinetics of the electrolysis process. And, the gaseous products which are released, they can also undergo crossovers or inter mixing.

And that result in loss of the electrical work, at the same time it can result into heating due to recombination. And, this is more prominent under high current densities and high operating pressures arises, because it is non-zero solubility of these gases inside the electrolyte and non-zero permeability of the separator. In the next class, we will see the different configurations, different the electrolyzer technologies which are there in detail.

Thank you.