#### **ELECTROCHEMISTRY AND APPLICATIONS**

(8h)

Electrodes –Reference electrodes (Hydrogen electrode and Calomel electrode), Electrochemical cell, Nernst equation.

Concept of pH, pH meter and applications of pH metry, Potentiometry- Potentiometric titrations (Redox titrations), Concept of Conductivity, Conductivity cell, Conductometric titrations (acid-base titrations),

Primary cells – Dry cell - Zinc-air battery,

Secondary cells – Lead acid battery, Lithium-ion batteries- working of the batteries including cell reactions, and button cells.

Fuel cells - Hydrogen-Oxygen and Methanol-Oxygen fuel cells - working of the cells.

#### **ELECTRO CHEMISTRY**

The branch of chemistry, which deals with the chemical changes caused by the passage of electric current; and production of electrical energy due to chemical changes, is known as electrochemistry.

**Electromotive force (emf):** The difference in electrode potentials which causes the flow of current from one electrode to another electrode is called Electromotive force emf of the cell

$$E_{cell} = E_{right} - E_{left}$$

- **Electrode potential**: Electrode Potential is the tendency of a metal electrode to lose or gain electrons, when it is contacted with a solution of its own salt. It is represented by E.
- Standard Electrode potential is the electrode potential measured at standard conditions i.e., at 298 K and 1M concentration of electrolyte and 1 atmosphere pressure. It is represented by E<sup>0</sup>

#### REFERENCE ELECTRODES

An electrode whose electrode potential is known is called standard electrode. These are also called as reference electrodes.

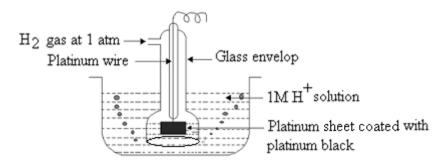
A reference electrode has a standard potential and it is used to compare the potential of other electrodes.

The two types of standard electrodes are

- Standard hydrogen electrode (SHE)
- Calomel electrode

#### Hydrogen electrode

- ♣ It has small thin platinum (Pt) sheet joined to the Pt wire and this Pt wire is closed in a glass tube.
- ♣ This tube is kept in another glass tube having an opening at the top and wide at the bottom as shown in diagram.
- **♣** The platinum sheet is coated with platinum black, it absorbs hydrogen gas and it speeds up the equilibrium between H<sub>2</sub> gas, H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup>.
- ♣ This electrode, when put in a 1N HCl solution and H<sub>2</sub> at 1 atm is passed through, gives a standard hydrogen electrode.
- ♣ The EMF of SHE is fixed at zero.



- ♣ pH of unknown solution can be measured by using two SHE electrodes as follows
- ♣ The concentration H<sup>+</sup> solution of the first SHE is 1M and the other is unknown.
- **Working:** when this Hydrongen electrode acts as anode following reaction takes place

$$H_2 \rightarrow 2H^+ + 2e^-$$

♣ When this hydrogen electrode acts as cathode following reaction takes place.

$$2H^+ + 2e^- \rightarrow H_2$$

- **↓** The chemical reaction takes place at Pt sheet is  $H^{\oplus}$  (aq)  $+ \overline{e} \rightarrow \frac{1}{2} H_2$  (g)
- ♣ Thus hydrogen electrode is reversible with respect to H+ ions.
- $\blacksquare$  This electrode is represented as Pt, H<sub>2</sub> (1atm) / H<sup>+</sup> (1M)

According to Nernst's equation,

$$E = E^{0} - \frac{2.303 \text{ RT}}{\text{nF}} \log \frac{[\text{H}_{2}]^{1/2}}{[\text{H}^{+}]}$$

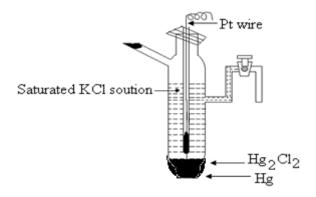
$$\Rightarrow E = 0.0592 \log \frac{1}{[\text{H}^{+}]} \quad (\because \text{E of right side SHE} = 0 \& [\text{H}_{2}] = 1)$$

$$\Rightarrow E = -0.0592 \text{ pH} \quad \text{at } 25^{0}\text{C}$$

#### **Calomel electrode**

- ♣ It is the commonly used mercury-mercurous chloride electrode. The potential of the calomel electrode varies with the concentration of potassium chloride used.
- ♣ A glass tube is filled with Hg then Hg<sub>2</sub>Cl<sub>2</sub> and saturated KCl solution as show in the diagram.
- ♣ A Pt wire is joined to the Hg layer and the electrode is shown as
- **♣** Hg, Hg<sub>2</sub>Cl<sub>2</sub> (S), KCl.
- ♣ The electrode reaction taking place in this half- cell is

$$Hg_2Cl_2(s) + 2\overline{e} \rightarrow 2Hg(l) + 2Cl^-(aq)$$



- ♣ P<sup>H</sup> of unknown solution can be measured by using calomel electrode and hydrogen electrode having solution of unknown pH.
- For the cell, Hg, Hg₂Cl₂(s), KCl (1N) || H+ (unknown), H₂ (1 atm), Pt
- ♣ The pH of the solution can be calculated as  $E_{cell} = -0.0591 \text{ pH} E_{calomel}$

Working: when this electrode acts as anode,

$$2Hg \leftrightarrow Hg_2^{2+} + 2e^{-}$$
 (oxidation)

These ions combine with chloride ions to form sparingly soluble mercurous chloride

$$Hg_2^{2+} + 2 Cl^- \leftrightarrow Hg_2Cl_2$$

When this electrode acts as cathode,

$$Hg_2Cl_2 \leftrightarrow Hg_2^{2+} + 2Cl^{-}$$

These mercurous ions discharges at the cathode as mercury

$$Hg_2^{2+} + 2 e- \leftrightarrow 2Hg$$

#### Calomel electrode is superior (always better than) to Hydrogen electrode:

- ♣ The hydrogen electrode is always affected by Hg, As, S and oxidizing agents.
- ♣ The hydrogen electrode cannot be used with redox reactions and many metal ion solutions.
- **♣** It is not easy to setup a hydrogen electrode.

The above problems are solved by using calomel electrode and hence it is always better than hydrogen electrode

#### **ELECTROCHEMICAL CELL**

• Electrochemical cell is a device, which convert chemical energy into electrical energy and vice-versa. Oxidation – reduction reactions take place in electrochemical cells for the generation of electrical energy.

There are two types of electrochemical cells.

- 1. **Galvanic or voltaic cells**. (These are devices which convert chemical energy into electrical energy. These reactions are spontaneous.
- 2. **Electrolytic cells.** (These are the devices in which electrical energy is converted into chemical energy (electrolysis). These are non spontaneous reactions.

#### **ELECTROLYTIC CELL**

#### **Electrolysis:**

• In this, electric current is passed through a substance in order to produce chemical changes in the substance.

#### **Electrolytic cell:**

- # It is a device that changes electric energy into chemical energy
- In this, electrolysis of a substance takes place to get chemical energy by breaking it.
- For example: when electric current is passed through water, it breaks water into H<sub>2</sub> and O<sub>2</sub>.
- It has cathode as the -ve electrode and anode as the +ve electrode. Oxidation takes place at anode and reduction takes place at cathode.

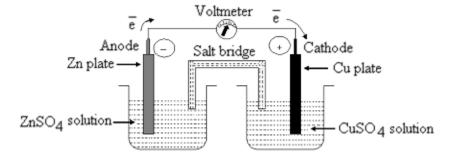
#### Galvanic cell

# ELECTRO CHEMICAL CELL (OR VOLTAIC CELL OR GALVANIC CELL):

- It is a device that changes chemical energy into electric energy by spontaneous redox reaction within the cell.
- It is also known as voltaic cell or galvanic cell.
- In this, electric energy is produced from a redox reaction that takes place inside the cell.
- It has cathode as the +ve electrode and anode as the -ve electrode. Oxidation takes place at anode and reduction takes place at cathode.
- The best example for a galvanic cell is **Daniel cell**.
- It has two half cells, one Zinc electrode put in ZnSO<sub>4</sub> solution (anode) and the other a copper electrode, put in CuSO<sub>4</sub> solution (cathode).
- The two solutions are separated by a salt bridge so that the solutions can flow out through it to touch each other.
- The EMF of the cell is 1.1 V and The electrode reactions in Daniel cell are:

At anode (-ve electrode): Zn 
$$\rightarrow$$
 Zn<sup>2+</sup> + 2 $\overline{e}$  (oxidation)  
At cathode (+ve electrode): Cu<sup>2+</sup> + 2 $\overline{e}$   $\rightarrow$  Cu (reduction)  
Cell reaction: Zn + Cu<sup>2+</sup>  $\rightarrow$  Zn<sup>2+</sup> + Cu

 $\Phi$  The cell shown as  $Zn/Zn^{2+}$  (aq)  $//Cu^{2+}$  (aq) //Cu



- Electrical current flows from Zn electrode to Cu electrode through external circuit.
- > Zinc rod loses its mass while the copper rod gains mass.
- ➤ Concentration of zinc sulphate solution increases while the concentration of copper sulphate solution decreases.
- > Solutions in both the compartments remain electrically neutral.

#### Representation of Galvanic cell:

- a) Anode half cell is written on left hand side and cathode half cell is written on right hand side.
- b) Anode is represented by writing the metal first and then the electrolyte. The two are separated by a vertical line or a semicolon. Concentration of the electrolyte can also be represented in bracket.
- c) Cathode is represented by writing the electrolyte first and then metal.
- d) The salt bridge is represented by two vertical lines, separating the two half cells.

Galvanic cell:  $Zn/Zn^{+2}$  (1M) //  $Cu^{+2}$  (1M) / Cu

#### **EMF** measurement of Daniel cell:

• The EMF of Daniel cell can be calculated from the reduction half cell potentials as:

$$E_{cell} = E_{right} - E_{left}$$

Where  $E_{right}$  = right hand side's electrode reduction potential  $E_{left}$  = reduction potential of left hand side electrode.

- We know that a +ve value of E<sub>cell</sub> shows that the cell reaction is feasible or possible. If E<sub>cell</sub> is -ve for particular cell then the electrodes must be reversed to bring about a cell reaction.
- Nernst's equation for a cell  $Zn(s)/Zn^{2+}$  (aq)  $//Cu^{2+}$  (aq) //Cu(s) and having cell reaction  $Zn + Cu^{2+}$   $Zn^{2+} + Cu$

$$E_{cell} = E^0 - \frac{2.303 \text{ RT}}{nF} log \frac{[zn^{2+}]}{[Cu^{2+}]}$$
 Where  $n = 2$ 

#### **NERNST EQUATION**

- ♣ Electrode potential varies with the change in concentration of ions and temperature. Hence, Walter Nernst derived a mathematical relation between standard electrode potential, temperature and concentration of ions.
- ♣ Nernst equation gives the relationship between standard electrode potential, temperature and the concentration of ions.
- ightharpoonup Consider a general redox reaction  $M^{n+}(aq) + n\overline{e} \rightleftharpoons M(s)$
- Now for a reversible reaction, the free energy change ( $\Delta G$ ) and it's equilibrium constant (K) are inter related as

$$\begin{array}{rcl} \Delta G &=& RT \ln K \, + \, RT \ln \frac{[Product]}{[Reactant]} \\ &&& \Delta G^0 &+& RT \ln \frac{[Product]}{[Reactant]} &----- &(1) \end{array}$$

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

➤ In a reversible reaction, the electrical energy is produced at the expense of the free energy decrease, i.e.

• 
$$-\Delta G = nFE$$
 and  $\Delta G^0 = -nFE^0 - - - - - - (2)$ 

- $\triangleright$  Where, E is the electrode potential, E<sup>0</sup> is the standard electrode potential,
  - F is Farady (or 96,500 coulombs).

➤ From 1&2 ⇒

$$-nFE = -nFE^{0} + RT ln \left(\frac{[M]}{[M^{n+}]}\right)$$

$$= -nFE^{0} + RT ln \left(\frac{1}{[M^{n+}]}\right) \qquad (\because [M] = 1)$$

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

$$\Rightarrow E = E^{0} + \frac{RT}{n^{n}} ln [M^{n+}] \qquad (dividing on both side by -nF)$$

The equation is known as Nernst's equation for electrode potential.

#### **Applications:**

- 1. The electrode potential can be calculated at 25°C from Nernst's equation as
- 2. The electrode potential of Galvanic cell can be calculated from the Nernst's equation.
- 3. For a chemical reaction like  $aA + bB \rightleftharpoons cC + dD$
- 4. Calculation of Equilibrium constant (K<sub>eq</sub>):

At equilibrium, E = 0 or  $\Delta G = 0$ 

For a chemical reaction  $aA + bB \rightleftharpoons cC + dD$ 

The Nernst's equation can be written as

$$\begin{array}{lll} 0 & = & E^{\,0} \, - \, \frac{2.303 \; RT}{nF} log \frac{[C]^{\,c}[D]^d}{[A]^a [B]^b} & (\because E = 0) \\ \\ \Rightarrow & E^{\,0} & = & \frac{2.303 \; RT}{nF} log \, K_{eq} & (\because \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}) \end{array}$$

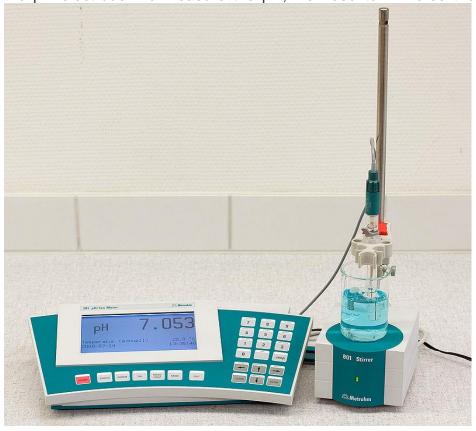
#### What is a pH Meter?

pH meter is a type of potentiometer we can use to measure the hydrogen ion activity in aqueous solutions.

The instrument can indicate the <u>acidity and basicity</u> of solutions as a pH value. The higher the pH value, the more the <u>alkaline</u> is the solution. The lower the pH value, the more acidic the solution is. Besides, it is a type of potentiometer because it measures the potential difference between the pH electrode and a reference electrode. However, this difference in electric potential relates to the pH of the solution.

When considering the principle behind the pH meter, it measures the voltage between two electrodes and displays the result as a pH value.

The meter contains a simple electronic amplifier and two electrodes for this purpose. Moreover, it has a display that is calibrated with pH units and a probe, which contains the pH electrode. To measure the pH, we need to immerse the probe into the test



The electrodes in this instrument are rod-like structures. Usually, manufacturers make these probes using glass.

The probe contains a bulb as the sensor at the terminal.

The glass electrode specifically contains a glass bulb that is sensitive to the hydrogen ion concentration

When we immerse the probe in the test solution, the hydrogen ions in the solution are exchanged with the positively charged ions in the glass bulb.

It creates an electrochemical potential across the glass bulb. Then, the electronic amplifier can detect this potential difference and converts it into pH units.

Furthermore, we commonly use pH meters for the determination of acidity and alkalinity of water, i.e. drinking water. Moreover, it is important in laboratory analysis. Besides, it is also important in soil pH measurement for agricultural purposes.

#### CONDUCTOMETRIC TITRATIONS OR CONDUCTOMETRY

- ♣ Conductometric titrations are used to detect the end point of the titration without using indicators.
- → These are based on the fact that the conductance of a solution at a constant temperature varies with the number and mobility of the ions present in it.
- ♣ The titration in which end point is identified with the help of conductivity measurement is known as conductometric titration.

**Procedure**: a solution (titrant) is added from the burette into a known volume of another solution (titrate) taken in a conductivity cell placed in a thermostat to keep constant temperature.

The conductivity readings are taken after each addition. The conductivity readings after each addition are plotted against the volume of titrant added; two linear curves are obtained, the interaction of which gives the end point of the titration. The point of interaction gives the volume of the titrant required to complete the reaction.

• It is a type of titration and in this conductivity of the reaction mixture is continuously checked as one reactant is added.

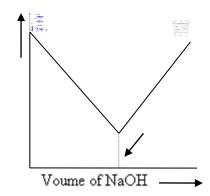
At the end point, the conductivity changes suddenly due to the change of concentration of H<sup>+</sup> and OH<sup>-</sup> ions in acid-base titrations

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#### **Acid-base Conductometric titrations:**

- Titration of a strong acid (HCl) with a strong base (NaOH):
- o The acid (HCl) is taken in the conductivity cell and the base (NaOH) in the burette.
- Before NaOH is added, the conductivity of HCl solution is high due to the presence of high moving H<sup>+</sup> ions. This is shown by point A on the curve of the graph.
- o On slow addition of NaOH, H<sup>+</sup> ions react with OH<sup>-</sup> ions to form non-conducting water molecules.

- o Hence, the conductivity of the solution decreases slowly, till the end point B is reached.
- Then the conductivity of solution increases as shown by point C (due to high moving OHions) as shown in the graph.

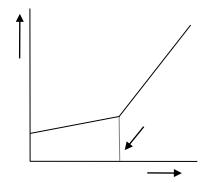


#### Titration of a weak acid (CH<sub>3</sub>COOH) with a strong base (NaOH):

- o The acid is taken in a conductivity cell and the base is taken in a burette.
- o Acetic acid has low conductivity. Since it is a weak acid.
- o Initially the conductivity of the solution is low because of its poor dissociation.
- As NaOH is added, the low conducting acid is changed into highly conducting salt (CH<sub>3</sub>COONa).

$$CH_3COOH$$
 + NaOH  $\rightarrow$   $CH_3COONa$  + $H_2O$   
low conducting acid High conducting salt

o After end point, sharp increase in conductance due to extra OH ions as shown in the graph.

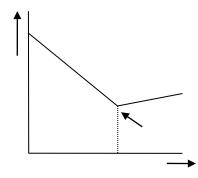


#### • Titration of a strong acid (HCl) with a weak base (NH<sub>4</sub>OH):

- o The acid (HCl) is taken in the conductivity cell and the base in the burette.
- Before **NH**<sub>4</sub>**OH** is added, the conductivity of HCl solution is high due to the presence of high moving H<sup>+</sup> ions. This is shown by point A on the curve of the graph.
- $\circ$  HCl has high conductivity at starting and it decreases slowly as NH<sub>4</sub>OH is added due to formation of low conducting NH<sub>4</sub><sup>+</sup> ions.

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$$

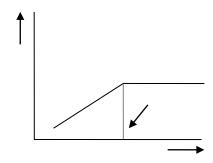
• There is not much increase in conductivity due to extra NH<sub>4</sub><sup>+</sup> ions as shown in the graph.



#### • Titration of a weak acid (CH<sub>3</sub>COOH) with a weak base (NH<sub>4</sub>OH):

- The conductivity of CH<sub>3</sub>COOH is low at starting.
- o An increase in conductivity is due to high conductance of salt NH₄<sup>+</sup> CH₃COO⁻ till end point.
- o After neutralization of the acid, addition of NH4OH does not increase the conductance as shown in the graph.

$$CH_3COOH + NH_4OH \rightarrow NH_4^+CH_3COO^- + H_2O$$



#### **Advantages of conductometry:**

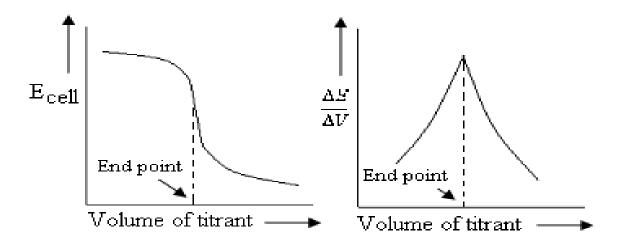
- It is very useful in case of colored solutions.
- More correct results are gotten from

#### **POTENTIOMETRIC TITRATION**

The titration in which the equivalent or end point of a reaction is determined with the measurement of the electrode potentials of the reaction mixture is known as potentiometric titration

- \* It is a direct titration of redox reaction
- \* In this, potentials of reaction mixture are measured to find out endpoint of a reaction.
- \* To do this, a combined glass electrode having glass electrode and a reference electrode is used.
- \* This glass electrode forms an electrochemical half cell with H<sup>+</sup> ions in the test solution.
- \* The reference electrode forms the other half cell with constant electric potential.
- \* The overall electric potential is calculated as  $E_{cell} = E_{glass} E_{ref}$
- \* E<sub>cell</sub> is recorded as titrant is added in constant volume.
- \* A graph of potential against volume added can be drawn and the end point of a reaction is halfway between the jumps in voltage.

 $\frac{\Delta E}{\Delta V}$  is also plotted against the volume of titrant as shown in diagram



### Types of potentiometric titrations:

#### • Redox titration:

- $\circ$  A platinum electrode is used in place H-electrode and The ferrous iron solutions is taken in the beaker and added dil H<sub>2</sub>SO<sub>4</sub>
- Pt electrode and calomel electrodes are put into solution and these are joined to the potentiometer.
- $\circ$  Emf of the solution after the addition of  $K_2Cr_2O_7$  is recorded.
- $\circ~$  A graph is drawn between volume of  $K_2Cr_2O_7$  added and observed emf , as shown above.

#### **BATTERIES**

- ♣ Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
- ♣ A device which converts chemical energy to electrical energy is called battery.
- **♣** Batteries are commercial electrochemical cells.
- **♣** Batteries are 3 types
  - 1. Primary cells
  - 2. Secondary cells
  - 3. Fuel cells

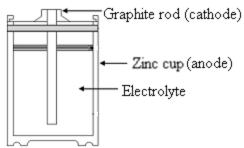
#### **Primary cells:**

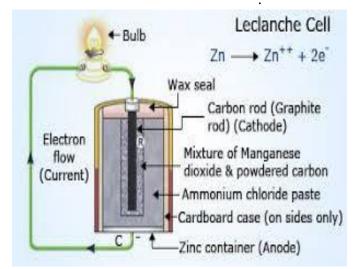
- These are disposable batteries, which are designed to use once and discard.
- > Cannot be recharged
- ➤ The cell reaction is not reversible; hence when all the reactants are converted into products, no more electricity is produced and the cell becomes dead and cannot be used after that. (the reactants are not return back to reactants by application of current)
- ➤ These batteries are used as a source of DC power.
- > These cells are convenient to use and inexpensive.
- > Used in ordinary gadgets like torch lights, watches and toys.
- Ex: Leclanche cell.

#### Leclanche cell (Dry cell):

- This is a primary cell without fluid component hence it is called dry cell.
- The basic design of the Leclanche cell dates to 1860's.
- In this, Zn cup acts as anode and graphite rod acts as cathode.
- A mixture of MnO<sub>2</sub>, Carbon, NH<sub>4</sub>Cl and ZnCl<sub>2</sub> is used as electrolyte.

• The cathode is kept in the electrolyte in the centre of the cell as shown





• The reactions at the Electrodes are

At anode:  $\operatorname{Zn}(s) \rightarrow \operatorname{Zn}^{2+} + 2\overline{e}$ 

Atcathode:

$$2MnO_2(s) + 2NH_4Cl(aq) + 2\overline{e} \rightarrow [Zn(NH_3)_2]Cl_2(s) + Mn_2O_3(s) + H_2O$$

Netreaction:

$$Zn(s) + 2MnO_2(s) + 2NH_4Cl(aq) \rightarrow [Zn(NH_3)_2]Cl_2(s) + Mn_2O_3(s) + H_2O + Zn^{2+}$$

• Dry cell is not costly to make and gives a voltage of 1.5 V.

#### **Applications:**

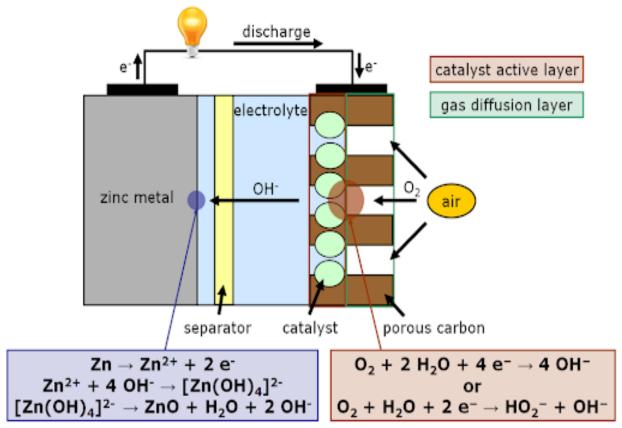
O Dry cells are used in flash light, portable radio, tape recorder, calculators, quartz wall clocks, etc.

#### **Limitations:**

- o Dry cell gives low voltage when it is used continuously.
- The cell gets discharged slowly even if it is not in use. Since Zinc is dissolved acidic electrolyte.

**Advantages**: low price, gives voltage of about 1.5 V; normally works without leaking (leak proof cells); possess high energy density; non toxic; contains no liquid electrolytes.





Voltage: 1.65 volts

Anode: Zinc plate

Cathode: A perforated Carbon plates treated with water repellants

Electrolyte: 5M NaOH/KOH

#### **Applications:**

Button cells are used in watches and in hearing aids ,in cameras and also used for the electric propulsion of vehicles.

#### **Secondary cells:**

- These are rechargeable batteries, which are designed to be recharged and used multiple times.
- ➤ The cells in which the cell reaction is reversed by passing direct current in opposite direction.
- ➤ The secondary batteries can be used through a large number of cycles of discharging and charging.
- ➤ They are used as source of dc power used to supply large, short term repetitive power requirements such as automotive and airplane batteries.
- ➤ These batteries have very large capacitance and long periods of low current rate discharge.
- ➤ The cell reaction is reversible; the reactants are return back to reactants by application of current
- These batteries are used as a source of DC power.
- > EX: Lead acid storage cell (Lead accumulator)

#### Lead accumulator or Lead storage battery:

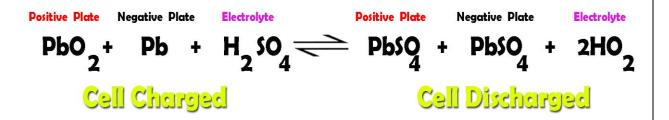
- A storage cell can operate both as a voltaic cell and as an electrolytic cell.
- When operating as a voltaic cell, it supplies electrical energy and as a result eventually becomes rundown, when being recharged; the cell operates as an electrolytic cell.
- This storage cell has the great advantage of working both as an electrolytic cell and as a voltaic cell.
- ▶ It has lead anode and PbO₂ cathode and dilute H₂SO₄ acts as electrolyte.
- These all are placed in a plastic container as shown in diagram.
- A number of lead plates (-ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel.
- The lead plates fit in between the lead dioxide plates. The plates are separated from adjacent one by insulators like wooden strips, rubber or glass fibre.
- The entire combination is immersed in 20% dilute H2SO4 corresponsing specific gravity of 1.2

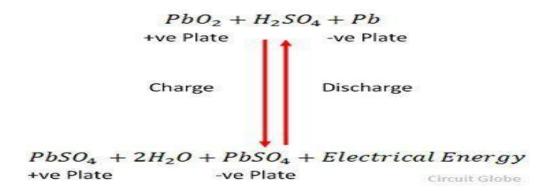
Anode: Pb grid coated with spongy Lead

Cathode: Pb grid coated with PbO2

Electrolyte: 5M Sulphuric Acid

The voltage of each cell is 2V.Hence the total voltage of six cells in series is nearly 12 volts.





#### Applications:

- o Lead storage batteries are used in cars, motor cycles, Lorries to start the engine.
- They are also used in invertors for electric supply in telephone exchanges, railway trains, hospitals and houses.

#### **Advantages:**

- 1. It has relatively constant potential i.e. 12V
- 2. It is portable and inexpensive.
- 3. When electricity is being drawn from the cell, to start the car it acts as a voltaic cell, when the car is running, the cell is being recharged as an electrolytic cell.

Lithium ion batteries (Rechargeable batteries): These cells do not contain metallic lithium hence they are called lithium ion cells and use lithium ions instead. In these cells actually oxidation and reduction reactions does not takes place, but transport of Li<sup>+</sup> 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 interchange between two layers of graphite and LiCoO2.

When the cell is in charging, lithium ions leave LiCoO, and travel through the electrolyte to the graphite( $C_8$ ).

Charging: 
$$LiCoO_2 + graphite(C_6) \rightarrow Li_{1-x}CoO_2 + Li_xC_6$$

When the cell discharges to provide power, Li<sup>+</sup>ions move 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.

Discharging: 
$$\text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \rightarrow \text{Li}_{1-x-y}\text{CoO}_2 + \text{Li}_{x-y}\text{C}_6$$

Thus charging and discharging cycle is simply migration of Li<sup>+</sup> ions from one electrode to another electrode with flow of electrons through the external circuit.

## **Applications:**

Li ion cells are used in electronic circuit boards ,military and space applications, medical devices such as neuro-simulators,drug delivery systems etc.

#### **Button cell**

A watch battery or button cell is a small single cell <u>battery</u> shaped as a squat <u>cylinder</u> typically resembling a <u>button</u>.

Stainless steel usually forms the bottom body and positive terminal of the cell.

An insulated top cap is the negative terminal.

Button cells are used to power small <u>portable electronics</u> devices such as <u>wrist</u> <u>watches</u>, and <u>pocket calculators</u>.

Wider variants are usually called coin cells.

Devices using button cells are usually designed around a cell giving a long service life, typically well over a year in continuous use in a wrist watch.

Most button cells have low self-discharge and hold their charge for a long time if not used.

Relatively high-power devices such as hearing aids may use a <u>zinc-air battery</u> which have much higher capacity for a given size, but dry out after a few weeks even if not used.

Button cells are single cells, usually disposable primary cells.

Common anode materials are zinc or lithium.

Common cathode materials are <u>manganese dioxide</u>, <u>silver oxide</u>, <u>carbon</u> <u>monofluoride</u>, <u>cupric oxide</u> or <u>oxygen</u> from the air.

## Chemistry of the Button Cell

- Half Equations
  - Cathode reaction

$$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-$$

Anode Reaction

$$\operatorname{Zn}_{(s)}$$
 + 2OH<sup>-</sup>  $\rightarrow$   $\operatorname{ZnO}_{(s)}$  +  $\operatorname{H}_2$ O + 2e<sup>-</sup>

Full Equation

$$\operatorname{Zn}_{(s)} + \operatorname{Ag_2O}_{(s)} \rightarrow \operatorname{2Ag}_{(s)} + \operatorname{ZnO}_{(s)}$$

#### FUEL CELL

- A fuel cell is an electrochemical cell which converts chemical energy contained in an easily available fuel oxidant system into electrical energy. The basic principles of fuel cells are identical to those of the electrochemical cells, the only difference is that in fuel cell the chemical energy is provided by a fuel and an oxidant stored outside the cell.
  - A fuel cell changes the chemical energy of the fuel into electricity. Since the electrons exchange takes place when a fuel gets oxidized.
- The essential process in fuel cell is

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Fuel + oxygen → oxidation products + electricity
```

#### Representation of fuel cell:

Fuel | electrode | electrolyte | electrode | oxidizer

- In this cell the fuel and oxidizer are continuously supplied separately to the electrodes of the cell.
- Fuel cells are capable of supplying current as long as the fuel and oxidizer are supplied.

#### • Principle:

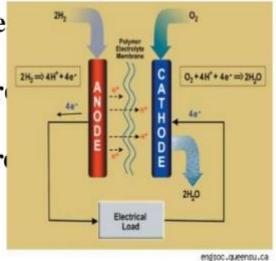
- The catalyst present in the anode pull off electrons from the H-rich fuel at the anode to produce H<sup>+</sup> ions then this H<sup>+</sup> ions travel through the electrolyte from anode to cathode.
- o Electrons formed at the anode travel through the circuit, give direct current and come to the cathode.
- $\circ$  There the electrons, H<sup>+</sup> ions and O<sub>2</sub> form water and this water comes out from the fuel cell as shown in the diagram.

#### H<sub>2</sub>-O<sub>2</sub> Fuel cell:

- It has as an electrolyte (2.5% KOH) and two inert electrodes having holes.
- H<sub>2</sub> and O<sub>2</sub> gases are passed through the anode and cathode rooms respectively.
- The electrodes made up of graphite are saturated with finely powdered platinum.
- A number of such fuel cells are joined together in series to make a battery.
- The following reactions take place in anode and cathode rooms are:

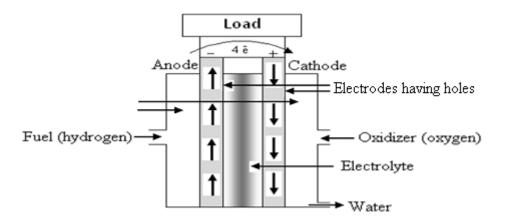
# GENERALIZED CHEMICAL REACTION

Anode side (an oxidation re  $2H_2 \Rightarrow 4H^+ + 4e^-$ Cathode side (a reduction re  $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ Net reaction (the "redox" re  $2H_2 + O_2 \Rightarrow 2H_2O$ 



11/13/2016

The standard EMF of the cell,  $E^0 = E_{oxd}^0 + E_{red}^0 = 0.83 + 0.40 = 1.23 \text{ V}$ 



#### o Applications:

- o H<sub>2</sub>-O<sub>2</sub> fuel cells are used as energy sources in space vehicles, submarines & military vehicles.
- $\circ$  250 kg of H<sub>2</sub> + O<sub>2</sub> is enough to produce electricity for 15 days
- o The water formed from fuel cell is very useful to austronauts.

#### **Advantages:**

- The energy conversion is very high (75-82%)
- Noise and thermal pollution are low.
- The maintenance cost is low for these fuels.
- The regenerative hydrogen oxygen fuel cell is an energy storage system for space applications.

#### **Limitations:**

- The life time of fuel cells are not accurately known.
- Their initial cost is high.
- The distribution of hydrogen is not proper.

# Direct Methanol Fuel Cell

- ❖Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel.
- ❖In the DMFC, the anode catalyst itself draws the hydrogen from the liquid methanol, eliminating the need for a fuel reformer.
- ❖ Efficiencies of about 40%.
- ❖This is operated at a temperature between 120-190°F.

#### Reactions

At Anode

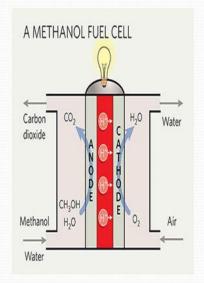
$$CH_3OH + H_2O \rightarrow 6 H^+ + 6 e^- + CO_2$$

At Cathode

$$\frac{3}{2}$$
O<sub>2</sub> + 6 H<sup>+</sup> + 6 e<sup>-</sup>  $\rightarrow$  3 H<sub>2</sub>O

Overall reaction

$$CH_3OH + \frac{3}{2}O_2 \rightarrow 2 H_2O + CO_2$$



He cell gives a voltage of nearly 1.2 volts.

It finds use in space craft for uninterrupted power supply and is also used by the Military.