Ganesh Institute of Engineering and Technology

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By

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Unit - 5

Electro-Chemistry

Oxidation and reduction

The chemical reaction during which electrons are lost is called an oxidation reaction and chemical reaction during which electrons are gained by a reactant is called reduction reaction.

Chemical reactions during which oxidation and reduction take place simultaneously is called redox reaction.

Electrolytes and Non-Electrolytes.

Electrolytes are substances that can carry electricity in its Fused state.

Ex- Nacl

Electrolytes are classified into two categories that is (i.e.) strong electrolyte and weak electrolyte

i) Strong electrolyte :-

Electrolyte that dissociates completely in their aqueous solution are called strong electrolytes

Ex - NaOH, HCl

ii) Weak electrolytes

The electrolytes that do not dissociate completely in their aqueous solution are called weak electrolytes.

Ex - NH_4OH, CH_3COOH

Non-electrolyte

Substances that do not carry electricity in their Few state are called non-electrolyte

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Faradey First law of Electrolysis

The law states that the amount of Substance deposited or liberated at the electrode as a result of electrolysis is directly proportional to the amount of Charge passing through the electrolyte.

Mathematically

$W \propto Q$

$W = ZQ$ Z = (electrochemical equivalent)

$W = ZIT$

Here, W = Weight of Substance
Q = Charge in coloumb
I = Current in ampere
T = Time in sec
Z = Electrochemical equivalent

when $I = 1A$
$T = 1s$
$W = Z$

So, electrochemical equivalent is equal to the amount of substance deposited at the electrode when 1 amp of Current is Flowing through the electrolyte For 1 sec.

Faradey

1 Faradey is the amount of Charge carried by 1 mole of electrons.

$1e^- = 1.6 \times 10^{-19} C$

$1M = 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$

$= 96450 \sim 96500 C$

When 1 Faraday of electricity is passed through electrolyte the amount of substance deposited at the electrode is equal to the equivalent weight of the substance.

We know,

$$W = ZQ$$

When $Q = 96500\ C$

$W = 1$ gram equivalent = Eq weight

So, $Z = \frac{\text{gram equivalent}}{Q}$

Ex

Gram eq of silver $= 108$

so, Z for silver $= \frac{108}{96500} = 0.00118$

15/9/25

Repeated

Faraday 1st law of Electrolysis

The law states that the amount of current passing through an electrolyte is directly proportional to the amount of substance deposited or liberated at the electrode as a result of electrolysis.

Mathematically

$$W \propto Q$$

But, $Q = I \times t$

So, $W \propto I \times t$

or $W = Z \times I \times t$

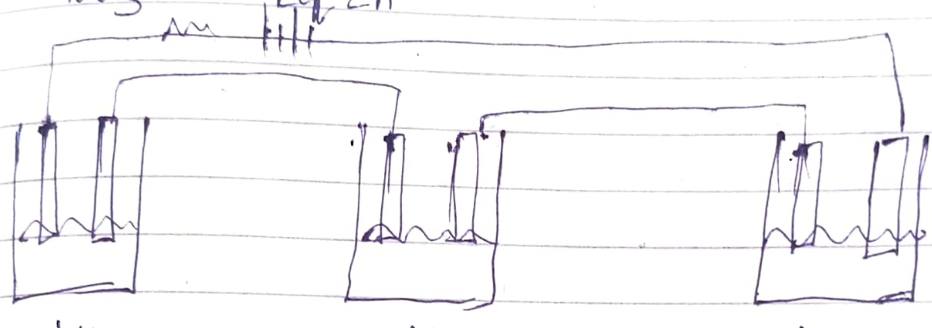
Faraday 2nd law of Electrolysis

The law states that when equal amount of current is passing through different electrolyte connected in series the amount of substance deposited is proportional to their equivalent weight.

Mathematically

$$\frac{w_1}{w_2} = \frac{Eq\ Cu}{Eq\ Ag}$$

$$\frac{w_2}{w_3} = \frac{Eq\ Ag}{Eq\ Zn}$$



w_1 Eq Cu w_2 Eq Ag w_3 Eq Zn

Industrial application of Electrolysis

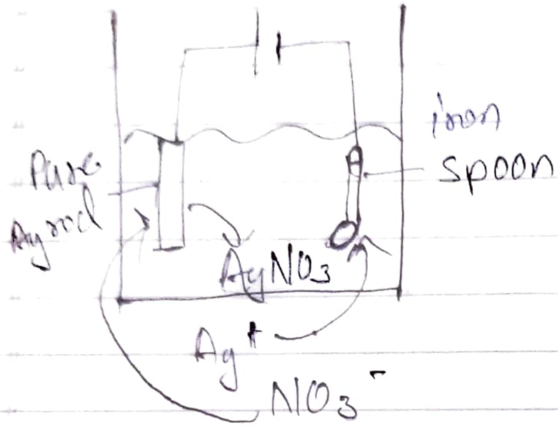
1) Metallurgy

During the process of Extraction of metals from its ore the highly reactive metals oxide can be reduced through electrolysis

Ex - The reduction of aluminium oxide into aluminium.

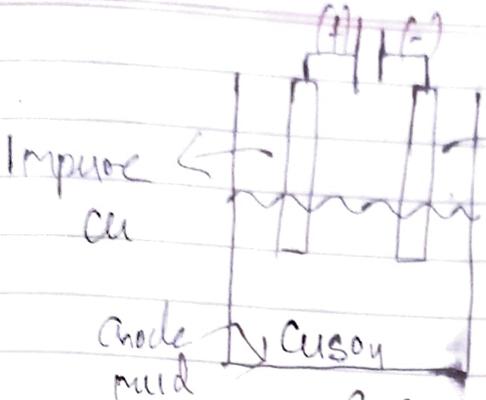
$$Al^{+3} + 3e^- \rightarrow Al$$

2) Electroplatting :-



As drawn in the diagram above the material to be coated is taken as cathode. The metal of which the coating is to be made is taken as anode. When the electricity starts flowing the Ag^+ ion migrates towards the cathode as a result a silver coating form over the iron spoon.
As the concentration of silver ion decreases from the solution the silver ion from the anode diffuse into the electrolyte.

3) Electro refining :-
In this method the impure metal is taken as the anode. A pure metal of the same compound is taken as cathode. The salt solution of the same metal is taken as the electrolyte or electrolysis as current charge flowing through the solution the pure metal gets deposited at the cathode the impurity in the metal gets deposited under anode this deposited impurity is refer to as anode mud



$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

Classification of Electrochemical cell :-

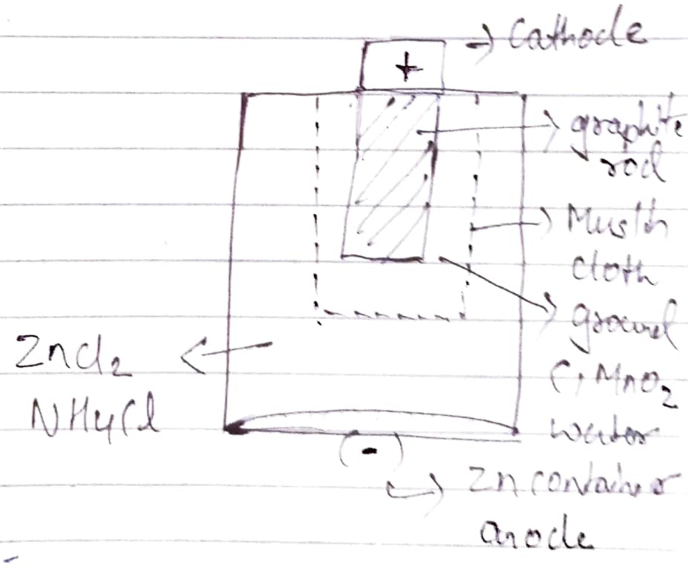
Electrochemical cell convert chemical energy into electrical energy. These cells are classified into two categories

i) Primary cell
ii) Secondary cell.

Primary cell :-

These cells are non rechargeble as the chemical reaction occuring inside the cell is irreversible

Dry cell



At anode

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

At cathode

$$MnO_2 + NH_4^+ + e^- \longrightarrow Mn_2O_3 + NH_3 + H_2O$$

Secondary cell:-

These cells are rechargeble.

Ex - Lead accumulator
Fuel cell
Solar cell

Solar cell

Solar cell converts solar energy into electrical energy. It is a renewable source of energy

Construction

- A solar cell consists of a P-N Junction which formed by combining P-type semiconductor with an N-type semiconductor. The p-type semiconductor can be formed by combining a group 14 element with 13 element.
  Ex - Combining silicon with aluminium.
- The N-type semiconductor is formed by combining ~~silicon with~~ group 14 elements with group 15 elements.
  Ex - Silicon (Si), Phosphorous (P)
- The process of adding aluminium and phosphorous to silicon is called dopping.

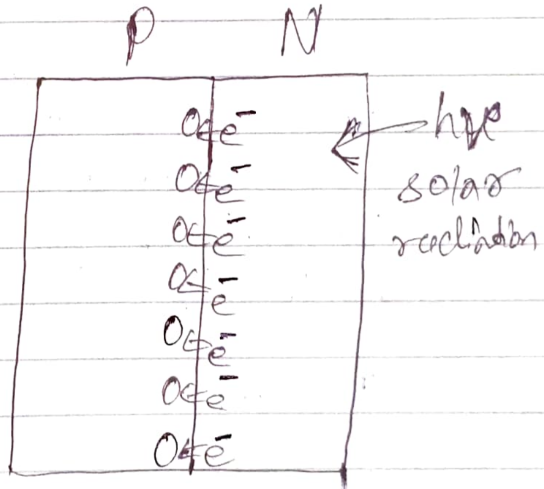
Working

- The number of valence electrons of group 13 and group 14 combined is 7. Similarly the no of valence electrons of group 14 and 15 combined is 9. All though all the elements here may neutral the P type semiconductor is one electron less to achieve octate and the n type semiconductor has one excess electron than octet.

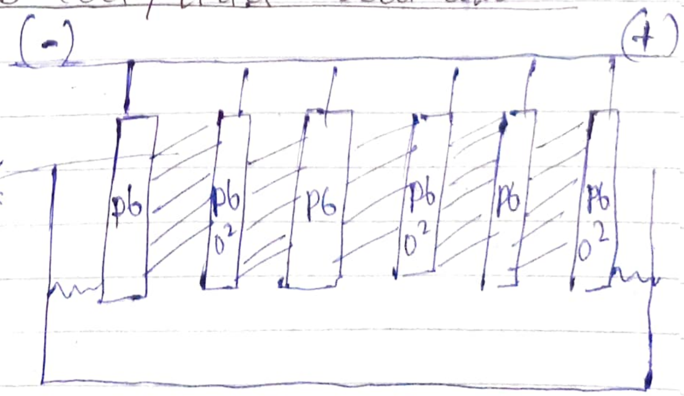
So P-type → Si + Al, 4 + 3 = 7

N-type → Si + P, 4 + 5 = 9

In a P-type Semiconductor the one less electron is considered as a hole and in N-type semiconductor this one excess electron is considered as a negative charge. This excess electron tries to occupy the hole in the P-type Semiconductor. The energy required for transition of the electron is provided by solar radiation.



Lead-acid storage cell / Lead accumulator



Lead acid storage cell or lead accumulator an example of a secondary that is rechargeable cell. this type of Cell acts as an electr cell during recharging process and acts as a Voltic or electrochemical cell during discharge cell.

Construction

lead accumulator consists of lead and as anode and lead oxide as cathode during discharge Electrodes are separated by insulator such as glass or wood. These are emerged in 20% solution of sulphuric acid.

Working

During discharge the cell converts ~~electrical~~ chemical energy into electrical energy the lead plate (Pb) gets oxidized into Pb^{2+} cation and releases two electrons This cation reacts with sulphuric acid to form lead sulphate ($PbSO_4$)

Discharge

At anode

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

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

At cathode the lead oxide gets reduced to Pb^{2+} cation which again reacts with sulphuric acid SO_4^- to form $PbSO_4$ (lead sulphate)

Discharge

at Cathode

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

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

Recharge

During recharge the lead accumulator converts electrical energy into chemical energy by reproducing lead and lead oxide (Pb), (PbO_2)

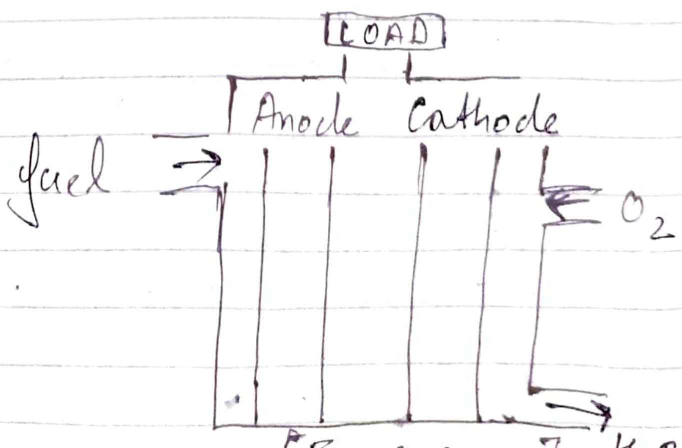
$$Pb^{2+} 2e^- \rightarrow Pb$$

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

Fuel cell

Fuel cell is an electrochemical cell that can convert chemical energy contained in a readily available fuel oxidant system into electrical energy by an electrochemical process in which fuel is oxidized at the anode. the fuel cell Consists of an electrolyte and two electrodes however the fuel and the oxidizing agent are Continuosly and separetely supplied to the cells electrodes at which they undergo reaction. Fuel cell work at high efficiency and the resulting emission level are far below the permissible limits.

In fuel cell electrical energy is obtained without combustion of oxygen. Hence, fuel cell converts the chemical energy of the fuel directly to electrical energy.



[Fuel Cell]

At anode

$2H_2 \rightarrow 4H^+ + 4e^-$

At cathode

$O_2 + 4e^- + H_2O \rightarrow 4OH^-$

$4H^+ 4OH^- \rightarrow 4H_2O$

- The basic arrangement in fuel cell can be represented as follows Fuel | Electrode | Electrolyte | Electrode | oxidant |
- The essential process in fuel cell is

  Fuel + O_2 → Product + Electricity

The following reactions takes place in a hydrogen - oxygen fuel cell.

At anode

$2H_2 \rightarrow 4H^+ + 4e^-$

$4H^+ + 4OH^- \rightarrow 4H_2O$

At cathode.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Redox $2H_2 + O_2 \rightarrow 2H_2O$

Application

Hydrogen - oxygen fuel cell are used as are auxillary energy source in space vehicles, submarines, or other military vehicles in hydrogen oxygen fuel cells the product water proved to be a valuable source of fresh water by the asteron...

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Corrossion

The process of detereanation and consequently loss of a solid metallic material through an unwanted chemical, electrochemical and biochemical attack by its environment at its surface is called corrosion.

Ex - Rusting of iron
Green Film on copper

Types of Corrosion

① Dry or chemical corrosion

Corrosion due to direct chemical attack by atmospheric gases such as oxygen, hydrogen sulphide, sulphur dioxide etc in absence of moisture or conducting electrolyte medium

② Wet or electrochemical Corrosion

- Wet Corrosion involves flow of electrons between anodic and cathodic areas
- Depending upon the nature of Corrosive environment Cathodic reaction consume electrons with either by

① Evolution of hydrogen - This type of reaction occurs in acidic medium
② Absorption of oxygen

Evolution of H_2

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

$2H^+ \rightarrow H_2 \uparrow$

Absorption of O_2

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

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow Fe(OH)_3$

or $Fe_2O_3 \cdot H_2O$

Factors influencing rate of Corrossion

→ **Position in galvanic cell series**
Higher in series means more active in nature therefore rate of corrossion is increased.

→ **Purity of Metal**
Impure metals creates heterogeneitic as a result a minute electrochemical cell is formed therefore rate of Corrosion is increased.

→ **Nature of Surface Film**
The ratio of volume of metal oxide to metal is called specific volume ratio. Greater specific volume ratio means lesser corrossion.

→ **Nature of Corrossive products**
If the Corrossive product is soluble and/or volatile rate of Corrossion is higher

→ **Physical state**
Smaller size means greater corrossion.

Nature of Corroding environment

- **Temperature** - with increase in temperature the rate of reaction of Corrossion increases as a result Corrossion becomes faster.

- **Humidity** - when humidity is high that indicates moisture content in the atmosphere is high. The moisture acts as a solvent for corroding elements such as oxygen Carbon dioxide etc. This salt acidic solution acts as an electrolyte in the corrossion as a result corrossion increases

- **PH** - When ph is greater than 10 the presence of hydrous oxide forms a protective coating over the metal surface as a result corrossion decreases. When ph is less than 10, the acidic medium is due to the presence of corroding elements such as oxygen which results in increasing rate of corrossion

- **Suspended particles** - Particles such as sodium chloride, ammonia absorb moisture and act as an electrolyte which results in increased corrossion rate

- **Impurity** - Impurities in the corroding environment such as carbon dioxide, sulphur dioxide etc create an acidic environment which results in increased corrossion rate.

Corrosion prevention method

Internal
- Purification
- Alloying
- Heat treatment

External
- Cathodic
- Anodic

Internal

→ **Purification** - when impurities are removed from the metal the susceptibility of the metal for corroding decreases. Purification can be done by methods such as distillation, liquation, electrolysis, ~~[illegible]~~ zone reffining etc.

→ **Alloying** - Alloy is a homogeneous mixture of two or more metals these alloys have improved chemical and physical properties than their constituent metal. As a result their are less susceptable to corrosion

→ **Heat treatment** - It has been observed that by heating an alloy homogenity increases therefore corrosion decreases.

External

Cathodic prevention

This can be done in the following two ways :-

(i) **Sacrificial anodic method**

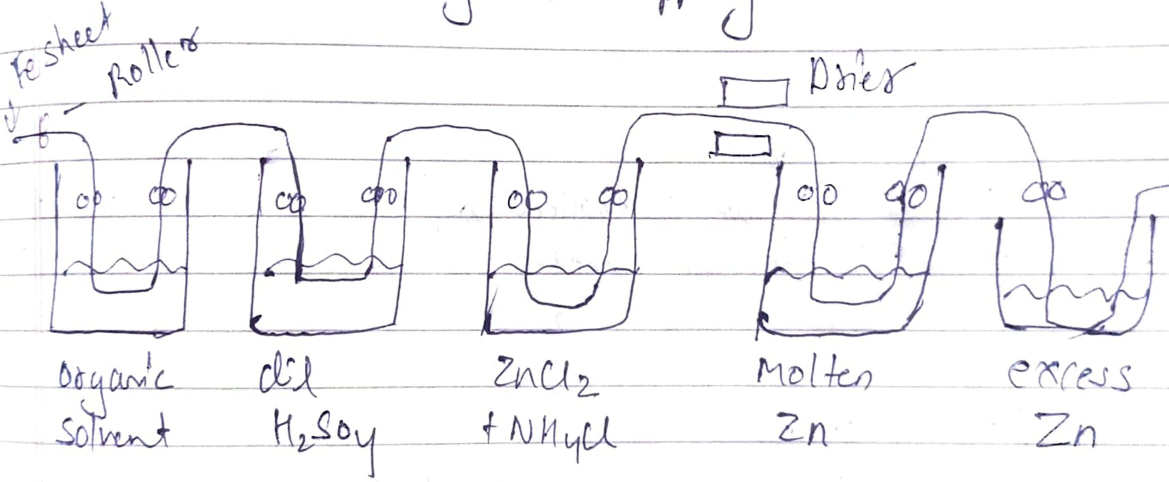
In this method a metal which higher oxidation potential is ~~false~~ connected to the protected metal through a wire. As a result the anodic metal undergoes corrosion and later remove by another anodic metal this way the cathodic metal is protected. The anodic metals can be zinc, magnessium, alluminium etc.

Impressed current cathodic protection

An impressed current is applied opposite to corrosion current and convert and corroding metal from anode to cathode this impressed current is derived from a direct current. The anode in this method is composed of coke bridged gypsum.

Anodic protection

For anodic protection galvanizing is commonly used galvanization is the process of coating a layer of zinc on iron by hot dipping.



- The iron sheet to be coated is dipt in organic solvent to remove oil and greece then it is dipped in dilute sulphuric acid to remove rust present on its surface later it is dipped in a mixture of zinc chloride and ammonium chloride, a mixture that acts as flux. The sheet is then dried and dipped in molten zinc. The excess zinc is removed.

Following methods can be applied to prevent Corr

i) anodic inhibition

Inhibitors which retard the corrosion of metal ~~perming~~ forming a sparingly soluble compoun with a newly produced metal cation are called anodic inhibitors. This compound will then absorb on the corroding metal surface forming a passi film or barrier

ii) Cathodic inhibitors

These are classified into

- acidic
- Neutral

Acidic solution

Corrosion can be controlled by slowing down the dif OF H^+ ion through cathode

$$2H^2 + 2e^- \rightarrow H_2$$

Neutral solution

Corrosion can be controlled by eliminating oxygen by adding reducing agent like sodium sulphate

$$1/2\, O_2 + H_2O + e^- \rightarrow 2OH^-$$

iii) Vapourphase inhibitor

These are the inhibitors that can ~~g~~ easily vapourise and form a protective layer on metal surface

dicyclohexyl ammonium nitrate