Electrochemistry

By
Dr. S. Khalid Hasan
Professor (Chemistry)
Institute of Technology & Management
GIDA, Gorakhpur (UP)
drskhasan@yahoo.com

Electrochemistry:

Electrochemistry is the branch of physical chemistry which deals with the interdependence of chemical change and electrical energy.

So, in electrochemistry we study chemical changes involving transport and transfer of electrons, accompanied by flow of an electrical current.

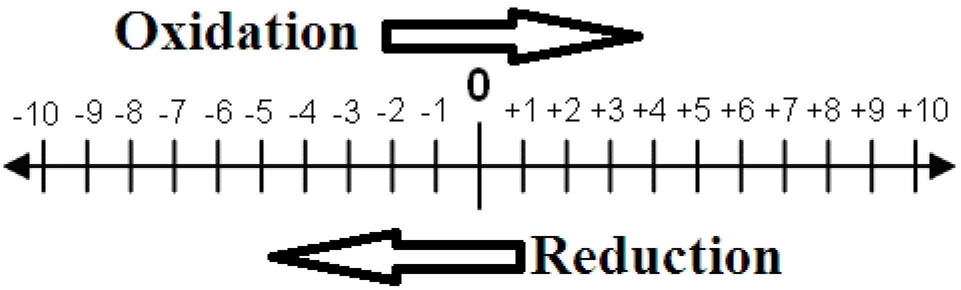
In 1793, Alessandro Volta discovered, electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper.

In 1800, Nicholson and Carlisle showed that an electric current could decompose water into oxygen and hydrogen. This was the first proof that water is composed of hydrogen and oxygen.

Important Terms

1. **Cation:** Positively charged ions are called as Cations.
   For example Na^+, K^+, Mg^{++}, Zn^{++}, Cu^+ etc.
2. **Anion:** Negatively charged ions are called as Anions.
   For example F^-, Cl^-, O^{--}etc.
3. **Oxidation:** Oxidation refers to loss of electron
   $Zn \rightarrow Zn^{++} + 2e^-$
4. **Reduction:** Reduction refers to gain of electron
   $Cu^{++} + 2e^- \rightarrow Cu$

Increase in oxidation number is referred as oxidation and decrease in oxidation number is referred as reduction.



Redox Reaction (Reduction and Oxidation)

Electron transfer reaction: Oxidation and reduction

Oxidation refers to loss of electron

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

Reduction refers to gain of electron

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

Overall reaction of reduction and oxidation is termed as Redox reaction

$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$

Reducing Agent: The substance which undergoes oxidation during a redox reaction, is called as reducing agent.

$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$

Since Zn undergoes oxidation, so it is reducing agent in above redox reaction.

Oxidizing Agent: The substance, which undergoes reduction during a redox reaction, is called as an oxidising agent.

$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$

Since Cu undergoes reduction, so it is oxidizing agent in above redox reaction.

Electrode:

It is a solid phase which can conduct electricity, such as metal strips or rods or graphite rod etc. Electrodes are of two types.

a. Cathode: The electrode where reduction reaction takes place.
b. Anode: The electrode where oxidation reaction takes place

Electrolyte or Electrolytic Solution:

Electrolytic solution is a conducting solution containing ions of soluble salts, acids or bases.

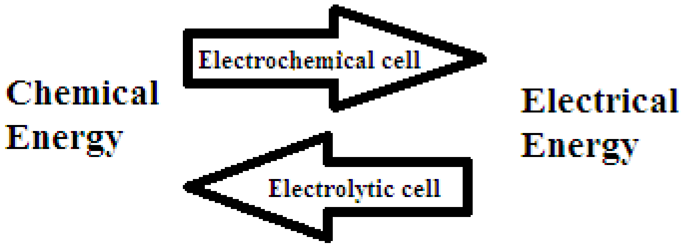
Cell: A device which can convert electrical energy into chemical energy or chemical enrgy into electrical energy is termed as a Cell. Cells are basically of two types.

i. **Electrochemical cell or Galvanic cell**

   The cell which can convert chemical energy into electrical energy is called as electrochemical cell. For example Voltaic Cell, Leclanche cell, dry cell etc.

ii. Electrolytic cell

   The cell which can convert electrical energy into chemical energy, is called as electrolytic cell.



Electro-neutrality Principle:

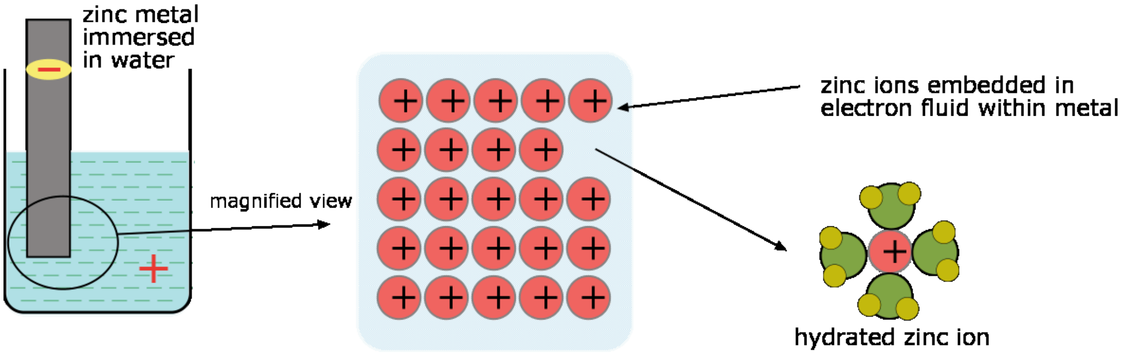
When a metal such as iron, copper or zinc is immersed in an electrolyte, a small quantity of metal cation will be released into the solution.

Suppose Zn metal is immersed in $ZnNO_3$ solution. The process can be described as;

$Zn(s) \rightarrow Zn^{++}(aq)$

A metal can be thought as an assembly of positive ions immersed in fluid-like sea of electrons.

The Zn^{++} ions leave the metal and attach themselves to water molecules, the electron left behind causes the metal to assume a negative charge.



For electrical neutrality, it is necessary to immerse Zinc in a solution of copper sulphate where zinc will get a coating of black finely divided metallic Copper. The reaction is simple as follows;

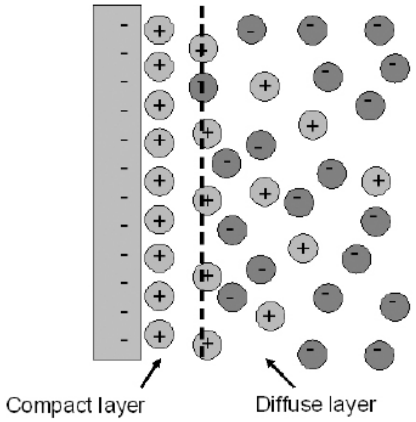
$Zn(s) \rightarrow Zn^{++} + 2e^-$

$Cu^{++} + 2e^- \rightarrow Cu(s)$

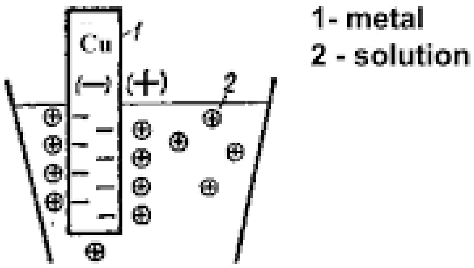
The Electric Double Layer:

The transition region between the metal electrode and the solution consists of a region of charge unbalance known as the electric double layer.

It consists of an inner adsorbed monomolecular layer of cations and an outer difuse region containing an excess of anion such as (NO_3^-). Electrode reaction takes place within the double layer. At that moment they alter the potential difference across this interfacial region.Helmholtz laid the theoretical foundations for understanding the double layer phenomenon. The formation of double layers is exploited in every electrochemical capacitor to store electrical energy.



Forming the double layer



Double Layer Capacitance

The electrical capacitance of an electrode is a surface related property, which reflects the separation of charge at the interface. **Double-layer capacitance** is the storing of electrical energy by means of the electrical double layer effect. This electrical phenomenon appears at the interface between a conductive electrode and an adjacent liquid electrolyte.

The value of the double-layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

Each electrode interface is composed of two sides:

1. The electrode side may be a metal or any other conducting material. The charge on the metal surface is formed either by the electrons (which are mobile) or lack of electrons (positively charged cores, which are not mobile). The adsorbed species may also influence the charge density on the electrode.
2. The other side of the interface is the electrolyte, which can produce a layer of ions or dipoles, due to chemical or electrostatic interactions with the charge accumulated at the electrode.

   As a result of the charge separation processes a double layer is formed, which can be characterised by its electrical capacitance usually called the double layer capacitance.

Cell Potential or Electrode Potential or Single Electrode Potential

Electrode potential of an electrode is the tendency of losing or gaining electron when t is in contact of a solution of its own ion. Tendency of losing electron is oxidation potential and tendency of gaining electron is reduction potential. The driving force that enables electrons to flow from one electrode to the other is called **electromotive force** (emf), or **cell potential** (E_{cell}), which has the unit **volt** (V). A volt is one Joule per Coulomb, where Coulomb is the unit of charge.

The electrode potential is defined as the potential difference of the electrical double layer formed at the contact (interface) of electrode metal and electrolyte. It is also called single electrode potential.

The electrode potential is the measure of tendency of an electrode to lose or gain the electrons when it is in contact of its own ions.

Origin of Electrode Potential

Nernst proposed the theory to explain how the electrode potential develops. The theory is called as Nernst's Theory.

According to this theory, a metal is regarded as an assembly of positive metal ions and free electrons. All the metallic elements have tendency to pass into solution in form of positive ions at constant temperature. This tendency is known as Solution Pressure or Solution Tension. It is a characteristic property of metal. Different metals have different solution tension.

When metal is placed in water, metal will pass into the solution in form of positive ions, the electrons will be left on the metal, making it negative charged.

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

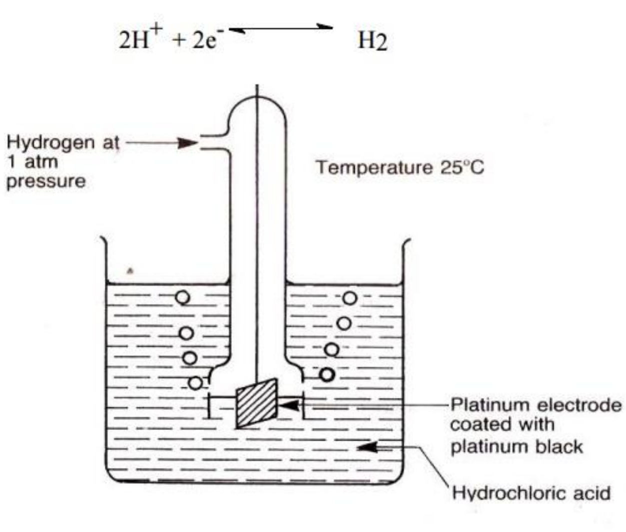
So, a double layer is formed. This electrical double layer prevents the further transfer of +ve ions from metal and an equilibrium state is reached with some definite value of potential difference, known as Single Electrode Potential or Electrode Potential.

Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (E°)

A standard hydrogen electrode in which concentration of hydrogen ions is unity, pressure of hydrogen is 1 atm., platinum plate with coating of platinum black is taken.

$$Pt, H_2\,(g)\ 1\ atm. \mid H^+\,(1M)$$

The potential of hydrogen electrode is arbitrarily given a value of zero volt at all temperatures.



A standard hydrogen electrode (S.H.E.)

Measurement of Electrode Potential

Standard hydrogen electrode can act as an anode or as a cathode when connected with a single electrode depending upon the tendency of losing or gaining electrons.

Since, potential of SHE is arbitrarily zero. So, when an electrode is coupled with SHE, the difference in potential in the Galavanic cell will be the potential of the given electrode.

Anodic reaction

$$H_2 \rightarrow 2H^+ + 2e^- \quad \textbf{(Oxidation)}$$

Cathodic reaction

$$2H^+ + 2e^- \rightarrow H_2 \quad \textbf{(Reduction)}$$

Metal undergoes oxidation and acts as anode

$$M(s) + nH^+ \rightarrow M^{n+} + n/2\ H_2$$

Metal undergoes reduction and acts as cathode

$$M^{n+} + n/2\ H_2 \rightarrow M(s) + nH^+$$

Standard Electrode Potential

The electrode potential at 298K temperature, 1 atm. Pressure and 1M concentration. It is denoted by E°.

Sign of Electrode Potential

According to IUPAC system

(i) The electrode potential is given positive (+ve) sign if the electrode reaction involves reduction when connected to SHE.

$$\begin{array}{l} \mathbf{H_2 \rightarrow 2H^+ + 2e^-} \\ \underline{\mathbf{Cu^{++} + 2e^- \rightarrow Cu}} \\ \mathbf{H_2 + Cu^{++} \rightarrow 2H^+ + Cu} \\ \mathbf{E^\circ_{Cu^{++}/Cu} = +0.34V} \end{array}$$

(ii) The electrode potential is given negative (–ve) sign if the electrode reaction involves oxidation when connected with SHE.

$Zn\ (s) + 2H^+ \rightarrow Zn^{++} + H_2$

$\mathbf{E°_{Zn++/Zn} = -0.76V}$

Value of reduction electrode potential and oxidation electrod potential are equal but opposite sign.

If, $\mathbf{E°_{Cu++/Cu} = +0.34V}$ **(reduction electrode potential)**

Then $\mathbf{E°_{Cu/Cu++} = -0.34V}$ **(oxidation electrode potential)**

The Electro-Chemical Cell or Galvanic Cell or Voltaic Cell

The device which converts chemical energy to electrical energy is called as an elctro-chemical cell. **Daniel Cell** is an example of Galvanic cell which can convert chemical energy to electrical enrgy. It consists of;

1. **An oxidation half cell:** Zn electrode partially dipped in $ZnSO_4$ solution
2. **A reduction half cell:** Cu electrode partially dipped in $CuSO_4$ solution
3. **A salt bridge or membrane:** Either the solutions are interconnected with the help of a salt bridge or they are separated by a porous membrane. A porous membrane is used to prevent mixing of the electrolyte.

Reaction at Oxidation Half Cell

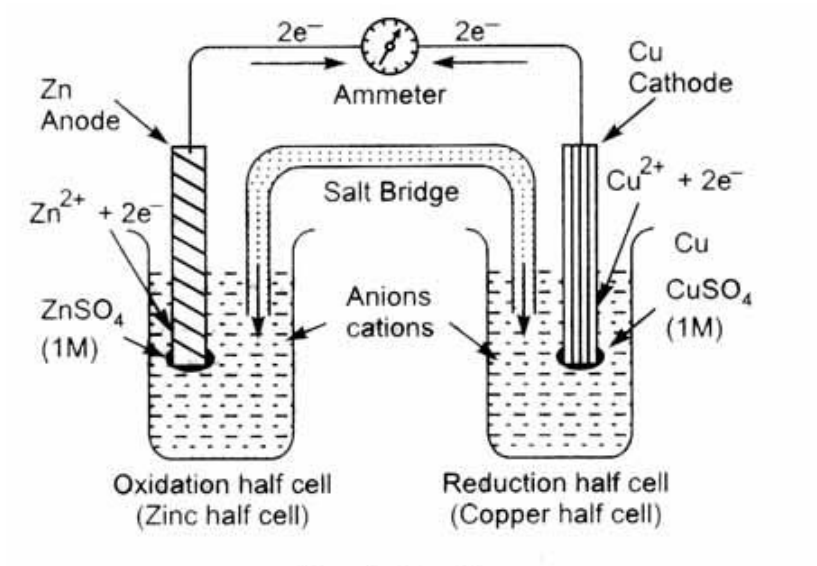
Zn electrode acts as anode and as convention it written on left side. Oxidation reaction takes place at anode.

$\mathbf{Zn(s) \rightarrow Zn^{++} + 2e^-}$ (Dissolution of Zn electrode)

Reaction at Reduction Half Cell

Cu electrode acts as a cathode and written on right side. Reduction reaction takes place on Cathode.

$\mathbf{Cu^{++} + 2e^- \rightarrow Cu(s)}$ (Deposition of Copper from solution on Cu electrode)



Daniell cell

Redox reaction takes place in an electro-chemical cell when both the electrodes are connected through a metal wire. Electrolyte in anode chamber is called as **Anolyte** and in cathode chamber it is called as **Catholyte.**

Salt bridge maintains electrical neutrality. A salt bridge is a U-shaped tube containing conc. Solution of KCl or KNO_3 or K_2SO_4 etc.

Net reaction in Daniel Cell $Zn + Cu^{++} \rightarrow Zn^{++} + Cu$

Transfer of ions

Accumulation of Zn^{++} takes place at Anode Electrolyte Interface (AEI) because of the dissolution of Zn. Very soon the anode gets completely surrounded by Zn^{++}.

Similarly, the copper deposition reaction gradually depletes Cu^{++} at cathode Electrolyte Interface (CEI). Resulting in a situation there is no Cu^{++} at the CEI. Thus the zinc dissolution reaction would stop at the anode. The absence of Cu^{++} at CEI means the copper deposition reaction will stop. But it has been observed that redox reactions continue in the galvanic cell which can happen in following three manners

i. Electromigration
ii. Diffusion
iii. And natural convection

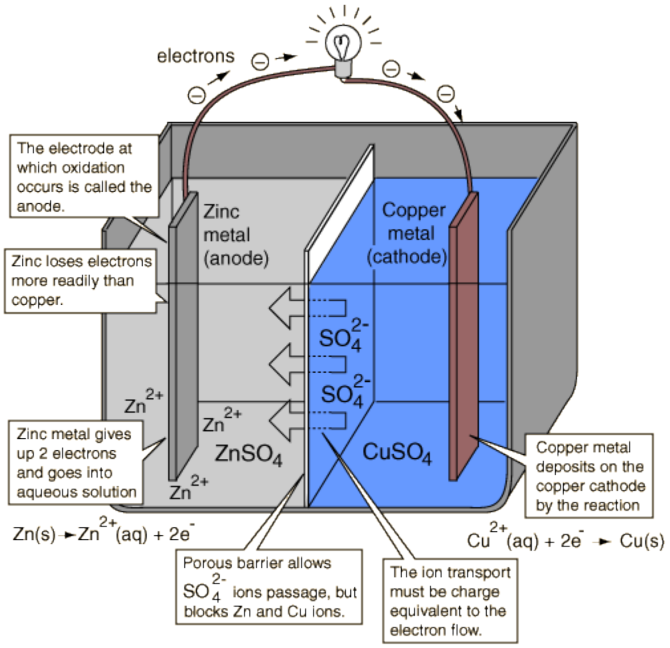


Fig. Transfer of ions

Representation of an Electro-chemical Cell

$Zn/Zn^{++}(C_1)//Cu^{++}(C_2)/Cu$

Overall reaction

Oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$

Reduction half-reaction: $Cu^{2+}(aq) + 2\ e- \rightarrow Cu(s)$

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

Kinetics of electrode processes and Current Density

The rate of electrochemical reactions are often expressed in terms of current density rather than in terms of the moles produced per unit time per unit area of the electrode surface. The current density is expressed as i which is A/m^2 s. The total current at the cathode is the same as the current at the anode.

The current density is related to the rate of reaction by the following equation which is a consequence of Faraday's law.

i = n F r

where, r is the rate of reaction in moles produced/m^2 s To provide an expression for the rate, r or the equivalent current density consider an electrode reaction represented as a reversible reaction of the type: $R \Leftrightarrow O + ne^-$,

where R and O represent the reduced and oxidized species and n is the number of electrons transferred.

Nernst Equation

Relationship between cell potential and concentration of electrolytes. The quantitative relationship between electrolyte concentration and cell potential is given by the following Reduction reaction for a half cell is given as

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

$E_{Electrode} = E^\circ_{Electrode} - (2.303RT/nF)\log 1/[M^{n+}]$ is called as Nernst equation.

$E_{cell} = E^o_{cell} - (RT/nF)\ \ln Q$;

E_{cell} is cell potential under non-standard conditions, while E^o_{cell} is cell potential under standard conditions (calculated from standard reduction potentials), R = 8.314 J/(mol.K), F = 96,485 C/mol, is the Faraday's constant; Q is the reaction quotient, such that, for the reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, $\quad Q = [Zn^{2+}]/[Cu^{2+}]$.

At 25 °C, $\dfrac{RT}{F} = \dfrac{(8.314\ \text{J/mol.K})(2\ 98\ \text{K})}{96{,}485\ \text{C/mol}} = 0.0257\ \text{J/C} = 0.0257\ \text{V}$

The expression for the Nernst equation becomes,

$$E_{cell} = E^o_{cell} - \frac{(0.0257\ \text{V})}{n} \ln Q\ ; \qquad (\ln = 2.303\ \log_{10})$$

$$= E^o_{cell} - \frac{(0.0591\ \text{V})}{n} \log[Zn^{2+}]/[Cu^{2+}]$$

$$\mathbf{E^o_{cell} = E^\circ_{cathode} - E^\circ_{Anode}}$$

The cell reaction will occur spontaneously until it reaches equilibrium, at which point Q = Kc (the equilibrium constant) and

$$E_{cell} = E^o_{cell} - (RT/nF)\ \ln(K) = 0\ ;$$

$$E^o_{cell} = (2.303RT/nF)\ \log Kc$$

Electrolysis and Electrolytic Cell

The chemical reaction that is carried out by passing electricity is called as the process of electrolysis. Electrolysis is commercially important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell. The voltage that is needed for electrolysis to occur is called the decomposition potential.

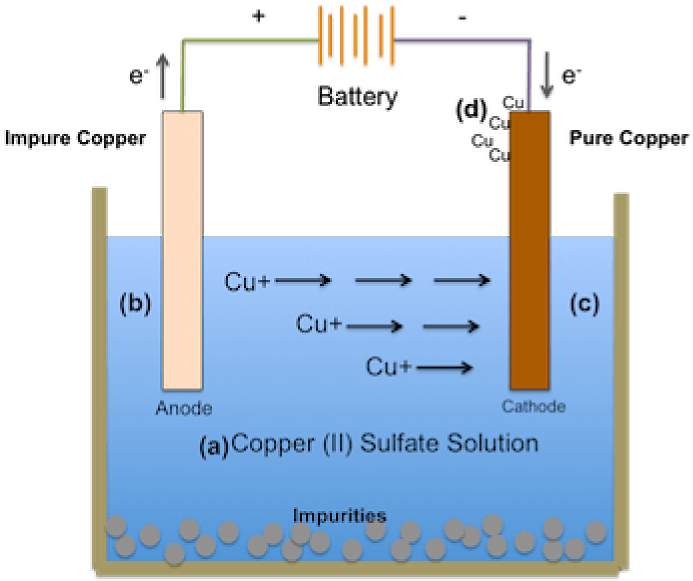


Fig.: **Electrolysis in Electrolytic cell**

Reaction at Anode (Oxidation)

$Cu \rightarrow Cu^{++} + e^{-}$ Dissolution of copper from impure rod

Reaction at cathode (Reduction)

$Cu^{++} + e^{-} \rightarrow Cu$ Deposition of pure copper on cathode

First law of electrolysis

In 1832, Michael Faraday reported that the quantity of elements separated by passing an electric current through a molten or dissolved salt is proportional to the quantity of electric charge passed through the circuit. The mass of the substance (m) deposited or liberated at any electrode is directly proportional to the quantity of electricity or charge (Q) passed.

$$m \propto Q$$

$$m = ZQ \qquad (Q = it)$$

thus, $m = Zit$

Where, Z is known as electrochemical equivalent of the metal deposited or of the gas liberated at the electrode.

Second law of electrolysis

Faraday's second law: According to this law, *"if same quantity of electricity is passed through different electrolytes, then the amount of substances liberated at the respective of electrodes are in the ratio of their equivalent masses".*

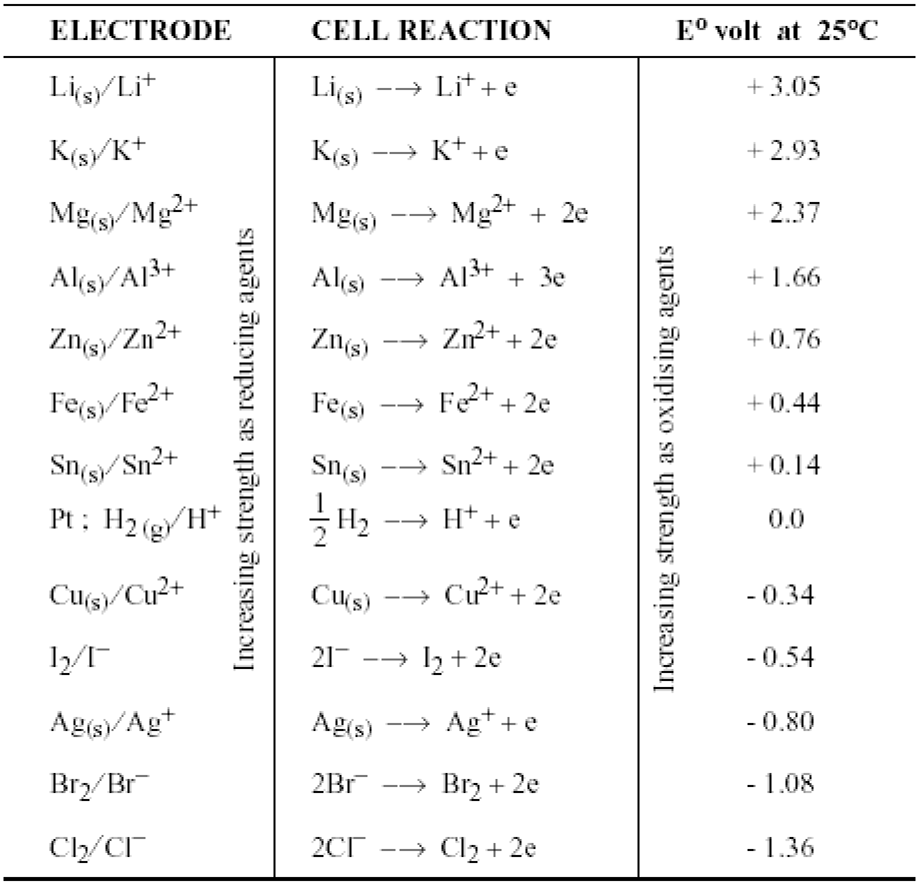
$$\frac{W1}{W2} = \frac{E1}{E2}$$

Electrochemical Series and Galvanic Series

The arrangement of elements in order of their increasing rates of ionization i.e. oxidizing and reducing strength is also called the activity series or the electrochemical series. Most of the elements of the periodic table can be arranged in such a fashion, which reflects their order of activity.

The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials (redox potentials). The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom.

The elctro chemical series comprising arrangement of metals and alloys in order of their standard reduction electrode potentials is called as Galvanic Series which is very useful in application of metallic structure manufacturing regarding corrosion.



ELECTRODE	CELL REACTION	E^o volt at 25°C
$Li_{(s)}/Li^+$	$Li_{(s)} \longrightarrow Li^+ + e$	+ 3.05
$K_{(s)}/K^+$	$K_{(s)} \longrightarrow K^+ + e$	+ 2.93
$Mg_{(s)}/Mg^{2+}$	$Mg_{(s)} \longrightarrow Mg^{2+} + 2e$	+ 2.37
$Al_{(s)}/Al^{3+}$	$Al_{(s)} \longrightarrow Al^{3+} + 3e$	+ 1.66
$Zn_{(s)}/Zn^{2+}$	$Zn_{(s)} \longrightarrow Zn^{2+} + 2e$	+ 0.76
$Fe_{(s)}/Fe^{2+}$	$Fe_{(s)} \longrightarrow Fe^{2+} + 2e$	+ 0.44
$Sn_{(s)}/Sn^{2+}$	$Sn_{(s)} \longrightarrow Sn^{2+} + 2e$	+ 0.14
$Pt ; H_{2\,(g)}/H^+$	$\frac{1}{2} H_2 \longrightarrow H^+ + e$	0.0
$Cu_{(s)}/Cu^{2+}$	$Cu_{(s)} \longrightarrow Cu^{2+} + 2e$	- 0.34
I_2/I^-	$2I^- \longrightarrow I_2 + 2e$	- 0.54
$Ag_{(s)}/Ag^+$	$Ag_{(s)} \longrightarrow Ag^+ + e$	- 0.80
Br_2/Br^-	$2Br^- \longrightarrow Br_2 + 2e$	- 1.08
Cl_2/Cl^-	$2Cl^- \longrightarrow Cl_2 + 2e$	- 1.36

Increasing strength as reducing agents

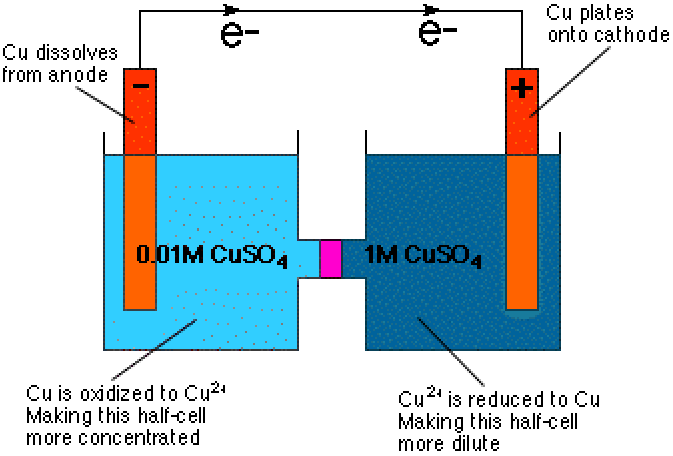
Increasing strength as oxidising agents

Table: Electrochemical Series

Concentration Cells

A concentration cell is an electrochemical cell in which both half-cells are of the same type, but with different electrolyte concentrations. The following cell notations are examples of concentration cells:

$Cu|Cu^{2+}(aq, 0.01\ M)||Cu^{2+}(aq, 1.0\ M)|Cu$



In concentration cells, the half-cell with the lower electrolyte concentration serves as an anode half-cell and one with the higher electrolyte concentration is the cathode half-cell. At the anode half-cell, oxidation reaction occurs to increase the electrolyte concentration and at the cathode half-cell, a reduction reaction occurs to decrease its electrolyte concentration. Oxidation-reduction reaction will continue until the electrolyte concentrations in both half-cells become equal.

At anode half-cell: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; (in 0.01 M Cu^{2+})
At cathode half-cell: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; (in 1M Cu^{2+})

Cell Potential and Free Energy

The cell potential measures the potential difference between the two half-cells. A potential difference of 1 V is equivalent to 1 Joule of work done per Coulomb of charge that flows between two points in the circuit. (1 V = 1 J/C or 1 J = 1 V.C)
Maximum work produced = charge x maximum potential

$W_{max} = -qE_{max} = \Delta G$

Electrical charge, $q = nF; \rightarrow \Delta G = -nFE_{cell}$; or $\Delta G^o = -nFE^o_{cell}$
Where, n = mole of electrons transferred or that flow through circuit,
and F = 96,485 C/mol e^- is called Faraday's constant

Significance:

(i) If E°_{cell} is positive (+ve), the cell reaction will be spontaneous.
(ii) If ΔG°_{cell} is negative (-ve), the cell acts as a source of electrical energy as cell reaction is feasible.

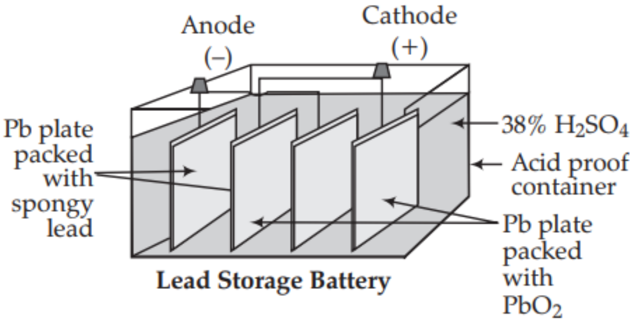
Lead Storage Batteries

These are batteries used in all types of automobiles. The lead storage batteries contain sulfuric acid as electrolyte. Each cell contains a number of grids of lead alloy. One set of alternating grids is packed with lead metal and the other with lead(IV) oxide, PbO_2. Each set of grids, which are the electrodes, are connected in a parallel arrangement, which enables the cell to deliver more current - the amount of current delivered depends on the surface area of the electrode. Each cell in a lead storage battery produces a potential of about 2.01 V. A standard 12-V battery used in most cars contains six cells connected in series.

Spontaneous Reactions that occur in the lead storage battery are:

Anode reaction: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$
Cathode reaction: $PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(m)$

Net reaction: $Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ ➔ discharging



Advantages: Recharging of Battery

The lead storage batteries are re-chargeable. When the engine is started, the discharge reaction occurs, but while the car is being driven, the battery obtains energy from the motor through the alternator and the following re-charging reaction occurs:

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq)$$

Lead storage batteries also have a longer lifetime and can deliver a relatively large amount of current and electrical energy within a short time.

Disadvantages

The major disadvantages are:

(1) They are very heavy and bulky - non-portable;

(2) Lead is a toxic metal and the disposal creates environmental problems;

(3) The battery must be kept upright and H_2SO_4 is very corrosive.

Fuel Cell

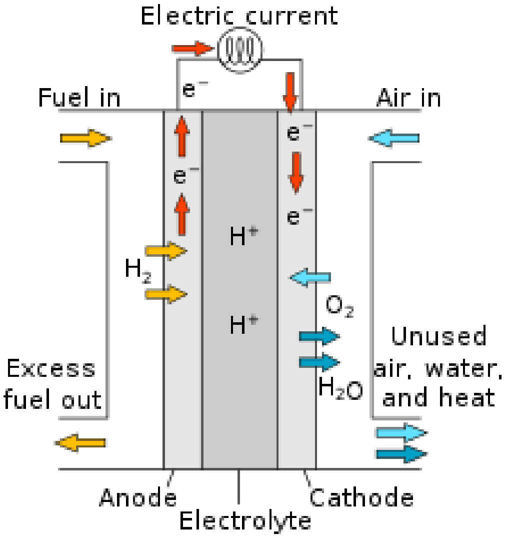
A fuel cell is a device that converts chemical potential energy (energy stored in molecular bonds) into electrical energy. A PEM (Proton Exchange Membrane) cell uses hydrogen gas (H_2) and oxygen gas (O_2) as fuel. The products of the reaction in the cell are water, electricity, and heat.

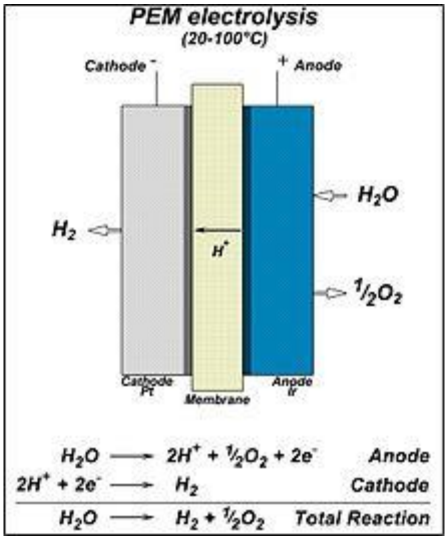
Proton Exchange Membrane Fuel Cell

Components of a PEM Fuel Cell

There are four basic elements of a PEM Fuel Cell:

1. **The anode**: The negative post of the fuel cell. It conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit.
2. **The cathode:**, The positive post of the fuel cell, has channels that distribute the oxygen to the surface of the catalyst. It also conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water.
3. **The electrolyte** is the proton exchange membrane. This specially treated material only conducts positively charged ions. The membrane blocks electrons.
4. **The catalyst** is a special material that facilitates the reaction of oxygen and hydrogen. It is usually made of platinum nanoparticles very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. The platinum-coated side of the catalyst faces the PEM.





A stream of hydrogen is delivered to the anode side of the MEA. At the anode side it is catalytically split into protons and electrons. This oxidation half-cell reaction or hydrogen oxidation reaction (HOR) is represented by:

At the anode: $H_2 \rightarrow 2H^+ + e$

At the cathode: $\frac{1}{2} O_2 + 2H^+ + e \rightarrow H_2O$

Overall reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$