

## **ELECTRO CHEMISTRY**

**Electro Chemistry** : Electro Chemistry is the study of the processes involved in the inter conversion of Electrical energy & chemical energy.

**Conductor** : A substance which allows electric current to pass through it is called a ' Conductor '.

Eg:- All metals, graphite, fused salts, aqueous solutions of acids, bases & salts.

Conductors are of two types :-

1. Electronic Conductors (or) Metallic Conductors: These are the substances which conduct electricity, but are not decomposed by it.

Eg: All metals, graphite etc.

2. Electrolytic Conductor (or) Electrolyte: It is a substance which in aqueous solution or in molten state (or fused state) liberates ions and allow electric current to pass through, there by resulting in its chemical decomposition.

Eg: Acids, bases, electrovalent salts (NaCl, AgNO<sub>3</sub> ) etc.

### **Difference between the Electronic conductors & Electrolytic conductors**

<b>Electronic conductors</b>	<b>Electrolytic conductors</b>
1. The conductance is due to flow of electrons.	1. The conductance is due to flow of ions.
2. No chemical change takes place.	2. Chemical change takes place.
3. No transfer of matter takes place.	3. Transfer of matter takes place.
4. The conductance decreases with increase in temperature	4. The conductance increases with increase in temperature

**OXIDATION**: The process which involves the loss of electrons by a substance is termed as 'Oxidation'.



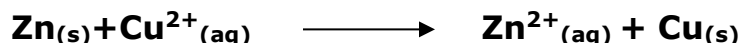
The addition of oxygen or Removal of H<sub>2</sub> is also termed as "Oxidation".

**REDUCTION**: The process which involves the gain of electrons by a substance is termed as "Reduction".



The addition of H<sub>2</sub> or removal of O<sub>2</sub> is also termed as "Reduction". If a substance loses electrons, some other substance must be involved in the reaction to accept these electrons, and vice versa. Thus oxidation and reduction must always go side-by-side. The overall reaction, obtained by

adding the oxidation & reduction is called as "Redox or oxidation -Reduction reaction".



The reaction in which loss of electrons takes place is called as "Oxidation Half reaction, & the reaction in which gain of electrons takes place is called as 'Reduction Half reaction'.

### **ELECTRODE POTENTIAL:**

The electrode potential of a Metal is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with the solution of its own ions.

**REDUCTION POTENTIAL:** The tendency of an electrode to gain electrons when it is in contact with the solution of its own ions.



**OXIDATION POTENTIAL:** The tendency of an electrode to lose electrons when it is in contact with the solution of its own ions.



The oxidation & reduction potentials of an electrode must have same magnitude but opposite signs.

### **STANDARD ELECTRODE POTENTIAL:**

The tendency of an electrode to lose or gain electrons when it is in contact with the solution of its own ions of unit molar concentration (or 1 atm pressure in case of gas electrode) at 25°C is called the 'STANDARD ELECTRODE POTENTIAL'.

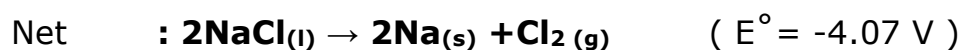
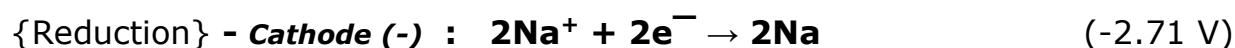
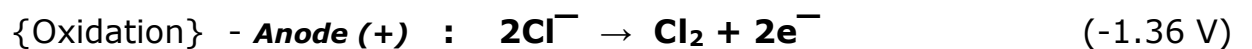
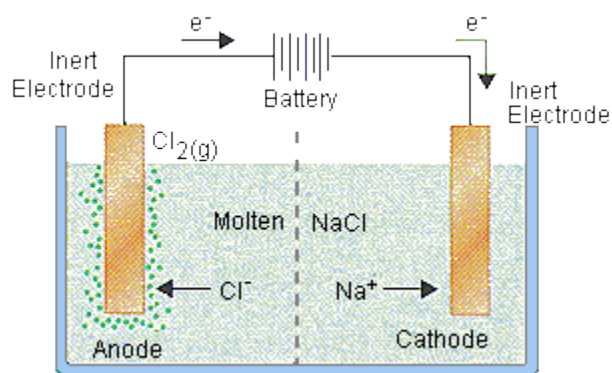
**ELECTROCHEMICAL CELLS :** An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions and facilitating chemical reactions through the introduction of electrical energy.

Oxidation-reduction or redox reactions take place in electrochemical cells. There are two types of electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; non-spontaneous reactions occur in electrolytic cells. Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the electrode termed the **anode** and reduction occurs at the electrode called the **cathode**.

**ELECTROLYTIC CELL :** An **electrolytic cell** is an electrochemical cell that undergoes a redox reaction when electricity is applied. It is most often used to decompose chemical compounds, in a process called 'electrolysis'.

Eg: Electrolysis of molten NaCl.

In the electrolysis of molten NaCl, a source of direct current is connected to a pair of inert electrodes immersed in molten NaCl. As the salt has been heated until it melts, the  $\text{Na}^+$  ion flow towards the negative electrode (Cathode) and the  $\text{Cl}^-$  ions flow towards the positive electrode (anode). When  $\text{Na}^+$  ions collide with the negative electrode, the battery carries a large enough potential to force these ions to pick up electrons to form sodium metal.  $\text{Cl}^-$  ions that collide with the positive electrode are oxidized to  $\text{Cl}_2$  gas, which bubbles off at this electrode.

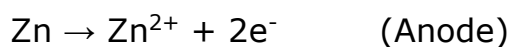


So, the battery used to drive this reaction must therefore have a potential of at least 4.07 V.

### **GALVANIC CELL:**

A galvanic cell (or a Voltaic cell) is an electrochemical cell that converts the chemical energy of a spontaneous redox reactions into electrical energy.

A Galvanic cell is made up of two half cells and are corresponding to oxidation reaction and hence called as 'Oxidation Half Cell'



and the other corresponding to reduction reaction and hence called as 'Reduction Half Cell'.



The two electrodes of half cells are joined by a copper wire through a volt meter and the electrolytes are joined by salt bridge.

### **Salt Bridge & its Role:**

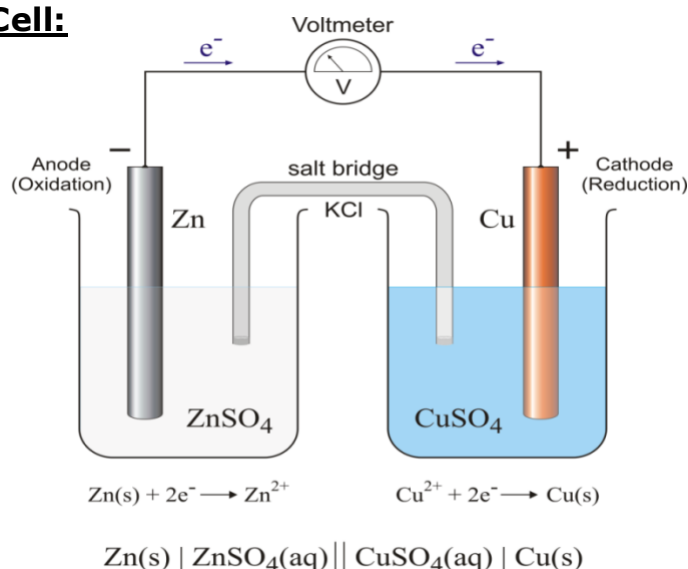
It is an inverted 'U' tube filled with Agar-Agar gel containing a saturated solution of KCl or KNO<sub>3</sub> or NH<sub>4</sub>NO<sub>3</sub> etc.

It does not react with the electrolytes but prevents the accumulation of charges of the electrodes. It allows the passage of ions from one electrolyte to the other there by facilitating the continuous production of electricity. It maintains the electrical neutrality.

In a galvanic cell a spontaneous redox reaction takes place. During the reactions at anode and cathode, the free energy of the reactants decreases and appears in the form of electricity.

### **Construction & working of Galvanic Cell:**

It consists of Zn electrode dipped in ZnSO<sub>4</sub> solution which acts as anode (Oxidation takes place) & Cu electrode dipped in CuSO<sub>4</sub> solution which act as cathode (Reduction takes place). The two electrodes joined by a copper wire through a volt meter and the two electrolytes are joined by salt bridge to complete the cell.



The following reactions take place at the electrodes:

At Anode :  $\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$

At cathode:  $\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu (s)}$

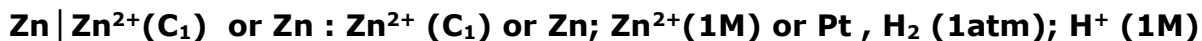
Cell reaction:  $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$

### **Representation of a galvanic cell (or) CELL NOTATION:**

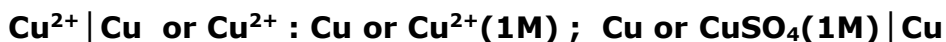
A Galvanic cell can be represented by the following sign conventions or cell notation:

1. Anodic half cell should be represented on the left side & the cathodic half cell should be represented on the right side.

2. Anodic half cell is represented by writing the symbol of the metal followed by the symbol of the electrolyte with its concentration in the brackets and the two are separated by a vertical line or a semicolon.



3. Cathodic half cell is represented by writing the symbol of the electrolyte with its concentration in the brackets followed by the symbol of the metal electrode & the two are separated by a vertical line or a semicolon.



4. A salt bridge is indicated by two vertical lines, separating two half cells.



### **EMF of an Electro Chemical cell:**

The difference between the reduction potentials of the two half cells of a galvanic cell is known as 'emf of a cell'. It is also known as cell potential.

Or

The difference of potential, which causes a current to flow from the electrode of higher potential to one of lower potential, is called as 'emf of the cell'.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \{\text{or } E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}\} \quad (\text{Bothe are reduction potentials})$$

The cell reaction is feasible, if  $E_{\text{cell}}$  is '+ ve' and it is not feasible, if  $E_{\text{cell}}$  is '- ve' and if it is not feasible, the electrodes will have to be reversed in order to bring about cell reaction.

### **Differences between a Galvanic cell and an Electrolytic cell**

<b><u>GALVANIC CELL</u></b>	<b><u>ELECTROLYTIC CELL</u></b>
<b>1)</b> It is a device to convert Chemical energy into Electrical energy.	<b>1)</b> It is a device to convert Electrical energy into Chemical energy
<b>2)</b> The redox reactions occurring at the electrodes are Spontaneous.	<b>2)</b> The redox reactions occurring at the electrodes are non-Spontaneous & it takes place only when electrical energy is supplied.
<b>3)</b> The electrodes are of dissimilar metals.	<b>3)</b> The electrodes used may be dissimilar or of the same metal.
<b>4)</b> Each electrode is inserted in its own ions and both have separate compartments.	<b>4)</b> Both the electrodes are inserted in the same electrolyte solution.
<b>5)</b> The two electrolyte solutions are connected by a salt bridge.	<b>5)</b> No salt bridge is needed.

<b>6)</b> The - ve electrode of the cell is an anode. The +ve electrode of the cell is a cathode.	<b>6)</b> The +ve electrode of the cell is an anode. The - ve electrode of the cell is a cathode.

### **ELECTRO CHEMICAL SERIES:**

When elements are arranged in increasing order of their standard electrode potential, then the series is called as 'Electro chemical series or electro motive series'.

#### STANDARD REDUCTION POTENTIALS @ 25°C

<b><u>METAL ION</u></b>	<b><u>SRP(E° VOLTS)</u></b>	
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.05	ANODE
$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.37	
$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66	
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.76	
$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	-0.74	
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.44	
$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.14	
$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$	-0.04	
$\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2}\text{H}_2$	0.00	REFERENCE
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34	
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.80	
$\text{Au}^+ + \text{e}^- \longrightarrow \text{Au}$	+1.69	
$\frac{1}{2} \text{F}_2 + \text{e}^- \longrightarrow \text{F}^-$	+2.87	CATHODE

### **Significance of Electro chemical series:**

**1. Relative Ease of Oxidation or Reduction** : A system with high SRP undergo reduction & low SRP undergo oxidation.

**2. Replacement Tendency:**

A metal with lower SRP will displace the metal with higher SRP from its solution.

### 3. Predicting Spontaneity of Redox Reactions:

The Redox reaction to be spontaneous if  $E_{\text{cell}}$  (EMF Value) = +ve &  $\Delta G$  must be -ve.

### 4. Calculation of Equilibrium Constant:

#### Displacement of $H_2$ from dilute acids by the metal:

A metal with lower SRP than  $H_2$  electrode potential will displace  $H_2$  from dilute acids i.e., all metals which are placed above  $H_2$  in the electrochemical series can displace  $H_2$  from dil. acids.



### TYPES OF ELECTRODES:

#### METAL – METAL INSOLUBLE SALT ELECTRODE:

As a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as 'Secondary reference Electrodes'.

The Metal – insoluble salt electrode consists of a metal (M) in contact with one of its sparingly soluble salts (MX) and a solution of a soluble salt having a common anion ( $X^-$ ), with the sparingly soluble salt.

Eg: 1. Calomel Electrode 2. Silver – Silver Chloride Electrode.

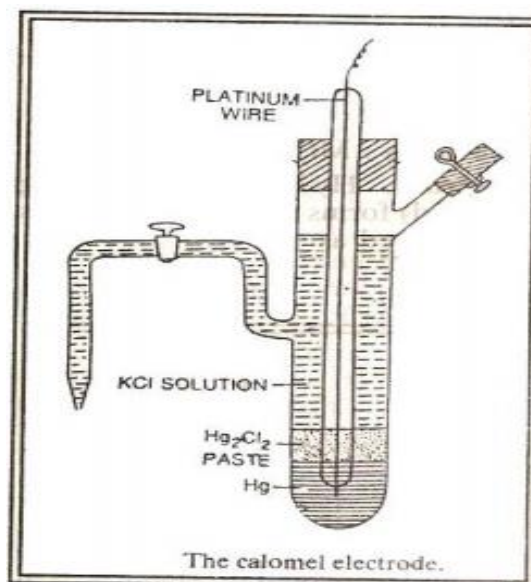
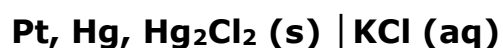
#### 1. Calomel Electrode:

It consists of a tube (glass) provided with two narrow side tubes, each on two sides. At the bottom of the tube, a small amount of Hg liquid of high purity is placed. It is covered with a paste of Hg +  $Hg_2Cl_2$ . The remaining portion of the tube is filled with a solution of KCl (0.1N for deci normal or 1N

for Normal or saturated solution for saturated calomel electrode SCE).

A platinum wire is sealed in a glass tube and is dipped in to the liquid Mercury layer for making electrical contact with the outer circuit. The side tube is used for making electrical contact with the salt bridge.

The electrode is represented as:



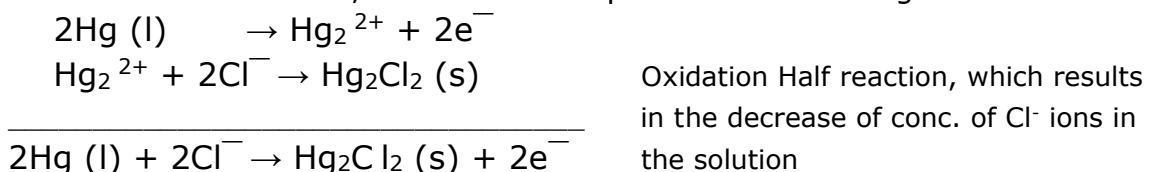
The potential of the calomel electrode depends upon the concentration of the KCl solution.

KCl Concentration	0.1 N	1.0 N	Saturated
Electrode potential (V)	0.3335	0.2810	0.2422

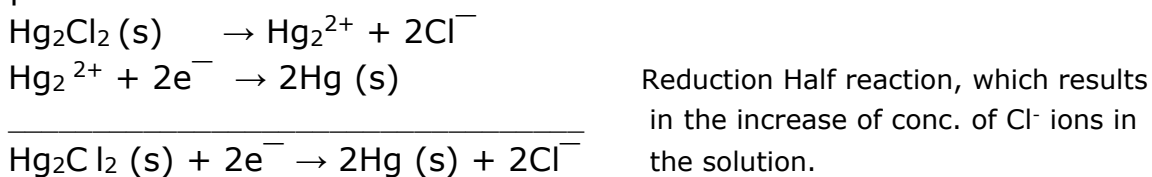
Calomel electrode acts as secondary reference electrode.

It acts as either anode or cathode w.r.t the other electrode connected to it.

If the electrode acts as anode, oxidation takes place & the following reactions occur:



If the electrode acts as cathode, reduction takes place & the following reaction takes place:

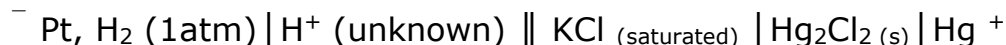


Thus, the Calomel electrode is reversible with respect to Cl<sup>-</sup> ions.

### **Measurement of P<sup>H</sup> using Calomel Electrode:**

When connected to SHE, the p<sup>H</sup> of an unknown solution can be determined using calomel electrode.

When saturated calomel electrode is connected through the potentiometer to standard hydrogen electrode dipped in the solution whose p<sup>H</sup> is to be determined.



The emf of the cell is

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} && (\text{since } E_{\text{H}^+/\text{H}_2} = -0.0591 \text{ p}^{\text{H}}) \\
 E_{\text{cell}} &= 0.2422 - (-0.0591 \text{ p}^{\text{H}}) \\
 E_{\text{cell}} &= 0.2422 + 0.0591 \text{ p}^{\text{H}} \\
 \mathbf{p^H} &= \frac{\mathbf{E_{\text{cell}} - 0.2422}}{\mathbf{0.0591}}
 \end{aligned}$$

### **Advantages:**

1. Its construction is very easy.
2. Potential Measurements does not vary with temperature
3. Results of cell potential Measurements are reproducible & stable over a long period.

### **Disadvantages:**



1. As  $\text{Hg}_2\text{Cl}_2$  degrades at about  $50^\circ\text{C}$ , it cannot be used above this temperature.

### **3. REDOX ELECTRODES:**

A Redox Electrode consists of an inert material like Pt or Au in contact with the solution of ions of two different oxidation states. The electrode potential is given by,

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[a_{\text{ox}}]}{[a_{\text{red}}]}$$

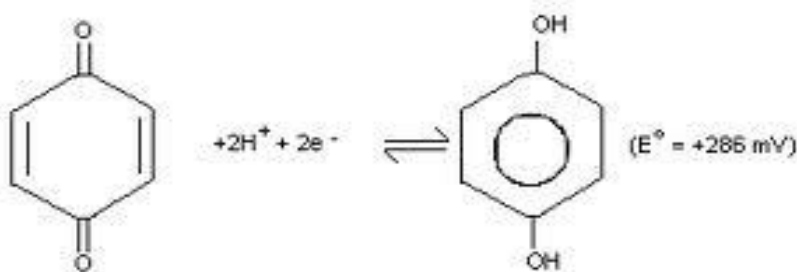
Where  $a_{\text{ox}}$  &  $a_{\text{red}}$  are activities of the oxidant & reductant.

Eg: 1. 'Pt' in contact with  $\text{Fe}^{+2}$  &  $\text{Fe}^{+3}$  ions of solution.

2. Quinhydrone Electrode

### **QUINHYDRONE ELECTRODE**

The Quinhydrone electrode consists of Pt wire immersed into a solution of saturated Quinhydrone, which is sparingly soluble in water & is formed by the combination of equimolar mixture of Quinone (Q) and hydroquinone ( $\text{QH}_2$ ). It is represented as **Pt, Q,  $\text{QH}_2$ ;  $\text{H}^+(\text{aq})$**  & is reversible with respect to  $\text{H}^+$  ions



It will either acts as anode or cathode depending on the other electrode connected to it.

If it acts as cathode, then the electrode reaction is



$$E_{\text{Q}} = E^\circ_{\text{Q}} - \frac{0.0591}{2} \log \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2}$$

$$= E^\circ_{\text{Q}} - \frac{0.0591}{2} \log \frac{[1]}{[\text{H}^+]^2} \quad (\text{ since } [\text{QH}_2] = [\text{Q}] )$$

$$= E^\circ_{\text{Q}} + 0.0591 \log [\text{H}^+]$$

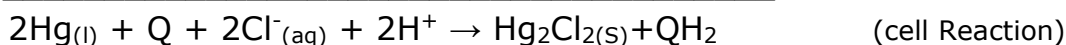
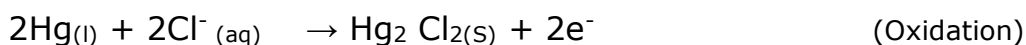
$$= E^\circ_{\text{Q}} - 0.0591 \text{pH}$$

$$\mathbf{E_{\text{Q}} = 0.6994 \text{ V} - 0.0591 \text{pH}} \quad (\text{ since } E^\circ_{\text{Q}} = 0.6994 \text{ V} )$$

Thus, the potential of Quinhydrone Electrode depends upon the  $P^H$  of the electrolyte solution with which it is in contact.

**Determination of  $p^H$  using Quinhydrone electrode:**

For determining the  $p^H$  of a solution, the Quinhydrone electrode is connected to saturated calomel electrode & the emf of the cell produced is determined potentiometrically. The Quinhydrone electrode acts as cathode ( $E^\circ = +0.6994$  v), While the SCE acts as anode ( $E^\circ = + 0.2422$  v).



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 0.6994 \text{ V} - 0.0591 \text{ p}^H - 0.2422 \text{ V}$$

$$= 0.4572 \text{ V} - 0.0591 \text{ p}^H$$

$$\text{p}^H = \frac{0.4572 \text{ V} - E_{\text{cell}}}{0.0591}$$

**Advantages:**

1. It is very useful for Acid – Base titrations.
2. Equilibrium is rapidly attained
3. It can be used in presence of ions of Many metals (Zn,Pb,Cu,Sn,Ni etc) which affect hydrogen electrode
4. It has low internal resistance
5. It is simple & free of errors due to the presence of Non – reducing gases or salts.
6. Very small quantities of solution are sufficient for the measurement.

**Disadvantages:**

1. It cannot be used in solutions of  $p^H > 8$ , since Hydroquinone ionizes as it is a weak dibasic acid ( $\text{QH}_2 \rightarrow \text{Q}^{-2} + 2\text{H}^+$ )
2. It is also oxidized by atmospheric oxygen

3. It cannot be used in solutions containing Redox systems, which would react with either Q or QH<sub>2</sub>.
4. It is not stable for a long time (above 30° C)

#### **4.ION SELECTIVE ELECTRODES:**

The electrodes which have the ability to respond to certain specific ions and develop a potential with respect to that species only in a mixture are called 'Ion Selective Electrodes'.

These electrodes use a membrane which is sensitive to particular chemical species. These are also referred to as 'membrane electrodes'.

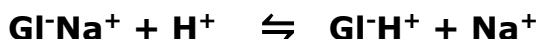
Eg : Glass membrane is H<sup>+</sup> ion selective only and does not respond to any other ion.

**GLASS ELECTRODE** –It is usually employed for p<sup>H</sup> measurement.

Construction: It consists of glass bulb made up of special type of glass called Corning glass (22% Na<sub>2</sub>O, 6% CaO, and 72% SiO<sub>2</sub>).It has low melting point and high electrical conductivity. The glass bulb is filled with 0.1 M HCl solution. A silver wire coated with AgCl is immersed in it. Ag/AgCl act as internal reference electrode.

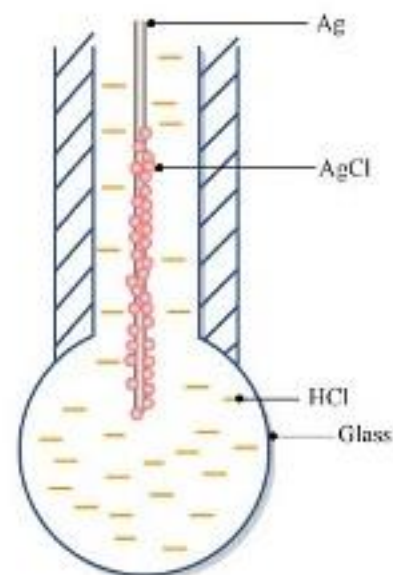
Glass electrode is represented as **Ag | AgCl (s) | HCl (0.1M) | glass**

Working : when glass electrode is dipped in the solution whose p<sup>H</sup> is to be determined there develops a potential difference between two surfaces of membrane then the potential difference developed is proportional to the difference in p<sup>H</sup> of the two solutions. Glass membrane functions as ion exchange resin and an equilibrium is set up between Na<sup>+</sup> ions of glass & H<sup>+</sup> ions of solution.



The electrode potential of glass electrode can be represented by

$$E_G = E_G^0 - 0.0591 \text{ p}^H$$



### Determination of $p^H$

For the determination of  $p^H$  of solution, glass electrode is coupled with saturated calomel electrode and is placed in the solution, whose  $p^H$  is to be determined and  $E_{\text{cell}}$  is measured. The cell is represented as



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \quad \text{or} \quad E_{\text{right}} - E_{\text{left}} \\ &= E_{\text{ref}} - E_G \quad (\text{where } E_{\text{ref}} = \text{Saturated calomel electrode} = 0.2422 \text{ V}) \\ &= E_{\text{ref}} - (E_G^0 - 0.0591 p^H) \\ &= E_{\text{ref}} - E_G^0 + 0.0591 p^H \quad \text{Or} \end{aligned}$$

$p^H = \frac{E_{\text{cell}} - E_{\text{ref}} + E_G^0}{0.0591}$
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### Advantages :

1. Glass electrode is simple & easy to operate,
2. Equilibrium is rapidly attained,
3. The results are accurate and is not easily poisoned,
4. It can be used in coloured, turbid or in colloidal solutions,
5. It can be used both in alkaline and oxidizing solutions.

### Limitations :

1. As the resistance of glass electrode is high, potentiometers containing vacuum tubes are required (Electronic potentiometers).
2. It is used up to a  $p^H$  range of 0-10. Special glasses can be used to measure up to 12. If  $p^H > 12$ , glass is attacked by an alkaline solution.
3. It only compares  $p^H$  values.

### NERNST EQUATION :

Nernst derived an expression for the determination of the electrode potential of any electrode at any concentration is called 'Nernst Equation'.

From Van't Hoff reaction isotherm, the free energy change accompanying a chemical reaction is given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{----- (1)}$$

$$\text{Since } \Delta G = -nFE \text{ \& } \Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{----- (2)}$$

Dividing Eq (2) by  $-nF$ , we get

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

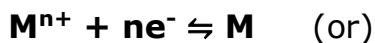
$$= E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{----- (3)}$$

Substituting the values of  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  (gas constant)  
 $T = 298 \text{ K}$  (Absolute Temperature)  
 $F = 96500 \text{ coulombs}$  (Faraday constant)

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{----- (4)}$$

Where  $E$  = Electrode potential,  
 $E^\circ$  = Standard Electrode potential  
 $N$  = no. of Electrons involved in the reaction

For a reaction taking place at the electrode **(Reduction)**



Oxidation state +  $ne^- \rightleftharpoons$  Reduced state

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[1]}{[M^{n+}]} \quad (\text{since } [M] = 1)$$

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \quad \text{----- (5)}$$

Or At any other temperature (  $T$  ),

$$\mathbf{E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]}$$

From this equation,

- 1) Electrode potential increases as the concentration of the solution  $[M^{n+}]$  increases & vice-versa.
- 2) Electrode potential increases as the temperature is increased & vice-versa.

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Reduced state}]}{[\text{Oxidation state}]}$$

For a reaction taking place at the electrode

**(Oxidation)**

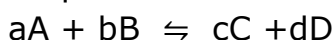


$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

$$E = E^{\circ} - \frac{2.303RT}{nF} \log [M^{n+}] \quad (\text{since } [M] = 1, \text{ for pure solid } )$$

$$\mathbf{E} = \mathbf{E}^{\circ} - \frac{2.303RT}{nF} \log [M^{n+}]$$

Nernst Equation can also be applied to any cell reaction such as



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

### **Applications of Nernst Equation:**

- 1) Nernst equation is applicable for the study of effect of Electrolyte concentration on electrode potential
- 2) It can also be used for the calculation of the potential of a cell under non-standard conditions
- 3) The unknown concentration of one of the ionic species in a cell can be known provided  $E^{\circ}_{\text{cell}}$  and the concentration of other ionic species are known.
- 4) The  $P^H$  of a solution can be calculated from emf measurements,

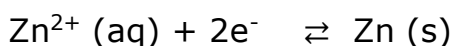
- 1)** A Zn rod is placed in a 0.1M solution of  $ZnSO_4$  at  $25^{\circ}C$ . Assuming that the salt is dissociated to the extent of 95% at this dilution. Calculate the potential of the electrode at this temperature ( $E^{\circ}_{Zn^{2+}/Zn} = -0.76V$ )

**Sol:** Concentration of  $ZnSO_4$  solution = 0.1 M

Percentage dissociation = 95

$$\therefore [Zn^{2+}] = 0.1 \times \frac{95}{100} = 0.095M$$

The electrode reaction in this case is

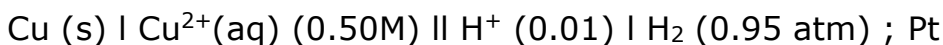


According to the Nernst equation, the potential of the electrode is given by,

$$E_{Zn^{2+}/Zn} = E^{\circ}_{Zn^{2+}/Zn} + \frac{2.303RT}{nF} \log [Zn^{2+}]$$

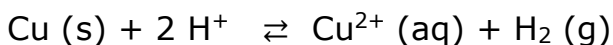
$$\begin{aligned}
 &= E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + \frac{0.0591}{n} \log [\text{Zn}^{2+}] \quad \text{at } 25^{\circ}\text{C} \\
 &= -0.76 + \frac{0.0591}{2} \log (0.095) = \underline{\underline{-0.79 \text{ V}}}
 \end{aligned}$$

**2)** Calculate the potential of the following electrochemical cell at  $25^{\circ}\text{C}$



$$\text{Given } E^{\circ}_{\text{cathode}} = 0.00\text{V} \text{ and } E^{\circ}_{\text{anode}} = 0.34\text{V}$$

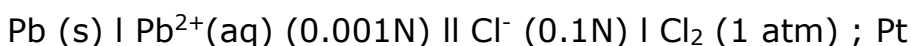
**Sol:** The overall reaction is



The potential of the cell is given by

$$\begin{aligned}
 E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]P_{\text{H}_2}}{[\text{H}^{+}]^2} \\
 &= (0.00-0.34) - \frac{0.0591}{2} \log \left[ \frac{(0.50)(0.95)}{(0.01)^2} \right] \\
 &= \underline{\underline{-0.449\text{V}}}
 \end{aligned}$$

**3)** Calculate the potential for each half cell and the total EMF of the following electrochemical cell at  $25^{\circ}\text{C}$



$$\text{Given } E^{\circ}_{\text{Pb}^{2+}/\text{Pb}} = -0.126\text{V} \text{ and } E^{\circ}_{\text{Cl}_2/2\text{Cl}^{-}} = +1.358\text{V}$$

**Sol:** The half cell reaction at anode is



$$\begin{aligned}
 E_{\text{Pb}^{2+}/\text{Pb}} &= E^{\circ}_{\text{Pb}^{2+}/\text{Pb}} - \frac{0.05916}{2} \log \frac{[\text{Pb(s)}]}{[\text{Pb}^{2+}]} \\
 &= -0.126 - \frac{0.05916}{2} \log \frac{1}{0.001} \\
 &= -0.126 - \frac{0.05916}{2} \times 3 = -0.126 - 0.09 = \underline{\underline{-0.216 \text{ V}}}
 \end{aligned}$$

Similarly, the half cell reaction at cathode is



$$E_{\text{Cl}_2/2\text{Cl}^{-}} = E^{\circ}_{\text{Cl}_2/2\text{Cl}^{-}} - \frac{0.05916}{2} \log \frac{[\text{Cl}^{-}]^2}{[\text{Cl}_2 (\text{g})]}$$

$$= 1.358 - \frac{0.05916}{2} \log(0.1)^2 \quad (\because P_{\text{Cl}_2} = 1 \text{ atm})$$

$$= 1.358 + 0.06 = \mathbf{1.418 \text{ V}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 1.418 - (-0.216) = \mathbf{1.634 \text{ V}}$$

### **THERMODYNAMICS of EMF of CELL :**

In an electrochemical cell, chemical energy is converted into electrical energy. As,  $\Delta G$  is the measure of the maximum useful work that can be obtained from a chemical reaction. Hence

$$\Delta G = \text{maximum work}$$

For a cell, whose electrodes differ in potential by 'E', the work done when charge  $nF$  is pushed along by the potential of the cell is given by ' $nFE$ '.

So, maximum work =  $nFE$ , where  $F$  = Faraday's constant,  
 $n$  = no. of electrons transferred

As the electrical energy of a cell is given by the decrease in the free energy ( $-\Delta G$ ), hence

$$\Delta G = W_{\text{max}} = -nFE \quad \dots\dots\dots (1)$$

From Gibb's-Helmholtz equation,

$$\Delta G = \Delta H + T \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P$$

Substituting  $\Delta G$  in the above equation, we get

$$-nFE = \Delta H + T \left[ \frac{\partial(-nFE)}{\partial T} \right]_P \quad \text{or} \quad -nFE = \Delta H - T.nF \left( \frac{\partial E}{\partial T} \right)_P$$

$$\text{or} \quad \Delta H = -nFE + nFT \left( \frac{\partial E}{\partial T} \right)_P$$

$$\text{or} \quad \Delta H = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_P - E \right]$$

comparing the relation with  $\Delta G = \Delta H - T\Delta S$  or  $\Delta H = \Delta G + T\Delta S$ ,

we get ,  $\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_P$  , where  $\left( \frac{\partial E}{\partial T} \right)_P$  = temperature coefficient of the cell

### **BATTERY CHEMISTRY**



**Battery:** The battery is a device consisting of one or more electrochemical cells connected with one another in a series that converts stored chemical energy into electrical energy.

Batteries are broadly divided into 3 types:

**(i) Primary Battery (or Primary cell):** The battery in which the cell reaction is not reversible is called 'a primary cell'. In primary cell when most of the reactants have converted to products, the cell no longer produce current and the cell is said to be 'dead'.

Eg: Dry Cell (Leclanche cell), Lithium Cell etc.

**(ii) Secondary Battery (or Secondary cell):** The battery in which the cell reactions are reversible is called 'a secondary cell'. These cells can be used by carrying a large no of cycles of charging & discharging.

Eg: Lead-Acid battery, Lithium ion cell, Ni-Cd battery etc

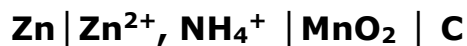
**(iii) Flow Battery ( or Fuel cell ):** It is an electro chemical cell that converts chemical energy into electrical energy, in which materials (reactants, products, electrolytes) pass through the battery.

Eg: Methanol-Oxygen fuel cell, hydrogen-oxygen fuel cell etc.

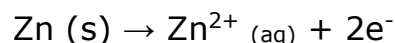
### 1) **ZINC-CARBON Battery (Dry Cell or Leclanche Cell):**

It consists of a Zinc anode which is shaped as a container containing an electrolyte consisting of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$  &  $\text{MnO}_2$  to which starch is added to make it thick paste – like to prevent the leakage. A carbon rod serves as a cathode, which is immersed in the electrolyte in the centre of the cell. Such a cell is known as 'dry cell' because of the absence of any mobile or liquid phase.

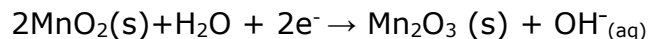
The Zn- $\text{MnO}_2$  (or dry) cell is represented as :



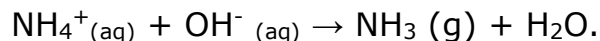
The oxidation reaction at anode is



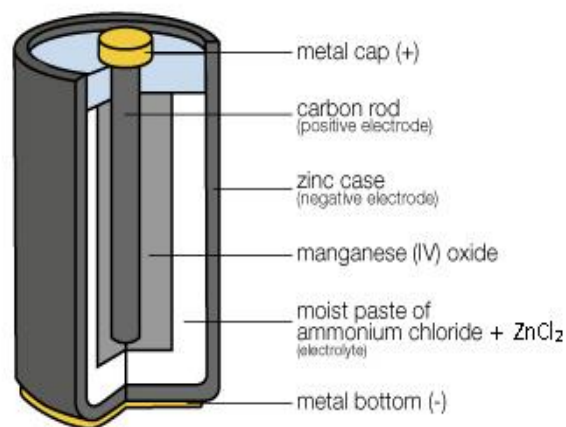
The reduction reaction at cathode is



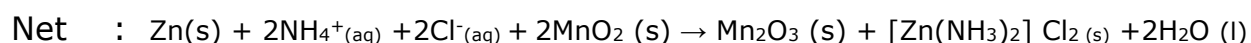
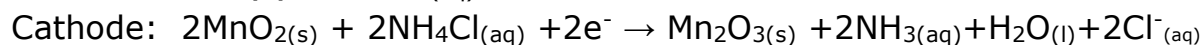
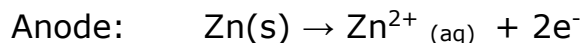
However, the reaction between  $\text{OH}^-$  formed at cathode and  $\text{NH}_4^+$  (derived from  $\text{NH}_4\text{Cl}$ ) evolves  $\text{NH}_3 (\text{g})$ , which disrupts the current flow



This is prevented by a reaction of  $\text{NH}_3(\text{g})$  with  $\text{Zn}^{2+}$  (from  $\text{ZnCl}_2$ ) to form the complex ion  $[\text{Zn}(\text{NH}_3)_2] \text{Cl}_2$ .



Hence the reaction at two electrodes are,



Since the reactions involved cannot be reversed by passing electricity back through the cell, it cannot be rechargeable.

### **Advantages:**

(i) It is cheap to make & gives voltage of about 1.5V

### **Disadvantages:**

(i) If current is rapidly drawn from it, products buildup on the electrodes there by causing drop in voltage.

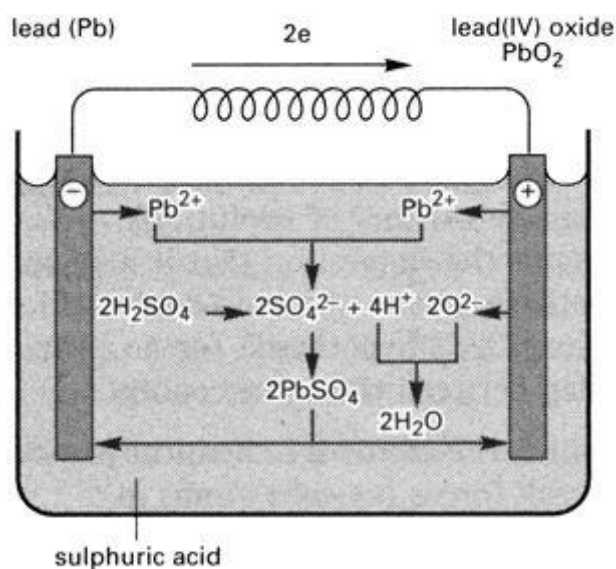
(ii) Since the electrolytic medium is acidic, so Zinc metal dissolves slowly, there by the cell run down slowly, even if it is not in use.

**Uses:** Dry cells are used in flashlights, transistor radios, calculators etc.

### **LEAD – ACID BATTERY:**

Lead-Acid battery is also called as lead-Acid storage cell and is one that can operate both as voltaic cell and as an electrical cell.

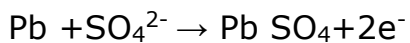
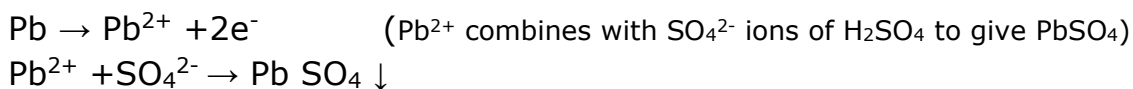
It consists of spongy lead anode and lead dioxide cathode. Lead dioxide is made into paste and passed into grid, made up of lead. A no. of lead plates (-ve) are connected in parallel and a no. of lead dioxide plates (+ve) are also connected in parallel. Lead plates fit in between lead dioxide plates. The plates are separated by adjacent ones by insulators like strips of wood, rubber or glass fibre etc. The entire setup is immersed in about 20% dil.  $\text{H}_2\text{SO}_4$  of density 1.20 to 1.30.



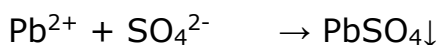
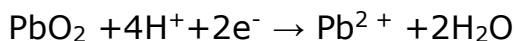
Cell notation :  **$\text{Pb, PbSO}_4 | \text{H}_2\text{SO}_4 | \text{PbSO}_4, \text{PbO}_2, \text{Pb}$**

**Discharging:** When cell is operating as voltaic cell then it is said to be discharging (Supplying of electrical energy)

**Anode:** (Oxidation of lead takes place at here) [Lead (-ve)]

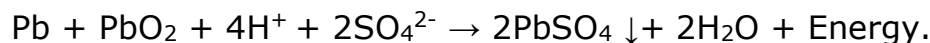


**Cathode:** ( $\text{PbO}_2$  (+ve))

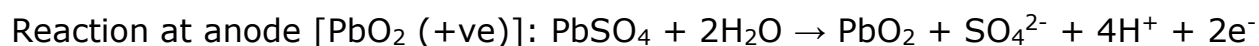
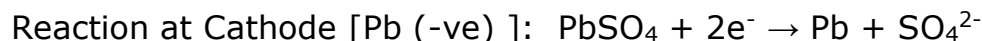


The electrons released from the anode flows to the dioxide electrode. Here  $\text{PbO}_2$  gains electrons to form  $\text{Pb}^{2+}$ . The  $\text{Pb}^{2+}$  ions then combine with  $\text{SO}_4^{2-}$  ions.

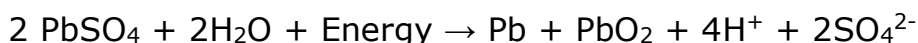
So, the net reaction during the discharging is



**Charging:** When both anode and cathode are covered by  $\text{PbSO}_4$ , the cell ceases to function as voltaic cell. The cell is then recharged by passing external emf greater than the cell emf (2volts). Then reverse of the discharging reactions takes place and anode become cathode and cathode become anode.



Net Reaction during charging is



During charging the electrodes restore their original conditions and the conc. of  $\text{H}_2\text{SO}_4$  increases, while during discharging the conc. of  $\text{H}_2\text{SO}_4$  decreases.

Generally lead – acid battery is a combination of six cells in series to form a battery of 12 volts (2 Volts each)

**Uses:** To supply current for electrical Vehicles, gas engine ignition, in telephone exchanges, railway trains, automobiles etc

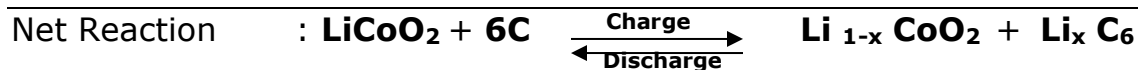
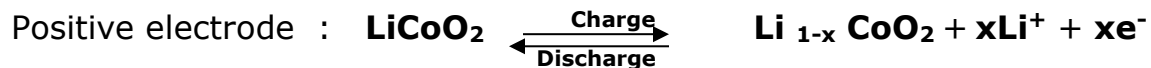
**LITHIUM – ION BATTERY (LIB):**

A LIB is a type of rechargeable battery in which intercalated Li compounds are used as the electrode materials.

### **Construction :**

The LIB consists of Lithium cobalt oxide (which offers high energy density) as the positive electrode and a highly crystallized specialty carbon (graphite) as the negative electrode. The electrolyte is an organic solvent like Lithium hexa fluoro phosphate ( $\text{LiPF}_6$ ). Lithium iron phosphate (LIP) & Lithium manganese oxide (LMO) can also be used as positive electrode.

The chemical reactions for charging & discharging are shown below :



In LIB, the Li ions move from the negative electrode (anode) to positive electrode (cathode) during discharge by reducing the cobalt from  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$  and from positive electrode (anode) to negative electrode (cathode) by oxidizing the cobalt from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$  during charging.

### **Advantages:**

- 1) Li – ion battery is lighter compared to all other equivalent energy density rechargeable batteries.
- 2) It has no memory effect. (i.e, discharge capacity of a battery is reduced when it is repetitively discharged incompletely & then recharged )
- 3) Self discharge is very less & environmentally friendly [(5-10%)/month]
- 4) The nominal cell voltage is higher than other batteries (3.6 V).

### **Disadvantages:**

- 1) Deep discharge reduces the life cycle & maintained with 40% charge in cold place.
- 2) It should be maintained with in safe voltage and current limits.
- 3) It should be often fully charged to prevent crystalline aging.
- 4) Restriction for transport due safety issue.

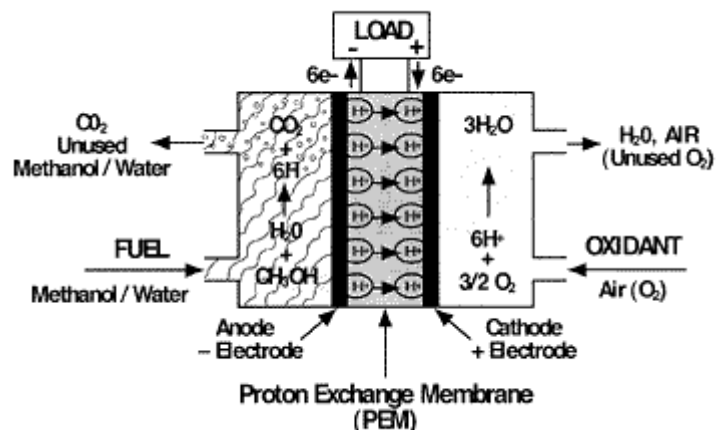
**FUEL CELLS:** A fuel cell is an electro chemical cell which converts chemical energy contained in a readily available fuel – oxidant system into electrical energy ( by oxidation of fuel at anode)

The basic principle of fuel cell is same as that of the electro chemical cell, the only difference is that the fuel and an oxidant stored outside the cell. These are supplied continuously and separately to the electrodes at which they undergo reactions. Fuel cells are capable of supplying current as long as the reactants are supplied.

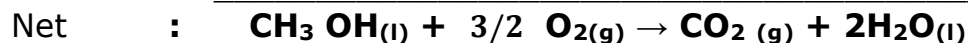


### **METHANOL – OXYGEN FUEL CELL:**

It is a sub category of proton – exchange fuel cells. The direct Methanol – fuel cell relies upon the oxidation of methanol on catalyst layer to form  $\text{CO}_2$ . Water is consumed at anode which is produced at the cathode. The positive ions ( $\text{H}^+$ ) are transferred across the proton exchange membrane 'Nafion', to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to a connected device. Currently Pt is used as a catalyst in both half-reactions. Methanol & water are absorbed on a catalyst usually made up of platinum particles & lose protons until  $\text{CO}_2$  is formed. Methanol or water mixture is circulated through an anode of cell while  $\text{O}_2$  or air is circulated at the cathode of the cell.



The half – reactions are:



**Advantages:**

- 1) Storage of methanol is much easier than H<sub>2</sub> as it does not need high pressure or low temp since it is liquid from -97°C to 64.7°C.
- 2) The energy density of methanol (the amount of energy contained in a given volume) is an order of magnitude greater than even highly compressed hydrogen.

**Advantages of Fuel cells:**

- 1) The energy conversion (from chemical to electrical) is highly efficient (75 to 82.8%) by fuel cells.
- 2) Noise and thermal pollution are low
- 3) They are modular and have low maintenance costs.
- 4) H<sub>2</sub>-O<sub>2</sub> fuel cell produces drinking water of potable quality

**Limitation of fuel cells:**

- 1) Life-times of fuel cells are not accurately known.
- 2) Their initial cost is high.
- 3) There is lack of infrastructure for the distribution of hydrogen.