

## UNIT-II

### **Electrochemistry and Applications:**

Electrochemical cell, Nernst equation, cell potential calculations and numerical problems, potentiometry- potentiometric titrations (redox titrations), concept of conductivity, conductivity cell, conductometric titrations (acid-base titrations)

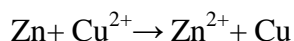
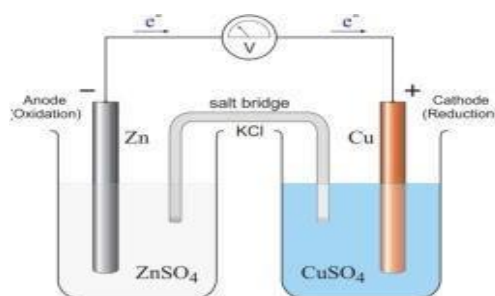
Electrochemical sensors–potentiometric sensors with examples, amperometric sensors with examples

Primary cells – Zinc-air battery, Secondary cells –lithium-ion batteries- working of the batteries including cell reactions; Fuel cells, hydrogen-oxygen fuel cell– working of the cells- Polymer Electrolyte Membrane Fuel cells (PEMFC)

## ELECTROCHEMISTRY

**Electrochemical cell:** Electrochemistry is defined as the branch of chemistry which deals with inter- conversion of chemical energy to electrical energy and vice versa. For example, in a battery, chemical energy is converted to electrical energy whereas in electroplating / electrolysis electrical energy is converted to chemical energy. Chemical energy is converted into electrical energy by Galvanic cell. These cells are known as electrochemical cells or voltaic cells. The best example of galvanic cell is Daniel cell. This cell is formed by combination of two half cells. One is oxidation half-cell or anodic half-cell and other one is reduction half-cell or cathodic half-cell. The oxidation half-cell consists of 'Zn' electrode dipped in  $\text{ZnSO}_4$  solution and reduction half-cell consists of 'Cu' electrode dipped in  $\text{CuSO}_4$  solution. Both the half cells are externally connected by metallic wire and internally connected by 'salt bridge'. Salt bridge is a U shaped tube containing solution of  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{KCl}$  or  $\text{NH}_4\text{NO}_3$  in agar-agar gel contained porous site. It maintains the electrical neutrality between two solutions.

The following reactions take place in the cell.



Presentation of galvanic cell:  $\text{Zn}|\text{Zn}^{2+}(\text{C1})||\text{Cu}^{2+}(\text{C2})|\text{Cu}$

### NERNST EQUATION

**Derivation of Nernst equation:** Nernst found that the single electrode potential varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. He derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation.

Consider the redox reaction:  $M^{n+} + ne^- \leftrightarrow M$

In the above reversible reaction the free energy change (G) and its equilibrium constant (K) are related by the following equation which is popularly known as Van't Hoff reaction isotherm.

$$\Delta G = RT \ln K + RT \ln \frac{\text{Product}}{\text{Reactant}}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{\text{Product}}{\text{Reactant}}$$

Where,  $\Delta G^0$  is the standard free energy change.

The free energy change is equivalent to the electrical energy –

$nFE$  Where  $n$  = valency

$F$  = Faraday (96500 coulombs)  $E$  = Electrode potential

$R = 8.314 \text{ Joules K}^{-1} \text{ mole}^{-1}$  (Gas constant)  $T$  = Temperature (K)

$-nFE = -nFE^0 + RT \ln([M])/([M^{n+}])$  (Concentration of  $M$  is unity)

$$-nFE = -nFE^0 - RT \ln [M^{n+}]$$

$$= -nFE^0 - RT 2.303 \log_{10} [M^{n+}]$$

Dividing the equation by  $-nF$

$$E = E^0 + 2.303RT/nF \log_{10} [M^{n+}]$$

Put the values of  $R$ ,  $T$  and  $F$  then

$$2.303RT/nF = 0.0591/n$$

$$\frac{2.303RT}{nF} = \frac{0.0591}{n}$$

$$E = E^0 + \frac{0.0591}{n} \log_{10} [M^{n+}]$$

**Single electrode potential:** If a metal is in contact with solution of its own ions, the metal either gains electrons or loses electrons. The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in the solution is called electrode potential. The tendency to gain electrons is called “reduction potential”. Similarly, the tendency to lose electrons is called “oxidation potential”. Oxidation and reduction potentials of an electrode

have same magnitude but opposite sign.

**EMF of electrochemical cell:** The difference between potentials of the two half cells is known as e.m.f.  $E_{\text{cell}} = E_R - E_L$  (Both are reduction potentials)

**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 (in case of gas electrode 1 atm pressure) at 25°C is called standard electrode potential.

**Measurement of electrode potential:** It is impossible to measure the absolute value of a single electrode potential. We can only measure the difference between two electrodes potentiometrically by combining them to form a complete cell. By arbitrarily fixing potential of one electrode as zero, it is possible to assign numerical values to potentials of various electrodes. Ex: "Standard Hydrogen Electrode": Pt, H<sub>2</sub>(g) (1 atm), H<sup>+</sup> (aq) (C=1M). All other single electrode potentials measured with respect to SHE are referred to as potentials on the hydrogen scale.

### Problems on Nernst's Equation: 1.

Calculate the Standard electrode potential of Cu<sup>+2</sup>/Cu if its electrode at 28°C is 0.296V and [Cu<sup>+2</sup>] is 0.03M

Solution :

$$\begin{aligned}
 E_{\text{Cu}^{+2}/\text{Cu}} &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + \frac{2.303RT}{nf} \log[\text{Cu}^{+2}] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log[0.03] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + 0.02986 [-1.5228] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 - 0.04547 \\
 E_{\text{Cu}^{+2}/\text{Cu}}^0 &= 0.296 + 0.04547 \\
 E_{\text{Cu}^{+2}/\text{Cu}}^0 &= 0.3414\text{V}
 \end{aligned}$$

2. Calculate the Standard electrode potential of Cu<sup>+2</sup>/Cu if its electrode at 25°C is 0.296V and [Cu<sup>+2</sup>] is 0.015M

Solution:

Given,  $E = 0.296\text{V}$   $[M^{n+}] = 0.015\text{M}$   $n = 2$

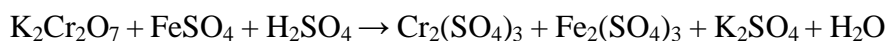
$$\begin{aligned}
 E &= E^0 + \frac{0.0591}{n} \log[M^{n+}] \\
 E_{\text{Cu}^{+2}/\text{Cu}} &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + \frac{0.0591}{n} \log[\text{Cu}^{+2}] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + \frac{0.0591}{2} \log[0.015] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 + 0.0295 [-1.8239] \\
 0.296 &= E_{\text{Cu}^{+2}/\text{Cu}}^0 - 0.0538 \\
 E_{\text{Cu}^{+2}/\text{Cu}}^0 &= 0.296 + 0.0538 \\
 E_{\text{Cu}^{+2}/\text{Cu}}^0 &= 0.3498\text{V}
 \end{aligned}$$

## POTENTIOMETRY

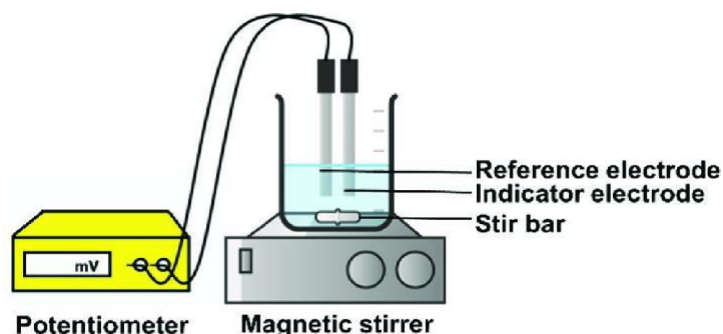
Potentiometric Titrations (Redox Titrations): The procedure of using a measurement of emf to determine the concentration of ionic species in solution is called as potentiometry.

Chemicals Required: Ferrous Ammonium Sulfate and standard K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution

**Principle:** The principle involved in potentiometric titration is the measurement of emf between two electrodes, an indicator electrode, (the potential of which is function of the concentration of the ion to be determined) and a reference electrode of constant potential. In this titration, the measurement of emf is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of emf readings against the volume of titrant.



**Procedure:** Take 25 ml of the given Ferrous Ammonium Sulfate solution into a beaker. Add one test tube of dilute sulphuric acid. Immerse the platinum and calomel electrode assembly into it. Connect the electrodes to potentiometer and measure the potential. Add  $\text{K}_2\text{Cr}_2\text{O}_7$  from the burette in increments of 0.5 ml and measure the potential after each addition. Plot a graph of  $\Delta E/\Delta V$  against volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  or plot a graph between emf and volume of  $\text{K}_2\text{Cr}_2\text{O}_7$ . The equivalence point can be obtained from the graph. Using the normality of  $\text{K}_2\text{Cr}_2\text{O}_7$  and volume of  $\text{K}_2\text{Cr}_2\text{O}_7$ , we can calculate the normality and weight of Ferrous Ammonium Sulfate.



#### Observations and Calculation:

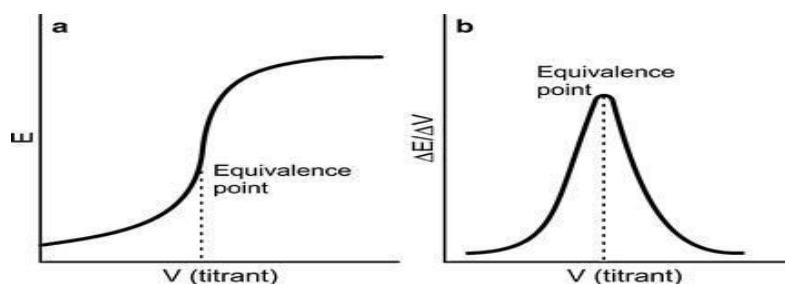
Volume of $\text{K}_2\text{Cr}_2\text{O}_7$	Emf (E) mv	$\Delta V$	$\Delta E$	$\Delta E/\Delta V$

$$N_{\text{FAS}} = \frac{N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7}}{\text{Volume of FAS}}$$

$$= \frac{0.5 \times}{25}$$

$$= \text{-----}$$

Graph:



## CONDUCTANCE

**Ohm's Law:** Ohm's law states that the current (I) flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of conductor.

$$E \propto I$$

$$\text{Thus } E = IR$$

## CONDUCTOMETRIC TITRATIONS

**Chemicals:** Stock acid solution, oxalic acid and Stock base solution.

**Principle:** Conductometric titrations works on the principle of Ohm's law. As current is inversely proportional to Resistance (R) and the reciprocal of resistance is termed as Conductance.

In the titration a strong base (NaOH) is added to a strong acid (HCl). Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as  $H^+$  ions react with  $OH^-$  ions to form un-dissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of  $OH^-$  ions.



### Procedure:

#### Step 1: Standardization of Sodium Hydroxide by Using Oxalic Acid

1. Rinse and fill the burette with the given NaOH solution
2. Pipette out 10 ml of 0.1 M oxalic acid solution into a clean conical flask
3. Add 1 or 2 drops of phenolphthalein indicator to oxalic acid solution.
4. Titrate the solution against sodium hydroxide solution drop wise with shaking till the

solution changes to pale pink

- Note the volume of NaOH used. It is the end point.
- Repeat the titration until the concordant readings are obtained
- Calculate the molarity of NaOH by using the formula mentioned above.

Volume of Oxalic acid ( $v_1$ ml)	Burette readings (ml)		Volume of NaOH Rindown ( $v_2$ ml)
	Initial	Final	

### Calculations

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2}$$

Molarity of NaOH =-----M

### Step 2: Determination of Molarity of Unknown HCl by Using Standard NaOH through Conduct metric Titration

- In 100 ml beaker take 25 ml of given unknown HCl solution and add 25 ml of distilled water. The contents are shaken thoroughly.
- Now, the conductivity cell is immersed in the beaker and the initial conductance of the solution is taken by stirring the solution and keeping it constant.
- Then, 0.5 ml portions of base is added from the burette and stirred well. The conductance of the solution for each addition is to be noted.
- The conductivity is corrected by multiplying with the factor  $[(v+V)/V]$ , where 'v' is the volume of base added and 'V' is the volume of solution initially taken in the beaker
- Plot the graph with respect to the volume of base consumed versus corrected conductance.

From the intersection point on the graph which gives value represents the equivalence points of acid and base.

### Observations and Calculations: Conductometric titration in between HCl & NaOH

Volume of base added	Conductance	Corrected conductance $C^1 = C[(v+V)/V]$

Calculation of Unknown molarity of HCl solution:

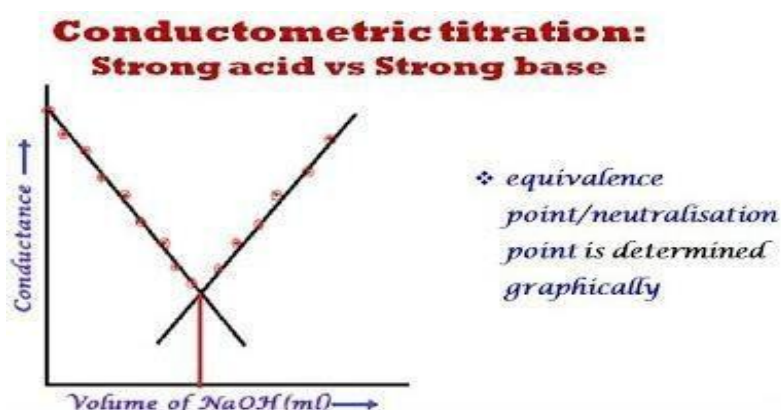
$$\frac{M_2 V_2}{n_2} = \frac{M_3 V_3}{n_3}$$

$$M_3 = \frac{M_2 V_2 n_3}{n_2 V_3}$$

Molarity of HCl =----- M

Amount of HCl =----- gms/l

**Graph:**

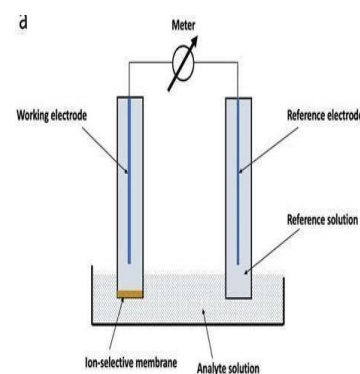
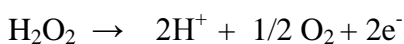
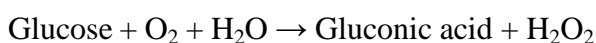


## ELECTROCHEMICAL SENSORS

**Potentiometric Sensors:** A potentiometric sensor is a type of chemical sensor that is used to determine the analytical concentration of test solution. These sensors measure the electrical potential of an electrode when no current is present. The sensor that measures the potential difference between working electrode and reference electrode is known as potentiometric sensors. Ion Selective Electrodes (ISE's) are used in Potentiometric sensors, these depends on the concentration of ionic species in the test solution used for electro analysis. In ISE's, the recognition of  $H^+$  ions is done by glass electrode sensing element. Potential of glass electrode will change according to the concentration of  $H^+$  ions in the test solution.

**Application: Analysis of glucose in blood:** Glucose is an electrically neutral molecule.  $C_6H_{12}O_6$  cannot be divided into ions. So, without ions signals are not obtained. Hence glucose has to be converted into ions, which are selectively detected.

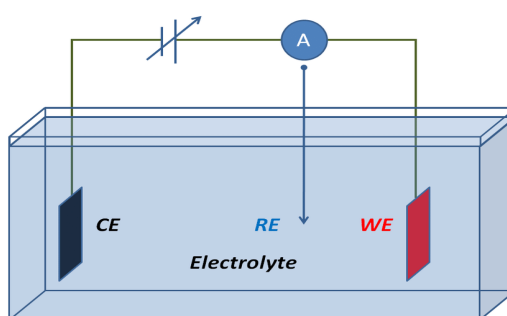
**Oxidation of glucose:** Glucose is oxidized to gluconic acid with liberation of  $H^+$  ions and electrons.





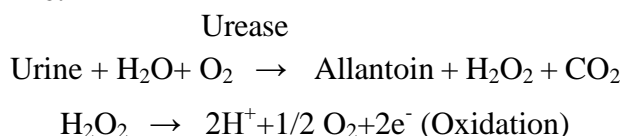
In the above chemical equation  $H^+$  ions were liberated and their concentration will be measured by glass membrane electrode and gives a value in the potentiometer. The obtained potential value gives the glucose concentration in blood.

**Amperometric Sensors:** This is a second kind of sensor in which it works based on the measurement of current between the working electrode and reference electrode, which is initiated by Redox reaction at working electrode. A redox reaction occurs during the measurement that generates current. This current is identified by working electrode and gives the signals.



### Application:

#### Analysis of uric acid in urine:

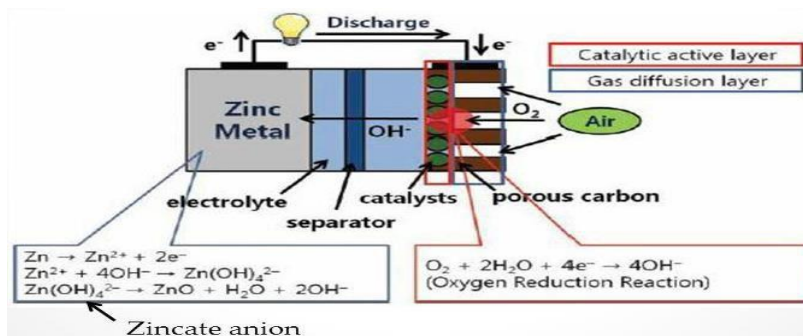


The produced electrons in the above reaction will be measured by working electrode and gives the value, which is directly proportional to the amount of uric acid present in the urine sample.

**PRIMARY CELLS:** These are irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means.

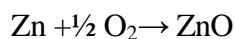
**Zinc-Air Battery:** Zinc-air battery is a primary battery, means they are non-rechargeable. Loose granulated Zinc acts as anode and porous carbon plate acts as cathode. The electrolyte used in this battery is NaOH/KOH. The cathode is activated by  $\text{MnO}_2$ . Two electrodes are separated using a gasket or a separator for insulation. The whole assembly is enclosed in a glass or ebonite container which contains gas permeable Teflon layer. The Teflon layer is hydrophobic, which allows only oxygen and prevents allowing moisture. During discharge, a mass of zinc particles forms a porous anode, which is saturated with an electrolyte. Oxygen

from the air reacts at the cathode and forms hydroxyl ions zinc oxide by releasing electrons to travel to the cathode. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed.



**At anode:**  $\text{Zn} + 2 \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$

**At Cathode:**  $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$



#### Advantages:

- Primary batteries have higher energy density than rechargeable secondary cells.
- High specific energy, long storage times (low self-discharge), and instant readiness give primary batteries a unique advantage over other power sources.
- They are usually the best choice for low-drain applications. They can be carried to remote locations and used instantly, even after long storage; they are also readily available and environmentally friendly when disposed.

#### Disadvantages:

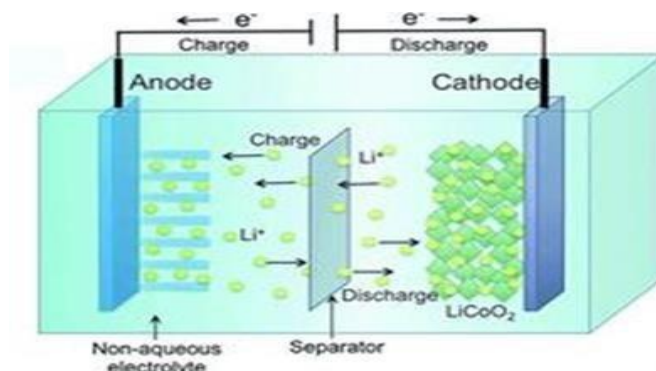
- They are non-rechargeable.
- They are less environment friendly batteries.
- Zinc-air batteries have limited power output, which is mainly due to the inadequate performance of air electrodes.
- The performance and operation of these batteries are depends on ambient conditions such as humidity and temperature.

#### Applications:

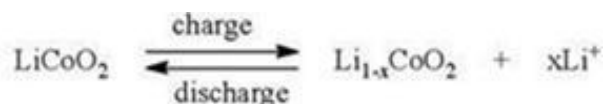
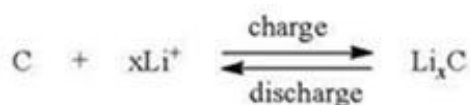
- Used as power source in hearing aids
- Used in electronic pagers
- Used in military radio receivers
- Used in voice transmitters
- 

**Secondary cells:** It can be recharged; in which cell reaction can be reversed by passing direct electric current in opposite direction. Thus, a secondary battery may be used through a large number of cycles of discharging and discharging.

Differences between primary cell (Non-Rechargeable Battery), and Secondary cell (Non rechargeable battery).

**Li-Ion Cell:**

This cell does not contain metallic lithium hence they called as lithium ion cells and use lithium ions instead. In this cell transport of  $\text{Li}^+$  ions through the electrolyte from one electrode to other electrode takes place through the external circuit to maintain charge balance. In this battery lithium ions interchanged between two layers of graphite and  $\text{LiCoO}_2$ . When the cell is in charging Lithium ions leaves  $\text{LiCoO}_2$  and travel through the electrolyte to the graphite ( $\text{C}_6$ ) and when the cell is discharges to provide power  $\text{Li}^+$  ions moved back through the electrolyte to the cobalt oxide while the electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.

**Anodic and Cathodic Reactions:****At Cathode:****At Anode:**

The charging and discharging cycle is simple migration of  $\text{Li}^+$  ions from one electrode to another electrode with flow of electrons through the external circuit.

**Advantages:**

- High energy density
- Lower self-discharge compared to other rechargeable batteries.
- Low Maintenance cost
- Good load characteristics

**Disadvantages:**

- Requires protection circuit to maintain voltage and current within safe limits.
- Subject to aging, even if not in use - storage in a cool place at 40% charge reduces the aging effect.

- Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
- Not fully mature - metals and chemicals are changing on a continuing basis

#### Applications:

- Pacemakers, defibrillators, watches, meters, cameras, calculators, portable, cellphones, Laptops, low-power use.

### FUEL CELL

**Introduction:** We know that voltaic cells convert the free energy change into electricity when a redox reaction is carried out. We also know that all ordinary combustion reactions of a fuel are redox reactions. However, when a fuel is burned, the electron exchange takes place when the oxidizing agent (oxygen) come in direct contact with the atoms of the substance being oxidized (fuel) and the energy is released in the form of heat.

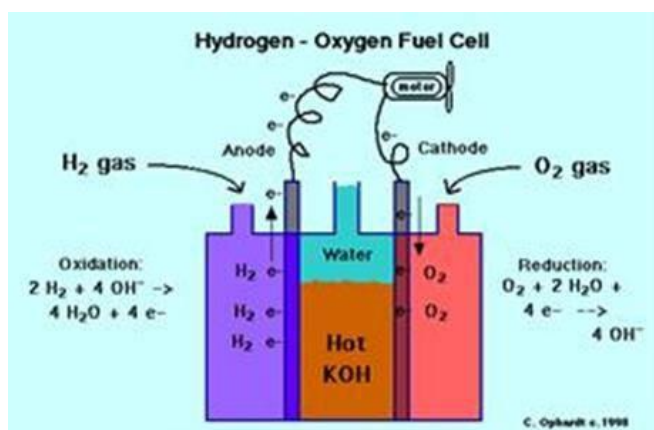
#### Working mode of fuel cell:

In a fuel cell, electricity is obtained by the oxidation of fuel without combustion. These fuel cells are much more efficient than thermal sources. These are used in space craft.

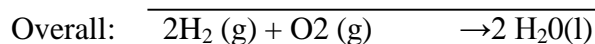
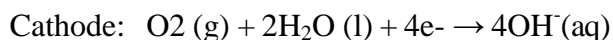
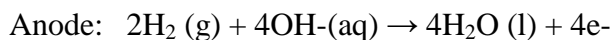


The mode of operation of fuel cells is fundamentally different from that of batteries. Batteries store electrical energy, while fuel cells convert energy obtained from chemical process directly into electricity. In fuel cells, in order to convert the maximum energy into electricity, the process which is almost reversible is selected.

**Hydrogen-Oxygen Fuel:** The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution



(25%). Hydrogen is oxidized at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:



### Applications and advantages:

- These types of cells are used in space-crafts.
- Fuel cells are efficient and pollution free.
- These types of cells are used in sub – marines or other military vehicles.
- The weight of the fuel battery sufficient for 15 days in space is approximately 250kg
- In case of hydrogen-oxygen fuel cells, the produced water is a valuable source of fresh water by astronauts.

### Disadvantages:

- Hydrogen Energy is Expensive.
- Storage Complications
- It's Not the Safest Source of Energy.
- Hydrogen Energy Cannot Sustain the Population.

### Polymer electrolyte membrane fuel cell (PEMFC):

It is also known as Proton-exchange membrane (PEM) fuel cell. In a PEMFC, hydrogen is oxidized at anode to produce  $\text{H}^+$  ions, which migrate through the PEM to the cathode. Reduction of oxygen takes place at cathode to form  $\text{O}^{2-}$  ions, which combine with the  $\text{H}^+$  ions to form  $\text{H}_2\text{O}$ . This develops a net cell potential that equals to the difference between electrochemical potentials of hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). When connected to an external load, a constant current can be drawn if the reactant gases are supplied and the reaction product ( $\text{H}_2\text{O}$ ) is removed continuously to maintain the system in steady state.

