

Electrochemistry

Electrochemistry deals with the chemical reactions produced by passing electric current through an electrolyte or the production of electric current through chemical reactions.

The cells which convert chemical energy to electric energy is called **electrochemical cells**.

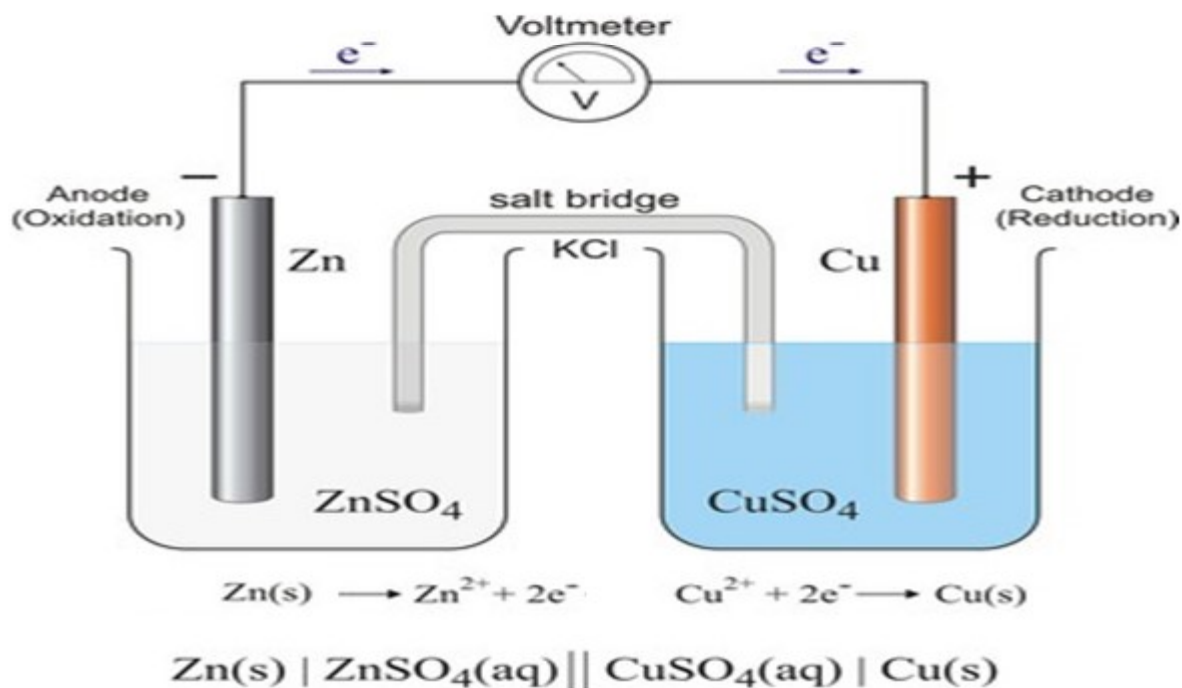
The cells that convert electric energy to chemical energy is called **electrolytic cells**.

Differences between electrochemical cells and electrolytic cells

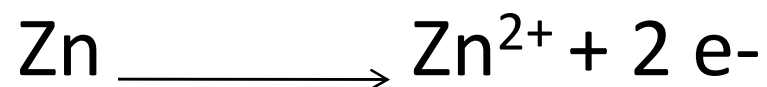
Electrochemical cells/ Daniel cells	Electrolytic cells
<ul style="list-style-type: none">• Convert chemical energy to electric energy.• Cell emf is positive• Free energy change ΔG is negative.• Anode is negative terminal.• Discharges of ions occur only at cathode.• Spontaneous reaction occurs.• These may be reversible	<ul style="list-style-type: none">• Convert electric energy to chemical energy.• Cell emf is negative• Free energy change ΔG is positive.• Anode is positive terminal.• Discharges of ions occur at both the electrodes• Non-spontaneous reaction occurs.• These may be irreversible

Electrochemical cell- Daniel cell/ voltaic cell/ galvanic cell

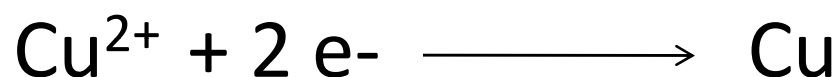
An electrochemical cell is a device in which the free energy of a physical or chemical process is converted into electrical energy. It consists of a Zn electrode immersed in ZnSO₄ Solution and Cu electrode dipped in CuSO₄ solution connected by means of salt bridge or porous partition.



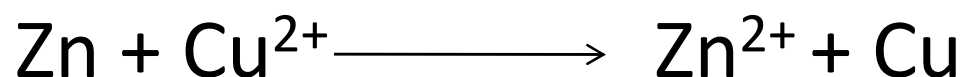
At anode, Zn metal leaves its electrons to the Zn electrode and goes to the solution as Zn^{2+} ,



At cathode, Cu^{2+} in the solution has a tendency of reduction, it accept electrons from Cu metal and get deposited on Copper electrode.



The overall cell reaction is :



The Daniel cell may be represented as



Electrode Potential

A potential difference is set up between the metal and the solution. This potential is called **single electrode potential**. This potential difference becomes a constant at equilibrium.

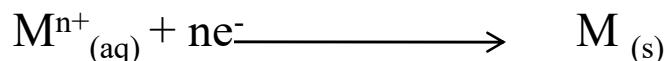
The tendency of the electrode to lose electrons is called **oxidation potential** and the tendency of the electrode to gain electrons is called **reduction potential**.

The potential difference developed when a metal is in contact with its own salt solution of concentration 1M at 25°C is called **standard electrode potential**.

Nernst equation

Nernst equation gives us the effect of electrolyte concentration on electrode potential.

Consider a general reduction reaction, taking place at the electrode,



The decrease in free energy, ΔG accompanying this process is : $\Delta G = \Delta G^{\circ} + RT \ln Q$
where Q is called reaction quotient, which is the ratio of activities of products to the reactants in a non equilibrium situation.

In a reversible cell, $\Delta G = - nFE$

Substituting the value of ΔG in above equation:

$$- nFE = - nFE^{\circ} + RT \ln Q$$

Dividing by $- nF$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Substituting the values of constants at the temperature $T = 298K$, $R = 8.314J/K/mol$,
 $F = 96500 C$

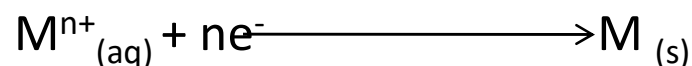
$$E = E^{\circ} - \frac{8.314 \times 298 \times 2.303}{n \times 96500} \log Q$$

$$E = E^{\circ} - \frac{0.0591}{n} \log Q$$

This is Nernst equation

Nernst equation for single electrode

For a single electrode,



Reaction quotient Q can be written as

$$Q = \frac{[M]}{[M^{n+}] [e]^n}$$

In dilute solution, activities are replaced by molar concentration, also concentration term (e) is one, for pure solid [M] is also taken as one.

Therefore,

$$Q = 1/[M^{n+}]$$

Thus , Nernst equation for single electrode is $E = E^{\circ} - \frac{0.0591}{n} \log 1/[M^{n+}]$

Nernst equation for a complete cell

For a cell reaction $aA + bB \longrightarrow cC + dD$
reaction quotient Q is

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Thus, Nernst equation for a complete cell is:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For a Daniel Cell, $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

The Nernst equation of Daniel cell is therefore

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

concentrations of pure solids are taken as one).

Applications of Nernst equation

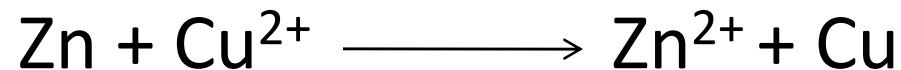
1. It can be used to study the effect of electrolyte concentration on electrode potential.
2. It can be used for the calculation of the potential of a cell under non-standard conditions.
3. The unknown concentration of one of the ionic species in a cell can be determined, provided that the E°_{cell} and concentration of other ionic species are known.
4. The pH of a solution can be calculated using this equation.
5. It can also be used for finding the valency of an ion or the number of electrons involved in the electrode reaction.
6. Solubility of sparingly soluble salt at any temperature can be determined.

Function of Salt Bridge

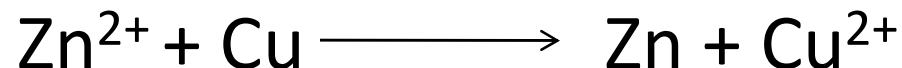
- Provides the continuity of electric circuit. When electrons flow through the external wire, there should be a flow of ions between the compartments.
- It prevents the diffusion of interfering ions from one compartment to another
- It prevents intermixing of solutions as well as ions in the two half cells.
- Since KCl is used in salt bridge, the mobility of K^+ and Cl^- ions are equal.

Reversible and irreversible cells

Reversible electrochemical cells are the cells whose reactions can be get reversed when an external emf better than its capacity is applied. For example, Daniel cell with capacity 1.1 volt, when an external emf of 1.1 volt is applied, the cell reaction stops.



But when an increased amount of emf better than 1.1 volt is applied, the cell reaction is get reversed.



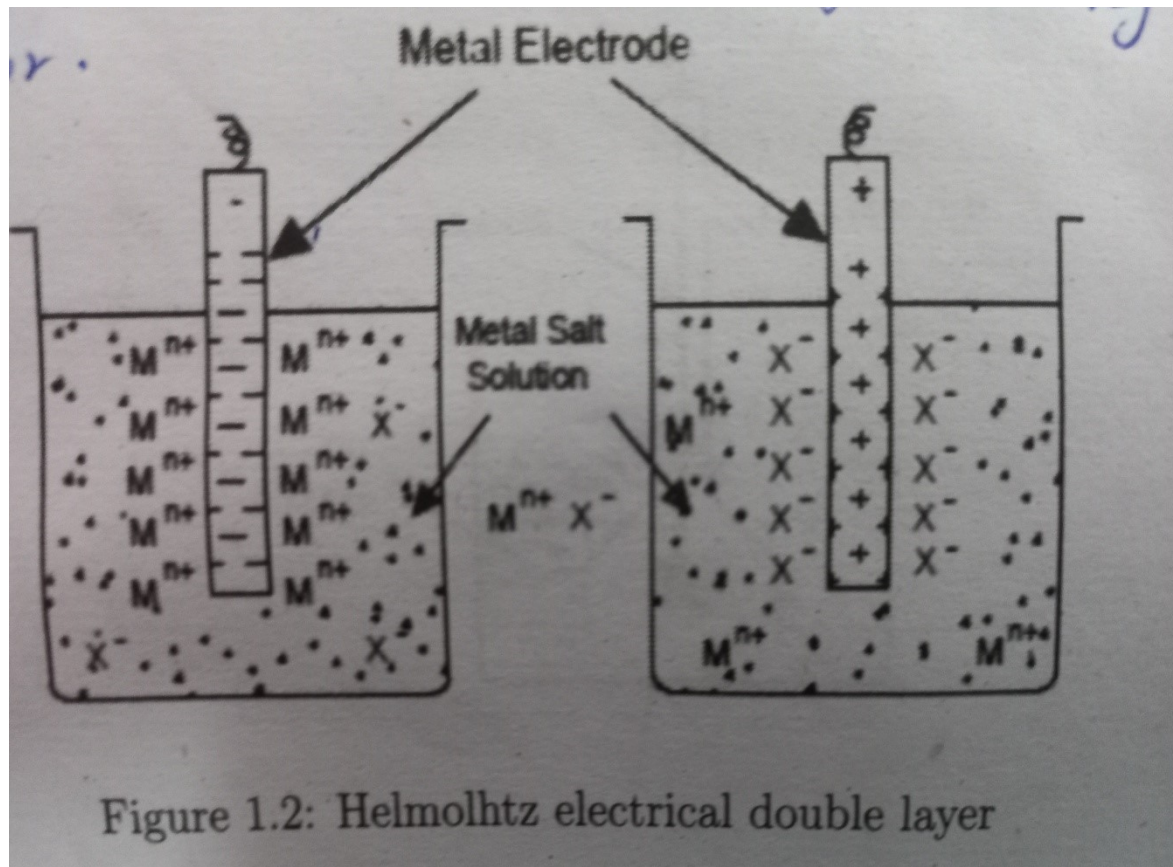
A cell is said to be reversible if the following two conditions are fulfilled-

1. The chemical reaction of the cell stops when an accurately equal emf is applied.
2. The chemical reaction of the cell is reversed and the current flows in a reversible direction when the external emf is somewhat higher than that of the cell.

Any other cell which does not obey the above two conditions is termed as irreversible cell.

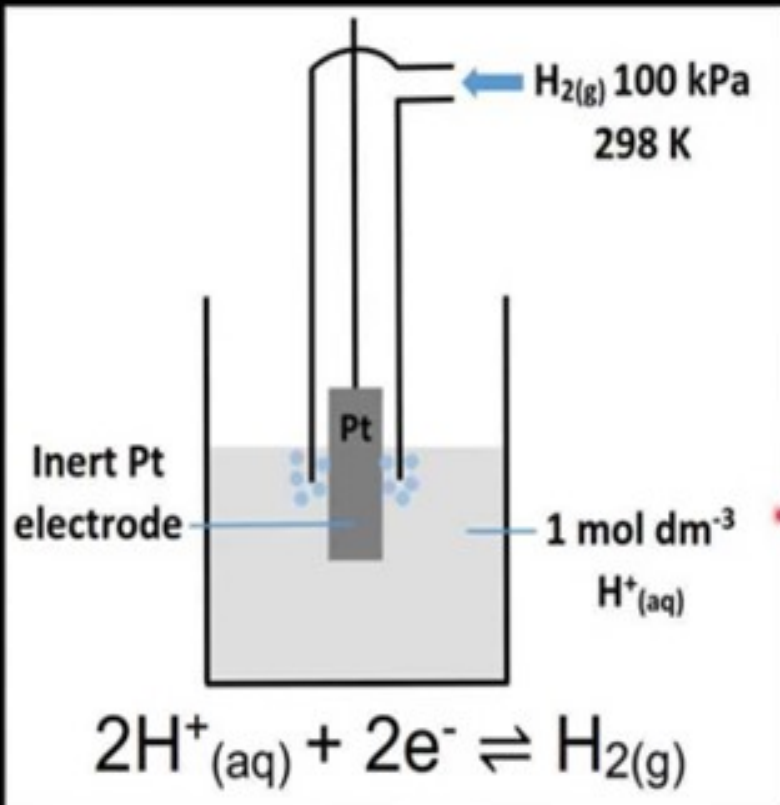
Example: Daniel cell is reversible cell and Volta cell is irreversible cell

Helmholtz electric double layer refers to the structural representation of the accumulation of electrical charges present at the boundary of an electrode and electrolyte when they are in contact with each other. The charge separation always occurs at the interface of the electrode in the solution. The excess charge on the electrode surface is accumulated by an accumulation of the excess ions of the opposite charge in the solution.



Reference Electrodes

Standard Hydrogen Electrode (SHE)/ Normal Hydrogen Electrode (NHE)



$\text{H}_2(\text{g})$ 100 kPa
298 K

Inert Pt electrode

Pt

$1 \text{ mol dm}^{-3} \text{H}^+_{(\text{aq})}$

$2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$

The standard hydrogen electrode (SHE) is assigned an electrode potential (E^\ominus) of 0 V. The SHE is used as a reference to measure the electrode potential of other half-cells.

SHE is an example of gas electrode. It consists of an inert platinum electrode dipped in 1M H^+ (HCl) solution, which is in contact with H_2 gas at 1 atm. pressure at 298K.

SHE is represented as $\text{Pt}/\text{H}_2 (\text{g}) 1 \text{ atm.}/\text{H}^+(1\text{M})$. It is also a reversible electrode

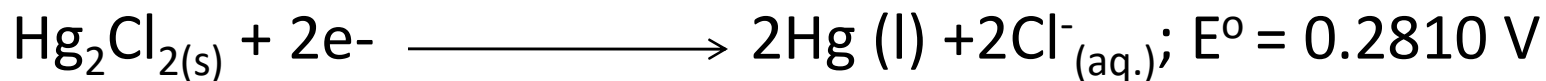
Limitation of SHE

1. It is very cumbersome to set up a SHE.
2. It requires considerable volume of solution.
3. The hydrogen electrode will be poisoned by compounds such as Hg, As, S, Fe^{3+} , etc.
4. It cannot be used in solutions containing redox systems.
5. Difficult to maintain pressure of H_2 gas at 1 atm and difficult to maintain the concentration of 1M HCl.

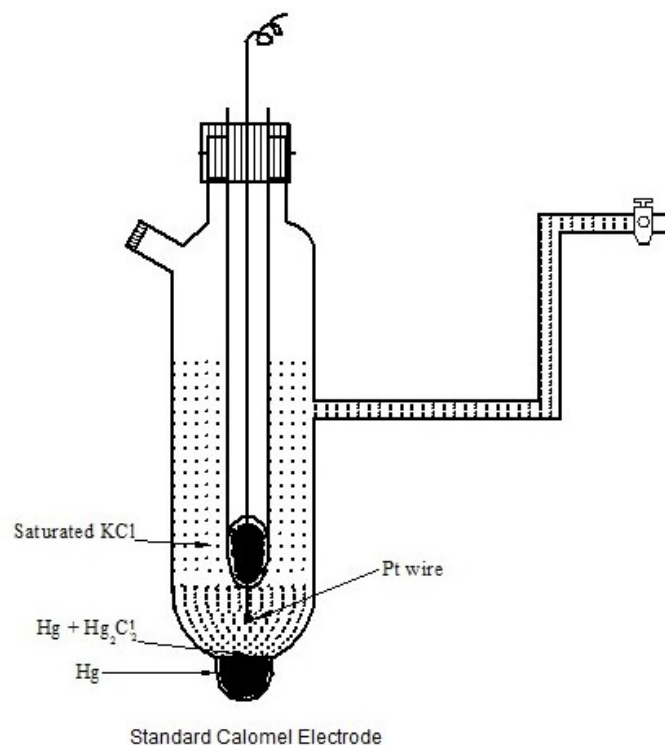
Calomel Electrode

Calomel electrode is a secondary reference electrode. This is a commonly used reference electrode since SHE is difficult to set up. This is an example of metal-metal insoluble metal salt electrode and a solution of its common ion (Mercury-mercurous chloride electrode, KCl). It consists of a glass tube at the bottom of which a small amount of Hg is placed. This is covered with a paste of solid mercurous chloride (Hg_2Cl_2 or calomel) which is further in contact with a solution of KCl. A Pt wire dipped into the Hg layer is used for making electrical contact. The electrode may be represented as $\text{Hg} / \text{Hg}_2\text{Cl}_{2(s)} / \text{KCl}$. The electrode potential of this electrode is 0.2422 volt.

The electrode cell reaction is :



Calomel electrode can act as anode or cathode depending on the electrode potential of the coupled electrode. It is used as left hand side electrode to measure the unknown potential of other electrode. Saturated calomel electrode is generally used, since it is easy to setup and its emf will not change with chemical reaction.



The Nernst equation of calomel electrode at 25°C is as given below:

$$E_{\text{cal}} = E^{\circ}_{\text{cal}} - \frac{0.0591}{2} \log [\text{Cl}^-]^2$$

$$\text{or } E_{\text{cal}} = 0.2810 - \frac{0.0591}{1} \log [\text{Cl}^-]$$

As chloride concentration increases, E value decreases.

KCl Concentration	0.1 N	1N	Saturated (SCE)
Electrode potential (in volt)	0.3335	0.2810	0.2422

Measurement of electrode potential using calomel electrode

In order to measure the standard electrode potential of Zn electrode, the Zn electrode is coupled with saturated calomel electrode through salt bridge and the emf of the cell is measured.

The electrode having higher reduction potential undergoes reduction and is the cathode and the electrode having lower reduction potential undergoes oxidation and is the anode.

Since, $E_{\text{SCE}} = 0.2422 \text{ V}$ and $E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, here calomel electrode is cathode and Zn electrode is anode.

The cell may be represented as $\text{Zn}/\text{Zn}^{2+} // \text{Cl}^- / \text{Hg}_2\text{Cl}_2 / \text{Hg}$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$E_{\text{cell}} = 0.2422 - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

By measuring cell emf $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$ can be calculated.

In order to measure the standard electrode potential of Cu electrode, the Cu electrode is coupled with calomel electrode. In this case, $E_{\text{SCE}} = 0.2422 \text{ V}$ and $E_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, here calomel electrode is anode and Cu electrode is cathode.

The cell may be represented as $\text{Hg}/\text{Hg}_2\text{Cl}_2 / \text{Cl}^- // \text{Cu}^{2+} / \text{Cu}$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{SCE}}$$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - 0.2422$$

By measuring cell emf, $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$ can be calculated.

What is the Electrochemical Series?

Electrochemical series also sometimes referred to as activity series is a list that describes the arrangement of elements in order of their increasing electrode potential values. The series has been established by measuring the potential of various electrodes versus standard hydrogen electrode (SHE).

In electrochemical series, the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction or oxidation potentials. Standard electrode potential is obtained by measuring the voltage when the half cell is connected to the standard hydrogen electrode under standard conditions.

Half Reaction

Standard Potential (V)

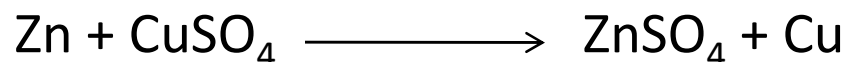
	F_2	+	2e^-	\rightleftharpoons	2F^-	+2.87
	Pb^{4+}	+	2e^-	\rightleftharpoons	Pb^{2+}	+1.67
	Cl_2	+	2e^-	\rightleftharpoons	2Cl^-	+1.36
	O_2	$+ 4\text{H}^+$	$+ 4\text{e}^-$	\rightleftharpoons	$2\text{H}_2\text{O}$	+1.23
	Ag^+	+	1e^-	\rightleftharpoons	Ag	+0.80
	Fe^{3+}	+	1e^-	\rightleftharpoons	Fe^{2+}	+0.77
	Cu^{2+}	+	2e^-	\rightleftharpoons	Cu	+0.34
	2H^+	+	2e^-	\rightleftharpoons	H_2	0.00
	Pb^{2+}	+	2e^-	\rightleftharpoons	Pb	-0.13
	Fe^{2+}	+	2e^-	\rightleftharpoons	Fe	-0.44
	Zn^{2+}	+	2e^-	\rightleftharpoons	Zn	-0.76
	Al^{3+}	+	3e^-	\rightleftharpoons	Al	-1.66
	Mg^{2+}	+	2e^-	\rightleftharpoons	Mg	-2.36
	Li^+	+	1e^-	\rightleftharpoons	Li	-3.05

stronger reducing agent

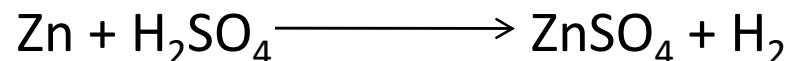
Application of Electrochemical Series

1. Reactivity of metals: The electrodes having negative standard electrode potential with respect to hydrogen undergo oxidation whereas electrodes with positive electrode potential undergoes reduction in aqueous solution.

2. To predict the displacement capacity of another metal from salt solution:- A metal having lower E° value will displace the metal having higher E° value from its salt solution.



3. Metals with negative E° value can displace hydrogen gas from acids.



4. Determination of standard emf of a cell from the standard electrode potentials of respective electrodes.

5. Decomposition potential of water can be calculated from electrochemical series.

Glass electrode

A glass electrode is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. It consists of low melting glass having high electrical conductivity. The glass electrode assembly consists of a long glass tube with a thin glass bulb filled with 0.1 M HCl. The inner surface of the glass is in contact with a AgCl coated silver electrode or simply a platinum contact electrode.

The electrode reaction is $\text{H}^+ + \text{Na}^+_{(\text{glass})} \longrightarrow \text{Na}^+ + \text{H}^+_{(\text{glass})}$
and electrode representation is:

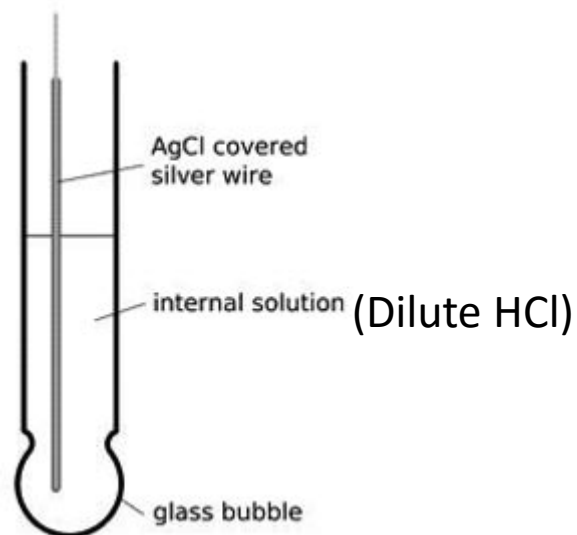


The Nernst equation for the electrode can be written as

$$E_G = E_G^0 - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$E_G = E_G^0 - 0.0591 \text{ pH}$$

Where E_G^0 is a constant for a particular variety of glass.



Measurement of pH

In order to measure the potential of glass electrode, it has to be coupled with secondary reference electrode like saturated calomel electrode. The cell can be represented as



The emf of the cell is measured and the pH can be calculated:

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

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

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

Since, the equation is in the form of $y = c + mx$, the pH of the test solution can be calculated by noting the E cell with test solution and knowing values of c and m .

Conductivity measurement using Digital conductivity meter

Conductivity is a measure of how well a solution conducts electricity. The conductivity is the inverse of resistivity and is determined from the voltage and current values according to Ohm's law

$$\text{Conductivity of the solution} = C \times l/a \text{ or } 1/R \times l/a$$

Thus for the measurement of conductivity of solution, resistance of the solution is to be determined. Wheat stone bridge method is used for this purpose. In this method, a conductivity cell containing the solution is made one arm of the wheat stone bridge apparatus. The electrodes of the cell are made up of platinum coated with platinum black. Then the conductivity cell is placed in a thermostat to keep the temperature constant. In order to prevent electrolysis, an Alternating Current is used. When current passes through the circuit, the resistors R2, R3 and R4 are so adjusted that a null point is obtained in the detector.

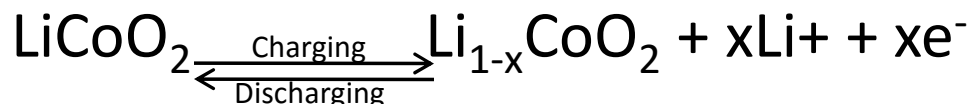
$$R_{\text{solution}} = \frac{R_2 R_3}{R_4}$$

The reciprocal of this resistance will give the conductance of the solution. From the conductance we get the specific conductance of the solution. Since conductivity of the solution = $C \times l/a$, where ' l ' is the distance between the electrodes and ' a ' is the area of cross section of electrodes. For a particular conductivity cell, ' C ' is constant and is called cell constant.

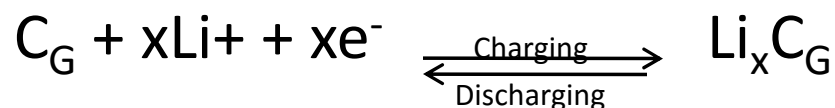
Lithium-ion cell (Li- ion battery)

Lithium ion cell is a secondary cell in which lithium ions moves between cathode and anode during charging and discharging. In this cell, anode is LiCoO_2 , cathode is graphite & electrolyte is an aprotic organic solution.

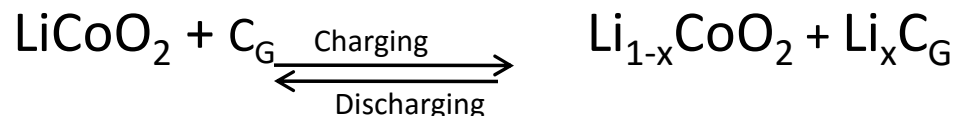
Anodic reaction:



Cathodic reaction:

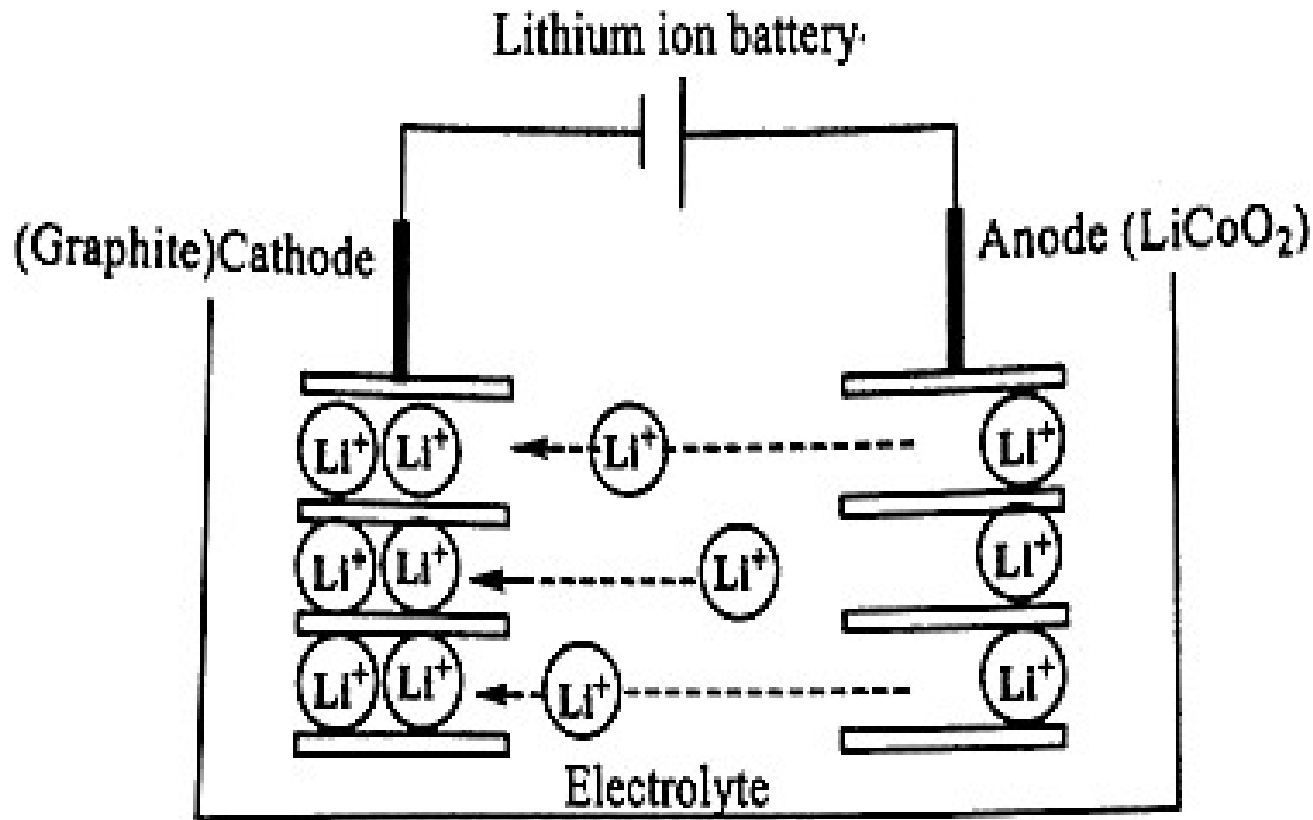


Overall cell reaction:



When Lithium ion cells are allowed to charge completely ($x=1$), then anodic material becomes $\text{Li}_{1-1}\text{CoO}_2$ or CoO_2 . This is an explosive material due to the liberation of oxygen gas on decomposition. Therefore, automatic built-in circuit breakers are there inside battery which allows charging only up to 90%.

Construction of Li-ion cell



Uses:

- It is used in Lap tops
 - It is used in mobile phones.
 - It is used in iPods.
- It is used in MP³ players.

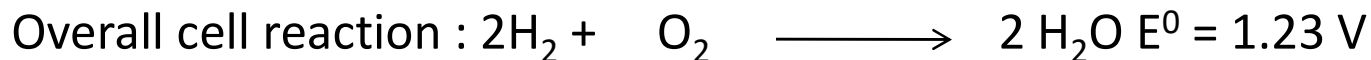
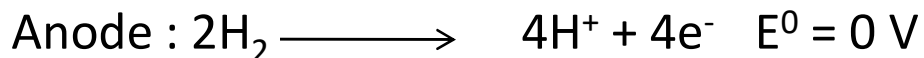
Hydrogen-Oxygen Fuel cell

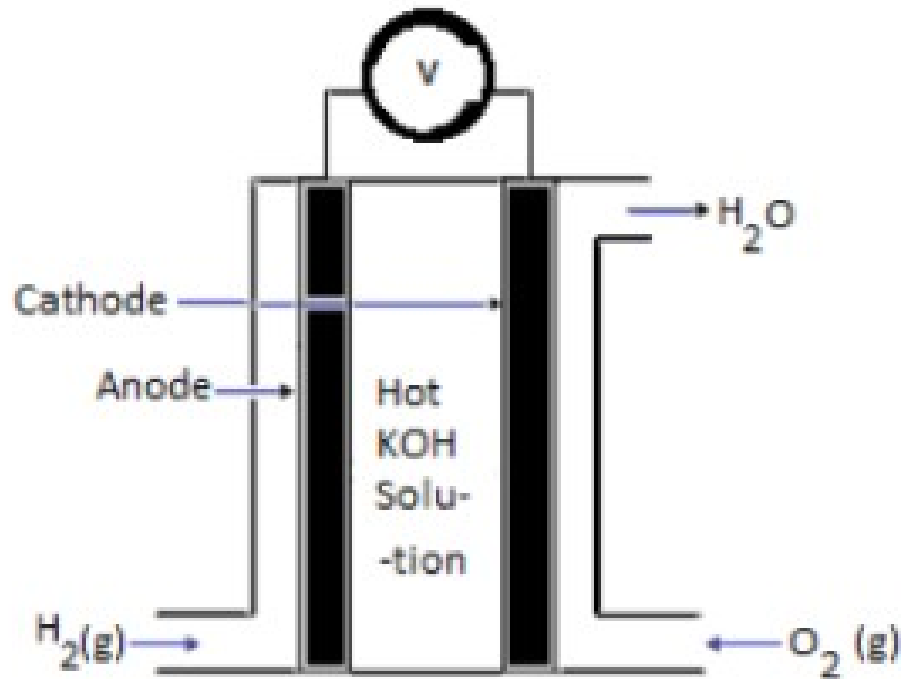
A fuel cell is an electrochemical system combining hydrogen and oxygen to generate energy, with the by-products of water and heat.

Construction and working

It consists of an anode, a cathode and an electrolyte. The two electrodes are made up of porous graphite impregnated with finely divided platinum catalyst. The electrolyte used is potassium hydroxide solution. Hydrogen is bubbled through the anode and oxygen is bubbled through the cathode. At Anode, hydrogen molecule gets split into electrons and protons. The protons pass through electrolyte and electrons generate electricity through circuit. At cathode electrons, protons and oxygen combine to form a water molecule.

Chemical Reaction





Advantages of H₂-O₂ fuel cell

1. The energy conversion efficiency is very high (75-83 %)
2. They are used as power sources in spacecrafts.
3. Noise and thermal pollution are very low.
4. It is light, compact, and simple to operate.
5. They can be stacked and connected in series to generate higher voltage.

Limitations

1. The cost of power from a fuel cell is high as result of the cost of electrodes and pure hydrogen gas.
2. As the fuels used are gases, they have to be stored in big tanks under high pressure.

Corrosion

Corrosion is the process of disintegration or deterioration of a metal by chemical or electrochemical reaction with the environment.

Example: Rusting of iron and tarnishing of silver or copper.

Based on mechanisms, corrosion can be explained by two main theories:

1) Dry or chemical corrosion and 2) Wet or electrochemical corrosion

Mechanism of Wet or Electrochemical corrosion

Electrochemical corrosion can occur when a conducting liquid is in contact with a metal or when two dissimilar metals or alloys are partially immersed in a conducting solution.

Hydrogen evolution corrosion in acid medium

This occurs when metals are in contact with acidic solution in the absence of sufficient oxygen.

Oxidation takes place at the anodic area, resulting in the corrosion of the metal.

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation) $E^0 = -0.44 \text{ V}$ The Fe^{2+} ions so formed dissolve in the solution.

Reduction occurs at the cathodic area. At the cathodic area, the dissolved constituents in the conducting medium accept electrons to form ions like OH^- , O^{2-} etc. The non-metallic ions so formed combine with the Fe^{2+} to form corrosion product. The electrons released at the anode flow through the metal and get consumed in the cathodic reaction, either for the evolution of hydrogen or for the absorption of oxygen. $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) ; E^0 = 0 \text{ V}$

Net reaction : $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 ; E^0_{\text{cell}} = 0 - (-0.44) = 0.44 \text{ V}$

Corrosion with evolution of H_2 occurs, when the anodic area is very large and cathodic area is small and it usually occurs in acidic environments.

Hydrogen evolution corrosion in alkaline medium

Hydrogen evolution corrosion does not take place in the case of iron immersed in alkaline medium. This is due to the fact that hydrogen electrode potential in alkaline medium ($E^{\circ} = -0.828 \text{ V}$) is lower than electrode potential of iron ($E^{\circ} = -0.44 \text{ V}$). Whereas metals like aluminum can give hydrogen evolution corrosion in alkaline medium. Upon considering cell reactions:

Anode: $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^{-}; E^{\circ} = -1.66 \text{ V}$

Cathode : $2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}; E^{\circ} = -0.828 \text{ V}$

Therefore, corrosion cell potential is

$$E^{\circ} \text{ cell} = E_{\text{cathode}} - E_{\text{anode}} = -0.828 - (-1.66) = 0.832 \text{ V}$$

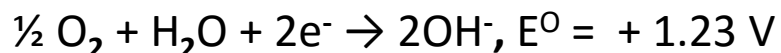
Oxygen absorption corrosion in acid medium

Rusting of iron occurs through this mechanism. Initially a thin film of iron oxide is formed on the surface of iron metal. Some cracks are developed on the iron oxide film. The surface of the metal acts as the anodic area, whereas the interior of the metal behaves as cathode.

At the anodic area, Fe dissolves as Fe^{2+} ions with the liberation of electrons.



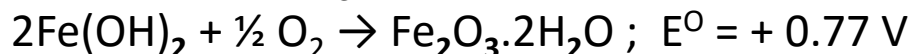
The electrons thus released from the anode move to the cathodic area through the metal. These electrons are then taken up by oxygen molecule to form OH^- ions.



$$\text{Corrosion cell potential } E^0_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 1.23 - (-0.44) = 1.67 \text{ V}$$

The Fe^{2+} ions formed at the anodic area and the OH^- ions formed at the cathodic area combine to form $\text{Fe}(\text{OH})_2$ precipitate. Fe^{2+} further gets oxidized to Fe^{3+} as its oxidation potential is more in acidic medium.

In the presence of excess of oxygen, $\text{Fe}(\text{OH})_2$ precipitate easily oxidises to get yellow rust having the formula, $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$



If the amount of oxygen is limited, then the corrosion product is black rust (Hydrated magnetite) $3\text{Fe}(\text{OH})_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$

The rust formation leads to intense localized corrosion called **pitting corrosion**. This is due to the formation of separate cathodic and anodic area. Thus the rate of corrosion of iron is more in acid medium than in alkaline medium as Fe^{2+} gets oxidized to Fe^{3+} in acidic medium.

Oxygen absorption corrosion in alkaline medium

This occurs when metals are in contact with water having dissolved oxygen in alkaline environment.

Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$; $E^\circ = -0.44 \text{ V}$

Cathode : $\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4\text{OH}^-$; $E^\circ = +0.40 \text{ V}$

Therefore, corrosion cell potential is

$$E^\circ_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.40 - (-0.44) = 0.84 \text{ V}$$

Here, Fe^{2+} produced can not further oxidized to Fe^{3+} , since oxygen electrode potential is less than

$E^\circ = +0.77 \text{ V}$ in alkaline medium. Here no insoluble precipitate of $\text{Fe}(\text{OH})_3$ is produce, thus no intense localized corrosion.

Galvanic series

Relative corrosion affinities of metals and alloys can be explained by using a series called galvanic series. This series can be prepared by studying the corrosion affinities of metals and alloys in unpolluted sea water without their oxide films. A metal high in this series is more anodic and undergoes corrosion faster than the metal below it. The position of a metal in the form of an alloy is different from that of the pure metal in this series.

Galvanic series is advantageous over electrochemical series in corrosion chemistry. The electrochemical series gives useful information regarding the reactivity of metals, but it does not provide sufficient information in predicting the corrosion behavior. In electrochemical series, the metal having lower reduction potential are more anodic and undergo corrosion faster. However, there are exceptions like Titanium and Aluminum.

Comparison of electrochemical series and galvanic series

Electrochemical Series	Galvanic series
<ul style="list-style-type: none"> • E° is measured only for metals and non- metals. • E° is measured by dipping pure metals in their 1M salt solution. • SHE is used as the reference electrode. • Position of the metals is fixed. • It predicts the relative displacement tendencies. 	<ul style="list-style-type: none"> • E° is measured only for metals and alloys. • E° is measured by dipping metals and alloys in unpolluted sea water. • Calomel electrode is used as the reference electrode. • Position of the metal and alloys may change. • It predicts the corrosion tendencies.

Corrosion prevention methods

1) Cathodic protection

In this method, the metal to be protected is made as cathode so that corrosion will not occur.

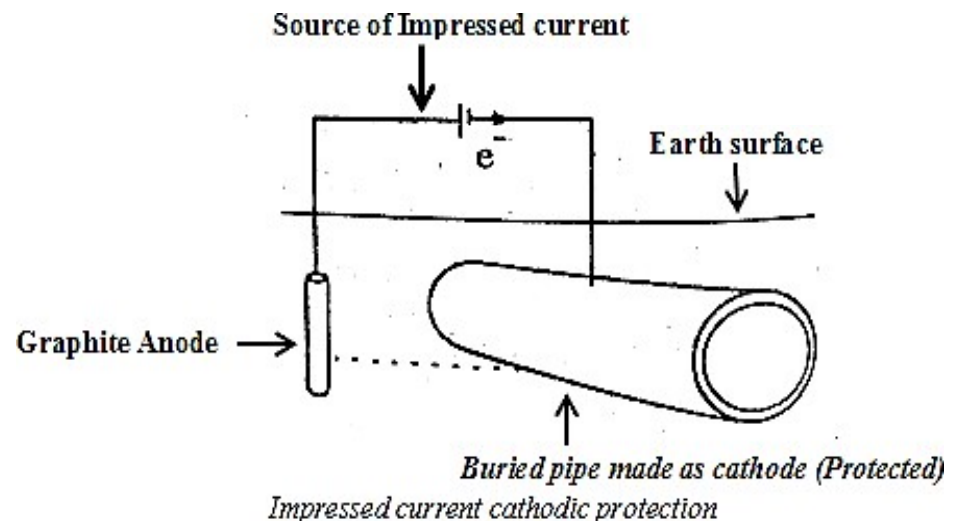
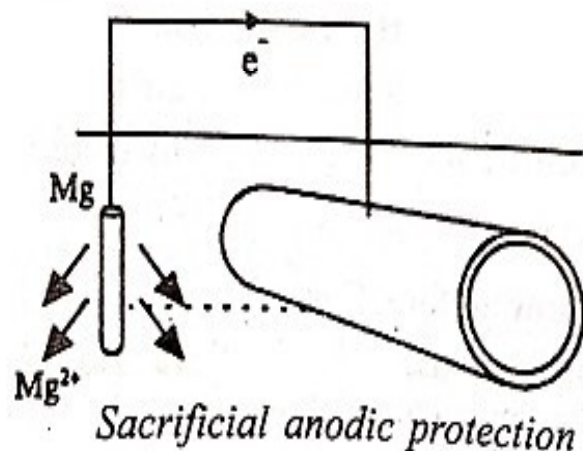
The following methods are employed for cathodic protection.

a) **Sacrificial anodic protection:**

In this method, the metal to be protected is connected by a wire to a more anodic or active metal. Then the more active metal will undergo corrosion and the cathode remains protected. Here the more active anodic metal sacrifices for the protection of cathodic metal and is called sacrificial anode. Metals commonly used for this purpose are Mg, Zn, Al and their alloys.

b) Impressed current cathode protection:

In this method an impressed current is applied in opposite direction to nullify the corrosion current. As a result corroding metal is converted from anode to cathode. The impressed current required can be obtained from a battery with an insoluble anode made of graphite or high silica iron. This method is used for the protection of open water box coolers, water tanks etc.

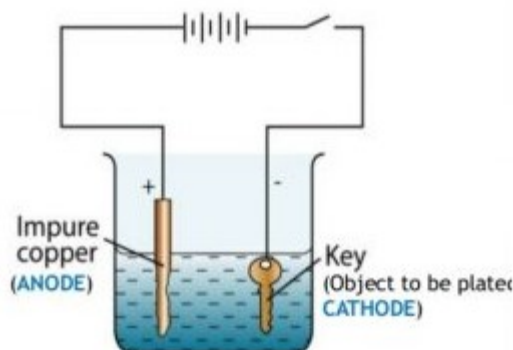


Electroplating

Copper Electroplating: Copper electroplating is a simple electrochemical process that results in a thin copper coating on any conductive surface with the help of an electrolyte bath. The article to be electroplated is first treated with organic solvents to remove oil, grease, etc. Then, treated with dil. HCl to remove surface scales. The cleaned article is made as the cathode and pure copper rod as anode. Both the electrodes are dipped in copper sulphate solution in an electroplating tank. Direct current is passed through the electrolyte, electrolysis occurs and Cu^{2+} ions move towards the cathode and gets deposited there.

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

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



2) Electroless copper plating (Autocatalytic plating)

It is the method of depositing copper from its salt solution on the catalytically active surface of the metal to be plated using a suitable reducing agent without using electrical energy.

The object to be plated is degreased using organic solvent and this followed by acid treatment. In this method, article to be plated is immersed in a plating bath containing CuSO_4 (As a source of Cu), formaldehyde (Reducing Agent), buffer solution of NaOH and Rochelle salt and a complexing reagent. Air is bubbled slowly through the medium to control the formation of cuprous oxide. Electroless plating of Cu takes place as follows.

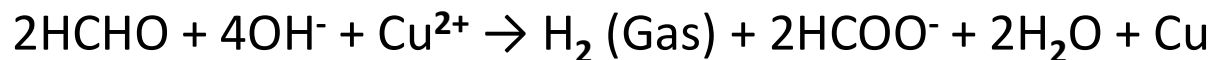
Oxidation (Anode)



Reduction (Cathode)



Net reaction



Applications of electroless Cu plating

- Widely used for metalizing printed circuit boards.
- Used for plating on non-conductors.
- It is also used for making decorative plating on plastics.

Advantages

- This method produces even coatings.
- It does not use electrical power.
- This coating is having improved hardness, strength, ductility and resistance to corrosion.

Disadvantages

- The reducing agent, formaldehyde is a human health hazard.
- The instability of the electroless copper bath creates difficulties in process control.