

Instruction Material
For
The Course: Engineering Chemistry
A.Y. 2018-19
CO1



K L E F
Department of Chemistry

Basic concepts of electrochemistry-Electrode Potential, Single electrode potential Galvanic cell, Measurement of Electrode Potential.

Single electrode Potential and its measurement

Introduction:

Electrochemistry is a Phenomenon which gives the relation between Chemistry and Electricity.

Single electrode Potential:

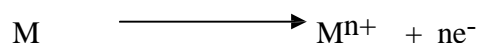
It is defined as the potential developed at the inter phase between the metal and the solution, when a metal is dipped in a solution containing its own ions. It is represented as E.

The origin of electrode Potential:

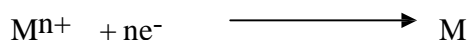
When a metal is dipped in a solution containing its own ions, the metal may undergo oxidation by losing electrons or the metal ions in solution may undergo reduction and get deposited on the metal surface.

Consider a metal 'M' is dipped in a solution containing its ions M^{n+} .

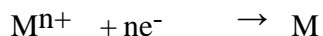
The tendency of metal to pass in to solution (oxidation) can be represented as,



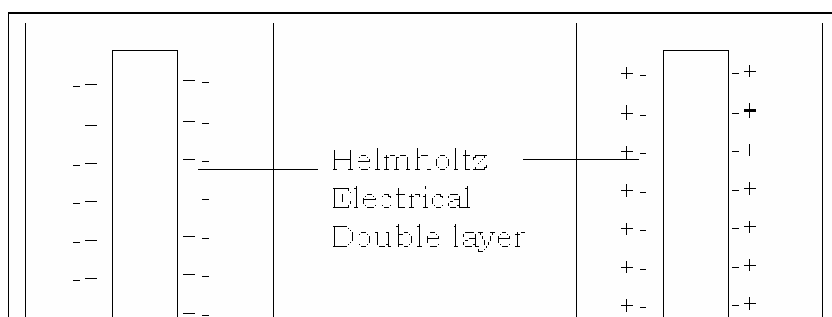
Simultaneously the metal ions from the solution tend to deposit on the metal as metal atoms (reduction)



The above two opposite tendencies will result in equilibrium as follows



When a metal undergoes oxidation it loses positive ions into solution leaving behind a layer of negative charges on its surface. This layer attracts positive charges and forms an electric double layer (EDL) because of the formation of EDL electrode potential arises.



When metal ions undergo reduction depositing metal atoms on the metallic surface the metal surface becomes positively charged. The accumulated positive charge on the metal surface attracts a layer of $-ve$ charges and forms an electrical double layer or Helmholtz EDL which causes the origin of electrode potential.

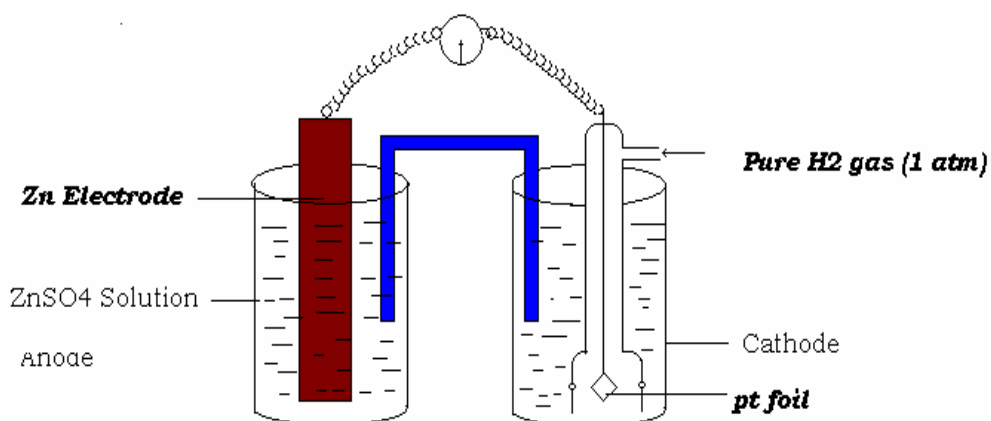
Measurement of electrode potential

The electrode potentials of any metal electrodes can be determined by using reference electrodes like standard hydrogen electrode (SHE).

The SHE is coupled with the electrode whose electrode potential is to be determined and the electrode potential of the electrode is determined by fixing the electrode potential and SHE as zero [at all temperatures]

Example: Consider the determination of Single electrode potential of Zinc electrode using Standard Hydrogen electrode.

To determine the Single electrode potential of Zinc electrode it is coupled with Standard Hydrogen electrode as follows:



The electrode potential of Zinc electrode can be calculated as

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

$$E_{\text{cell}} = E_{\text{SHE}} - E_{\text{Zn}}$$

$$0.76 = 0 - E_{\text{Zn}}$$

$$E_{\text{Zn}} = -0.76 \text{ V}$$

The electrode potentials can also be determined by using secondary reference electrode such as calomel electrode and Ag / AgCl electrode.

Electrochemical Cells, Reversible and Irreversible cells and Cell EMF

Electro Chemical Cell:

An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vice versa.

These electrochemical cells are classified into two types as follows.

- 1) Galvanic or Voltaic cells (Reversible): These are the electrochemical cells, which convert chemical energy into electrical energy.

Ex: Daniel cell, Dry cell, etc.

- 2) Electrolytic cell (Irreversible): These are the electrochemical cells, which are used to convert electrical energy into chemical energy.

Ex: Lead acid battery, Nickel cadmium battery etc.,

Electron Motive Force (EMF)

It is defined as the potential difference between the two electrodes of a galvanic cell which causes the flow of current from an electrode with higher reduction potential to the electrode with lower reduction potential. It is denoted as E_{cell} .

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

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

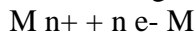
Problems:

- 1) Calculate emf of a cell constructed by combining Cu & Zn electrodes dipping in their respective ionic solutions. The standard electrode potential of Cu and Zn are 0.34 V and 0.76 V respectively at 298K.

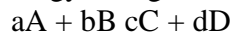
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Cu}} - E_{\text{Zn}} = 0.34 - (-0.76) = 1.1 \text{ volt}$$

Nernst Equation

Consider a general redox reaction,



For a general reversible chemical reaction, according to Vant-Hoff's isotherm, Gibb's free energy change, ΔG of the reaction and its equilibrium



and is given by,

$$\Delta G = -RT \ln K + RT \ln [\text{Product} / \text{Reactant}] \dots\dots\dots 1$$

$$\text{We know that } \Delta G^0 = -RT \ln K$$

Substituting the above in Van't - Haff's isotherm equation,

$$\Delta G = \Delta G^0 + RT \ln [\text{Product} / \text{Reactant}] \dots\dots\dots 2$$

Where ΔG^0 = Standard free energy change.

For reversible reaction involving M electrons, the decrease in free energy ($-\Delta G$) will produce electrical energy (E) coulombs and is given by

$$nFE = -\Delta G$$

$$\Delta G^0 = -nFE^0$$

$$\text{or } -\Delta G^0 = nFE^0 \dots\dots\dots 3$$

ΔG^0 = Standard free energy change

n = the number of electrons

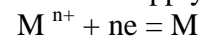
F = Faraday = 96,500 Coulombs of electricity

E^0 = the standard potential and

Substituting Eq. (3) in Eq. (2), we get,

$$-nFE = -nFE^0 + RT \ln [M] / [M^{n+}] \dots\dots\dots 4$$

When we apply this equation to an electrode reduction equation



We get,

$$-nFE_{\text{red}} = -nFE^0_{\text{red}} + RT \ln [M] / [M^{n+}]$$

Rearranging the above equation, we get

$$E_{\text{red}} = E^0_{\text{red}} - RT/nF \ln [M] / [M^{n+}]$$

$$E_{\text{red}} = E^0_{\text{red}} - RT/nF \ln [1] / [M^{n+}] \text{ (since } [M] = 1 \text{ the activity of the solid metal)}$$

The above equation may be written as,

$$E_{\text{red}} = E^0_{\text{red}} + RT/nF \ln [M^{n+}]$$

where $R = 8.314 \text{ J/K/mole}$, $T = 2980 \text{ K}$, $F = 96500 \text{ coulombs}$. Now substituting the value of R , T and F we get,

$$E_{\text{red}} = E^0_{\text{red}} + 0.0591/n \log [M^{n+}] \dots\dots\dots 5$$

The above equation is known as the Nernst Equation.

In general,

$$E = E^0_{\text{red}} + 0.0591/n \log C \dots\dots\dots 6$$

Similarly for oxidation potential,

$$E = E^0_{\text{oxi}} - 0.0591/n \log [M^{n+}] \dots\dots\dots 7$$

The Eqs (5) and (7) are known as Nernst Equation for single electrode potential.

Applications of Nernst Equation:

Electrode potential of unknown metal can be determined using the Nernst equation.
It is used to predict the corrosion tendency of metals.

Problems:

(1) Calculate the reduction potential of Cu/Cu^{2+} electrode which is dipped in 0.5M of its own salt solution at 250 C and the standard electrode potential or its is 0.337.

Find out the emf.

$$E = E^0 + 0.0591/n \log (\text{Cu}^{2+}) \text{ Volts } n=2 ;$$

(Ans): Reduction Potential= 0.3230 V

(2) Find out the oxidation potential of Zn/Zn^{2+} which is in contact with 0.2 M of its own salt solution at 250C and the std. electrode potential is 0.763 V.

$$E = E^0 + 0.0591/n \log (\text{Zn}^{2+}) \text{ V } n=2;$$

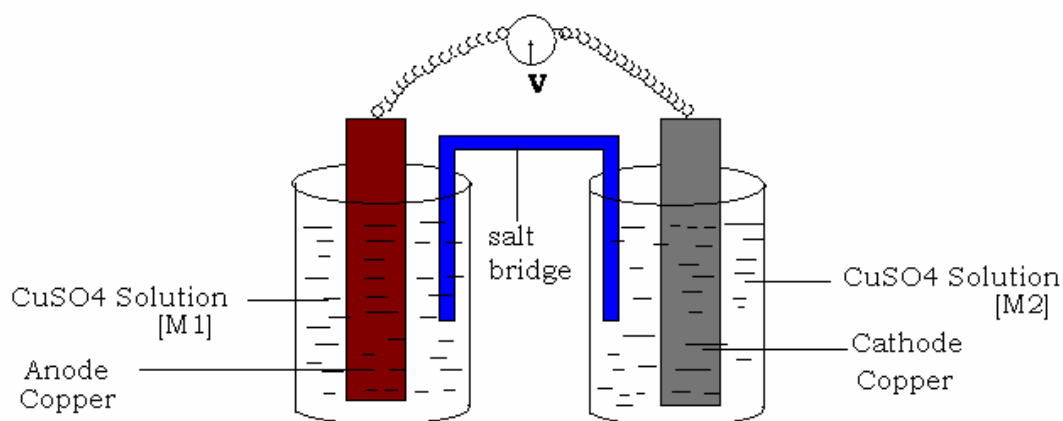
(Ans) : Oxidation potential = 0.7836 V

Concentrations cells

These are the galvanic cells consisting of same metal electrodes dipped in same metal ionic solution in both the half cells but are different in the concentration of the metal ions.

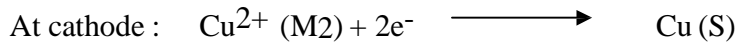
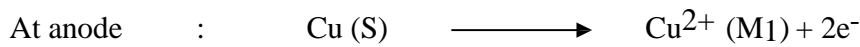
Ex: Consider the following concentration cell constructed by dipping two copper electrodes in CuSO_4 solutions of M_2 molar and M_1 molar where $M_2 > M_1$

The two half-cells are internally connected by a salt bridge and externally connected by a metallic wire through voltmeter or ammeter.



Concentration Cell

The electrode, which is dipped in less ionic concentrations solutions (M1) act as anode and undergoes oxidation. The electrode, which is dipped in more ionic concentration (M2) act as cathode and undergoes reduction.

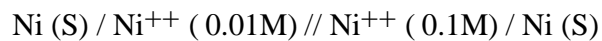


E of cell = E cathode – E anode.

$$E_{\text{cell}} = \left[E^{\circ} + \frac{0.0591}{n} \log (\text{M2}) \right] - \left[E^{\circ} + \frac{0.0591}{n} \log (\text{M1}) \right]$$

Where, (M2) > (M1)

1. Calculate emf of the following concentration cell at 25⁰ C

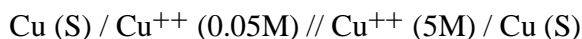


Where, (M2) > (M1)

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{(0.1)}{(0.01)}$$

$$= 0.02955\text{V}$$

2. Calculate emf of the following concentration cell at 25⁰ C



Where, (M2) > (M1)

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{(5)}{(0.05)}$$

$$= 0.0591\text{V}$$

Reference Electrodes and pH determination using Glass Electrode

Different types of single electrodes

i) Metal-Metal ion electrode: These electrodes consist of a metal dipped in a solution of its own ions.

Example: Zn/Zn⁺⁺, Cu/Cu⁺⁺, Ag/Ag⁺

ii) Metal-Metal salt electrode

These electrodes consists of a metal in contact with its salt

Example: Calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-$), Silver – Silver Chloride electrode ($\text{Ag}/\text{AgCl}/\text{Cl}^-$), Lead – Lead sulphate electrode($\text{Pb}/\text{PbSO}_4/\text{SO}_4^{2-}$)

iii) Gas electrode

Example: H_2 electrode ($\text{H}_2/\text{Pt}/\text{H}^+$) Chlorine electrode ($\text{Pt}/\text{Cl}_2/\text{Cl}^-$)

iv)Amalgam electrode

Example: Lead amalgam electrode ($\text{Pb-Hg}/\text{Pb}^+$)

v) Oxidation– Reduction electrode

Example: $\text{Pt}/\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Pt}/\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Pt}/\text{Sn}^{2+}, \text{Sn}^{4+}$

vi) Ion selective electrode

Example: Glass electrode

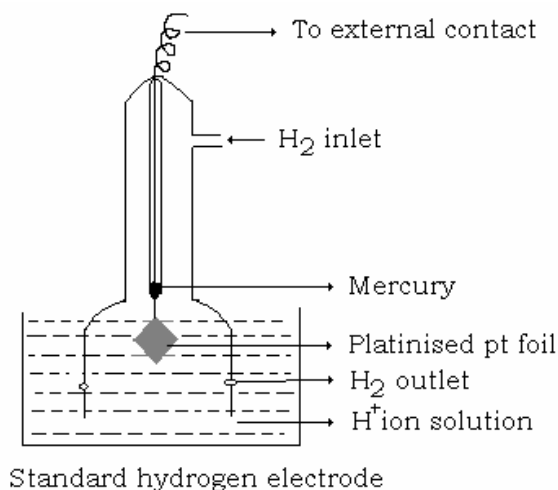
Reference Electrodes

These are the standard electrodes with reference to these, the electrode potentials of any other electrode can be determined.

The Reference Electrodes can be classified in to two types

- i) Primary reference electrodes Ex: Standard hydrogen electrode
- ii) Secondary reference electrodes Ex: Calomel and Ag/AgCl electrodes

Construction, working and limitations of standard hydrogen electrode



The standard hydrogen electrode consists of platinised platinum foil fused to the glass tube. Mercury is placed at the bottom of the tube and a copper wire is used for electrical connections. The platinum foil is immersed in a solution containing unit

molar hydrogen ions. Pure hydrogen gas is bubbled about the electrode through the H_2 gas inlet at 1atm pressure.

The electrode is represented as $Pt/H_2(g)/H^+$

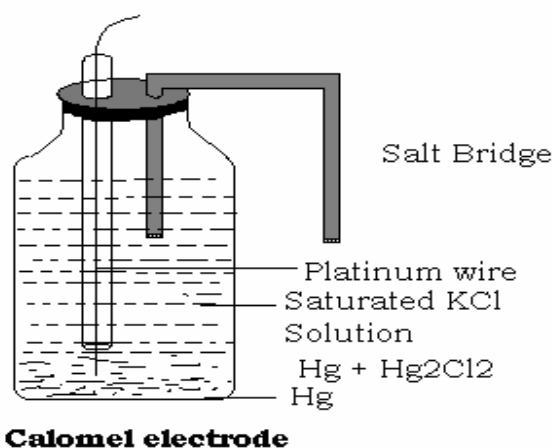
If the concentration of H^+ is 1M, H_2 gas bubbled at 1atm pressure and at temperature 298k, then the electrode is called standard hydrogen electrode. And the electrode potential is arbitrarily fixed as zero.

The electrode reaction is:

Limitations of SHE

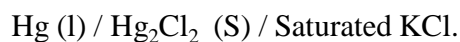
- i) The construction of SHE is difficult.
- ii) It is very difficult to maintain the concentration of H^+ as 1M and Pressure H_2 gas at 1atm
- iii) Platinum electrode is poisoned by the impurities of the gas
- iv) It cannot be used in the presence of oxidizing agents.

Construction and working of Calomel electrode



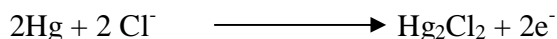
Calomel electrode consisting of a glass container at the bottom of which mercury is placed above which a layer of mercury and mercurous chloride (called calomel) is placed with $\frac{3}{4}^{th}$ of bottle is filled with saturated KCl solution. Electrode potential

of the cell depends on the concentration of KCl used. The calomel electrode can be represented as.

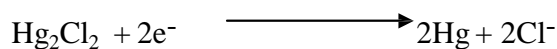


The calomel electrode acts as both anode and cathode depending upon the other electrode used. The platinum wire is used for electrical connections. Salt bridge is used to couple with other half cell.

When it acts as anode the electrode reactions is,



When it acts as cathode the electrode reaction is



Advantages of Calomel Electrode: It is simple to construct.

The electrode potential is reproducible and stable. It is used as a reference electrode.

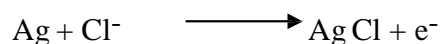
Construction and working of Silver-Silver chloride electrode.

Ag/AgCl electrode is a metal metal salt electrode. It consists of narrow glass tube at the bottom of which agar is placed above which saturated solution of KCl is placed. The silver wire is used for electrical connections and it is coated electrolytically with AgCl. The cell can be

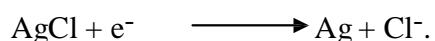
Represented as: $\text{Ag(s) / AgCl (s) / Saturated KCl.}$

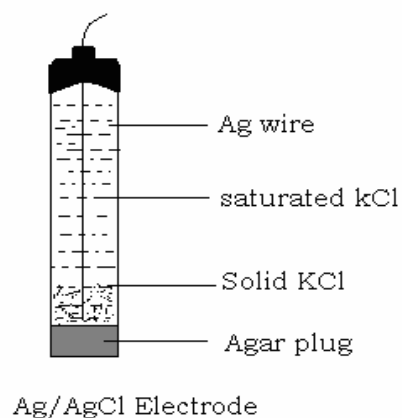
Electrode acts as both anode and cathode depending on the other electrode used.

When it acts as anode the electrode reaction is



When it acts as cathode the electrode reaction is

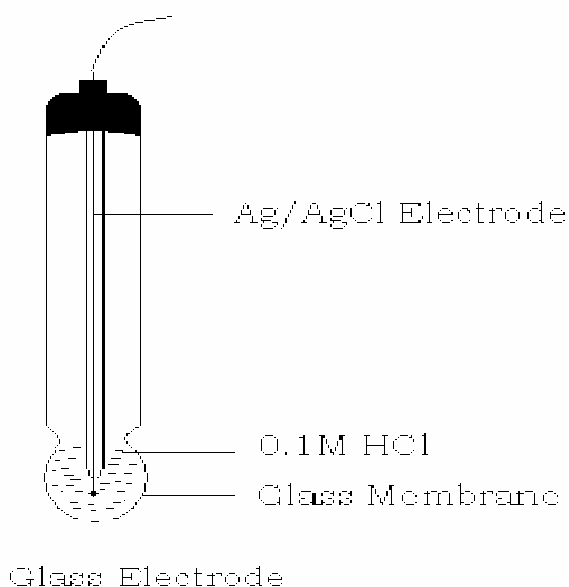




Ion Selective Electrodes

These are the electrodes, which responds to specific ions only and develop potential against that ion while ignoring the other ions present in the solution.

Ex: Glass electrode.



Glass electrode is a pH sensitive electrode widely used for pH determinations. It is consisting of a long glass tube at the bottom of which a thin and delicate glass bulb, which made up of special type of glass (12 % Ba_2O , 6% of CaO , 72% of SiO_2) with low melting point and high electrical conductance is used. The glass bulb is filled

with 0.1M HCl and Ag – AgCl is used as a internal reference electrode. A platinum wire is used for electrical contact. The glass electrode can be represented as:



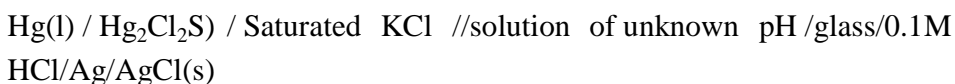
$$E_{\text{Glass}} = E^{\circ}_{\text{Glass}} + 0.0591 \log [\text{H}^+]$$

$$= E^{\circ}_{\text{Glass}} - 0.0591 \text{ pH}$$

Determination of pH using glass electrode.

To determine pH of unknown solution the glass electrode is combined with secondary reference electrode such as calomel electrode and the glass - calomel electrode assembly is dipped in the solution whose pH is to be determined. The two electrodes are connected to potentiometer or pH meter.

The combined electrodes can be represented as.



The emf of the above cell is given by

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

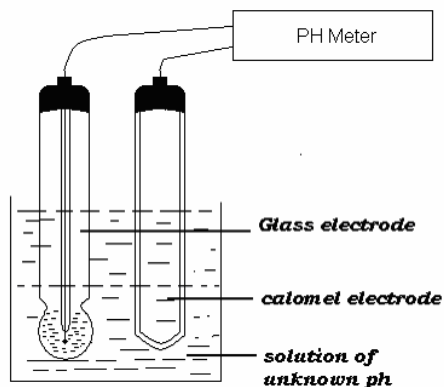
$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$= E_{\text{SCE}} - E_{\text{G}}$$

$$= 0.2422 - (E^{\circ}_{\text{Glass}} - 0.0591 \text{ pH}) \quad [E_{\text{G}} = E^{\circ}_{\text{G}} - 0.0591 \text{ pH}]$$

$$E_{\text{cell}} = 0.2422 - E^{\circ}_{\text{G}} + 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} + E^{\circ}_{\text{G}} - 0.2422}{0.0591}$$

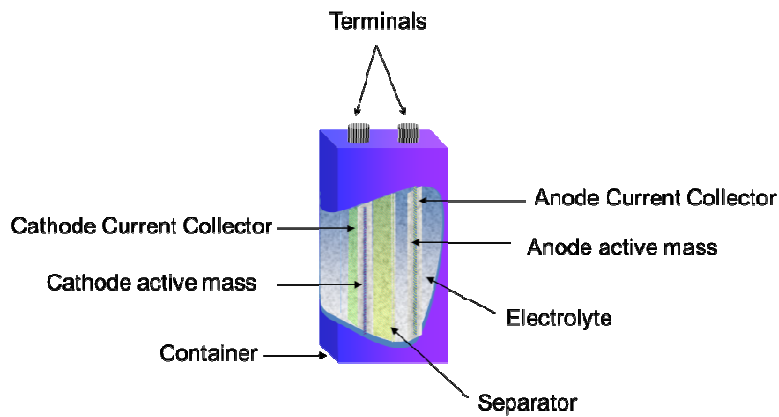


Session-6

Introduction to Batteries and Chemistry of Primary Battery (Hg-Battery)

A **battery** is an Electrochemical cell or often several electrochemical cells which are connected in series to produce a constant voltage to run portable goods.

Principle Components of a Battery



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Mainly batteries are of three types:

- 1) Primary Battery is the one in which cell reactions are irreversible.

E.g. Leclanché cell, Zn-Carbon Battery, Hg-Battery

- 2) Secondary Battery is the one in which cell reactions can be reversed by passing external emf in opposite direction. i.e. it can be used for many cycles of charging and discharging.

E.g. Lead – Acid battery, Ni-metal-hydride (NiMH) etc.

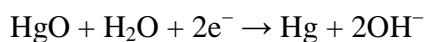
- 3) Flow battery is the one in which all the constituents of the battery flow throughout the battery.

E.g. Hydrogen-Oxygen Fuel cell.

Primary Cell (Mercury Battery)

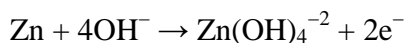
Mercury batteries use either pure mercury (II) oxide (HgO)—also called mercuric oxide—or a mixture of HgO with manganese dioxide (MnO_2) as the cathode. Mercuric

oxide is a non-conductor, so some graphite is mixed with it; the graphite also helps prevent collection of mercury into large droplets. The half-reaction at the cathode is:

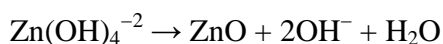


with a standard potential of +0.0977 V vs. NHE.

The anode is made of zinc (Zn) and separated from the cathode with a layer of paper or other porous material soaked with electrolyte; this is known as a salt bridge. Two half-reactions occur at the anode. The first consists of an electrochemical reaction step:



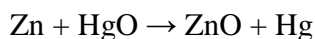
followed by the chemical reaction step:



yielding an overall anode half-reaction of:



The overall reaction for the battery is:



In other words, during discharge, zinc is oxidized (loses electrons) to become zinc oxide (ZnO) while the mercuric oxide gets reduced (gains electrons) to form elemental mercury. A little extra mercuric oxide is put into the cell to prevent evolution of hydrogen gas at the end of life.

Secondary Battery (Lead Acid and Nickel metal hydride)

Storage cell: it is the one which can act both as voltaic cell and electrolytic cell. When it functions as voltaic cell, it supplies electric current and the process is known as discharging. When it functions as electrolytic cell, it receives electric current and this process is known as charging. So it can be used for a large no. of cycles of charging and discharging. The best example for storage cell is lead acid battery or lead acid accumulator.

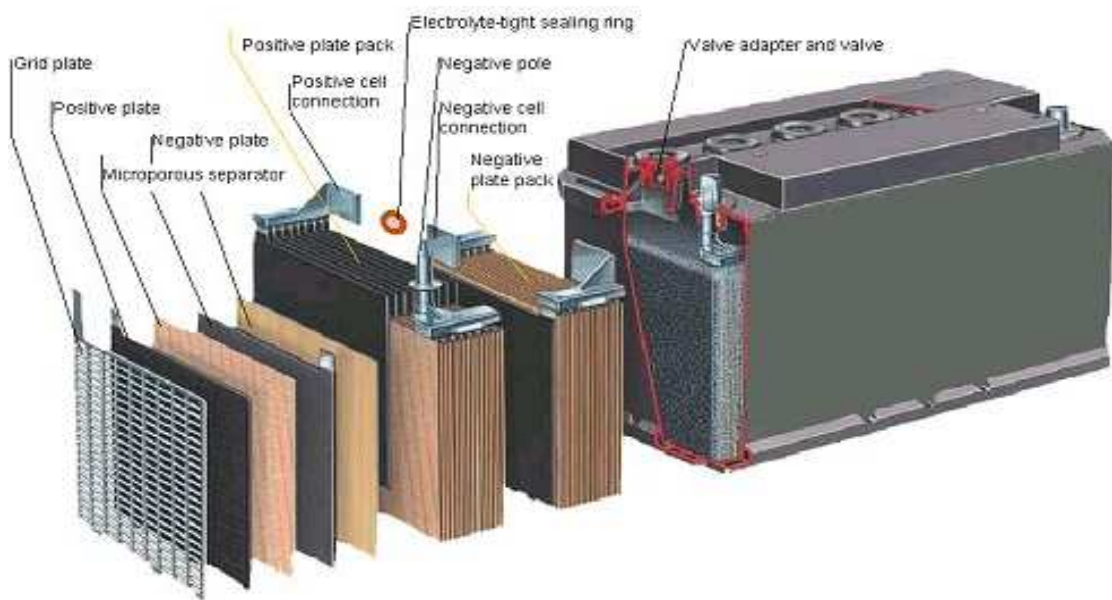
1. Lead-acid battery: Lead-acid is the oldest rechargeable battery in existence. Invented by the French physician Gaston Planté in 1859, lead-acid was the first rechargeable battery for commercial use. 150 years later, we still have no cost-effective alternatives for cars, wheelchairs, scooters, golf carts and UPS systems.

Construction: Large number of anodes and cathodes are arranged alternatively in a series separated by insulators as shown above. The entire set up is immersed in dilute sulphuric acid solution.

Anode: lead plate

Cathode: lead dioxide plate

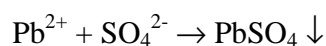
Electrolyte: 25% H_2SO_4 solution



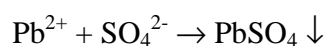
Discharging:

Reactions taking place during discharging: During discharging, it acts as voltaic cell and supplies electrical energy.

Anode: $\text{Pb} \rightarrow \text{Pb}^{2+} + 2 \text{e}^-$ (oxidation)



Cathode: $\text{PbO}_2 + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$ (Reduction)



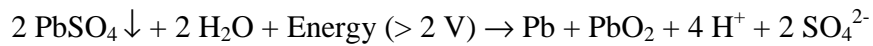
Net reaction: $\text{Pb} + \text{PbO}_2 + 4 \text{H}^+ + 2 \text{SO}_4^{2-} \rightarrow 2 \text{PbSO}_4 \downarrow + 2 \text{H}_2\text{O} + \text{Energy} (= 2 \text{ V})$

The following points can be noticed from the above reaction:

- The concentration of sulphuric acid decreases in course of reaction.
- Both the electrodes are covered with lead sulphate.
- As lead sulphate is insoluble in sulphuric acid, it acts as a protective layer and prevents the further corrosion of lead.

As the lead sulphate deposited at both the electrodes is solid, the cell reactions can easily be reversed by passing emf just above the voltage of the cell i.e. $> 2 \text{ V}$.

Charging:



Application: Car battery

2. Nickel Metal Hydride (NiMH)

NiMH Principles of Operation

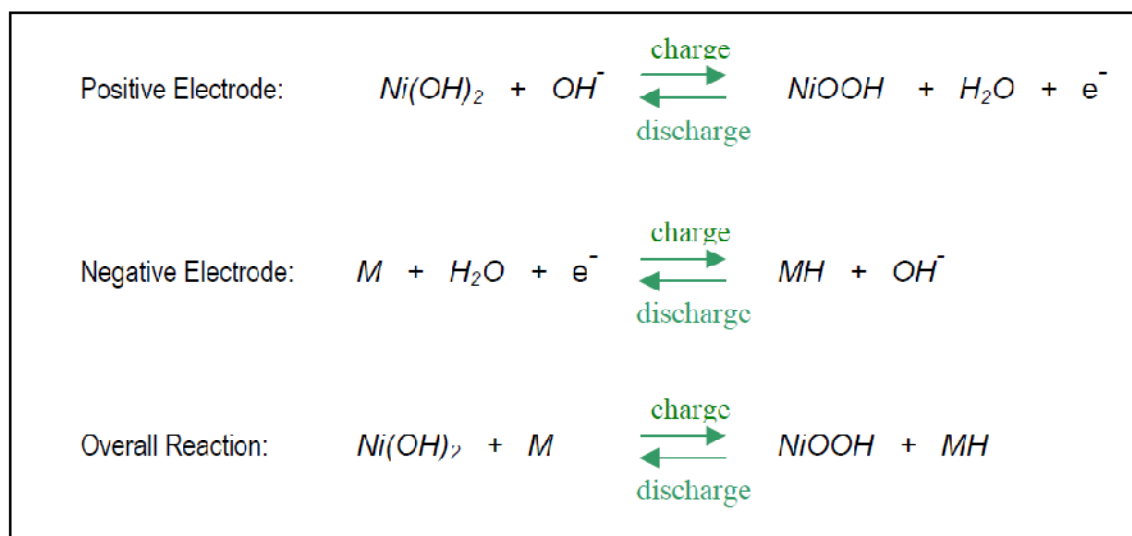
The principles in which NiMH cells operate are based on their ability to absorb, release, and transport (move) hydrogen between the electrodes within the cell. The following sections will discuss the chemical reactions occurring within the cell when charged and discharged and the adverse effects of overcharge and overdischarge conditions.

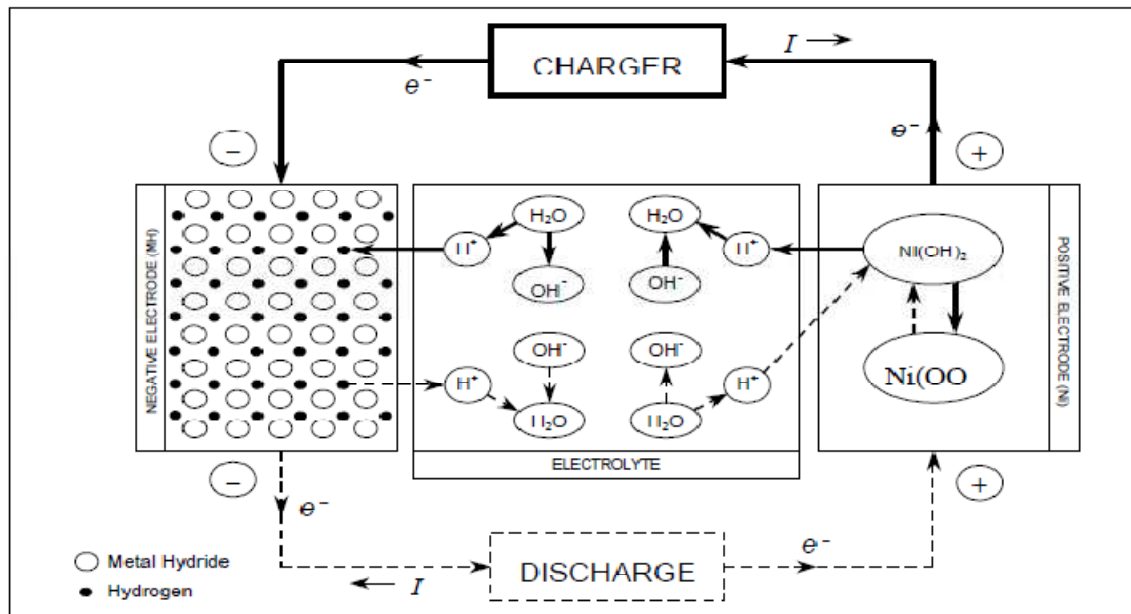
The success of the NiMH battery technology comes from the rare earth, hydrogen-absorbing alloys (commonly known as Misch metals) used in the negative electrode. These metal alloys contribute to the high energy density of the NiMH negative electrode that results in an increase in the volume available for the positive electrode. This is the primary reason for the higher capacity and longer service life of NiMH batteries over competing secondary batteries.

Charging Chemical Reaction

When a NiMH cell is charged, the positive electrode releases hydrogen into the electrolyte. The hydrogen in turn is absorbed and stored in the negative electrode. The reaction begins when the nickel hydroxide ($\text{Ni}(\text{OH})_2$) in the positive electrode and hydroxide (OH^-) from the electrolyte combine.

This produces nickel oxyhydroxide (NiOOH) within the positive electrode, water (H_2O) in the electrolyte, and one free electron (e^-). At the negative electrode the metal alloy (M) in the negative electrode, water (H_2O) from the electrolyte, and an electron (e^-) react to produce metal hydride ($M\text{H}$) in the negative electrode and hydroxide (OH^-) in the electrolyte.





Li-ion battery, H₂-O₂ Fuel cell

Lithium ion Battery

A lithium-ion battery (sometimes Li-ion battery or LIB) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

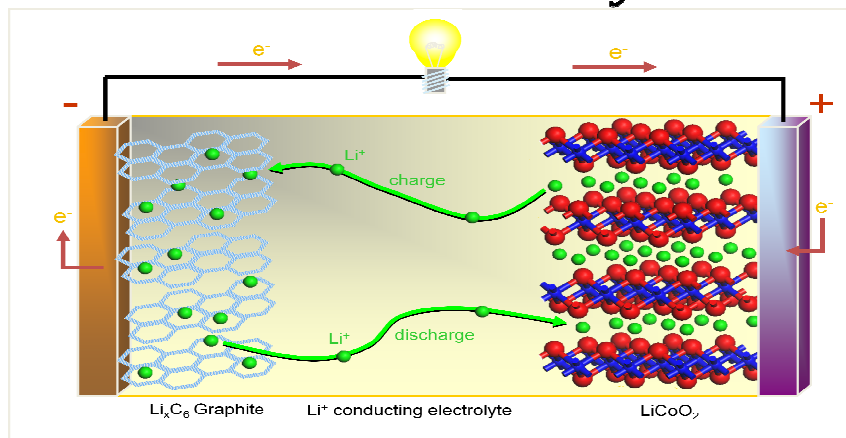
During discharge, lithium ions Li^+ carry the current from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

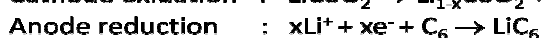
The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During insertion or intercalation lithium moves into the electrode. During the reverse process, extraction or deintercalation, lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Li-ion Battery



- **Electrode redox reactions on charge:**



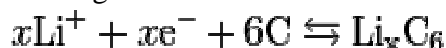
discharge is the opposite

Useful work can only be extracted if electrons flow through a closed external circuit. The following equations are in units of moles, making it possible to use the coefficient x .

The positive electrode half-reaction (with charging being forwards) is:



The negative electrode half-reaction is:



The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide possibly by the following irreversible reaction:



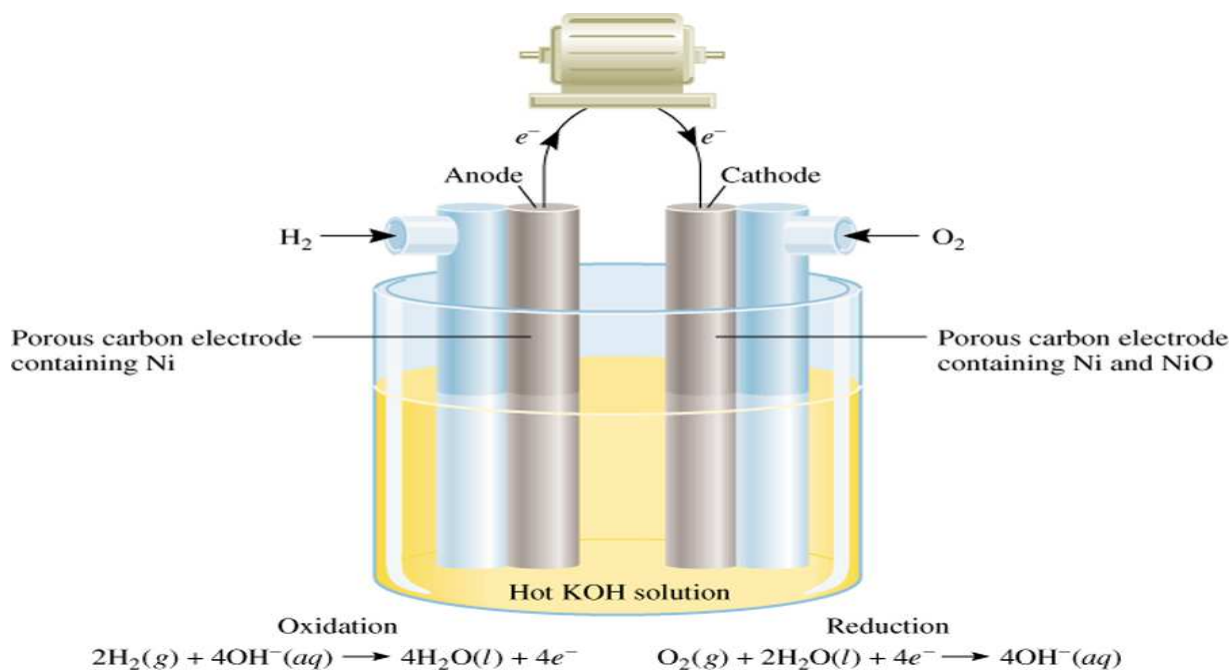
Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction



In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in Li_xCoO_2 being oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

3. Fuel Cell: A galvanic cell where there is a continuous supply of reactants.

It consists of two inert porous electrodes made of graphite impregnated with finely divided Pt and 25% KOH solution as electrolyte. Hydrogen gas is bubbled through one inert electrode, acts as anode. Oxygen gas is bubbled through another electrode, acts as cathode. The hydrogen-oxygen fuel cell produces water as a product and hence is an ideal power source for zero-emission vehicles. Hence it is called an eco friendly battery.



Redox Reaction in a Hydrogen- oxygen Fuel Cell

At Anode: $2(\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-)$ (Oxidation)

At Cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ (Reduction)

Net Reaction: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 1.0\text{V}$