ELECTROCHEMISTRY

"The branch of chemistry that deals with the relationship between electricity and chemical reactions i.e. with the conversion of electrical energy in to chemical energy and chemical energy into electrical energy is known as electrochemistry."

ELECTROLYTES:

"The chemical compound which conducts electricity in molten condition or through its aqueous solution with chemical change is called an electrolyte."

Examples:

All acids, bases and salts are electrolytes (in aqueous solutions or fused state).

Hydrochloric acid (HCl).
Sulphuric acid (H_2SO_4).
Sodium hydroxide (NaOH).
Sodium chloride (NaCl).
Copper sulphate ($CuSO_4$) etc.

Explanation:

No substance can be electrolyzed unless it conducts electricity. But all the conductors are not electrolytes. Electric current can pass through a metal for years but it will not decompose. Metals are good conductors but are not electrolytes.

All electrolytes are ionic compounds or polar compounds like acids and bases. Salts are ionic compounds and are solids. These solids do not conduct electricity because in the solid state these ions are tightly packed or held together showing no movement of the ions. They cannot move. However when an ionic solid is melted or dissolved in water, its ion become free to move. Thus ionic compounds in molten states or in aqueous solution conduct electricity. This conduction due to the free movement of ions

NON-ELECTROLYTES:

"The chemical compounds which do not conduct electricity in molten or in aqueous solution are called non-electrolytes."

Example:

Sugar, petrol. Benzene etc.

ELECTROLYSIS OR ELECTROLYTIC CONDUCTION:

Movement of the ions of an electrolyte to towards their respective electrodes and their deposition or liberation as neutral species under the influence of electric current is called electrolysis.

The cell used for the reaction to occur by passing electric current is called electrolytic cell. Thus electrolytic cell is a device which is used to convert electrical energy into chemical energy (a non-spontaneous chemical reaction takes place by the loss and gain of electrons) for example: a device or electroplating or electrolysis of water in the presence of an acid. The process is called electrolysis or electrolytic conduction.

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE:

Sodium chloride (salt) does not conduct electricity in the solid state. To make it conduction electricity, either fuse or melt the salt or dissolve it in water. So there are two ways of doing electrolysis of sodium chloride. We are doing electrolysis of molten sodium chloride. Sodium chloride melts at 800°C. It is easy to predict the result of electrolyzing a molten electrolyte. The salt just splits into two parts. Sodium (metal) positive ion (Na^+) and chloride (non-metal) negative ion (Cl^-). We can write the ionization reaction as.

$$NaCl \qquad Na^+ + Cl^-$$

In sodium chloride, the ions are held together tightly in a regular lattice arrangements. In solid the ions cannot move but when sodium chloride is melted, the ions are free from their lattice and they can move freely to conduct electricity. Some fused NaCl is taken in an electrolytic cell i.e. in a glass vessel. Two platinum rods (electrodes) are dipped in to the used salt (NaCl). The two electrodes are connected to a source of electricity i.e. to a battery outside the cell by wires. The electrode connected to the negative i.e. to a battery outside the cell by wires. The electrode connected to the positive terminal of the battery is called anode.

When an electric potential is applied through the molten sodium chloride salt, electrolysis starts. The positive ions i.e. Cat ions (Na^+) are attracted towards cathode and the negative ions i.e. anions (Cl^-) are attracted towards anode. At the two electrodes following chemical reactions are taken place.

At Cathode:

Sodium ions (Na+) which are positively charged move towards cathode and gain electrons to get neutralized. Thus Na^+ ions are discharged at cathode and form neutral molten sodium metal. We can represent the happening at cathode as:

Sodium ion + electron Sodium metal

$Na^+ + e^-$ Na

At Anode:

Chloride ions which are negatively charged moved towards anode i.e. Cl^- ions have one electron in excess. The anode has a shortage of electrons and is positively charged. When Cl^- ions arrive at anode, forming neutral chlorine (Cl) atoms but we know that Cl atoms do not exist in Free State. They combine to form Cl_2 molecules. So Cl^- ions are discharged at anode to liberate Cl_2 gas by the loss of electrons at anode.

Chloride ion Chlorine atom + e^-

Cl $Cl + e^-$

Then $Cl + Cl$ Cl_2

Overall it amounts to $2Cl^-$ $Cl^2 + 2e^-$

The overall reaction can be described as:

$2Na^+ + 2e^-$ 2Na cathode reaction

$2Cl$ $Cl_2 + 2e^-$

On adding the two reactions, the loss and gain of electrons cancel we get final result:

$2Na^+ + 2e^-$ 2Na cathode reaction

$2Cl^-$ $Cl_2 + 2e^-$

NET ELECTROLYSIS REACTION:

$2Na^+ + 2Cl^-$ $2Na + Cl_2$

The electrolysis of molten sodium chloride shows that we get sodium metal at cathode and Cl_2 gas is liberated at anode.

FARADY'S FIRST LAW OF ELECTROLYTES:

"The mass of an element discharged during electrolysis is directly proportional to the magnitude of electric current and the time of flow of current."

Explanation:

According to the law

$W \propto A \times t$

$W = Z \times A \times t$

Where

W	=	mass of element deposited
Z	=	electrochemical equivalent of the substance
A	=	amount of electric current in ampere
T	=	time in seconds

FARADY'S SECOND LAW OF ELECTROLYSIS:

It states that:

"The mass of different substance deposited or liberated when same quantity of current is passed through different electrolytes, connected in series are proportional to their chemical equivalent masses."

Explanation:

Consider three different electrolytes $AgNO_3$ $CuSO_4$ and $Al_2(NO_3)_3$ solutions connected in series. Same quantity of current is passed through them and then the masses of Ag, Cu and Al deposited on their respective electrodes would be directly proportional to their equivalent masses.

According to faraday if exactly 96500 coulombs of electric charge is passes then the mass of an element deposit would equal to their equivalent masses.

For example:

By passing 96500 coulombs Ag deposited would be equal to 108g, that of copper is 31.75g and Al is 9g which are their equivalent masses respectively.

ELECTRO CHEMICAL EQUIVALENT (Z):

The amount of deposited or liberated substance during electrolysis when one coulomb charge is passed through an electrolyte is called electrochemical equivalent of that substance.

S.I unit of it is expressed in Kg/coulomb.

Each element has its own chemical equivalent.

Relationship between equivalent and electrochemical equivalent:

Since 96500 C electric charge is required to liberate one gram equivalent mass of substance, so it is clear that the 1 gram equivalent mass of a substance is 96500 times greater than its electrochemical equivalent.

Gram Eq. mass $=96500 \times Z$

In other words

$C = 96500 \times Z$ or $e = F \times Z$

Z = e/96500 or Z=e/F

Where e = Gram equivalent mass
F = Faraday = 96500 coulombs
Z = E.C.E = electrochemical equivalent

EQUIVALENT MASS OF SOME ELEMENT:

Equivalent mass of an element =Atomic mass of the element /valency of the element

i. Equivalent mass of silver Ag = 108/1 = 108
ii. Equivalent mass of copper = 63.5/2 = 31.75

ELECTRIC CURRENT:

"The flow of charge in the unit of time is called electric current and its S.I unit is Ampere."

Ampere:

The current when passed through a circuit for one second, can liberate 0.001118 gram from silver nitrate solution is called an Ampere.

COULOMB:

Coulomb is the S.I unit of electric charge.

If one ampere of electric current is passed for one second, then the quantity of charge is known as a coulomb.

Electric charge = A x t
1 Coulomb = 1 Ampere x 1 Second

FARADAY:

The current of 96500 coulombs charge is called one faraday (F) charge. The name is given after the name of faraday.

USES OF ELECTROLYSIS:

Electrolysis is an important process,

i. For the extraction of certain metals from their ores.
ii. Electroplating.

i. EXTRACTION OF ALUMINIUM:

Aluminum is a reactive metal which makes it difficult to extract it from its ore. Earlier it was obtained by heating its salt aluminum chloride with sodium metal. Sodium itself as expensive which made it even more expensive.

$$AlCl_3 + 3Na \rightarrow Al + 3NaCl$$

Now a days Al is extracted by the electrolysis of Alumina which is obtained from cheap ore of Al bauxite. Due to the process of electrolysis. Aluminum is so cheap that it is used in dispose able plates for eating.

ii. EXTRACTION OF SODIUM:

Sodium metals is extracted by the electrolysis of molten sodium chloride to deposit sodium (Na) metal at cathode by Down's process. Many metals are purified into pure metals by the process of electrolysis.

iii. EXTRACTION OF COPPER:

Impure copper is purified by the process of electrolysis. In this process. The impure copper i.e. blister copper is made as anode in the electrolytic cell.

Cathode is a thin plate or sheet of pure copper metal and the two electrodes are dipped in the electrolytic solution of copper sulphate containing few drops of sulphuric acid. The two electrodes are connected with a battery. When an electric current is passed through the electrolytic solution. The copper anode dissolves in the solution as Cu^{++} ions which move towards cathode and gain electrons to get neutralized, depositing pure copper metal over cathode plate. Most of the impurities of anode fall to the bottom of the cell, called as "anode mud". Copper thus deposited at cathode is 99.99% pure. In this way copper anode dissolves completely to form pure copper at cathode. This process of electrolysis is similar to electroplating.

ELECTROPLATING:

"The coating of one meta on other metal through the process of electrolysis in order to protect the baser metal from corrosion and to make them more attractive is called electroplating."

EXPLANATION:

Electroplating is the process of electrolysis which is used to coat one metal onto another. Usually the object to be electroplated is made up of cheaper or baser metal, such as iron, steel etc. It is then coated with a thick layer of more attractive corrosion – resistance and costly metal, like silver, gold, chromium, tin etc. The cost of the finish product is far less than the object entirely made of these metals. Gold coated object is much cheaper than the gold object.

Nickel Plating:

A cell is used for electroplating of nickel. A piece of pure metal is the anode and the spoon or any object to be plated is cathode. A solution of sulphate ($NiSO_4$) is used as the electrolyte in the electrolytic cell. The two electrodes are joined with a battery. On passing the electric current, the anode which is Ni dissolves in the electrolytic solution forming Ni^{2+} ions by the loss of electrons. Ni^{++} ions from the solution move towards the cathode, where they gain electrons and are reduced to Ni metal on the surface of spoon (cathode).

$$Ni\ (anode) \rightarrow Ni^{++} + 2e^{-}\ (Anode\ reaction\ oxidation)$$
$$Ni^{++} + 2e^{-} \rightarrow Ni\ (Cathode\ reaction\ reduction)$$

The net reaction is simply the transfer of Ni as Ni through $NiSO_4$ solution towards the cathode i.e. spoon and get it coated with Ni metal on the surface. The sum of reduction and oxidation is:

$$\underset{(Anode)}{Ni} \rightarrow \underset{(Cathode)}{Ni}$$

ELECTROCHEMICAL CELLS:

"The cell which is used to convert chemical energy into electrical energy or vice versa is called electrochemical cell."

GALVANIC OR VOLTAIC CELL:

"An electrochemical cell which converts chemical energy into electrical energy is known as Galvanic or voltaic cell."

The simplest of the cell Galvanic or Voltaic cells is Daniel cell.

DANIELL CELL:

A Daniel cell is the simplest of the Galvanic or Voltaic cell which is used to convert chemical energy into electrical energy spontaneously.

Construction:

Daniel cell consists of two half cells. One half cell is Zinc rod dipped in 1M $ZnSO_4$ Solution and the other half cell is copper rod dipped in 1M $CuSO_4$ solution. The two half cells are connected together to form a complete cell. The two half cells or single electrodes are connected together to form a complete cell. The two half cells are separated from each other by a porous partition or a salt bridge (KCl).

Process:

When both the electrodes are connected externally through a voltmeter by means of metal wire. The cell starts producing electric current at once. Zn undergoes oxidation to form Zn^{2+} ions by the loss of two electrons to go in to $ZnSO_4$ solution. Zn acts as anode or negative electrode. The electrons which are free at Zn electrode travel through the wire externally to cu electrode. These electrons are accepted by $Cu2^{+}$ ions of $CuSO_4$ solution and Cu^{2+} ions undergo reduction to deposit copper metal at Cu electrode which acts as cathode or positive electrode. In this process Zn electrode dissolves in the solution of $ZnSO_4$ and reduces in size, while copper electrode grows in size due to the deposition of Cu metal.

Cell reaction at Zn electrode (Anode)

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

At Cu electrode (Cathode)

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

The total cell reaction is the sum of two half-cell reactions.

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

The function of salt bridge or porous partition is to prevent the mixing of two solutions ($ZnSO_4$& $CuSO_4$) and allows the ions to move through from one part to another. Zn^{2+} ions from the anode compartment move in to the cathode compartment through the porous partition or salt bridge. It maintains the electrical neutrality in the two electrolytic solutions.
The cell voltage in Daniel cell is 1.10 volt.

BATTERIES:

In everyday life, we use the devices to produce electricity by the chemical reactions. Known as batteries. A flash light battery consists of single voltaic cell with two electrodes in contact with one or more electrolytes.
Sometimes a distinction is made between the terms cell and battery. A battery is an assembly of two or more voltaic cells, connected together in series. By this

definition automobile or motor battery is a true battery. The most common types of cells or batteries are described as follows:

Dry cell:

It is a primary cell, which is used to convert chemical energy into electrical energy. It is used in most of the flash lights, calculators, clocks and in portable devices. It is an irreversible cell.

Construction:

In a dry cell there is an outer zinc vessel which acts as anode and inner carbon (graphite) rod which acts as cathode. The graphite rod is surrounded by a mixture of manganese dioxide and carbon powder. The electrolyte is a moist paste of Ammonium chloride and zinc chloride. The cell is called a dry cell into a gel like paste by an agent such as starch. The upper top position of the cell is sealed with wax. A copper cap is fitted on the top of carbon rod (cathode) to make the electrical contact. The whole cell is covered with a safety cover.

Working:

When a zinc and graphite electrodes are connected by a metallic wire, Zn gets oxidized to form Zn^{2+} which pass into the wet paste leaving behind electrons on the Zn container and the electrons move from Zn electrode to carbon electrode through the external circuit. The cell reactions are complex.

Lead-storage battery (Motor-Battery):

Lead storage battery is used in automobiles. It is a secondary battery and is a reversible cell which can be restored to its original condition. The battery can be used through repeated cycles of discharging and recharging.

Construction:

There are several anodes and several cathodes which are connected together in series; about six cells are connected together. Each cell has a voltage of 2V and overall voltage when six cells are connected together in series would be 12V.

In lead storage battery anodes are lead alloy and cathodes are made up of red lead oxide. The electrolyte is dilute sulphuric acid. Which having concentration of 30%.

Discharging:

As the cell reaction proceeds $PbSO_4$ precipitates and partially coats both the electrodes, sulphuric acid is diluted because more and more water is formed. The battery is said to be discharged.

Recharging:

Now by connecting the battery to an external electrical source, we can force the electrons to flow in the opposite direction i.e. the net cell reaction can be reversed and the battery is recharged.

EXERCISE

Q1. A current of 0.5 ampere was passed through a solution $CuSO_4$ for one hour. Calculate the mass of copper metal deposited on the cathode. Electrochemical equivalent of Cu= 0.000329 g/C = 3.29×10^{-4} or 3.29×10^{-7} Kg/C.

DATA:

Given:

Current in ampere (A) = o.5 ampere

Time in second (1 hr.) = 1 x 60 x 60 = 3600s

Z for Cu metal = 3.29×10^{-4} g/C or 3.29×10^{-7} Kg/C Required:

Mass of copper deposited = W? **FORMULA**:

$W = Z \times A \times t$

Solution:

$W = 3.29 \times 10^{-7} \times 0.5 \times 3600$

$W = 5.929 \times 10^{-4}$ Kg

Mass of copper metal deposited 5.929×10^{-4} Kg

Q2. A current of 10A was passed for 15 minutes in a solution of silver nitrate. The mass of silver deposited was found to be 1.0062×10^{-2} Kg. Calculate the electrochemical equivalent (Z) of Ag metal.

DATA:

Given:

Current = 10 A

Time in seconds = 15 x 60 = 900 s

Mass of Ag metal (W) = 1.0062×10^{-2} Kg or $1.0062 \times 10^{-2} \times 1000$ g

Required:

Electrochemical equivalent = Z=? **FORMULA**:

$W = Z \times A \times t$

$Z = W/ (A \times t)$

Solution:

$Z = 10.062/ (10 \times 900)$

Z = 0.001118 g/c ANSWER

Q3. If constant current was passed for 5 hours and 404 mg of Cu was deposited. Calculate the current passed through $CuSO_4$

Given:

Amount of Cu deposited = W = 404mg = 0.404g
Time = 5 hours = 5 x 60 x 60 = 18000 seconds
Gram equivalent mass of Cu = 63.5/2 = 31.75

Required:

The amount of electric current =?

A = (96500 x W) / (e x t)
A = (96500 x 0.404) / (31.75 x 18000)
A = 0.0682 Ampere

1. Fill in the blanks:

The substance used for electrolysis is called **Electrolyte.**
When molten sodium chloride is electrolyzed **sodium metal** is formed at cathode.
One faraday is equivalent to **96500** coulombs.
The electrolyte in lead storage battery is **sulphuric acid.**
Dry cell is a **primary** cell.