MODULE-3

Electrochemistry and Battery Technology

CONTENTS

Introduction, electrochemical cells – Definition, Types of electrochemical cells, Construction, working & representation of galvanic cell. Modern sign conventions, single electrode potential, standard electrode potential. E.M.F of a cell, standard E.M.F of a cell, derivation of Nernst's equation.

Concentration cell- Definition with example, derivation of EMF of concentration cells.

Electrodes - Types of electrodes-Metal-metal ion electrode, Metal- metal salt ion electrode, gas-electrode and ion selective electrode.

Secondary reference electrodes – Calomel electrode-construction, working and applications.

Ion selective electrode- construction and working of glass electrode. Determination of pH of a solution using glass electrode. Numerical problems on E, E^0, E_{cell}, E^0_{cell} and concentration cells.

Potentiometric estimation of FAS using $K_2Cr_2O_7$ solution.

Battery technology

Batteries- Definition, classification of batteries- primary & secondary batteries.

Secondary batteries - construction, working and industrial applications of Lead-acid battery and Nickel-metal hydride battery.

Modern battery- construction, working and industrial applications of Li-ion batteries.

Fuel Cells- Introduction, definition, construction, working and industrial applications of H_2-O_2 fuel cell& Methanol-O_2 fuel cell.

10 hours

ELECTROCHEMISTRY

Electro-chemistry is a branch of science, which deals with conversion of chemical energy into electrical energy and vice-versa.

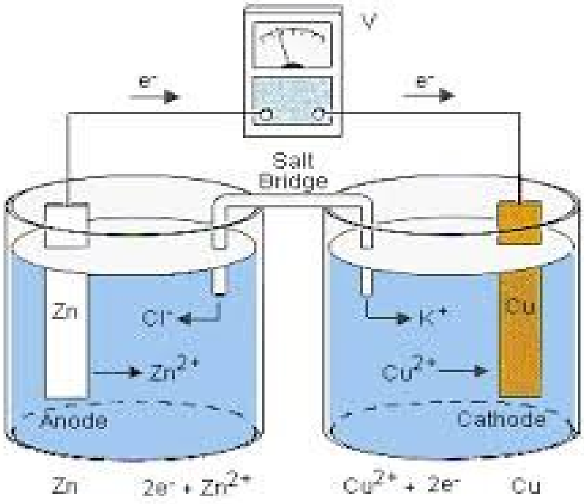
Electro chemical cell

An electro chemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy.

Classification: Electrochemical cells can be classified into 2 types. They are-
(1). Galvanic cells or voltaic cells (converts chemical energy into electrical energy).
(2). Electrolytic cells (Converts electrical energy into chemical energy).
A galvanic cell is a device which converts chemical energy into electrical energy.
Electrolytic cell is a device which converts electrical energy into chemical energy.

Galvanic cells or Voltaic cells

Galvanic cell generally consists of two electrodes dipped in two electrolyte solution which are connected through a salt bridge.
Example: Daniel cell



Daniel cell consists of Zn electrode dipped in $ZnSO_4$ solution and Cu electrode dipped in $CuSO_4$ solution. The two solutions are connected by a salt bridge. The salt bridge is a U-tube filled with saturated solution of KCl or $NH_4NO_3$and it provides a passage of ions from one half cell to another without mixing of two solutions. When Zn and Cu electrodes are connected externally through an ammeter by using a wire, the following reactions are observed.

At anode zinc passes into the solution (dissolution) as Zn^{2+}ion and liberating 2 electrons.

$Zn \longrightarrow Zn^{2+}+2e^{-}$ (oxidation)

At cathode Cu^{2+}ions gains electron and reduce to metallic copper(deposition), which is deposited at the copper electrode.

$Cu^{2+}+2e^{-}Cu$ (Reduction)

The overall chemical reaction may thus be represented by,

$Zn \longrightarrow Zn^{2+}+2e^{-}$

$Cu^{2+}+2e^{-}Cu \longrightarrow$

$Zn+Cu^{2+}Zn^{2+}+Cu$

In the construction of galvanic cell the electrode with high reduction potential acts as cathode (Cu = +0.34V) and electrode with low reduction potential acts as anode (Zn = -0.76V).

Cell notation and conventions or Representation of galvanic cell

According to present conventions a galvanic cell is represented by keeping in view of the following points,

1) Anode is written on left hand side, while cathode is written on the right-hand side.
2) The anode is written by writing the metal first (or solid phase) and then the electrolyte. The two are separated by vertical line. The electrolyte may be represented by the formula of the whole compound or by the ionic species and concentration may also be mentioned in bracket.

   Example: $Zn_{(s)}/ZnSO_{4(solution)}1M$

   OR

   Zn/Zn^{2+} (1M)

3) The cathode of the cell is written on the right-hand side. In this case the electrolyte is represented first and the metal (or solid phase) thereafter. The two are separated by a vertical line.

   Example: $CuSO_4$ (solution)1M/Cu(s)

   Or

   Cu^{2+}(1M)/Cu
4) A salt bridge is indicated by two vertical lines separating the two half cells.

Example:Daniel cell is represented as,

$Zn / ZnSO_4$ (solution)1M // $CuSO_4$ (solution)/cu

OR

Zn/Zn^{2+}(1m)// Cu^{2+} (1m)/ Cu.

5) EMF of the cell is calculated using the equation

$E_{cell}= E_{RHSE}-E_{LHSE}$

$E_{cell}= E_{Cathode}-E_{Anode}$

Or

Standard emf = $E^0_{Cell}=E^0_{(cathode)}-E^0_{(anode)}$

Problems:

1) Give the representation of a standard cadmium copper cell, write the electrode and cell reactions and calculate standard emf of the cell. If standard electrode potentials of cadmium and copper are -0.4 and +0.34 V respectively.

Ans:E^0_{cd}=0.4v

E^0_{cu}=0.34 $E^0_{cd}<E^0_{cu.}$Therefore cadmium acts as anode and copper acts as cathode.

Cell representation;-

$Cd/Cd^{2+}//Cu^{2+}/Cu$

Electrode reactions:

At anode,Cd $Cd^{2+}+2e^-$ $\longrightarrow$

At cathode,$Cu^{2+}+2e^-$ Cu $\longrightarrow$

Cell reaction (overall reaction), $Cd+Cu^{2+} \longrightarrow Cd^{2+} + Cu$

Standardemf of cell,

$E^0_{Cell}= E^0_{cathode}-E^0_{Anode}$

$=E^0_{cu}-E^0_{cd}$

$=0.34-(-0.4)$

$=0.34+0.4$

$E^0_{Cell} = 0.74$ V.

2) Calculate the standard emf of the following cell at 25^0C, writing its half cell reaction and net cell reaction.
   $Zn/Znso_4//cuso_4/cu$
   Standard potential of copper and zinc electrodes are +0.34 and -0.76 volts respectively.
   Answer: 1.1v

   Single electrode potential (E): The tendency of a electrode to loose or gain electrons when it is in contact with its own ions is called electrode potential or single electrode potential and it is denoted by 'E'.

   Standard electrode potential (E^0): Standard electrode potential is the electrode potential is in contact with a solution of unit concentration at 298 K (25^0C) and 1atms.pressure. It is denoted by E^0.

   Electromotive force (EMF) of a cell (E_{Cell}): The difference of potential, which causes a current to flow from the electrode of higher potential to another of lower potential is called the electromotive force (emf) of the cell and is expressed in volts. It is denoted by E_{cell}.

   Standard emf (E^0_{Cell}): Standard emf of a cell is defined as the emf of a cell when the reactants and products of the cell reaction are at unit concentration at 298 K and at 1 atmospheric pressure and is denoted by $E^0_{cell.}$

Nernst Equation

Derivation of Nernst equation:

Consider an electrode metal M dipped in its own ionsM^{n+}, the reversible redox electrode reaction is

$$M^{n+} + \quad ne^- \quad \rightleftharpoons M$$

reactant electrons product

The change in free energy of the electrode reaction is related to the electrode potential as follows

$$\Delta G = nFE$$

$$\text{or}\Delta G = - nFE$$

In its standard state,

$$\Delta G^\circ = - nFE^\circ$$

Where ΔG° is known as the standard free energy change (i.e. the change in free energy, when the concentrations of the reactants and products are unity each.),

E° is the standard electrode potential, F is the faraday constant and n is the no. of electrons involved in the electrode reaction.For a spontaneous reaction (reversible reaction), the change in free energy, ΔG and itsequilibrium constant K, are interrelated as,

$$\Delta G = \Delta G^\circ + RT\ln K_c$$

Where R= gas constant and T= absolute temperature

Since $K_c = \frac{[product]}{[reac\tan t]}$

Therefore,

$$\Delta G = \Delta G^\circ + RT \ln \frac{[product]}{[reac\tan t]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

Substitute nFE for ΔG and- nFE° for ΔG°

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

$$- nFE = - nFE^\circ + RT \ln[M] - R T \ln [M^{n+}]$$

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

Since, the concentration of the metal is unity under standard conditions i.e. [M] = 1

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

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

Divide throught by –nF

$$- \frac{n F E}{-nF} = - \frac{n FE^\circ}{-nF} - \frac{R T}{-nF} \ln[M^{n+}]$$

$$\boxed{E = E^\circ}$$

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

Or

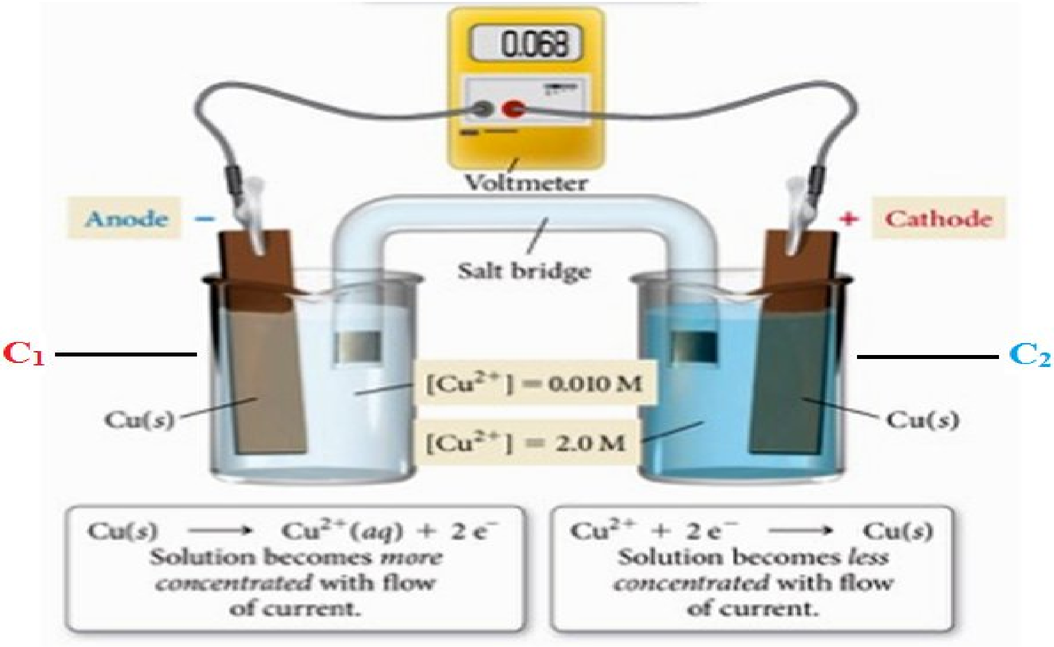
$$\boxed{E = E^{\circ} + \frac{0.0591}{n}\log[M^{n+}]}$$

This equation is known as the Nernst equation for electrode potential.

Concentration cells:

These are the cells, which consists of the two electrodes made of same metal dipped in same ionic solutions of the metal of different concentrations. The two solutions are in contact through a salt bridge. Because of difference in concentration of two solutions, a potential is developed.

Ex: Two Cu electrodes are dipped in $CuSO_4$ solution of different concentrations 0.1 M (C1) and 1M (C2).



The cell is represented as,

$Cu/cu^{2+}_{(C1)}//cu^{2+}_{(c2)}/cu$ [where c_1 and c_2 are the concentrations of metal ions (Mn^+) in contact with two electrode and $c_2>c_1$]

At anode cu gets converted into cu^{2+}ions and goes in to the solution liberating 2 electrons (oxidation taken place).

$$Cu \longrightarrow Cu^{2+}+2e^-$$

At cathode cu^{2+} ions deposited as copper metal.

$Cu^{2+}+2e^{-} \longrightarrow Cu$

The emf of the cell is given by,

$E_{Cell}=E_{Cathode}-E_{Anode.}$ (Or) $(E_{cell}=E_{right}-E_{left})$.

Note: 1) As long as $C_2>C_1$ cell reaction taken place.
2) $C_2>C_1$ cell potential becomes zero.
3) $C_2>C_1$ cell reaction is not spontaneous.

PROBLEMS

(1). Two copper rods are placed in $CuSO_4$solution of concentration 0.1M & 0.01M separately in the form of a cell. Write the scheme of the cell and calculate its emf at 298^0K.

Answer: Cell representation,

$Cu/Cu^{2+}_{(0.01M)}//Cu^{2+}_{(0.1M)}/ Cu$

$E_{Cell} = \frac{0.0591}{n}\log \frac{C2}{C1}$ $[(c_2>c_1)]$

$=\frac{0.0591}{2}\log\frac{0.1}{0.01}$

$= 0.02955 \log 10$

$=0.02955x1$

$\mathbf{E_{Cell} = 0.02955V}$

(2). A concentration cell is constructed by dipping Cu rod in 0.001M & 0.1M $CuSO_4$ solution. Calculate the emf of the cell at 298^oK.

Answer: Cell representation,

$Cu /Cu^{2+}_{(0.001M)}// Cu^{2+}_{(0.1M)}/Cu$

$E_{Cell}= \frac{0.0591}{n}\log \frac{C2}{C1}$

$= \frac{0.0591}{2}\log\frac{0.1}{0.001}$

$= \frac{0.0591}{2} \log 100$

$\mathbf{E_{Cell}= 0.0591V}$

(3). A cell is formed by dipping Nickel rod in 0.01M Ni^{2+} solution and lead rod in 0.5M Pb^{2+} solution. The standard electrode potentials of Ni & Pb are -0.24V & -0.13V respectively. Write the cell representation, cell reaction & calculate the emf of the cell.

Answer: Cell representation,

$Ni/Ni^{2+}{}_{(0.01M)}//Pb^{2+}{}_{(0.5M)}/Pb$

Cell reaction,

At anode, $NiNi^{2+}+2e^{-} \longrightarrow$

At cathode, $Pb^{2+}+2e^{-}Pb \longrightarrow$

Net cell reaction, $Ni+Pb^{2+} \longrightarrow Ni^{2+}+Pb$

$E^0_{Cell}=E^0_{Cathode}-E^0_{Anode}$

$=E^0_{Pb^{2+}/Pb}-E^0_{Ni/Ni^{2+}}$

$=-0.13-(-0.24)$

$\mathbf{E^0_{Cell}=0.11V}$

$$E^0_{Cell}=E^0_{cell}+\frac{0.0591}{n}\log\frac{[\text{concentration at cathode}]}{[\text{concentration at anode}]}$$

$$=E^0_{cell}+\frac{0.0591}{2}\log\frac{[pb^{2+}]}{[Ni^{2+}]}$$

$$=0.11+\frac{0.0591}{2}\log\frac{[0.5]}{[0.01]}$$

$=0.11+0.02955 \log 50$

$=0.11+0.02955x1.6989$

$=0.11+0.0502$

$\mathbf{E_{Cell}=0.1602V}$

(4). An electro chemical cell consists of iron electrode dipped in 0.1 M $FeSO_4$& silver electrode dipped in 0.05 M $AgNO_3$.Write the cell representation, cell reaction & calculate emf of the cell at 298K. Given that the standard reduction potential of iron & silver electrodes are -0.44 & +0.80V respectively.

Answer: Cell representation,

$Fe/Fe^{2+}{}_{(0.1\ M)}//Ag^{+}{}_{(0.05M)}//Ag$

Half-cell reaction,

At anode, $Fe Fe^{2+}+2e^{-} \longrightarrow$

At cathode, $(Ag^{+}+e^{-} Ag)\ x2 \longrightarrow$

$E^{0}_{Cell}=E^{0}_{Cathode}-E^{0}_{Anode}$

$=E^{0}_{Ag^{+}/Ag}-E^{0}_{Fe/Fe^{2+}}$

$=0.80-(-0.44)$

$\mathbf{E^{0}_{Cell}=1.24V}$

$$E_{Cell}=E^{0}_{Cell}+\frac{0.0591}{n}\log\frac{[\text{concentration at cathode}]}{[\text{concentration at anode}]}$$

$$=1.24+\frac{0.0591}{2}\log\frac{[Ag^{+}]^{2}}{[Fe^{2+}]}$$

$$=1.24+0.02955\log\frac{[0.05]^{2}}{[0.1]}$$

$$=1.24+0.02955\log 0.025$$

$$=1.24-0.0473$$

$\mathbf{E_{Cell}=1.1927\ V}$

(5). Calculate the E_{Cell}, when Al & Cu electrodes are in contact with 0.02M Aluminium and copper ions solutions respectively at 298 K. Write the cell representation & cell reactions. Given $E^{0}_{cu^{2+}/cu}=+0.34$ V & $E^{0}_{Al^{3+}/Al}=-1.66$ V.

Cell representation

$Al/Al^{3+}{}_{(0.02\ M)}\ //\ Cu^{2+}{}_{(0.25\ M)}/\ Cu$

Reaction,

$(Al \longrightarrow Al^{3+}3e^{-})\ 2$

$(Cu^{2+}+2e^{-} Cu)\ 3 \longrightarrow$

$2Al+3Cu^{2+} 2Al^{3+}+3Cu \longrightarrow$

$E^0_{Cell}=E^0_{Cu}-E^0_{Al}$

$=0.34-(-1.66)$

$=2.0\ V$

$$E_{Cell}=E^0_{Cell}+\frac{0.0591}{n}\log\frac{[3cu^{2+}]}{[2Al^{3+}]}$$

$$=2+\frac{0.0591}{n}\log\frac{[0.25]^3}{[0.02]^2}$$

$$=\frac{0.0625}{0.0004}=2.1938=0.00648$$

E_{Cell}= 1.99 V

Types of electrodes

Electrodes are mainly classified into four types, depending upon the purpose for which they are used.

1) Metal-Metal ion electrodes.
2) Metal-Metal salt ion electrode.
3) Gas electrode.
4) Ion selective electrode.

(1) **Metal-Metal ion electrode:** An electrode of this type consists of a metal dipped in a solution containing its own ions.
Example: Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^+

(2) **Metal-Metal salt ion electrode:** These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution containing anion of the salt.
Example: Calomel electrode ($Hg/Hg_2cl_2/cl^-$), Silver-Silver chloride electrode ($Ag/AgCl/Cl^-$)

(3) **Gas electrode:** These are the electrodes where gas will be in equilibrium with its ion present in an electrolyte.
Example: Hydrogen electrode ($Pt/Hg/H^+$), Chlorine electrode ($Pt/Cl_2/Cl^-$)

(4) **Ion selective electrode:** In an ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions.
Example: Glass electrode (exchange H^+ ions with the solution).
(These are the electrodes which are sensitive to particular ion species and will develop a potential, when a membrane is in contact with an ionic solution).

Reference electrodes

Reference electrodes arethe electrodes with reference to these, the electrode potential of any electrode can be measured. The best reference electrode used in standard hydrogen electrode, whose electrode potential at all temperatures is taken as zero.

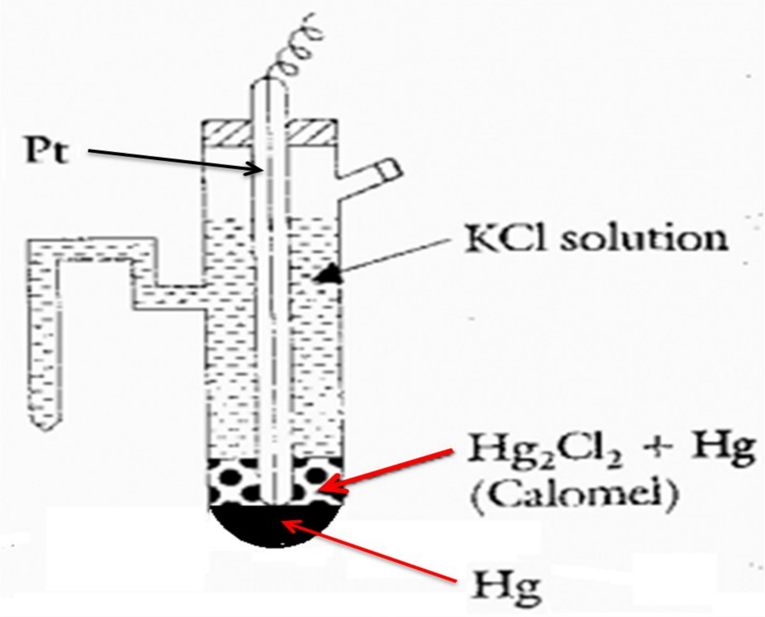
Classification of reference electrodes:Reference electrodes are classified into two types. They are,

1) Primary reference electrodeExample: Hydrogen electrode.
   (It is very difficult to set up because pure H_2 gas is required and production of pure H_2 gas is a problem, due to impurity it gets poisoned very quickly and also it is difficult to maintain H_2 gas uniformly at 1atmosphere).
1) Secondary reference electrode (Subsidiary reference electrode).
   Example: Calomel electrode, Ag-AgCl etc.

Secondary reference electrode:

Because of the difficulties involved in the use of standard hydrogen electrode as reference electrode, some other electrodes of constant electrode potential are used they are called as secondary reference electrodes. The commonly used reference electrodes are calomel electrode and silver-silver chloride electrode.

Calomel electrode:



Calomel electrode is a metal-metal salt ion electrode. It consists of Hg, mercurous chloride and a KCl solution. Mercury is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride with mercury and potassium chloride solution. A solution of KCl is introduced above the paste through the side tube. A platinum wire dipping into the mercury layer and is used for making electrical contact. The concentration of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode respectively.

Calomel electrode can be represented as,

$Hg/Hg_2Cl_{2(s)}/Cl^-$ or $Hg/Hg_2Cl_{2(s)}/KCl_{(sat).}$

The calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

When it acts as anode, the electrode reaction is,

$2Hg\,Hg^{2+}+2e^- \longrightarrow$

$Hg_2^{2+}+2Cl^-\,Hg_2Cl_2 \longrightarrow$

$2Hg^+ + 2Cl^-\,Hg_2Cl_2+2e^- \longrightarrow$

When it acts as cathode, the electrode reaction is,

$Hg_2^{2+}+2e^-\,2Hg \longrightarrow$

$Hg_2Cl^2Hg_2^{2+}+2cl^- \longrightarrow$

$Hg_2Cl_2+2e^- \longrightarrow 2Hg+2Cl^-$

Therefore, the net reversible electrode reaction is,

$Hg_2Cl_2+2e^-\,2Hg + 2Cl^- \longrightarrow$

The electrode potential of calomel electrode depends upon the concentration of KCl solution used. The reduction potentials of various KCl concentrations at 25^0C.

0.1N KCl = 0.334 V

1N KCl = 0.281 V

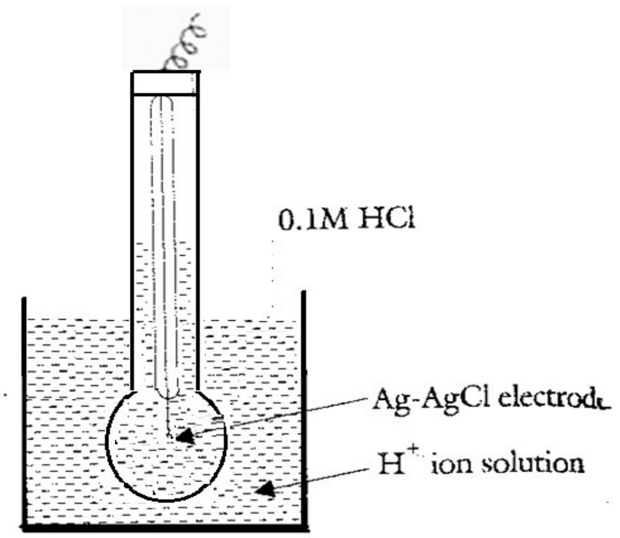
Saturated KCl = 0.2422 V

Uses

1. Used as secondary reference electrode in the measurement of single electrode potential. It is commonly used as reference electrode in all potentiometric determinations.

Glass electrode

Glass electrode is a P^H sensitive electrode therefore it is widely used for P^H determination.



The glass electrode consists of a glass bulb made up a special type of glass (corning glass 72%, silicon dioxide (Sio_2) 22%, sodium oxide (Na_2O) and 6% Calcium oxide (CaO)) with high electrical conductance. The glass bulb is filled with a solution of constant P^H (0.1 M HCl) and is inserted with Ag-AgCl electrode, which acts as internal reference electrode and also serves for the external electrical contact. The electrode is dipped in a solution containing H^+ ions (HCl in the bulb furnishes a constant H^+ ion concentration).

The glass electrode system can be represented as follows,

$Ag/AgCl_{(s)}//0.1M\ HCl/glass$

The potential of glass electrode depends upon the concentration of hydrogen ions present in the experimental solution. The expression which relates the glass electrode potential E_G with concentration of H^+ ions is,

$$E_G = E_G^0 + \frac{2.303RT}{F} \log [H^+] \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} \quad (1)$$

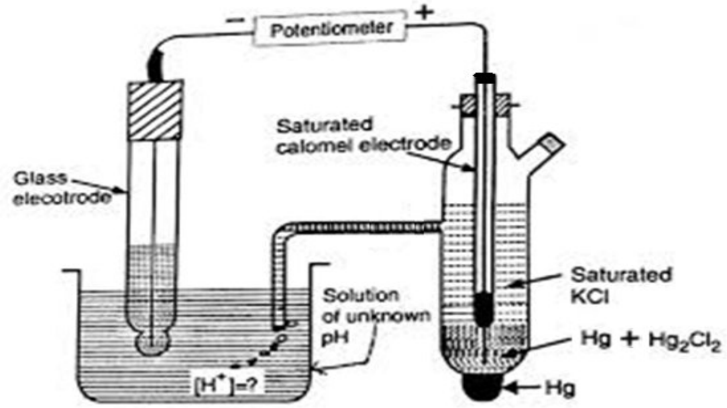
Where E_G^0 is standard glass electrode potential. The value of E_G^0 depends on the nature of glass used in the construction of the glass bulb.

The equation (1) can be written as, $E_G = E_G^0 + 0.0591 \log [H^+]$

$E_G = E_G^0 - 0.0591\ P^H$

$$P^H = \frac{E_G^0 - Eg}{0.0591} \text{ ——————————— } (2)$$

Determination of P^H of a solution using glass electrode



Glass electrode calomel electrode

Glass electrode is used as the internal reference electrode for determining the $P^H$of solutions, especially coloured solutions containing oxidizing or reducing agents. Usually calomel electrode is used as the second electrode. In order to determine the $P^H$of a solution, the glass electrode is placed in the experimental solution and this half-cell is coupling it with a saturated calomel electrode. The emf of the cell is measured. Since the resistance is very high, so potentiometer is used to measure the emf of the cell.

The emf of the cell is given by,

$E_{Cell} = E_{Calomel} - E_{Glass}$

$=0.2422-[E_G^0+\frac{2.303RT}{F} \log [H^+]]$ $[H^+=1]$

$=0.2422-[E_G^0+0.0591 \log [H^+]]$ $[n=1]$

$=0.2422-[E_G^0-0.0591\ P^H]$

$E_{Cell}=0.2422-E_G^0+0.0591\ P^H$

$$P^H = \frac{0.2422 - E_{Cell} - E_G^0}{0.0591}$$

E_G^0 is the value of glass electrode can be determined by using a solution of unknown P^H.

Battery Technology

The conversion of chemical energy into electrical energy is a function of cells or batteries. A cell designates a single unit consisting of anode, cathode and an electrolyte. The arrangement of two or more cells connected in series or parallel is called battery. Batteries are used in digital watches, calculators, electric bells, electric clocks, alarm systems, photoflash devices, emergency lighting, tape recorders, toys, telephone systems, digital camera, mobile phones, laptops, electric vehicles, space vehicles, military applications, etc,. They are also used in automobiles to start engines, UPS systems to run computers, etc.

Principal components of a battery:

The main components of a battery are:

1. Anode: It is a negative electrode where oxidation takes place. It gives out electrons to the external circuit during electrochemical reaction.

2. Cathode: It is a positive electrode where reduction takes place. It accepts electrons from the external circuit.

3. The electrolyte (Active mass in anode and cathode): It is an ionic conductor. The electrolyte is commonly a solution or slurry of acids or alkalis or salts having high ionic conductivity.

4. The separator: The material which electronically isolates anodes and cathodes in a battery to prevent internal short circuiting are referred to as separators. They are permeable to the electrolyte so as to maintain desired ionic conductivity. Thus, their main function is to transport ions from the anode compartment to the cathode compartment and vice-versa.

Classification of batteries:

Batteries are classified into two types

a) **Primary batteries:**

These are the batteries in which the cell reaction (chemical reaction) is irreversible. In primary batteries, as long as the active material is present, the electrical energy is obtained. These batteries cannot be recharged or reused because after some times the cell reaction stops and cell becomes dead.

Ex: Zn-MnO_2 battery, Li-MnO_2 battery, etc,

b) Secondary batteries:

These are the batteries in which the cell reaction (chemical reaction) is completely reversible. These are also known as rechargeable batteries or reversible batteries. They can be recharged to their original condition by passing the current through them in the direction opposite to that of discharge current. As a result a secondary battery can be used again and again for a long time by charging after discharge. Red-ox reaction gets reversed during recharging.

Ex: Lead – acid battery, Ni – Cd battery, etc.

Characteristics of a battery:

A battery is specifically designed, constructed and used based on the following characteristics.

Voltage or emf of the battery:

The voltage available form a battery depends upon the emf of the cell which constitutes the battery system. The emf of a battery is calculated using the Nernst equation

$$E_{cell} = E^o_{cell} - \frac{2.303\ RT}{nF} \log Q$$

$$E_{cell} = E^o_{cell} - \frac{2.303\ RT}{nF} \log [product]/[reactant]$$

Where $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ and Q is the reaction quotient for the cell reaction at any stage of reaction, which is the ratio of molar concentrations of product molecules to that of reactant molecules.

Current:

Current is a measure of the rate at which the battery is discharging. A battery can deliver high current only when there is a rapid electron transfer reaction. Rapid electron transfer reaction is possible when the battery contains large quantities of active materials.

Capacity:

The capacity is the charge or amount of electricity that may be obtained from the battery during discharge and is measured in ampere hours (Ah). Capacity depends on the size of the battery and is determined by Faraday relation-

$$C = \frac{WnF}{M}$$

Where W is weight of the active material, M is the molar mass of the active material, C is the capacity in ampere hours and n is the no. of electrons involved in the reaction.

Cycle life:

It is applicable only to secondary batteries, which can be recharged. Primary batteries are not rechargeable (designed for single discharge) but secondary batteries are rechargeable and their cycle life must be high.

Cycle is a single charge and discharge of a secondary/rechargeable battery and the number of charging cycles to discharge cycles that are possible before failure occurs in the case of secondary batteries is termed as cycle life.

Energy density:

Energy density is a measure of how much energy can be extracted from a battery per unit weight or volume of a battery.

Power density:

It is a measure of how much power can be extracted from a battery per unit weight of a battery.

Energy efficiency:

It is also known as cell efficiency. It is applicable only for secondary batteries.

The energy efficiency of a storage battery (in percent) is defined as

% energy efficiency = energy released on discharge/ energy required for charge X 100.

It is given by a ratio of energy released on discharge to energy required for charge.

Higher the energy efficiency, better is the battery (batteries should have high energy efficiency). As the energy efficiency increases, then the quality of the battery also increases.

Shelf life or storage life:

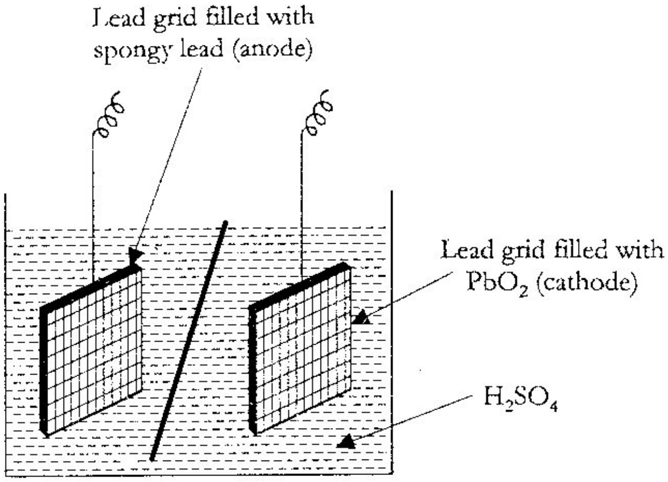
Shelf life is the maximum time for which a given battery can be stored without self discharge or corrosion or loss of performance. Good Shelf life is expected when there is no self discharge or

corrosion. Self discharge takes place when there is a reaction between the anode and cathode active materials. Self discharge and corrosion reduce the shelf life of a battery. A good battery is one which has high shelf life or storage life.

Construction, working and applications of some commercially important batteries:

Lead-acid battery:

Construction:



Lead-acid battery consists of two electrodes made of flat grids of lead. The anode grid is filled or packed with a paste of spongy lead metal (Pb) and other additives such as graphite powder (0.25 %), lignin sulphonate (0.2%), and barium sulphate (0.35%). The cathode grid is packed with a paste consisting of equal amount of lead dioxide (PbO_2) and lead. Several such pairs of anode & cathode grids are immersed or dipped alternatively in 5M or 37 % H_2SO_4, which acts as the electrolyte. The anode and cathode grids are separated by micro porous polyethylene separators.

Cell reactions during discharging of the battery:

At Anode, Lead electrode loses electrons, which flow through the external circuit. In this reaction oxidation of lead takes place.

$Pb \rightarrow Pb^{+2} + 2e^-$ ----------------- oxidation

$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$

$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^-$

At Cathode, PbO_2 undergo reduction.

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{+2} + 2H_2O$

$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$

$PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \rightarrow PbSO_4 + 2H_2O$

The net cell reaction is: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Recharging of the battery:

The condition of the battery can easily checked by measuring the density of the solution. When the density falls below 1.20 gm/cm^{3,} the battery needs charging. The battery is recharged by connecting it to an external source of direct current.

The net recharging reaction is,

$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

In general, the charging and discharging reaction is given by

Discharging

$Pb + PbO_2 + 2H_2SO_4 \qquad 2PbSO_4 + 2H_2O \longrightarrow$

Charging

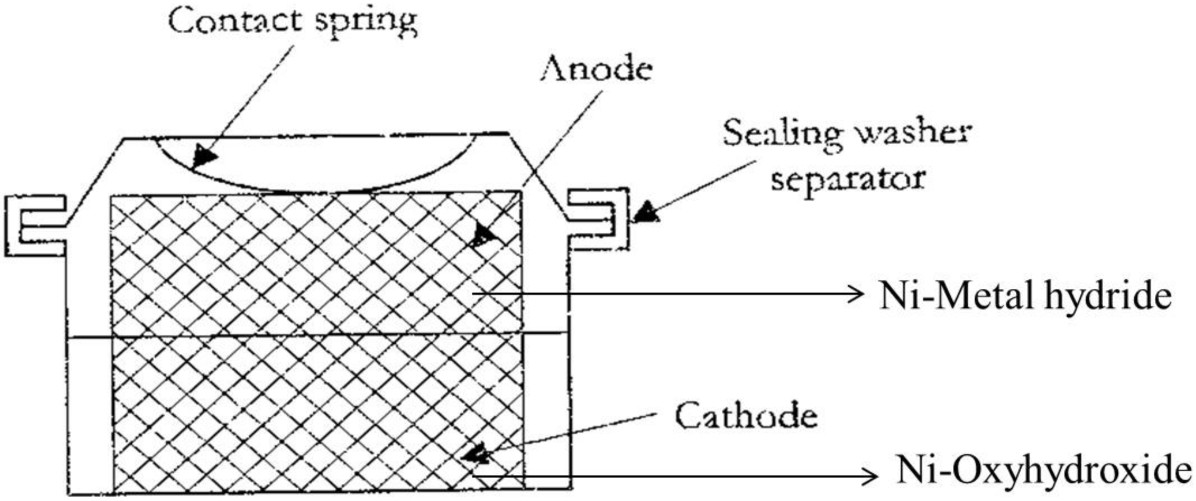
A lead-acid battery produces a potential of about 2.0 V/ cell. A typical 12V lead acid battery consists of six individual cells connected in series.

Applications:

Lead acid batteries are extensively used in automobiles to start the engine. It is also used in UPS systems to run the computers, used as a power source for laboratories, hospitals, emergency lighting, telephone exchangers, broadcasting stations, etc,.

Modern Batteries

Ni-MH battery:



It consists of rectangular Ni wire gauze electrode grids. The anode grid is coated with metal-hydride as active material. The cathode grid is coated with Ni-oxy hydroxide as active material. The anode and cathode grids are PP porous separator containing 21% KOH, which acts as electrolyte.

Cell reactions during discharging of battery are:

At anode:

$$MH + OH^- \longrightarrow M + H_2O + e^-$$

At cathode:

$$NiOOH + H_2O + e \longrightarrow Ni(OH)_2 + OH^-$$

The net cell reaction is

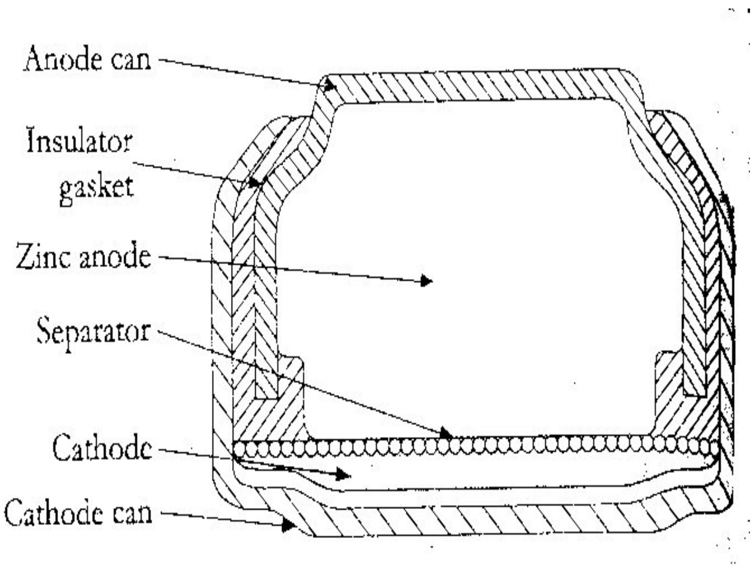
$$MH + NiOOH \longrightarrow M + Ni(OH)_2$$

This battery produces a potential of 1.25 v to 1.35v/cell

Applications:

It is used in digital camera, potable music player, cordless phones, cordless mouse, cordless key boards, laptops, electric vehicles, etc.

Zinc-air battery:



It is a secondary battery or rechargeable battery. Zinc- air battery belongs to the class of metal-air batteries, which use oxygen directly from the atmosphere to produce electrochemical energy. Oxygen diffuses into the cell and is used as the cathode reactant.

The Zn- air battery consists of an anode can and cathode cup. The loose, granulated powdered zinc is mixed with aqueous alkaline electrolyte (30 % KOH or NaOH) and a gelling agent (to immobilize the composite and ensure adequate contact with zinc granules). This mixture is filled completely into the anode can and is kept inverted over cathode cup. Pores carbon mixed with pallets of MnO_2 is taken at the bottom of cathode cup and is covered with nickel wire gauze mesh, which is coated or laminated with gas permeable Teflon layer. The two containers (anode cover and cathode cup) are separated by plastic gasket insulator. The two electrodes are separated by a porous separating membrane. The separating membrane is placed directly over the air access holes to uniform air distribution across the air electrode. Teflon layer allows oxygen, diffuse into and out of the cell and also provides resistance to leakage. The separator acts as an ionic conductor between the electrodes and as an insulator to prevent internal short circuiting. Holes in the battery allow the oxygen from the air to enter the cathode and be reduced on the carbon surface. At the same time, the Zn in the anode is oxidized.

During the cell reaction, pure air is admitted into the battery through the cavities of cathode, the oxygen of air diffuses through Teflon layer and adsorbed on the surface of MnO_2 and acts as cathode reactant. When air is passed through the cell, Zn is oxidized to ZnO at anode, during discharge. The oxygen of the air reacts with water at the cathode.

- **Electrode reactions are:**

At anode: $Zn \text{®} Zn^{+2}+2e^{-}$

$Zn^{+2}+2OH^{-} \text{®} ZnO+H_2O$

$Zn + 2\ OH^{-} \text{®} ZnO+H_2O +2e^{-}$

At cathode: $\frac{1}{2} O_2 +H_2O+2e^{-} \text{®} 2OH^{-}$

Net cell reaction $Zn + \frac{1}{2} O_2 \text{®} ZnO$

- This cell produces a potential of 1.4 V.
- During charging the above cell reaction is reversed.

Uses

- ✓ Used in hearing aids. It is used as a power source for hearing aids.
- ✓ In voice transmitters
- ✓ Used in military radio receivers
- ✓ In railway signals
- ✓ In remote communications,

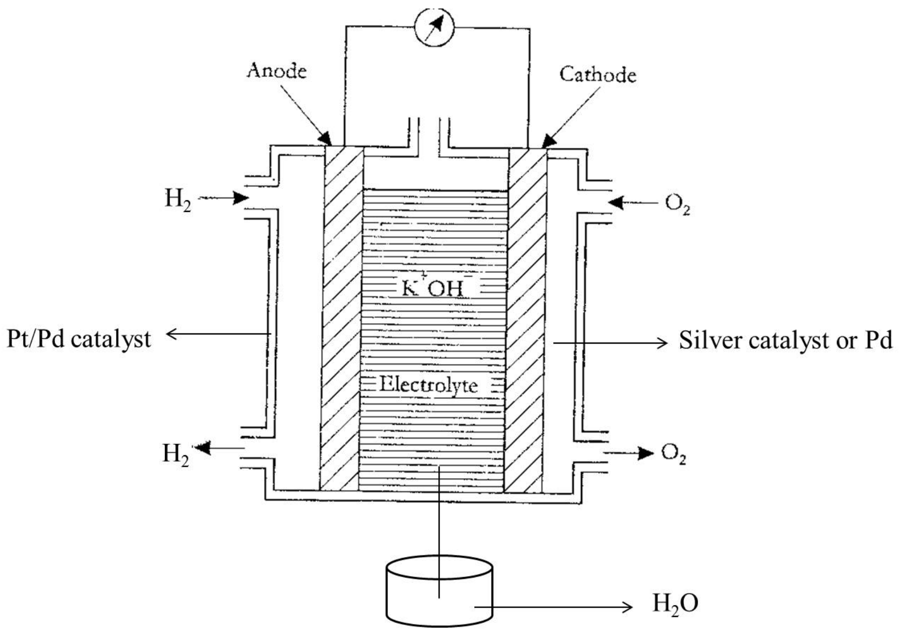
FUEL CELLS

Fuel cells are the galvanic cells in which the chemical energy of fuel is directly converted into electrical energy.

or

Fuel cell can be defined as galvanic cell in which the electrical energy is directly derived by the combustion of fuels supplied continuously.

H_2 - O_2 fuel cell



In this H_2 - O_2 fuel cell, hydrogen gas is used as a fuel and oxygen gas is used as oxidant. The

H_2 - O_2 fuel cell consists of two electrodes made of porous carbon or graphite. The anode is coated with finely divided platinum or palladium catalyst. The cathode is coated with platinum or silver catalyst. These two electrodes are placed in aqueous solution of KOH (30 %), which acts as electrolyte.

Cell reactions

At anode, hydrogen gas diffuse through the anode, it is absorbed on the electrode surface and reacts with hydroxyl ions to form water

$$2H_2\,(g) + 4\,OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4\,e^-$$

At cathode, O_2 diffuses through the cathode (electrode) and reacts with water molecules to form OH^- ions (reduction of oxygen takes place to OH^- ions).

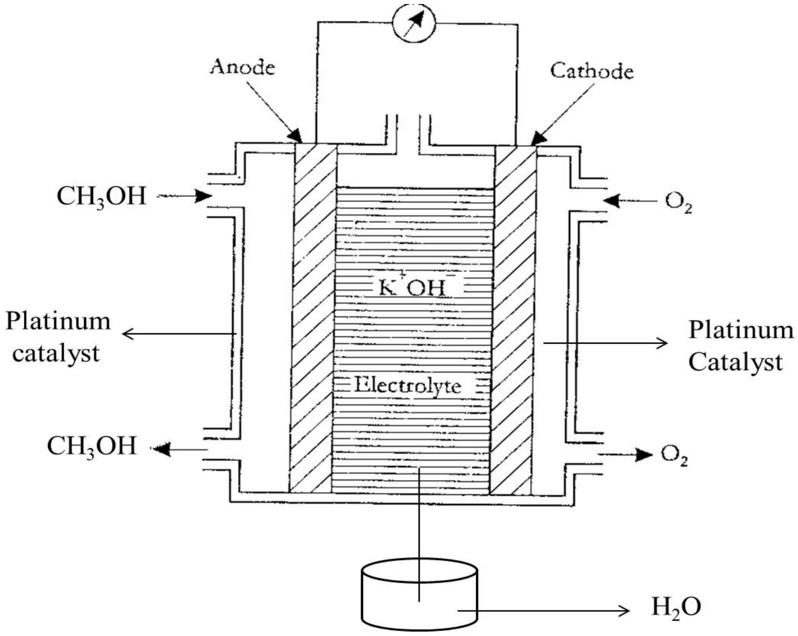
$$O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4\,OH^-$$

Net cell reaction: $H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$

The net cell reaction is nothing but the combustion of H_2 and O_2. The water formed as the product, which dilutes the KOH. As a result, the cell becomes inactive. Therefore, the electrolyte is always kept hot so that water evaporates as fast as it is formed. A wick placed inside the electrolyte is also helps in removing and maintaining water balance. The cell produces an emf of 1.23V.

Uses: It is used as electric power source for space vehicles, military and mobile power system.

Methanol- O_2 fuel cell:



In this Methanol- O_2 fuel cell, hydrogen gas is used as a fuel and oxygen gas is used as oxidant. The Methanol- O_2 fuel cell consists of two electrodes made of porous Ni. The anode is coated with finely divided platinum or palladium catalyst. The cathode is coated with platinum or silver catalyst. These two electrodes are placed in aqueous solution of KOH (30 %), which acts as electrolyte.

Cell reactions

At anode, hydrogen gas diffuse through the anode, it is absorbed on the electrode surface and reacts with hydroxyl ions to form water.

$$CH_3OH + 6\,OH^- \longrightarrow CO_2 + 5H_2O + 6\,e^-$$

At cathode, O_2 diffuses through the cathode (electrode) and reacts with water molecules to form OH^- ions (reduction of oxygen takes place to OH^- ions).

$$3/2\,O_2 + 3H_2O + 6\,e^- \longrightarrow 6\,OH^-$$

Net cell reaction $CH_3OH + 3/2\,O_2\,(g) \longrightarrow CO_2 + 2H_2O$

The cell produces an emf of 1.23V.

Uses: It is used as electric power source for space vehicles, military and mobile power system

Differences between battery and fuel cell

Sl. No.	Battery	Fuel cell
1.	It is an effective energy storage system i.e. chemical energy is stored in the battery	It is an effective energy conversion system i.e. the energy is not stored in fuel cell.
2.	The reactants are not freely available and hence the production cost is more.	Fuels and oxidants are freely available, hence they are cheaper.
3.	It needs charging again and again.	No need of charging.
4.	The byproducts may be harmful and cause pollution.	Byproducts are eco-friendly and not cause any pollution.
5.	Efficiency of the battery is low	Efficiency of the fuel cell is high
6.	Reactants are used during the construction of battery	Reactants are introduced from outside the cell
7.	Battery operates until the reactants stored in it are completely used up	Fuel cell operates as long as the reactants are supplied to the electrodes from outside
8.	Ex: lead acid battery, Zn- air battery, Ni-Cd battery, etc.	Ex: Hydrogen- oxygen fuel cell. Methane- Oxygen fuel cell, methanol- oxygen fuel cell, etc.

TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers (2001 edition).
2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)

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2. Industrial Chemistry by B. K. Sharma, GOEL Publishing House (2014 edition).
3. Industrial Electrochemistry, Second Edition by Derek Pletcher & Frank C. Walsh publisher: Chapman & Hall, USA (1993 edition).