

MODULE 1: SENSORS AND ENERGY SYSTEM

Sensors

Sensors are basically devices which “read” a physical stimulus, and then convert that reading into an electrical signal output.

Physical Stimulus: heat, light, sound, weight, attraction

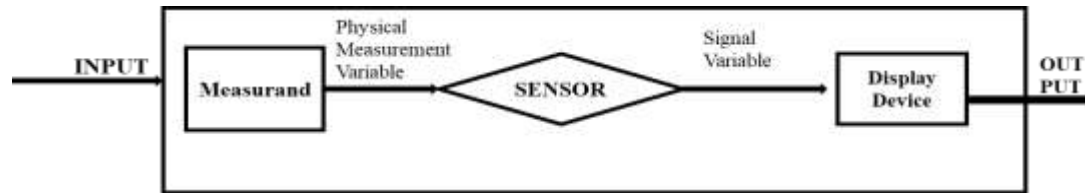


Fig: 1.1 Function of Sensor

- Sensor - observe and acquire information
- Transducer- Converts one form of energy into another form
- An actuator- Converts electrical energy into mechanical energy

Measurement process for the instrumentation model

- 1) Sensor input - the physical value or measurand (X) is observed by the sensor device
- 2) Sensor output - The sensor generates a signal variable (S) output which is normally electrical
- 3) Signal conditioning - The signal is transmitted and conditioned if needed (amplified, converted, filtered, etc.)
- 4) Display of measurement – the measurement is then displayed by the output device.

Electrochemical sensors

Sensors which convert the effect of electrochemical reaction between analyte and electrode surface into a useful signal are known as electrochemical sensors.

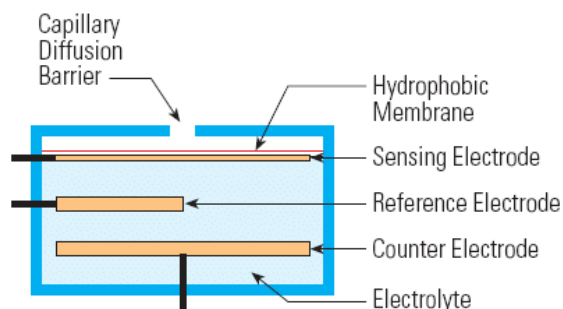
In Electrochemical sensors the electrode is used as transducer element.

They are divided into several types:

- Potentiometric (measure voltage)
- Amperometric (measure current)
- Conductometric (measure conductivity)

Working Principle:

Working Principle:



Electrochemical sensor consists of a transducer element covered by a recognition element. The recognition element interacts with target analyte and signal is generated. Electrochemical transducers transform the chemical changes into electrical signals. The electric signals are related to the concentration of analyte. Electrochemical sensing always requires a closed circuit. Current must flow to make a measurement. Since we need a closed loop there should be at least two electrodes. These sensors are often called an electrochemical cell.

Applications

1. Electrochemical sensors used for the detection of blood glucose
2. Electrochemical sensors are used for pH measurements
3. Used to detect pesticides
4. Used in the detection of hydrocarbon pollutants
5. Optical sensors are used to measure the concentration of coloured analyte.

Conductometric Sensors

Conductometric sensors are two electrode devices, measures the electrical conductivity in sample solution between two electrodes.

Principle:

The basic principle of conductometric detection involves **a reaction that can change the concentration of ionic species**. This reaction leads to changes in electrical conductivity or current flow. In this method, two inert metal electrodes are used. The ions or electrons produced during an electrochemical reaction may change the conductivity or resistivity of the solution.

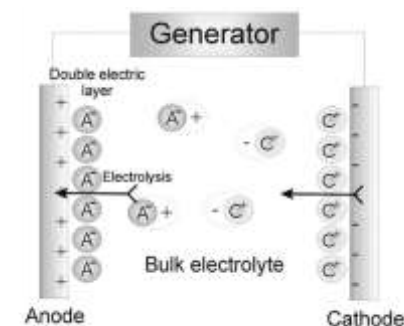
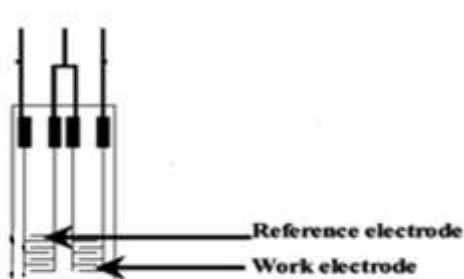


Fig:1.5 Migration of charges in Conductometric Sensors

Working

The conductivity is result of dissociation an electrolyte, into ions. The migration of the ions is induced by an electrical field. When a potential difference is applied to the electrode, there is an electrical field within the electrolyte, so the positively charged ions move towards cathode and negatively charged ions are move towards anode. (**Figure**). Thus, the current in the electrolyte is caused by the ion movement towards the electrodes where the ions are neutralized and isolated as neutral atoms (or molecules). This chemical change is recognized by working electrode and transducers converts this chemical change into electrical signal.

Applications:

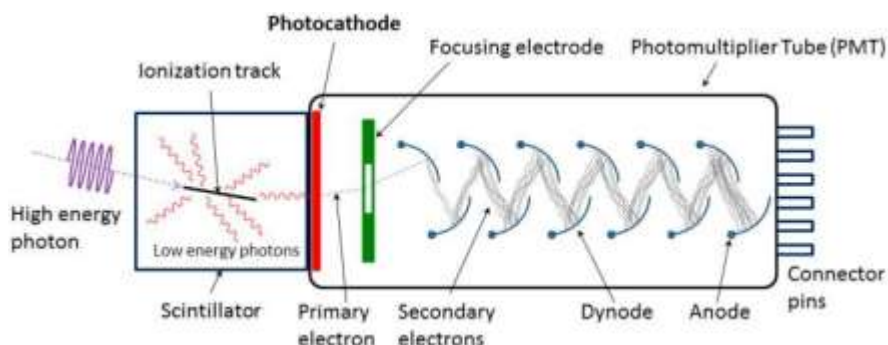
- The conductometric measuring method can be used in enzyme catalysis to determine analyte concentration and enzyme activity and selectivity.
- Screen-printed conductometric sensor with inter digital gold electrodes on glass substrate coated with molecularly imprinted polyurethane layers was fabricated to detect polycyclic aromatic hydrocarbons (PAHs) in water.
- A conductometric sensor consisting of a silicon substance with a pair of gold inter digitized and serpentine electrodes is used to determine urea.
- The conductometric biosensor based on inhibition analysis, was intended for the determination of organophosphorous pesticides.

Optical sensors

Optical sensors are electronic components designed to detect and convert incident light rays into electrical signals.

Example: Colourimetric Sensors

Principle: When a sample solution is interacted with a light of suitable wavelength, certain quantity of light is absorbed by the analyte solution and it is observed by a sensor and transducer converts intensity of absorbed light into electrical signal. The change in intensity at certain wavelength within visible (400–800nm) range can be determined using special instrumentation.



A photon (ultraviolet, visible, or near-infrared light) is converted in the photocathode into a low-energetic electron, emitted into the vacuum. This electron is accelerated towards and focused onto the first dynode, releasing secondary electrons. This multiplication is repeated in subsequent dynodes, resulting in a measurable electric charge at the anode.

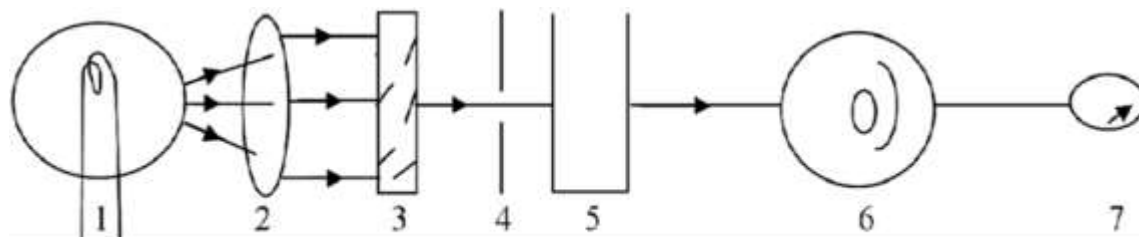


Fig.1.6 Components of Colourimetric Sensors

A monochromatic light is made to pass through analyte solution where certain quantity of light is absorbed and it is a function of concentration of analyte. The change in the intensity of light is detected by photodetector (sensing). The light source generates an intense and stable radiation signal needed to probe an optical property of the molecular recognition element in the sensor. **The amount of absorbance is governed by Beer-lamberts law.**

Electrochemical Sensor for the measurement of Dissolved Oxygen (DO)

Brief introduction to different sensors for DO

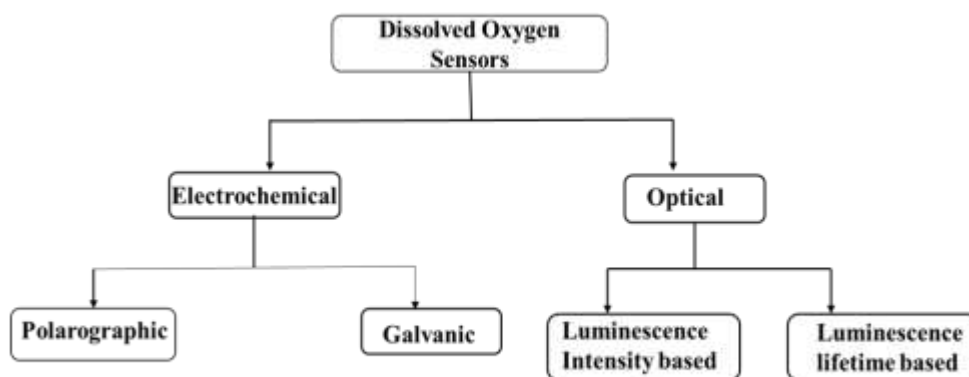


Fig: 1.8 Chart showing different types of DO sensors

Electrochemical DO sensors, also known as **amperometric** or **Clark-type sensors**, measures dissolved oxygen concentration in water based on electrical current produced.

Galvanic Sensor is a **Electrochemical sensor**, which is used to measure DO

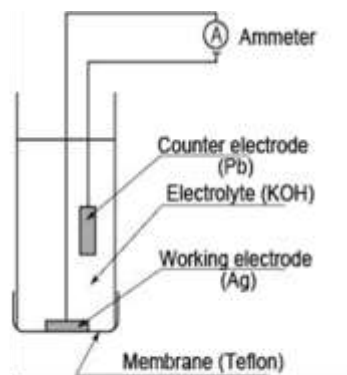


Fig:1.9 Galvanic Sensor for DO measurement

Components:

Cathode : Working electrode-Ag

Anode : Zn, Pb or any other active metal

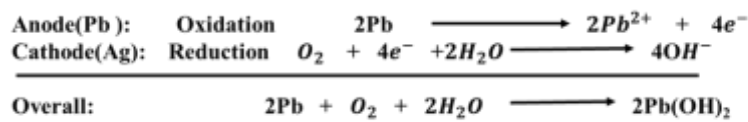
Electrolyte: KOH, NaOH or any other inert electrolyte

Membrane: Teflon

Working Principle

The difference in potential between the anode and the cathode should be at least 0.5V. DO sensor is immersed in water sample. Oxygen molecule diffuses across the oxygen-permeable membrane (Teflon) and the rate of diffusion is proportional to the pressure of oxygen in the water. Molecular Oxygen reduces to OH^- at cathode. This reaction produces an electrical current that is directly related to the oxygen concentration. This current is carried by the ions in the electrolyte and runs from the cathode to the anode.

Reactions:



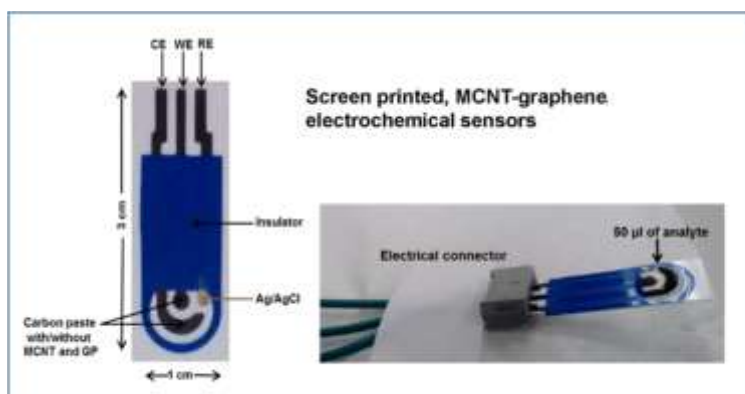
Electrochemical sensors for the detection of Pharmaceuticals (diclofenac)

Electrochemical detection occurs at the interface between an analyte (diclofenac) of interest and the working electrode to which a potential is applied with respect to the reference electrode, while the corresponding current is measured.

Different sensors are developed for the detection of Diclofenac such as

- 1) Potentiometric sensor (low sensitivity)
- 2) Electrochemical sensor with unmodified carbon electrode
- 3) **Electrochemical sensor with modified carbon electrode**
- 4) Bio-sensor

Components of disposable screen printed Carbon paste electrode for diclofenac detection (Three electrode sensor)



Working electrode: Carbon Paste with MWCNT or Graphene

Counter Electrode: Carbon Paste with MWCNT or Graphene

Reference Electrode: Ag/AgCl

Process: Screen Printing Technique on PVC substrate. Insulating ink was printed on the remaining PVC surface.

Working: The electrochemical oxidation of DCF on carbon-based sensor at pH 7.0 is reversible reaction. Oxidation of Diclofenac occurs at carbon electrode to release e^- , to form radical intermediates and followed by hydrolysis of radical intermediate species. The products formed are 2,6-dichloro aniline and 2-(2-hydroxyphenyl) acetic acid. Reactions on the electrode cause the current to flow. The intensity of this current is a function of the number of oxidized / reduced molecules.

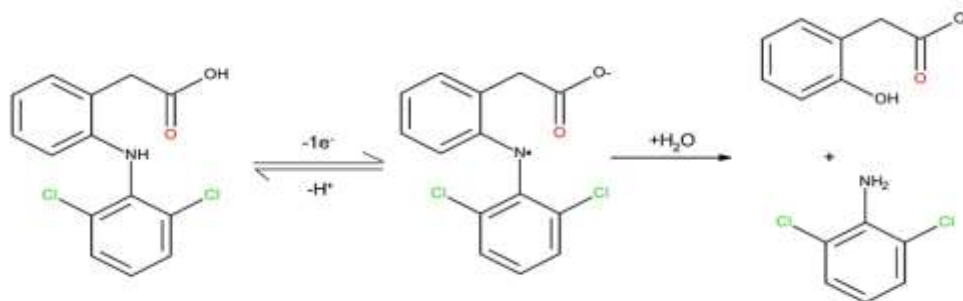


Fig:1.12 The Oxidation mechanism for diclofenac

Products: 2,2 Hydroxy-Phenyl-Acetic Acid and 2,6 Dichloro Aniline

Electrochemical sensors for the detection of Hydrocarbon: 1- Hydroxypyrene(Screen Printed Sensor)

Working electrode: PAMAM/Cr-MOF/GO (Composite)

Counter Electrode: PAMAM/Cr-MOF/GO

Reference Electrode: Ag/AgCl

Operating Voltage: +0.7 to -0.5 V

PAMAM: Dendrimer polyamidoamine

Cr-MOF: Chromium-centered metal–organic framework

GO: Graphene Oxide

Working

When this electrode is used to detect the sample containing 1-Hydroxypyrene (water sample) the following changes takes place. At the electrode surface electro-oxidation takes place to yield several hydroxylated species and then hydroquinone by losing $2e^-$ and $2H^+$

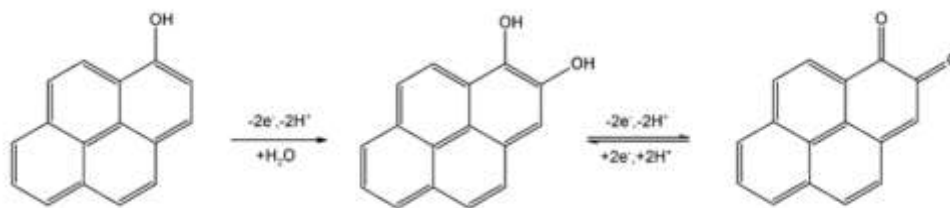


Fig:1.13 The electro-oxidation scheme for 1-Hydroxypyrene

Reactions on the electrode cause the current to flow. The quantity of this current is a function of the number of oxidized / reduced molecules. Current produced is directly proportional to the concentration 1-Hydroxypyrene.

Electrochemical gas sensors for SO_x and NO_x

The major contributors to traditional air pollution are NO_x, SO_x, and H₂S while NH₃ and Volatile organic compounds are of increasing concern recently. Traditional air quality monitors based on mass spec, infra-red spectroscopy and gas chromatography are expensive and not suitable for large scale deployment. Electrochemical gas sensors provide a cheap alternative option for widespread air quality monitoring. Electrochemical gas sensor interacts with a gas to measure its concentration and each gas has a unique voltage; the electric field at which it is ionized. Sensor identifies gases by measuring these voltages.

Sensor for NO_x

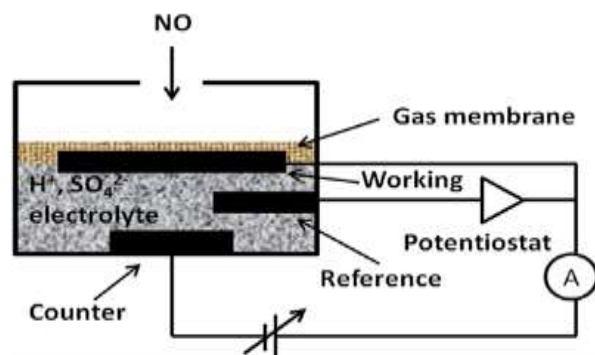


Fig: 1.14 NO_x Gas Sensor

Chemiresistive sensors based on graphene and its derivatives have been used to measure NO_x. Chemiresistive sensors measure the change in resistance upon exposure to analyte gases and can detect toxic gases at very low concentrations.

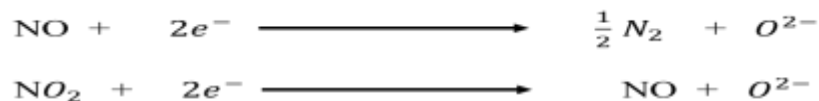
$$R_{\%} = \frac{(R_0 - R_g)}{R_0} * 100$$

R% is the reported sensor response

R₀ is the resistance in dry clean air (Back ground Correction)

R_g is the new resistance observed under analyte gas

Reactions



The concentration of electrons decreases due to the reaction between the electrons in the sensing materials and NO_x gas, as shown and resistance offered by e⁻ decreases and current increases.

“Higher the concentration of NO_x, lesser would be the resistance”

Detection of SO₂: The sulfur dioxide sensor works on the electrochemical

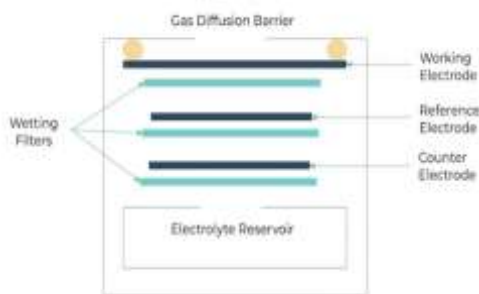
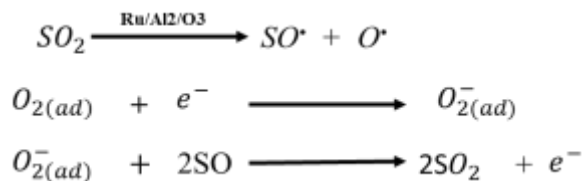


Fig:1.15 SO₂ Gas Sensor

It works based on the diffusion of SO₂ gas into the sensor. Initially SO₂ oxidizes to produce oxygen free radical and converted to molecular oxygen. Electrons are consumed from sensor for the reduction of O₂ and number of electrons decreases on the electrode surface. Resistance of the electrode is a function of Concentration of SO₂



$$R\% = \frac{(R_0 - R_g)}{R_0} * 100$$

R% is the reported sensor response,

R₀ is the resistance in dry clean air (background condition),

R_g is the new resistance observed under analyte gas.

Disposable sensors

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single-point measurements.

Advantages of disposable sensors:

1. They transduce physical, chemical, or biological changes in their environment to an analytical signal.
2. Disposable sensors are biodegradable and sustainable
3. They have a short duration of analysis and fast response times.
4. It provide digitized chemical and biological information.
5. Prevents the contamination of samples.

Detection of Ascorbic acid using disposable electrochemical sensor

L-Ascorbic acid (AA) or adsorbate, commonly known as vitamin C, is an important water-soluble vitamin derived from green vegetables, fruits, and other dietary supplements. AA improves the immune system. It enables collagen synthesis, which is needed to maintain healthy bones, teeth, skins, cartilages, enhances antibody levels and acts as an antioxidant; reduces necrosis

At the same time

Abnormal AA levels in bodily fluids have been reported to cause cancer, cardiovascular diseases, and Alzheimer's and Parkinson's diseases. Extended use of AA could cause urinary oxalate calculus, increase infertility in a woman, and affect embryo development. Excessive AA use has been reported to cause diarrhoea, nausea, vomiting, headache, insomnia, gastric irritation, renal problems, loss of food taste, and vomiting.

Disposable screen-printed carbon electrodes sensor (CNT with gold nanoparticles) for biomolecule detection- Ascorbic acid

It is comprising three disposable electrodes: one working electrode, one auxiliary or counter electrode, and one reference electrode. Each one includes a contact or terminal, a section and an active area. All electrodes have been manufactured by silkscreen printing with conductive material ink on a **plastic polyester (PET) sheet**. The active surfaces of the **counter electrode** and **working electrode** have been printed with a **conductive ink of C** (MWCNT) and modified with **gold nanoparticles**. Active surface of the **reference electrode** has been printed with an **Ag/AgCl ink**.

Working

The electrochemical sensor can catalyze the **two-electron electro catalytic oxidation** and **hydrogen dissociation of AA** to L-dehydroascorbic acid in the presence of oxygen in solution. The carboxyl MWCNTs act as electron transfer mediators promoting the electron transfer between AA molecules and the matrix interface Increases the electro catalytic oxidation of AA during electrochemical detection and transduce their presence into measurable signals. The electric current or voltage produced is proportional to the concentration of the ascorbic acid.

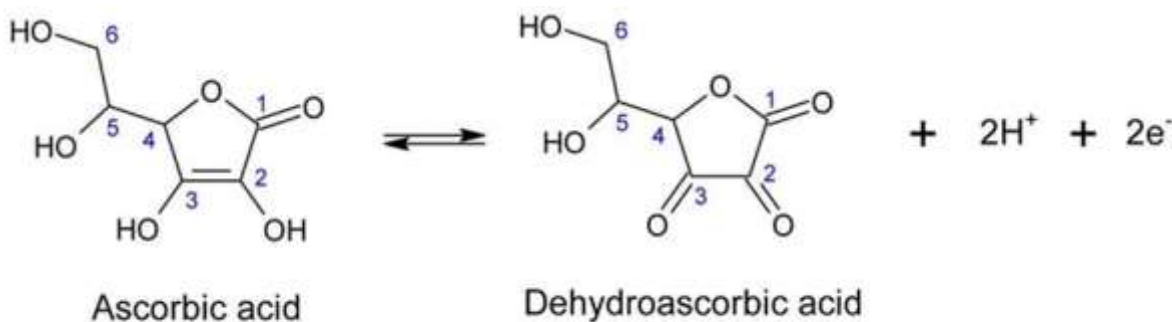


Fig: 1.18 Oxidation of Ascorbic acid

Detection of pesticide such as Glyphosate by electrochemical oxidation method

One of the most commonly used pesticides is glyphosate. Glyphosate has the ability to attach to the soil colloids and degraded by the soil microorganisms. As glyphosate led to the appearance of resistant species, the pesticide was used more intensively. As a consequence of the heavy use of glyphosate, residues of this compound are increasingly observed in food and water. Recent studies reported a direct link between glyphosate and chronic effects such as tetrogenic, tumorigenic.

Electrochemical Sensor for Glyphosate Detection

The sensor is a silicon- based chip comprising of three-electrode system. It is fabricated by electro deposition technique.

Working Electrode: A gold electrode of 4 mm diameter coated with 200nm thickness gold nanoparticles

Counter electrode: A gold electrode of 4 mm diameter coated with 20nm thickness gold nanoparticles

Reference Electrode: Ag/AgCl/Cl⁻

Electrolytes are added to increase the conductivity of the solution and minimizes the resistance between the working and counter electrode.

Working:

The electrochemical detection is based on the oxidation of Glyphosate on gold working electrode. A potential of 0.78V is applied on working electrode, there is a interaction between analyte and electrode surface. Glyphosate oxidizes on the working electrode brings a change in current in the electrolyte medium. The change in the current is a measure of concentration of Glyphosate.

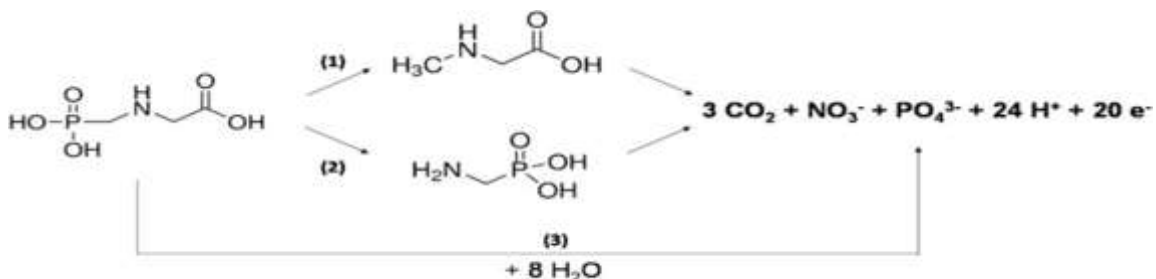


Fig:1.19 Electrochemical oxidation of Glyphosate

ENERGY SYSTEM

A battery is a device consists of two or more galvanic cells arranged in series or parallel or both that can convert chemical energy into electrical energy.

Classification of batteries

Primary (single-discharge) Batteries:

These are the batteries in which net cell reaction is not completely reversible, therefore these are not rechargeable. The primary battery contains a finite quantity of the reactant materials participating in the reaction; once this quantity is consumed (on completion of discharge), it cannot be used again.

Example: Leclanche cell (Zn-MnO₂), Magnesium cell (Mg-MnO₂), Zn-air cell (Zn-O₂), Lithium primary cell etc.

ii).Secondary Batteries (Storage or Rechargeable Batteries):

These are the batteries in which net cell reaction is completely reversible and therefore these are rechargeable. On the completion of discharge, a storage battery can be recharged by forcing an electric current through it in the opposite direction; this will regenerate the original reactants from the reaction (or discharge) products.

iii).Reserve Batteries: In this battery, one of the key components is separated from the remainder of the cell until activation. The electrolyte is the component that is usually isolated, activation of the reserve battery is accomplished by adding the electrolyte just prior to use.

Example: Zinc/Silver Oxide, Mg-AgCl, lithium-thionyl chloride batteries, etc,

Construction and working of Li-Ion battery

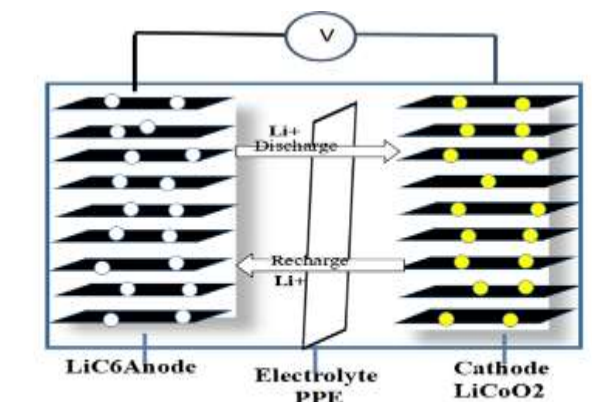


Fig: 1.20 Li-ion battery

Anode: Lithiated carbon or graphite and a binder coated on a copper foil.

Cathode: Lithiated transition metal oxide like LiCoO_2 mixed with a conductor and binder and coated in an Aluminium foil.

Electrolyte: Lithium salt in ethylene carbonate propylene carbonate

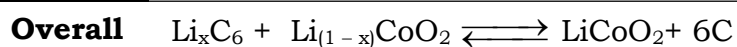
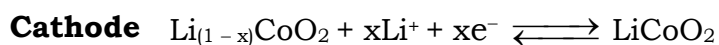
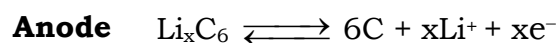
Separator: micro porous polythene film

Binder: poly vinylidene fluoride

Battery Representation:

$\text{Li}_x\text{C}_6 \mid \text{LiX, Polypropylene} \mid \text{Li}_{(1-x)}\text{CoO}_2$

Working



Simply, the Li -ion is transfers between anode and cathode through lithium Electrolyte. Since, neither the anode nor the cathode materials essentially change, the operation is safer than that of a Lithium metal battery.

Uses

Cellular phones, Portable CD player, Note PC, DVC/DSC/DVD/Portable LCD TV etc. MD player, Semiconductor-driven audio etc and Portable electric vehicles.

Advantages	Disadvantages
High Energy Density	They require protection from being over charged and discharged too far.(integrated circuit technology is required to monitor)
High Voltage compared to other batteries	LCO battery or cell needs to be stored it should be partially charged - around 40% to 50% and kept in a cool storage area. (-15°C)
Low self-discharge (long shelf life)	A major lithium ion battery disadvantage is their cost.(40% more than Ni-MH batteries)
Low maintenance	

Sodium Ion Battery

Anode: Sodium metal intercalated on graphite is used as anode

Cathode: Chalcogenides, fluorides, polyanion compounds and chromium cathodes have been used as cathode material.

Electrolytes: Commonly used electrolytes are PEC, PPC

The electrode reactions in a Na-ion battery utilizing hard-carbon (C_6) anode and a layered transition metal oxide, $NaMO_2$, cathode are depicted in [eq 1](#).

The discharged electrodes are on the right-hand side of eq1

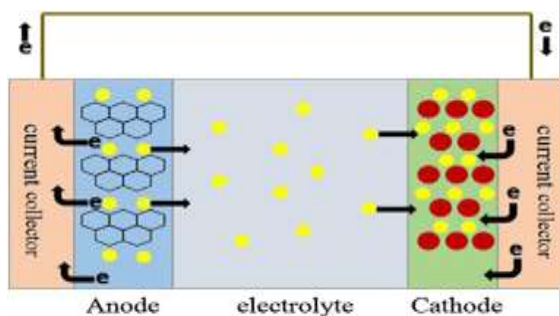


Fig:1.20 Sodium ion battery

Sodium Ion Battery

It stores energy in the chemical bonds of anode. When battery is recharging sodium ions moves from cathode to the anode. Meanwhile charge balancing electrons pass from the cathode through the external circuit containing the charger and into the anode. During discharge process electrons

move from anode to external circuit, it can be used for various applications. Meanwhile, Na^+ ions move from anode to the cathode. Voltage obtained from every sodium ion cell is 3.6V.

Advantages

Sodium resources are more abundant,

The cost of sodium-ion batteries is about 30% lower than that of lithium batteries,

Sodium-ion batteries are safer and are not easy to produce lithium dendrites.

Disadvantages of sodium ion batteries:

Lower energy density of sodium ion batteries

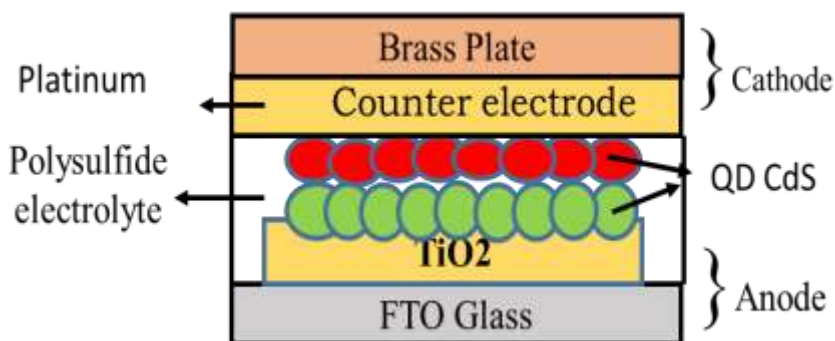
Short cycle life;

The industrial chain is still incomplete.

Quantum dot-sensitized solar cells (QDSCs)

A semiconductor device which convert sunlight into direct current is called solar cell or PV cell. A quantum dot solar cell (QDSC) is a solar cell design that **uses quantum dots as the absorbing photovoltaic material**.

Construction of QDSSC- Quantum Dot Sensitized Solar Cell



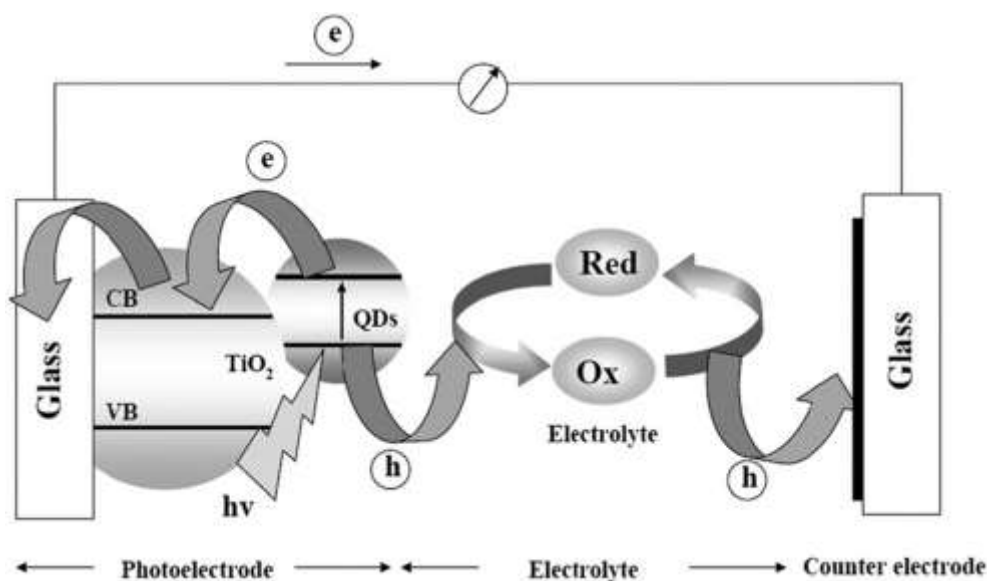
Working Electrode: Fluorinated Tin Oxide substrate is taken and coated with mesoporous wide band gap semiconducting TiO_2 . TiO_2 is coated with quantum dots such as CdS by CBD method. TiO_2 act as electron conductors (or acceptors) and transport layers. CdS facilitates the charge separation.

Counter Electrode: A platinum and carbon based materials are coated on a brass substrate. Counter electrode is acting as cathode and it transfers electrons from external circuit to electrolyte and catalyze the reduction reaction of the oxidized electrolyte at the electrolyte/ counter electrode interface.

Electrolyte: Polysulfide is used as electrolyte ((S^{2-}/S_x^{2-})). It is a redox electrolyte or hole conductor. Redox electrolyte significantly influences both stability and efficiency of QDSSC. It is a medium which transfers charges between counter electrode and photo anode for the regeneration of oxidized quantum dots.

Sensitizer: CdS is a sensitizer, it is a Quantum dot nano crystal made of semiconductor materials.

Working of QDSSC



Working of QDSSC

1. Upon light irradiation the photosensitizer is photo excited.
2. The excited electron of QD are injected into the conduction band of TiO₂.
3. The electrons penetrate through nano crystalline TiO₂ film to the back contact of the conducting substrate and flow through an external circuit to the counter electrode.
4. At the counter electrode the oxidized (S^{2-}/S_x^{2-} component of the redox couple in the electrolyte is reduced.

The oxidized form of the sensitizer (QD) are finally regenerated by the reduced component of the redox couple in the electrolyte.

Properties of QDs

1. Quantum dots has narrow bandgap.
2. It exhibits tunable bandgap.
3. Strong light absorption and
4. High multiple electron generation.

Application

1. QDSSC is mainly used to harness solar energy.

MODULE-2 Materials for Memory and Display Systems

1 What are Memory Devices? Explain the Classification of electronic memory devices with examples

A memory device is a piece of hardware made of semiconducting materials used to store data.

Example: CD, DVD, USB and external hard disc.

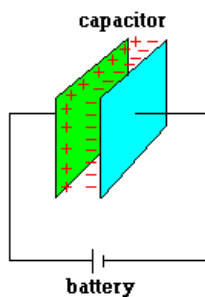
Classification of Memory Devices:

1. Transistor-Type Electronic Memory
2. Capacitor-Type Electronic Memory
3. Resistor-Type Electronic Memory
4. Charge Transfer Effects

1. Transistor-Type Electronic Memory:

A transistor is a miniature electronic component that can work either as an amplifier or a switch. A computer memory chip consists of billions of transistors, each transistor is working as a switch, which can be switched ON or OFF. Each transistor can be in two different states and store two different numbers, ZERO and ONE. Since chip is made of billions of such transistors and can store billions of Zeros and Ones, and almost every number and letter can be stored.

2. Capacitor-Type Electronic Memory



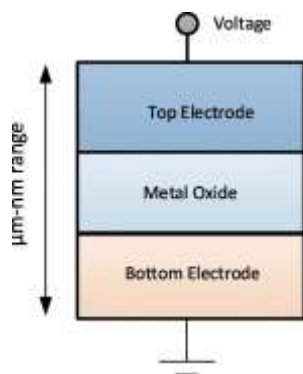
A capacitor consists of two metal plates which are capable of storing an electric charge. It is like a battery that holds data based on energy.

If the capacitor is charged, it holds the binary numeral, "1" and holds "0" when the cell is discharged.

If the parallel plates of a capacitor are separated by dielectric layer, charges dissipate slowly and memory would be **volatile**.

On the other hand, if the medium between the electrodes is ferroelectric in nature, can maintain permanent electric polarization that can be repeatedly switched between two stable states (bistable) by an external electric field. Thus, memory based on ferroelectric capacitors (FeRAM) is **non-volatile memory**.

3. Resistor-Type Electronic Memory



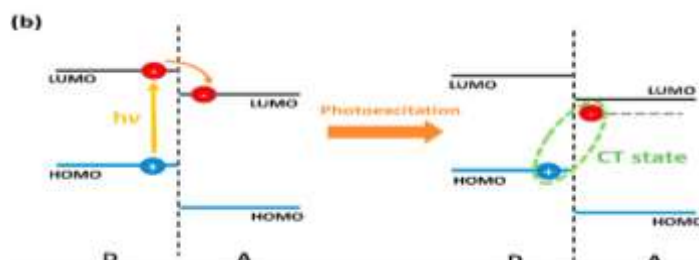
Memory devices containing switchable resistive materials are classified as resistor-type memory, or resistive random access memory (RRAM).

Resistor-type electronic memory usually has a simple structure, having a metal-insulator-metal structure generally referred to as MIM structure. The structure comprises of an insulating layer (I) sandwiched between the two metal (M) electrodes and supported on a substrate (glass, silicon wafer, plastic or metal foil).

Initially, the device is under high resistance state or "OFF" and logically "0" state, when resistance changed or under external applied field changes to low resistance state or "ON" logical value "1".

4. Charge Transfer Effects

A charge transfer (CT) complex is defined as an electron donor–acceptor (D–A) complex, characterized by an electronic transition to an excited state in which a partial transfer of charge occurs from the donor moiety to the acceptor moiety. The conductivity of a CT complex is dependent on the ionic binding between the D–A components.



If the donor has intermediate size and ionization potential, it tends to form a weakly ionic salt with the acceptor, which possesses incomplete CT ($0.4 < \delta < 0.7$) and thus is potentially conductive.

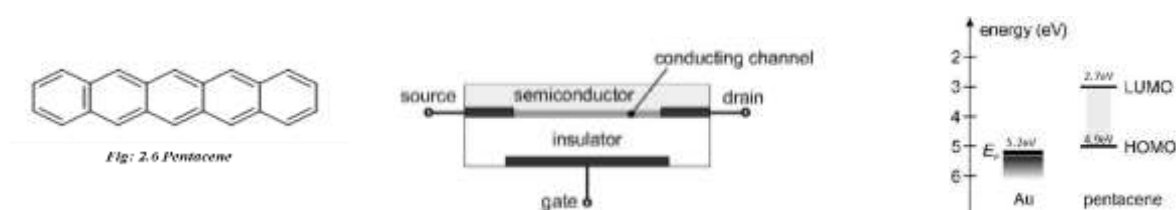
2. Explain the types of organic memory devices by taking p- type and n-type semiconducting materials.

Organic electronic memory device uses organic semiconductors and stores data based on different electrical conductivity states (ON and OFF states) in response to an applied electric field.

The p-Type Organic Semiconductor Material “Pentacene”

An Organic molecule with π conjugated system and possess holes as major charge carrier is called p-type semiconductor.

Example: Pentacene



When a positive voltage was applied between gate and source, it was found no flow of electrons to drain due to higher energy gap between the Fermi level of gold (source) and LUMO of Pentacene. On the other hand, when a negative voltage is applied between the drain and source, **holes** are induced at source. This permits a channel of charges (holes) to drain through semiconductor and insulator interface when a secondary voltage is applied. Therefore it called as P-type semiconductor

The n-type organic semiconducting material Perfluoropentacene

An Organic molecule with π conjugated system with electron withdrawing substituent groups and possess electrons as major charge carrier is called n-type semiconductor.



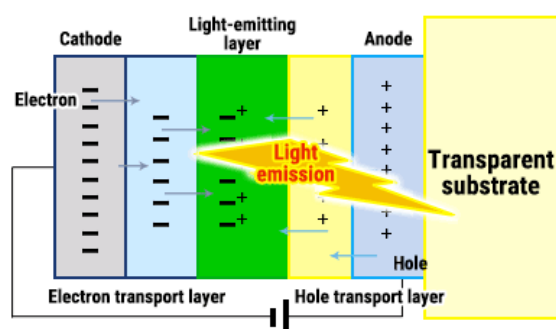
In Pentacene, when hydrogen atoms are substituted by highly electronegative fluorine atoms, it is called Perfluoropentacene and acts as N-type of semiconductor. When a positive voltage is applied between source and drain, **electrons** are induced in the source (gold). This permits the channel of charges to drain through semiconductor-insulator interface as the bandgap between Fermi level of gold (source) LUMO energy of Perfluoropentacene is 1.95eV which is lesser than LUMO energy of Pentacene. Therefore, it is n-type semiconductor.

3 Define photoactive and electroactive materials and write their working principle in display system.

Photoactive and electroactive organic materials are the semiconductors composed of π -electron systems which are used in electronic and optoelectronic devices.

Working Principle

Photoactive and electroactive material absorb and emit light in the UV to IR region. Display system (OLED) consisting of photoactive and electroactive material absorb light and allows an electron to jump from HOMO of a Donor to LUMO of an Acceptor. This phenomenon generates and transports charge carriers.



When electrons move from cathode, anode allows movement of holes towards light emitting layer under an applied field. Electron-hole pairs are created at the Light-Emitting-Layer and energy is released due to recombination. This energy is sufficient to excite an electron from HOMO to LUMO in the light emitting layer made of photoactive and electroactive materials. There is a re-emission of light while electron is returning to HOMO level. This light is extracted by a transparent substrate placed adjacent to either of the electrode.

4 What are nanomaterials? Explain any four properties and applications of Polythiophenes (P3HT) suitable for optoelectronic devices.

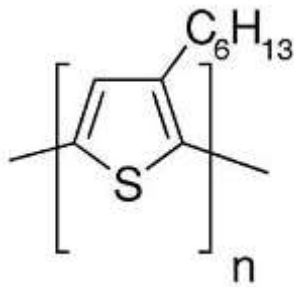
Any substance in which at least one dimension is less than 100nm is called nanomaterials.

The properties of nanomaterials are different from bulk materials due to:

1. Quantum Confinement effect
2. Increased surface area to volume ratio

Polythiophenes are conjugated polymers, environmentally and thermally stable material. Chemical structure of P3HT Poly (3-hexylthiophene) is a polymer with chemical formula $(C_{10}H_{14}S)_n$. It is a polythiophene with a short alkyl group on each repeat unit. Highly ordered (P3HT) are composed of closely packed, p-p stacked (p-p distance of 0.33 nm).

Structure of P3HT



The improved electronic properties yielded for nanostructured P3HT suitable for optoelectronic devices are listed as follows:

1. P3HT is a semiconducting polymer with high stability and exhibits conductivity due to holes therefore considered as p-type semiconductor.
2. Poly-3-hexylthiophene (P3HT) have great capability as light-absorbing materials in organic electronic devices.
3. P3HT has a crystalline structure and good charge-transport properties required for Optoelectronics.
4. P3HT has a direct-allowed optical transition with a fundamental energy gap of 2.14 eV.
5. Fundamental bandgap of P3HT is 490nm visible region, corresponding to $\pi \rightarrow \pi^*$ transition, giving electron-hole pair.

Applications:

1. P3HT-ITO forms a p-n junction permit the charge carriers to move in opposite direction and hence, used in Photovoltaic devices.
2. It can be used as a positive electrode in Lithium batteries.
3. Used in the construction of Organic Solar Cells.
4. Manufacture of smart windows.
- 5.
6. Used in the fabrication new types of memory devices.

5 What is QLED? Mention any four properties and applications of QLED.

Quantum dot light emitting diodes are a form of light emitting devices consisting of nano-scale crystals that can convert light energy into electrical energy or vice-versa.

Properties of QLED

1. QLEDs are capable of producing highly accurate and vibrant colors due to their use of quantum dots.
2. QLEDs are more energy-efficient than traditional LCD displays because they do not require as much backlighting.
3. QLED displays have high contrast ratios and produce more detailed and lifelike images.
4. QLEDs have a longer lifespan than traditional LCD displays because they do not suffer from the same issues of backlight burnout or color fading over time.

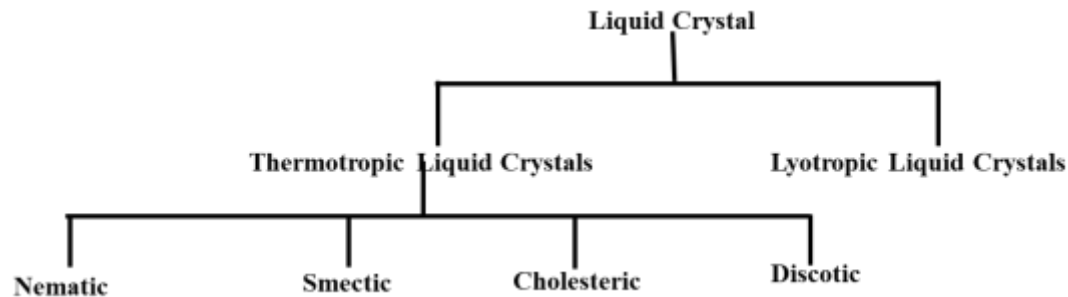
Applications of QLED

1. QLED displays are commonly used in televisions, monitors, smartphones, and other electronic devices.
2. QLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting, and architectural lighting.
3. QLEDs can be used in medical imaging applications, such as in MRI machines, to produce high-resolution and accurate images.

4. QLED displays can be used in advertising displays, such as digital billboards and signage, to produce high-quality and eye-catching visuals.

6 Explain the classification of liquid crystals. Mention any four properties and applications of liquid crystals.

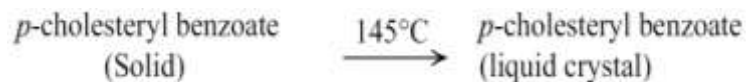
The liquid crystals are a unique state of matter between solid (crystalline) and liquid (isotropic) phases.



i) **Thermo tropic liquid crystal**

A liquid crystal is said to be thermo tropic if molecular orientation is dependent on the temperature.

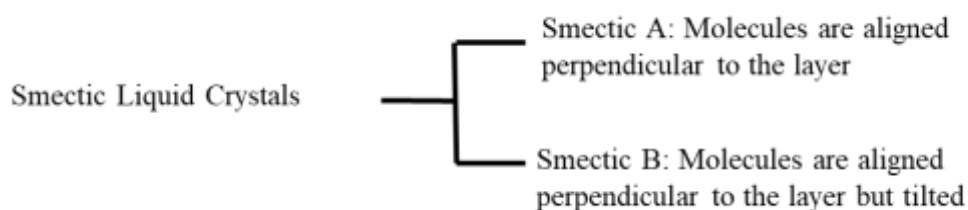
Example:



a) **Nematic (or thread-like liquid crystals)** : The molecules move either sideways or up and down. Increase in temperature decreases the degree of orientation.

Example: p-azoxyphenetole

b) **Smectic (or soap-like liquid crystals):** The molecules in smectic crystals are oriented parallel to each other as in the nematic phase but in layers.



c) **Cholesteric liquid crystals:** Molecules in successive layers are slightly twisted and form helical pattern.

d) **Discotic liquid crystal:** Molecules are arranged in a column arranged with disc like structure.

2) **Lyotropic liquid crystals:** The orientational behaviour of Lyotropic crystals is a function of concentration and solvent. These molecules are amphiphilic – they have both hydrophilic and hydrophobic ends in their molecules. At low concentrations, molecules are randomly arranged and higher concentration produces a definite pattern heads out and tail in. Soaps and detergents form Lyotropic crystals when they combine with water

Properties of liquid crystals

1. They exhibit optical anisotropy which is defined as the difference between refractive index parallel to the director and refractive index perpendicular to the director.
2. The intermolecular forces are rather weak and can be perturbed by an applied electric field.
3. They interact with an electric field, which causes them to change their orientation slightly.
4. Liquid Crystal can flow like a liquid, due to loss of positional order.

Applications of liquid crystals

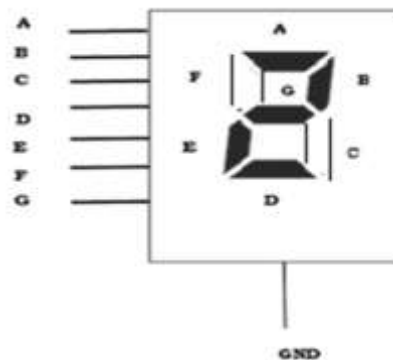
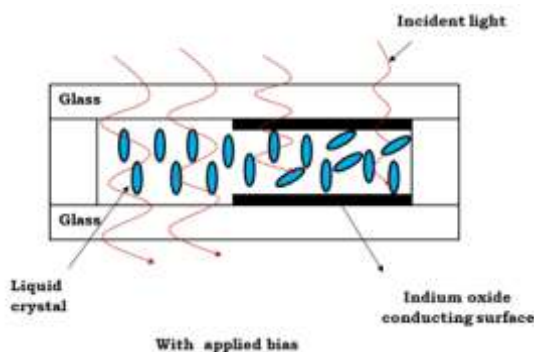
1. The liquid crystal layer in LCDs allows for the display of images and text through the use of electrical currents that control the orientation of the crystals.
2. Liquid crystal sensors are used in various applications such as temperature sensing, humidity sensing, and chemical sensing.
3. Liquid crystals are used in various optical devices such as variable optical attenuators, phase shifters, and tunable filters. These devices are used in optical communication systems, spectroscopy, and imaging.
4. Liquid crystals have been used in drug delivery systems, where the drug is encapsulated in the liquid crystal matrix and delivered to specific target cells.

7 Discuss the working of Liquid Crystal Display.

Liquid-crystal displays (LCDs) consist of multiple layers. Light produced by a light-emitting diode passes through polarizing filters, color filters, and a liquid-crystal layer to produce an image.

The basic working principle of LCD is blocking of light. When the external light passes from one polarizer to the next polarizer, external supply is given to the liquid crystal, the polarized light aligns itself so that the image is produced in the screen.

The indium oxide conducting surface is a transparent layer which is placed on both the sides of the sealed thick layer of liquid crystal. When no external bias is applied the molecular arrangement is not disturbed.



When the external bias is applied the molecular arrangement is disturbed and that area looks dark and the other area looks clear. In the segment arrangement, the conducting segment looks dark and the other segment looks clear. To display number 2 the segments A,B,G,E,D are energized.

The LCD can display images in colour by using filters that absorb different colours of light. First, a white light-emitting diode shines light toward the front of the display, generating each pixel. The pixels actually

consist of three sub pixels, one for each color—red, blue, and green. These sub pixels are made up of a liquid-crystal layer and the appropriate color filter sandwiched between two polarizing light filters. Transistor arrays switch the structural states of the liquid crystals to control whether or not a sub pixel gets lit up, which in turn produces all the colors in an image.

- 8 Explain any four properties and applications of Light emitting materials - Poly[9-vinylcarbazole] (PVK)] suitable for optoelectronic devices.

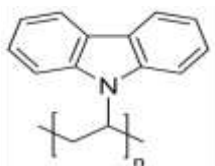


Fig: 2.13 Poly[9-vinylcarbazole] (PVK)]

Poly (N-vinyl carbazole) (PVK) is a polymers and an efficient hole transport material to prepare highly efficient and stable planar heterojunction perovskite solar cells.

Properties of PVK

1. It is a semiconducting polymer and an electron acceptor converts ultra-violet (UV) light into electricity.
2. PVK has a band gap of 3.4 eV, optical absorption edge stating at 350 nm capable of absorbing Ultra-Violet light.
3. The PVK film is hydrophobic, thermally stable with a relatively high glass transition temperature (T_g) of 200 °C
4. The PVK solution also showed good wettability, and provide uniform thin films on glass/ITO substrates.

Applications

1. PVK is used in OLEDs for light harvesting applications.
2. Used in the fabrication of light-emitting diodes and laser printers.
3. Used in the fabrication of organic solar cells when combined with TIO on glass substrate.
4. Used in the fabrication of solar cells when combined with Perovskite materials.
5. PVK-Perovskite junction is used in Light-Emitting Diodes with Enhanced Efficiency and Stability.

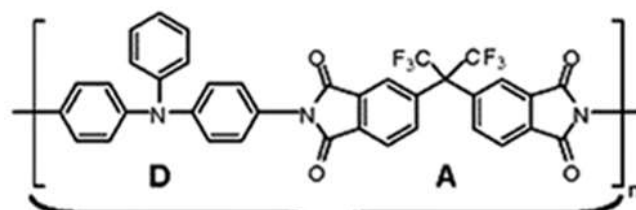
- 9 Discuss the use of Polyimide Polymeric material for Organic memory device.

Organic polymer used for polymer used for organic memory device is Polyimide with Donor- Triphenylamine and Acceptor- phthalimide.

Donor: Triphenyl Amine group (TPA)

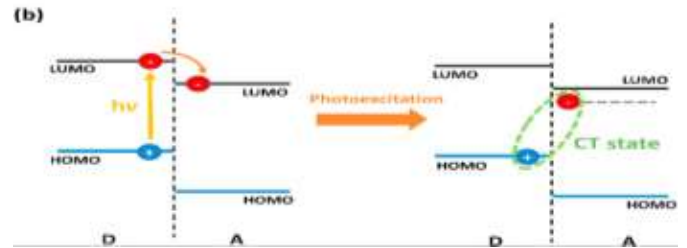
Acceptor: Phthalimide group

Hexafluoroisopropylidene (6F): Increases the solubility of PI



The donors and acceptors of PIs contribute to the electronic transition based on an induced charge transfer (CT) effect under an applied electric field.

1. When an electric field more than threshold energy is applied, the electrons of the HOMO (TPA unit) is excited to LUMO.
2. The energy of LUMO of donor and acceptor are similar and therefore, after excitation the electron transferred to LUMO (acceptor), generating a CT state.

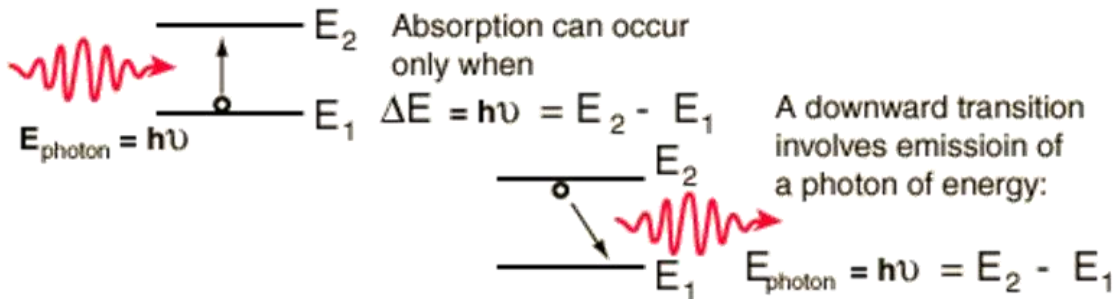


3. This permits the generation of holes in the HOMO, which produces the open channel for the charge carriers to migrate through.
4. Therefore, Field-induced charge transfer from Triphenylamine to Phthalimide exhibit the switching behavior (bistable states ON/OFF).

10 Define Optoelectronic device. Explain the working principle of Optoelectronic device.

A hardware device that converts electrical energy into light and light into energy through semiconductors is called Optoelectronic device. Optoelectronic devices are primarily transducers i.e. they can convert one energy form to another.

Working principle



If the photon has an energy larger than the energy a gap, the photon will be absorbed by the semiconductor, exciting an electron from the valence band into the conduction band, where it is free to move. A free hole is left behind in the valence band. When the excited electron is returning to valence band, extra photon energy is emitted in the form a light. This principle is used in Optoelectronic devices.

11 Write the properties and applications of Silicon Nano Crystals for Optoelectronic devices

Properties of Silicon Nanocrystals for optoelectronics

1. Silicon Nano crystal has wider bandgap energy due to quantum confinement.
2. Si NCs shows higher light emission property (Photoluminescence)
3. Si NCs exhibit quantum yield of more than 60%.
4. Si-NCs exhibit tunable electronic structure

Applications:

1. Si NCs are used in neuromorphic computing and down-shifting in photovoltaics
2. Si NCs are used in the construction of novel solar cells, photodetectors and optoelectronic synaptic devices.

12 **What is OLED? Mention any four properties and applications of OLED.**

“OLEDs are thin film devices consisting of a stack of organic layers sandwiched between two electrodes. OLEDs operate by converting electrical current into light via an organic emitter”.

Properties of OLED

1. OLEDs are very thin and flexible, which makes them suitable for use in curved or flexible displays.
2. OLEDs have a high contrast ratio, and produce images with vivid and rich colours.
3. OLEDs have a fast response time, resulting in smooth and seamless motion in video content.
4. OLEDs have a wide viewing angle, and image quality is maintained even when viewed from different angles.
5. OLEDs are energy efficient, as they do not require a backlight like traditional LCD displays.

Applications of QLED

5. QLED displays are commonly used in televisions, monitors, smartphones, and other electronic devices.
6. QLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting, and architectural lighting.
7. QLEDs can be used in medical imaging applications, such as in MRI machines, to produce high-resolution and accurate images.

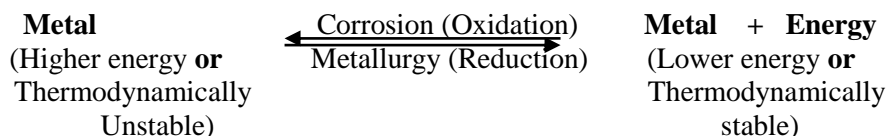
QLED displays can be used in advertising displays, such as digital billboards and signage, to produce high-quality and eye-catching visuals.

MODULE-3

CORROSION AND ELECTRODE SYSTEM

Definition of corrosion:

Corrosion is defined as “the destruction or deterioration of metals or alloys by the surrounding environment through chemical or electrochemical reactions is known as corrosion.”



Examples:

- (i) **Rusting of iron:** When iron rod is exposed to the environment for a long time, a layer of reddish brown powder of Fe_2O_3 (final oxidation product) is formed on the surface of iron rod.
- (ii) **Formation of green layer on copper metal:** A green color of copper carbonate layer consisting of $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ is formed on the surface of copper when exposed to moist air.
- (iii) Based on the environment, corrosion is classified into (i) Dry or Chemical Corrosion (ii) Wet or Electrochemical corrosion

Difference between dry corrosion and wet corrosion:

Dry corrosion	Wet corrosion
The corrosion occurs in the absence of moisture.	The corrosion occurs in the presence of moisture or conducting medium.
It involves direct attack of chemicals on the metal surface.	It involves formation of galvanic cells.
It is a slow process.	It is a fast process.
Corrosion is uniform.	Corrosion is not uniform. It depends on the size of anodic part of metal.
It occurs on both heterogeneous and homogeneous surfaces.	It occurs only on heterogeneous metal surfaces.

Electrochemical theory of corrosion:

When a metal such as iron is exposed to atmospheric air for long time, the following electrochemical reactions occur gradually on the surface of iron metal.

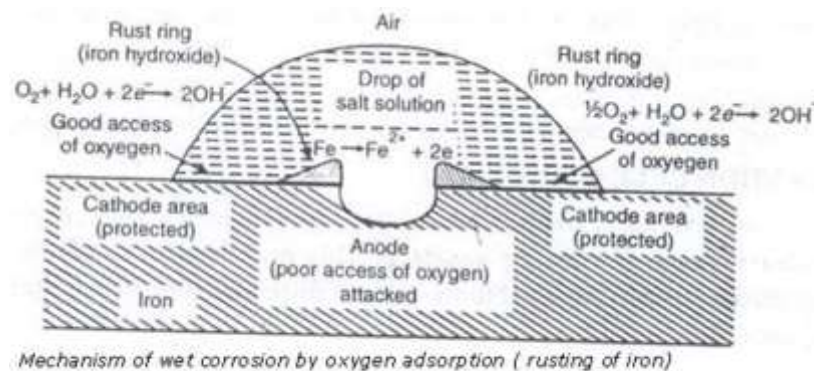
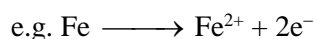


Fig: 3.1 Rusting of Iron mechanism

Reaction at anodic region

As mentioned above, oxidation of metal takes place at anode.



Reactions at cathodic region

At cathode, the reaction is either

(a) Liberation of hydrogen

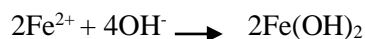
or

(b) Absorption of oxygen.

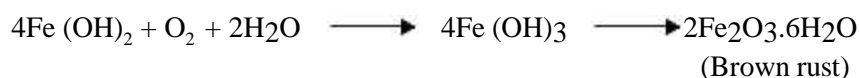
Liberation of hydrogen (in the absence of oxygen)	Absorption of oxygen (in the presence of oxygen)
<p>In acidic medium the reaction is</p> $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$ <p>In neutral or alkaline medium, the reaction is</p> $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2\uparrow$	<p>In acidic medium, the reaction is</p> $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ <p>In neutral or alkaline medium, the reaction is</p> $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$

Overall reaction

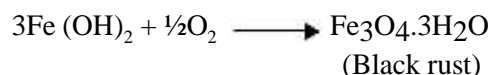
The metal ions (Fe^{2+}) liberated at anode and some anions (OH^-) formed at cathode diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and cathode as



In an oxidizing environment, the insoluble $\text{Fe}(\text{OH})_2$ oxidized to ferric oxide as following reaction.



If the concentration of oxygen is limited then $\text{Fe}(\text{OH})_2$ is converted into magnetic oxide of Fe and is known as black rust.



Factors affecting the rate of corrosion:

The rate of corrosion is mainly dependent upon environmental conditions. The following are the factors which decide the rate of corrosion.

i).Primary factors (Related to nature metal)

a. Ratio of anodic to cathodic areas: The rate of the corrosion is mainly depends on relative sizes of anodic and cathodic areas. If the metal has smaller the anodic area and larger the cathodic area results, intense and faster corrosion takes place at the anodic area. This process makes the anodic reaction to takes place at maximum rate thus increasing the corrosion rate.

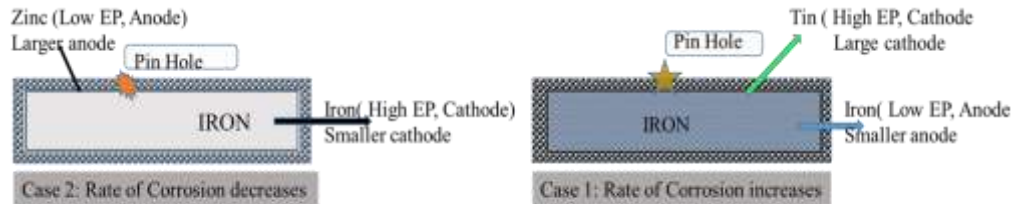


Fig: 3.2 Ratio of anodic to cathodic areas on the rate of corrosion

Example: coating of tin (Sn) on iron (Fe) surface: in this case if coating is not uniform and some areas are not covered, a small anode and a large cathode areas are formed. An intense corrosion occurs at the anodic area.

On the other hand, coating of Zn on Fe sheet gives an anodic coating to iron. Even if zinc coating peels off at some areas the rate of corrosion of iron is low. This is because of the formation of large anodic and small cathodic areas (Fig.3.2).

b. Nature of corrosion product

Usually product of corrosion is metal oxide. The metal oxide covers the metal and form a thin metallic layer. This metallic layer determines the speed of corrosion. If the corrosion product is highly ionic, porous, conducting, non-stoichiometric & unstable then, the rate of corrosion increase. On the other hand, if corrosion product is less ionic, nonporous, non-conducting, stoichiometric and stable then the corrosion product deposited on the metal surface prevents further corrosion.

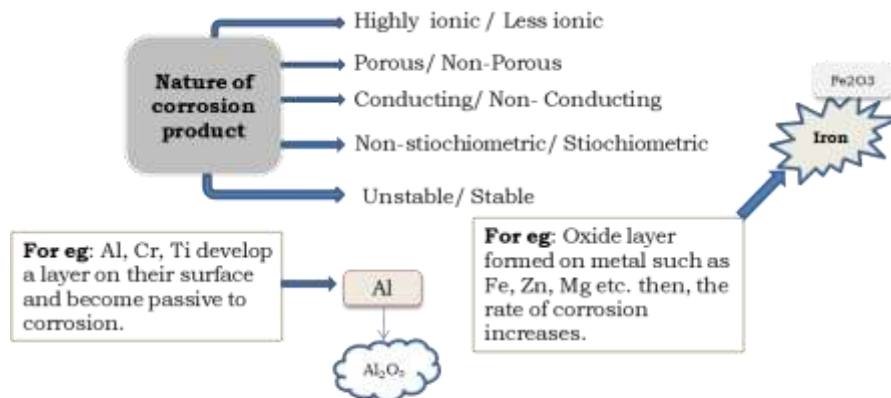


Fig.3.3 Nature of corrosion product and rate of corrosion

ii).Secondary factors (Related to nature of the medium)

a.pH of the medium:

In general, the rate of corrosion increases with decrease in pH. In case of metal such as iron, at very high pH (pH above 10) protective layer of iron oxide is formed which prevents further corrosion. Between pH 3 and 10, in the presence of oxygen is essential for corrosion of iron. But, if the pH of the medium is 3 or lower than 3 severe corrosion occurs even in the absence of air, due to the continuous evolution of H_2 gas at cathode.

b. Temperature

The rate of corrosion is directly proportional to temperature i.e., rise in temperature, increases the rate of corrosion. This is because the rate of diffusion of ions increases with rise in temperature. In some cases the rise in temperature decreases the passivity leading to an increase in the corrosion rate. Example: Steel and other metals corrode at faster rates at higher temperatures than at lower temperatures.

a. Conductance of the medium:

The corrosion rate increases in the presence of conducting species in the corroding environment. The speed of corrosion in dry medium is less than that in a wet medium. Because wet medium contains more conducting species compared to wet medium.

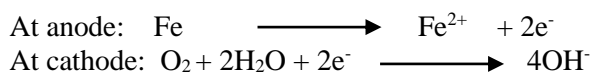
Types of corrosion:

1. Differential metal corrosion: Differential metal corrosion arises when two dissimilar metals such as iron and copper are in contact with each other in a corrosive medium. The potential difference between two metals is the cause or driving force for corrosion. The metal with lower electrode potential or more active metal (top in electrochemical series) acts as anode and undergoes corrosion quickly. Other metal (cathode) is unaffected from the corrosion. Example: In Fe-Cu galvanic cell, iron ($E^\circ = -0.44V$) with lower reduction potential than copper ($E^\circ = +0.34V$), hence zinc acts as anode and the electrons flow from anodic metal to cathodic (Cu) Fig.2.3.



Fig: 3.4 Galvanic Corrosion

In corrosive medium,



Factors affecting rate of galvanic corrosion:

- Higher the potential difference between the anodic and cathodic metals, higher is the rate of corrosion.
- Smaller anodic area and larger cathodic area increases the rate of galvanic corrosion.

This type of corrosion can be observed in the following examples:

- (i) Steel screw's in a brass marine hardware.
- (ii) Steel pipe connected to copper plumbing.
- (iii) Zinc coated mild steel structures.

2. Differential aeration corrosion

This type of corrosion occurs when two different parts of the same metal are exposed to different oxygen concentrations.

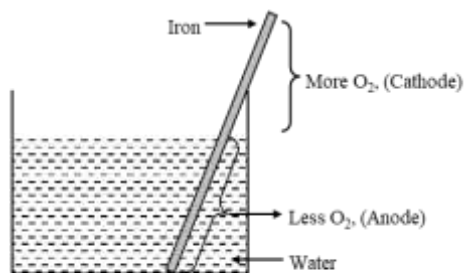
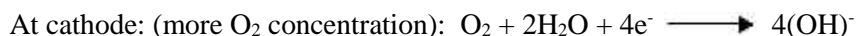


Fig: 3.5 Differential aeration corrosion

The reactions may be represented as follows:



Examples of differential aeration corrosion are the *waterline corrosion* and *pitting corrosion*.

2. a. Water line corrosion: This is an example of differential aeration corrosion.

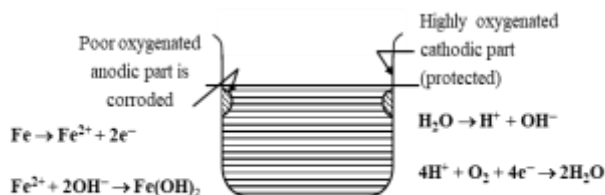
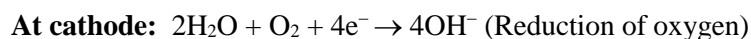
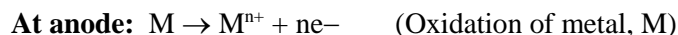


Fig:3. 6 Waterline Corrosion

When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to DO, whereas, the portion above the water line is exposed to more oxygen. Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected. A distinct brown line is formed just below the water line due to the deposition of rust as shown in Fig 3.6.

The reactions may be represented as follows:



Other example: Ships which remain partially immersed in sea water for a long time undergo water line corrosion.

2. b. Pitting Corrosion

When a small dust particle gets deposited on a steel surface, the region below the dust particle is exposed to less oxygen compared to the remaining part. As a result, the region below the dust particle acts as anode and undergoes corrosion and forms a pit as shown in Fig: 3.7. The remaining region of the metal acts as cathode and is unaffected. Formation of a small anodic area and a large cathodic area results in intense corrosion below the dust particle.

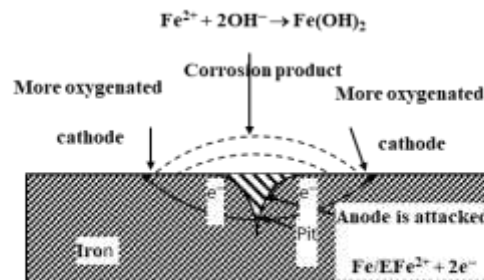
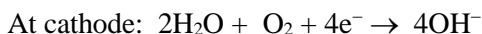


Fig: 3.7 Pitting Corrosion

The reactions may be represented as follows:



Corrosion Control

Due to corrosion, there is a great loss of material and money. Therefore, it is essential to protect metals from corrosion. Since, there are two components involved in corrosion; the metal and environment both are considered in corrosion protection. Following methods have been adopted for the protection of metal from corrosion.

Galvanizing

Galvanizing is the process of coating a metal surface such as iron with zinc metal. Galvanizing of iron is an example of anodic metal coating on the surface of a cathodic metal.

Process: Galvanization is carried out by hot dipping method as shown in Fig.2.6. It involves the following steps

1. Solvent Cleaning: The metal surface is washed with organic solvents to remove organic impurities on the surface.
2. Alkali Cleaning: Residual organic impurities are removed by treating the object with alkali such as NaOH.
3. Pickling: Rust and Scale is removed by washing the object with dilute sulphuric acid H_2SO_4
4. Finally, the article is washed with water and air-dried.
5. The article is then dipped in a bath of molten zinc at $430^{\circ}C$ to $470^{\circ}C$ (Molten zinc is covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.)
6. The excess zinc on the surface is removed by passing through a pair of hot rollers.

Application

Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

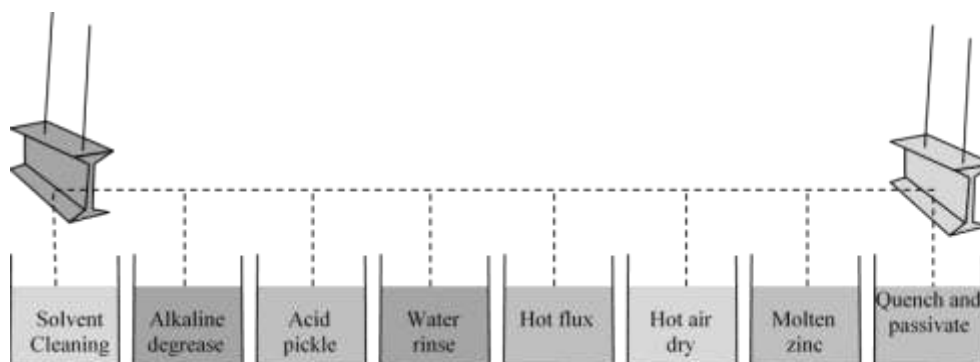


Fig: 3.8 Galvanizing

Note: Even if the Zn coating falls off at some places, the base metal (Fe) does not get corroded at those places. (This is because the base metal acts as cathode. In corrosion process, the cathodic metal always remains unaffected.) And because of the formation of small cathodic area and larger anodic area corrosion process will not be there.

(**Note:** Galvanized articles are not used for preparing and storing food because zinc dissolves in dilute acids producing toxic zinc compounds)

Anodizing

(Anodizing of aluminum): It is a type of inorganic coating. A process in which top layer of a metal is converted to its oxide, which acts as a protective barrier and reduces corrosion is called as anodizing.

Process: The article is subjected to degreasing and polishing and then made as anode, refer fig 16. Chromic acid electrolyte is maintained at about 35°C and suitable voltage is applied to get desired thickness of the oxide film. Anodised article is sealed by treating with boiling water or steam containing salts of Nickel or Cobalt. The $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ layer on the surface acts as a protective coating, hence corrosion is prevented.

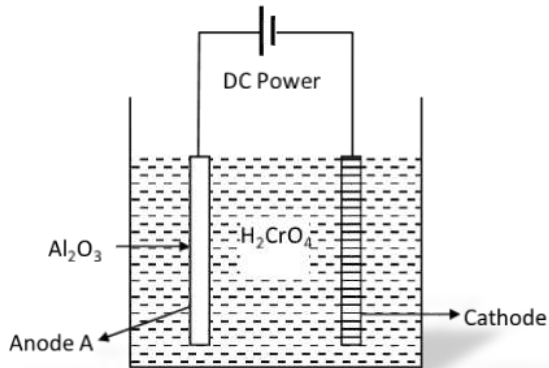
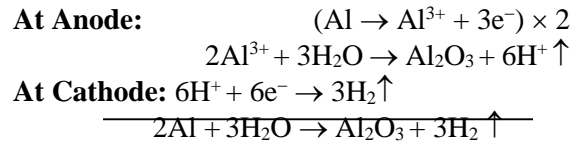


Fig: 3.9 Anodizing of aluminium



Other metals such as Mg, Ti etc. can also be anodized.

Applications: Metals such as Al, Mg, Ti etc. are anodized to control corrosion.

3.5.2 (b) Phosphating

It is generally obtained on steel surface by converting surface metal atoms into their phosphate by chemical or electrochemical process.

Phosphate bath contains three essential components 1. Free phosphoric acid 2. Primary phosphate like Fe, Mn, or Mg phosphate. 3. Accelerator such as nitrates, nitrites hydrogen peroxide and PH usually in the range of 1.8-3.2 if the process is immersion type. If the process is spraying type then PH is in an around 3.2 to 7.8 and temperature maintained at 35°C.

The mechanism of Phosphating involves following steps.

1. First dissolution of the metal as metal ions.
2. Metal ions reacting with phosphate ions to form a metal phosphate.
3. Deposition of the metal phosphate on the surface of the metal.

Phosphating is always given as underline (under coating) before the finishing, because Phosphating along with corrosion resistance it also imparts the surface a good paint adhesion quality.

Application: An undercoating before painting of automotive bodies, refrigerators, washing machines etc.

One of most important application of Phosphating is of galvanized iron which is otherwise difficult to paint.

3.6 Cathodic protection

A method of converting the metallic structure into cathode by supplying electrons from external source is called cathodic protection.

- i) A metallic structure is converted to cathode by connecting it to another highly reactive metal.

ii) A metallic structure is converted to cathode by supplying electrons DC source.

3.6.1 Sacrificial anode method:

In sacrificial anode method, the metal to be protected is electrically connected to a more active metal using insulated copper wire. For example, when steel is to be protected, it may be connected to a block of Mg or Zn. In such a situation, steel acts as **cathode** (high electrode potential) and is unaffected as shown Fig.3.10. Mg and Zn act as anode (low electrode potential) and undergo sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

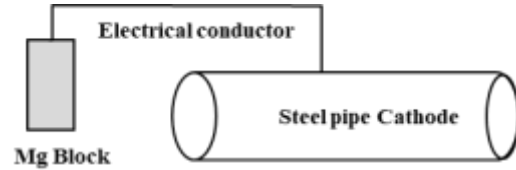


Fig: 3.10 Sacrificial anode technique

Other examples: Mg bars are fixed to the sides of ships to act as sacrificial anode.

Mg blocks are connected to underground pipe lines.

Mg blocks are connected to underground oil storage tank.

3.6.2 Impressed current method:

In cathodic protection, the metal to be protected is completely converted into a cathode. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.

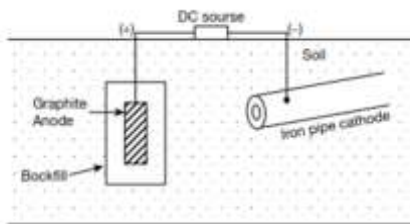


Fig: 3.11 Impressed Current Technique

In impressed current method, the metal to be protected is connected to the negative terminal of an external DC. Power supply. The positive terminal is connected to an inert electrode such as graphite. Under these conditions, the metal acts as cathode and hence does not undergo corrosion. The inert electrode acts as anode; but it does not undergo corrosion because it is inert refer Fig: 3.11.

3.7 Corrosion Penetration Rate (CPR)

Definition: The Corrosion penetration rate is the speed at which any metal or alloy deteriorates in a specific corrosive environment through chemical or electrochemical reactions.

It is also defined as the **amount of weight loss per year in the thickness of metal or alloy due to corrosion**. The Corrosion penetration rate also referred as corrosion rate.

Corrosion penetration rate depends on following factors;

1. Nature of metal.

2. Nature of corrosive environment/medium.
3. Nature of corrosion product.
4. Speed at which corrosion spreads in the inner portion of metal.

The Corrosion penetration rate is calculated using the following formula;

$$\text{CPR} = \frac{k \times W}{D(\rho) \times A \times T}$$

Where,

W-is weight loss after exposure time

T-is exposure time in corrosive medium.

D- is the density of metal or alloy.

A-is surface area of exposed specimen.

K -is constant.

The CPR is conveniently expressed in terms of either mils (0.001 inch) per year (mpy) or milli meters per year (mmpy).

	CPR in mpy	CPR mmpy
K	534	87.6
W	Mg	Mg
(D)ρ	g/cm ³	g/cm ³
A	inch ²	cm ²
Hrs	Hrs	Hrs

Numerical Problems on CPR

1. A sheet of carbon steel one meter wide by three meters long has lost 40g to corrosion over the past six months. Convert that mass loss to a penetration rate of the steel in mm units and mpy units. What would be the corrosion rate? (Carbon steel density=7.8g/ cm³) To calculate CPR in mmpy

Solution:

To calculate CPR in mmpy

	Given	CPR in mmpy
K		87.6
W	40 g	40 x1000 mg
(D)ρ	7.8g/cm ³	7.8g/cm ³
A	1mx3m=3m ²	3x100x100cm ²
T	6 months	6 x30x24 hrs

$$\text{CPR} = \frac{k \times W}{D(\rho) \times A \times T} \quad \text{To calculate CPR in mpy}$$

	Given	CPR in mpy
K		534
W (wt loss)	40 g	40 x1000 mg

P	7.8g/cm ³	7.8g/cm ³
A	1m x3m = 3m ²	3 x1550 inch ²
T	6 months	6 x30x24 hrs

1sqmt=1550 sq inch

$$CPR = \frac{k \times W}{D(\rho) \times A \times T}$$

$$CPR = \frac{534 \times 40 \times 1000}{7.8 \times 3 \times 100 \times 100 \times 6 \times 30 \times 24}$$

$$CPR = 0.0503 \text{ mpy}$$

2. Calculate the CPR in both mpy and mmpy for a thick steel sheet of area 100 inch² which experiences a weight loss of 485g after one year. (Density of steel=7.9g/cm³).

Solution:

To calculate CPR in mmpy

	Given	CPR in mmpy
K		87.6
W	485 g	485 x1000 mg
ρ	7.9g/cm ³	7.9g/cm ³
A	100 inch ²	100 x6.45cm ²
t	1year	365 x24 hrs
1 inch ² =6.45 cm ²		
1cm ² =0.155 inch ²		

$$CPR = \frac{k \times W}{D(\rho) \times A \times T}$$

$$= \frac{87.6 \times 485 \times 1000}{7.9 \times 100 \times 6.45 \times 365 \times 24}$$

$$= 0.9518 \text{ mmpy}$$

To calculate CPR in mpy

	Given	CPR in mpy
K		534
W	485 g	485 x1000 mg
ρ	7.9g/cm ³	7.9g/cm ³
A	100 inch ²	100 inch ²
t	1year	365 x24 hrs

$$\begin{aligned}\text{CPR} &= \frac{k \times W}{D(\rho) \times A \times T} \\ &= \frac{534 \times 485 \times 1000}{7.9 \times 100 \times 365 \times 24} \\ &= 37.42 \text{ mpy}\end{aligned}$$

3. A thickness of brass sheet of area 400 inch² is exposed to air near the ocean. After two years period it was found to experience a weight loss of 375g due to corrosion. If the density of Brass is 8.73g/cm³. Calculate the CPR in mm/year mpy.

Solution:

To calculate CPR in mmpy

	Given	CPR in mmpy
K		87.6
W	375 g	375 x1000 mg
ρ	8.73g/cm ³	8.73g/ cm ³
A	400 inch ²	400 x6.45cm ²
t	2year	2 x365x24 hrs
1 inch ² =6.45 cm ²		
1cm ² =0.155 inch ²		

$$\begin{aligned}\text{CPR} &= \frac{k \times W}{D(\rho) \times A \times T} \\ &= \frac{87.6 \times 375 \times 1000}{8.73 \times 400 \times 6.45 \times 365 \times 2 \times 24} \\ &= 0.083 \text{ mmpy}\end{aligned}$$

To calculate CPR in mpy

	Given	CPR in mpy
K		534
W	375 g	375 x1000 mg
P	8.73g/cm ³	8.73g/ cm ³
A	400 inch ²	400 inch ²
T	2year	2 x365x24 hrs

$$\begin{aligned}\text{CPR} &= \frac{k \times W}{D(\rho) \times A \times T} \\ &= \frac{534 \times 375 \times 1000}{8.73 \times 400 \times 365 \times 2 \times 24} \\ &= 3.27 \text{ mpy}\end{aligned}$$

Electrochemical cell

Electrochemical cell

A device which converts chemical energy into electrical energy and vice versa is known as Electrochemical cell. There are two types of electrochemical cell: galvanic and electrolytic cell.

Parameter	<u>Galvanic cell</u>	<u>Electrolytic cell</u>
Type of device	A device which converts chemical energy into electrical energy.	A device which converts electrical energy into chemical energy.
Assembly	It is the combination of two half cells, containing the same or different electrodes dipped in the same or different electrolytes.	It is a single cell containing same electrodes present in the same electrolyte.
Nature of electrodes	Anode – Negative (-ve) Cathode – Positive(+ve)	Anode – Positive (+ve) Cathode – Negative (-ve)
Movement of electrons	From anode to cathode in external circuit.	Electrons entered through cathode and leave by anode.
Salt bridge	Salt bridge is required.	Salt bridge is not required.

Cell terminology: Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current: The flow of electrons through a wire or any conducting medium is called current.

EMF (Electromotive force): The potential difference between the two electrodes of the cell when no current is drawn from the cell is known as electromotive force. SI unit is volt or milli volt.

Potential difference: The difference of potentials between any two points in a closed circuit is called as potential difference.

Anode The anode is the negative or reducing electrode that releases electrons to the external circuit and oxidizes during the electrochemical reaction.

Cathode The cathode is the positive or oxidizing electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.

Half-cell A device consisting of a single electrode immersed in an electrolytic solution and thus developing a definite potential difference.

Galvanic Cell (Daniel cell): It is an electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy.

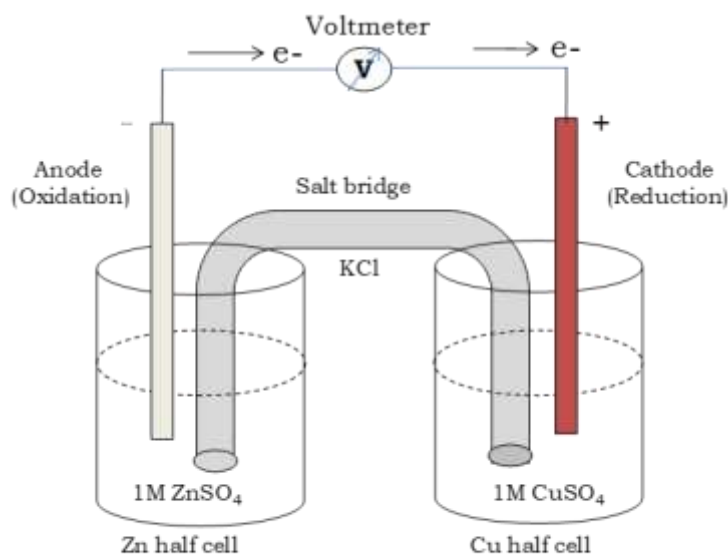
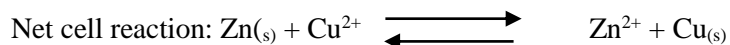
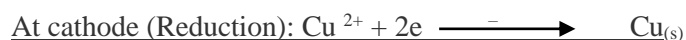
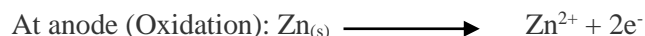


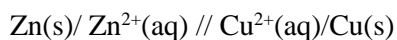
Fig:3.12 Galvanic Cell

Construction of galvanic cell: Galvanic cell consist zinc and copper half cells. The zinc half-cell consists of zinc rod immersed in 1molar zinc sulphate solution. Similarly, the copper half- cell consists of a copper rod immersed in 1molar copper sulphate solution. The two half cells internally connected by a KCl salt bridge. A salt bridge is a U-tube filled with jelly containing KCl or NH_4NO_3 solution or saturated KCl solution. Both ends of the U-tube fitted with porous plugs. The salt bridge allows the flow of ions but prevents the mixing of the solution that would allow direct reaction of the cell reactants. Two half cells are connected externally through an ammeter or voltmeter by using a conducting wire.

Cell reaction:



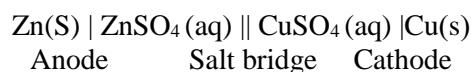
The galvanic cell mentioned above is represented in a short IUPAC cell notation as follows:



It is important to note that:

1. A single vertical line “/” indicates a phase boundary, while “//” indicates salt bridge.
2. The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

For example the Daniel cell can be represented as,



3. “Conventional current flow” is from positive to negative, which is opposite to the electron flow. This means that if the electrons flow. This means that if the electrons are flowing from the left electrode to right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

Single electrode potential: *The tendency of an electrode to lose or gain electrons when it is in contact with a solution of its own ions is called single electrode potential.* The tendency of an electrode to lose electrons is called *oxidation potential*, while the tendency of an electrode to gain electrons is called *reduction potential*. (denoted by E)

Standard electrode potential: Standard electrode potential is defined as the potential developed on the electrode at the interface when it is in contact with a solution of its own ions at equilibrium, at unit ionic concentration and 298K. If the electrode involves a gas, then the gas is at one atmospheric pressure. (denoted by E°)

TYPES OF ELECTRODES:

METAL-METAL ION ELECTRODE: This type of electrode consists of a metal in contact with a solution of its own ions.

- Eg: 1. Zinc in a solution of zinc sulphate.
2. Copper in a solution of copper sulphate.

METAL-METAL SALT ION ELECTRODE: This type of electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt.

- Eg: 1. Calomel electrode $\text{Hg} / \text{Hg}_2\text{Cl}_2 / \text{Cl}^-$
2. Silver-Silver chloride electrode $\text{Ag} / \text{AgCl (s)} / \text{Cl}^-$

GAS ELECTRODE: A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which it is reversible.

- Eg: SHE $\text{Pt} / \text{H}_2 (1\text{atm}) / \text{H}^+ (1\text{M})$

OXIDATION-REDUCTION ELECTRODE: This type of electrode consists of an inert electrode (Pt or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion.

- Eg: $\text{Pt} / \text{Fe}^{2+} : \text{Fe}^{3+}$
 $\text{Pt} / \text{Sn}^{2+} : \text{Sn}^{4+}$

AMALGAM ELECTRODES: Amalgam electrode is one in which amalgam of a metal is in contact with solution containing its own metal ions. Highly reactive metals are used in the form of amalgam Example: $\text{Zn(Hg)} / \text{Zn}^{2+}$, $\text{Cu(Hg)} / \text{Cu}^{2+}$

ION SELECTIVE ELECTRODE: In ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions. (Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution)

Example- Glass electrode.

3.9 REFERENCE ELECTRODE:

Reference electrodes are those whose potentials are known.

3. 9.a PRIMARY REFERENCE ELECTRODE [SHE]: Hydrogen gas at a pressure of one atmosphere in equilibrium with one molar hydrochloric acid in the presence of platinum is called standard hydrogen electrode.

Construction of normal hydrogen electrode [nhe or she]:

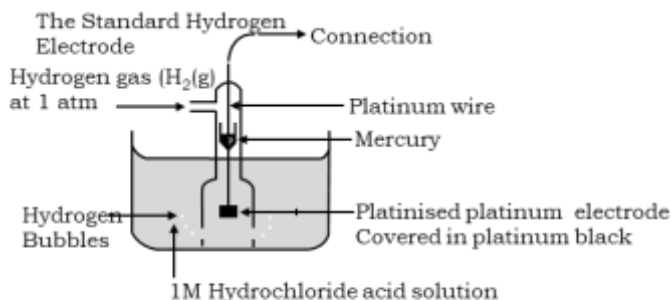
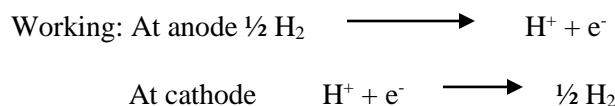


Fig: 3.12. a Standard Hydrogen Electrode

It consists of a rectangular piece of platinum foil, which is covered with finely divided Pt black, which adsorbs large quantity of hydrogen and so acts as hydrogen electrode. The electrode is immersed in a solution of HCl containing hydrogen ions at unit activity Fig:3.12.a Pure hydrogen gas is bubbled at one atmospheric pressure. The temperature is maintained at 298K. By convention the potential of such electrode has been taken as zero.

This electrode is represented as
 $\text{Pt, H}_2 (1\text{atm}); \text{H}^+(1\text{M})$



Limitations of hydrogen electrode:

1. It is difficult to maintain the pressure of hydrogen gas uniformly at one atmosphere.
 2. It is difficult to maintain the hydrogen ion concentration 1M throughout the experiment.
 3. Platinum foil is easily poisoned by the adsorption of impurities present in the solution.
 4. The adsorptions of impurities on the platinum foil decrease the adsorption of hydrogen and hence equilibrium between hydrogen gas and hydrogen ions gets disturbed.
 5. Hydrogen electrode cannot be used in the presence of oxidizing agent.
- These limitations lead to the construction of secondary reference electrode.

3.9. b Secondary reference electrode: 1. Calomel electrode 2. Ag-AgCl electrode

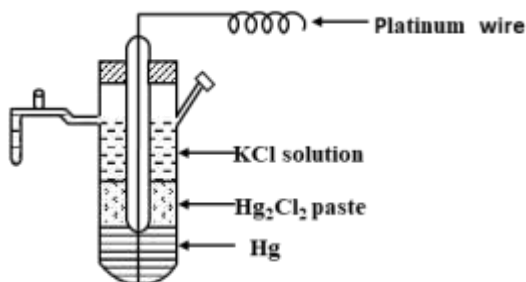
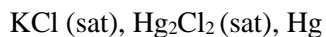


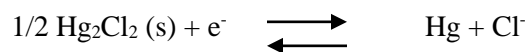
Fig: 3.13 Calomel Electrode

CALOMEL ELECTRODE: The calomel electrode consists of a glass vessel containing a layer of Hg over which is placed a paste of an Hg, Hg_2Cl_2 and KCl. Above this there is a solution of KCl saturated with the Mercurous salt. A platinum wire is fused in the glass tube for electrical connection Fig:3.13. A salt bridge is used to couple with other half-cell.

The half-cell is represented as



The half-cell reaction is



The potential of the calomel electrode depends on the concentration of KCl used. For saturated KCl, the potential is +0.241V, FOR 1M and 0.1M KCl the values are 0.280V and +0.334V respectively.

USES: The calomel electrode is simple to construct, the cell potential is reproducible and stable over a long period and does not vary with temperature. Hence it is commonly used as a secondary reference electrode for potential measurements.

3.10 Ion selective electrode:

Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution”

Glass electrode: A glass electrode is an ion selective electrode where potential depends upon the pH of the medium.

Construction of glass electrode:

A glass electrode is an ion selective electrode where potential depends upon the pH of the medium. The glass electrode consists of a glass bulb made up of special type of glass which consisting of 72% of SiO₂, 22% Na₂O and 6% CaO, has low melting point and relatively high electrical conductivity. (Fig:1.3) The glass bulb is filled with a solution of constant pH (0.1 M HCl) and insert with a Ag-AgCl electrode, which is the Internal reference electrode and also serves for the external electrical contact. The electrode dipped in a solution containing H⁺ ions (Fig:)

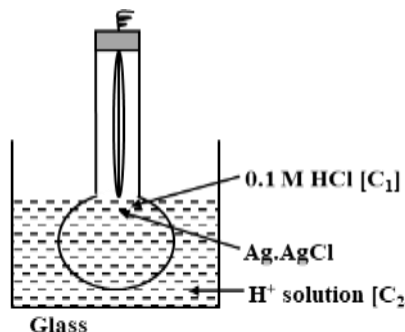


Fig: 3.14 a Glass Electrode

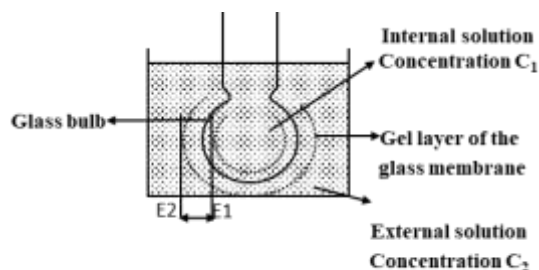
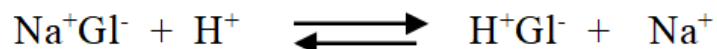


Fig:3.14 b Boundary Potential

The electrode representation is, **Ag-AgCl | 0.1 M HCl | Glass.**

Principle:

If a thin walled glass bulb containing an acid is immersed in another solution containing H⁺ ions, a potential is developed across the glass membrane. This is due the ion exchange reaction taking place at the gel layers of glass membrane. This is called boundary potential **E_b**



The boundary potential is due to the difference in potential ($E_1 - E_2$) developed across the gel layer of the membrane between the two liquids.

WORKING

Consider, $C_2 > C_1$

The boundary potential is given by Nernst equation at membrane $E_b = E_2 - E_1$

$$E_b = \frac{2.303RT}{nF} \log C_2 - \frac{2.303RT}{nF} \log C_1$$

Therefore $E_b = 0.0591 \log C_2 - 0.0591 \log C_1$

$E_b = K + 0.0591 \log C_2$ where $K = -0.0591 \log C_1$

$E_b = K - 0.0591 \text{pH}$

Since $\text{pH} = -\log [H^+]$

The glass electrode E_G has 3 three components

1. Boundary Potential E_b
2. Potential of the internal reference electrode $E_{Ag|AgCl}$
3. Asymmetric Potential E_{asy}

Therefore, $E_G = E_b + E_{Ag|AgCl} + E_{asy}$

$E_G = K - 0.0591 \text{pH} + E_{Ag|AgCl} + E_{asy}$

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

Advantages

1. This electrode can be used to determine pH in the range 0 – 9, with special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

Limitations

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the pH above 12

Applications of Glass electrode:

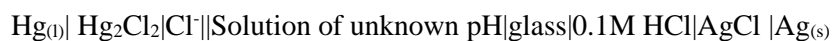
- pH measurement.
- Food Analysis.
- Cosmetic analysis.
- Environmental regulations.
- Soil acidity determination.

Determination of pH using glass electrode:



Principle: When a thin glass membrane is placed between two solutions of different pH values, a potential difference arises across the membrane. The potential difference varies as the pH of these solutions varies. In practice, pH of one of these solutions is kept constant and therefore the electrode potential depends on pH of the other solution i.e. experimental solution.

Procedure: glass electrode is immersed in the solution; the pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as,



The emf of the above cell, E_{cell} is measured using an electronic voltmeter with a pH meter.

The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \dots\dots\dots 1$$

$$E_{\text{cell}} = E_G - E_{\text{SCE}} \quad \dots\dots\dots 2$$

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

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

$$\text{pH} = \frac{E_G^0 - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}$$

Concentration Cells

A concentration cell is an electrochemical cell in which the electrode material and the solution in both the electrodes are composed of the same substances but only the concentration of the two solutions is different”

A typical example of Zinc concentration cell is shown below

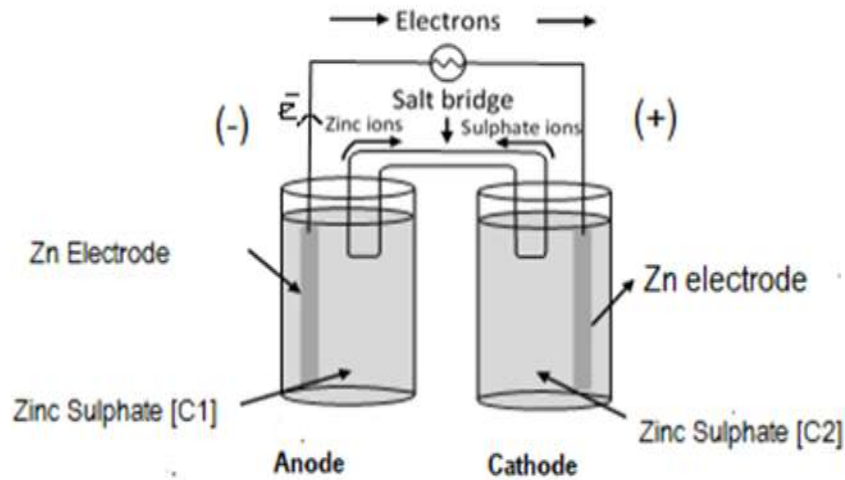
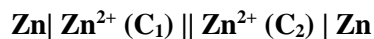
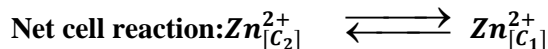
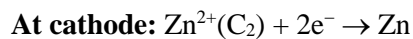
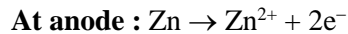


Fig: 3.16 Concentration Cell

It consists of two zinc electrodes are immersed in two different concentrations of ZnSO_4 solutions. These two electrodes are externally connected by metallic wire and internally by a salt bridge as shown in Fig:7. The cell can be represented as,



By convention left hand electrode is the anode and right hand electrode is cathode.



The net cell reaction is merely the change in concentration as a result of current flow.

EMF of Concentration Cell

We know that electrode potential depends upon the concentration of the electrolyte. By convention, the potential of the cell is

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \dots (1)$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log[\text{C}_2] - \frac{0.0591}{n} \log[\text{C}_1] \quad \dots (2)$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[\text{C}_2]}{[\text{C}_1]} \text{ at } 298 \text{ K} \quad \dots (3)$$

From equation (3) following conclusions may be drawn.

1. When the two solutions are of the same concentration, then $\log \frac{[C_2]}{[C_1]}$ and no electricity flows.
2. Hence, $E_{\text{cell}}=0$
3. When $C_2 | C_1 > 1$ i.e., $C_2 > C_1$, $\log C_2 | C_1$ is positive & electrode potential is positive.
4. Higher the ratio of $C_2 | C_1$, higher is the value of cell potential.

Numerical Problems

1. Calculate the emf of Copper concentration cell at 25 °C, where the copper ions ratio in the cell is 10.

Solution

Given: $\frac{[Cu^{+2}]_{\text{cathode}}}{[Cu^{+2}]_{\text{anode}}} = \frac{C_2}{C_1} = 10$

w.k.t $E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$; at 298 K

$$E_{\text{cell}} = \frac{0.0591}{2} \log(10)$$

$$E_{\text{cell}} = 0.0296 \text{ V}$$

2. A concentration cell was constructed by immersing two silver electrode in 0.05 M and 1 M $AgNO_3$ solution. Write the cell representation, cell reactions and calculate the EMF of the cell. **(July-06)**

Solution

Cell representation: $Ag(s) | AgNO_3 (0.05 \text{ M}) || AgNO_3 (1 \text{ M}) | Ag(s)$

At anode: $Ag (0.05 \text{ M}) \rightarrow Ag^+ (0.05 \text{ M}) + e^-$

At cathode: $Ag^+ (1 \text{ M}) + e^- \rightarrow Ag (1 \text{ M})$

Net cell reaction: $Ag (0.05 \text{ M}) + Ag^+ \rightarrow Ag^+ (0.05 \text{ M}) + Ag$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{1}{0.05} \right)$$

$$E_{\text{cell}} = 0.0768 \text{ V}$$

3. The spontaneous galvanic cell $Tin | Tin \text{ ion } (0.024 \text{ M}) || Tin \text{ ion } (0.064 \text{ M}) | Tin$ develop an emf of 0.0126 V at 25 °C, Calculate the Valency of Tin **(Jan-06)**

Solution

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$$

$$n = \frac{0.0591}{E_{\text{cell}}} \log \left(\frac{C_2}{C_1} \right)$$

$$n = \frac{0.0591}{0.0126} \log \left(\frac{0.064}{0.024} \right)$$

$$n = 2 \text{ (Valency of tin)}$$

4. Calculate the concentration of the unknown, given the equation below and a cell potential of 0.26 V and cell $\text{Ag} | \text{Ag}^+ (x \text{ M}) || \text{Ag}^+ (1.0 \text{ M}) | \text{Ag}$

Solution

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$$

$$0.26 = \frac{0.0591}{1} \log \frac{1.0}{x}$$

$$4.362 = -\log (1.0) + \log(x)$$

$$x = 4.341 \times 10^{-5} \text{ M}$$

5. The emf of a cell $\text{Ag}/\text{AgNO}_3 (0.02\text{M})//\text{AgNO}_3(\text{X})/\text{Ag}$ found to be 0.084V at 298 K. Write the cell reactions and calculate the value of X.

Solution:

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \left(\frac{X}{0.02} \right)$$

$$\text{Log} \left[\frac{X}{0.02} \right] = \frac{E_{\text{cell}} \times n}{0.0591}$$

$$\frac{X}{0.02} = \text{Antilog} \frac{E_{\text{cell}} \times n}{0.0591} \quad \frac{X}{0.02} = \text{Antilog} \frac{0.084 \times 1}{0.0591}$$

$$\frac{X}{0.02} = \text{Antilog} (1.421)$$

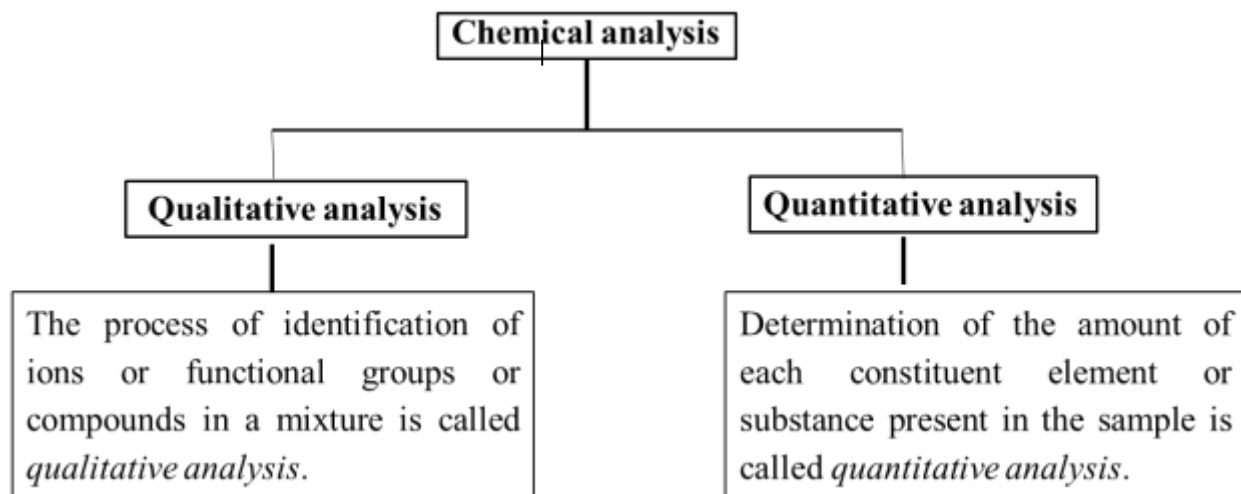
$$\frac{X}{0.02} = 26.36$$

$$\boxed{X = 0.5272 \text{ M}}$$

ANALYTICAL TECHNIQUES

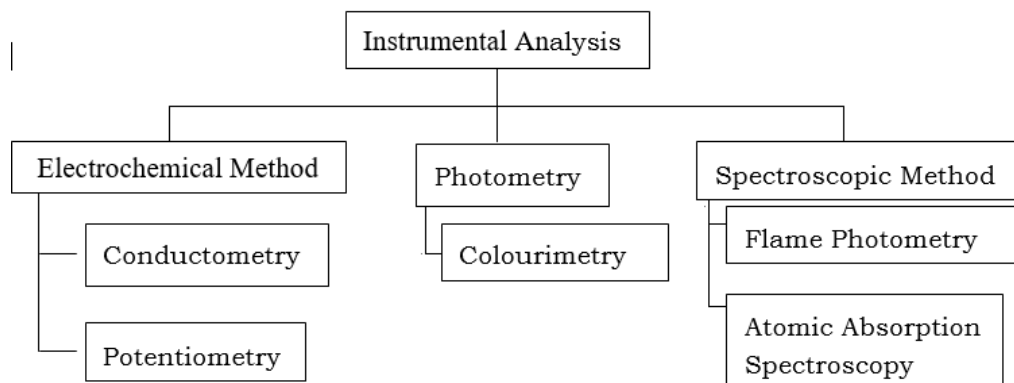
Introduction

The study of the chemical composition and structure of substances is known as chemical analysis. Chemical analysis deals with method of identification, quantification and determination of molecular structure of a substance. Two types of chemical analysis,



Advantages of instrumental methods:-

1. Milligram or microgram quantity of analyte is sufficient for analysis.
2. Very dilute solutions can be titrated and results are accurate.
3. Use of additional reagents and indicator are avoided.
4. Complex mixture can be analyzed either with or without their separation.
5. Sufficient reliability and accuracy of results are obtained by instrumental method.
6. Personal errors are avoided as the results are obtained from the graph.



a Conductometric Titration

The electrochemical method of analysis used for the determination of the electrical conductance of an electrolyte solution by means of a conductometer.

Theory

The conductance of the solution is explained by considering ohm's law. According to ohm's law the current flowing through the conductor is directly proportional to voltage and inversely proportional to the resistance.

$$E = I R$$

The resistance of the conductor is directly proportional to the length and inversely proportional to the area of cross section.

Specific conductance is also called conductivity.

$$\text{Further, } \rho = \frac{A \times R}{l}$$

$$\Rightarrow \frac{1}{\rho} = \frac{l}{A} \times \frac{1}{R}$$

$$\Rightarrow \kappa = \frac{1}{A} \times C$$

Or Specific conductance = Conductance \times cell constant

Specific conductance is defined as the conductance of a solution enclosed in a cell having two electrodes of unit area separated by one centimeter apart. The conductance of the solution depends on mobility of the ions and number of the ions present in the solution.

Unit of specific conductance: **$\text{Ohm}^{-1} \text{cm}^{-1}$**

Types of conductance: Conductance is classified into three types, i.e., specific conductance, equivalence conductance and molar conductance.

Equivalence conductance (λ_{eq}): is the conductance of the solution when 1g equivalent weight of solution is placed between two electrodes of area 1cm^2 at 1cm apart.

Molar conductance (λ): is the conductance of the solution when 1g molecular weight of solute is placed between two electrodes of area 1cm^2 at 1cm apart.

$$\lambda = 1000\kappa/c$$

κ = specific conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)

C = molar concentration (moles/cm^3)

The unit of molar conductance is **$\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$**

Principle: Conductometric titrations are based on the measurement of conductance of solution, which is mainly depends on number of ions, charge on the ions and mobility of the ions. During the titration fast moving ions are replaced by slow moving ions and alter the conductance of a solution. Conductance values upon addition of titrant vs volume of titrant are plotted and equivalence point is obtained from the graph.

Instrumentation:

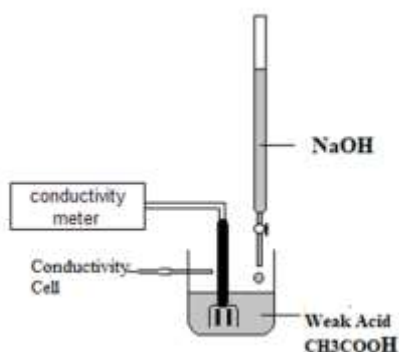


Fig:3.17 Instrumentation of Conductometry

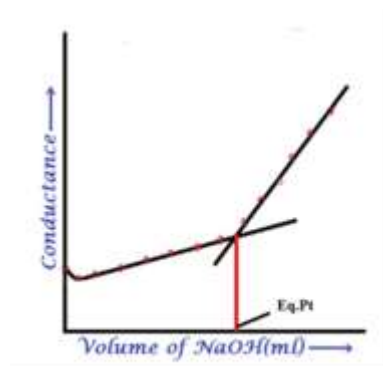


Fig:3.18 Graph of weak acid Vs strong base

Applications of conductometric titration: Estimation of weak acid

Since the acid is weak, its conductivity is relatively low. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions.

In the above graph, point (B) represents the equivalent point or the neutralization point.

b Potentiometric Titration

Potentiometric titrations involve the measurement of the potential of a suitable indicator electrode with respect to a reference electrode as a function of titrant volume. Potentiometry is usually employed to find the concentration of a solute in solution.

Potentiometry is the field of electro analytical chemistry in which potential is measured under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the analytic solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied. These methods rely on the measurement of E_{cell} for quantification.

Principle: Redox titrations can be carried out potentiometrically using platinum and calomel electrode combination in a manner similar to acid-base titrations.

For the reaction; Reduced form \rightarrow Oxidised form + n electrons

The potential is given by Nernst equation

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Where, E° is the standard electrode potential of the system. The potential of the system is controlled by the ratio of concentration of the oxidized to that of the reduced species. A plot of change in potential against volume is characterized by a sudden change of potential at the equivalent point. At the end point, potential is determined by large jump in the potential value. Hence there is large increase in potential at the end point.

Instrumentation:

Procedure: 25.0 cm³ of FAS was Pipetted out into a clean beaker and 5.0cm³ of dilute sulphuric acid was added, and the platinum-calomel electrode assembly was immersed into the beaker containing the test

solution. The electrodes are connected to potentiometer and initial potential was recorded without the

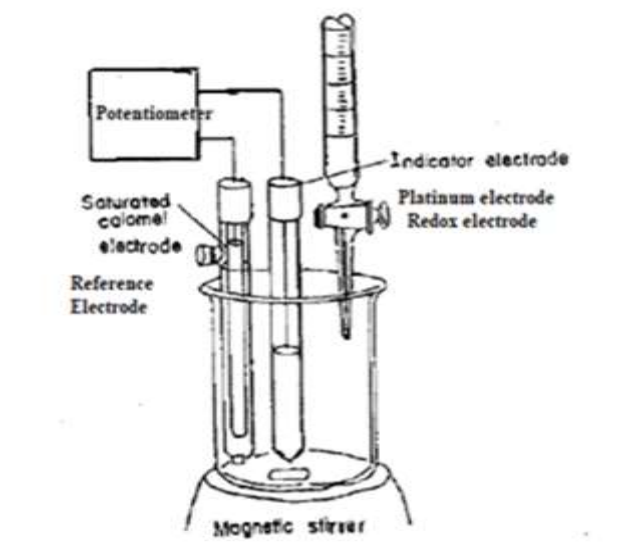


Fig: 3.19 Instrumentation of Potentiometry

addition of $K_2Cr_2O_7$. $K_2Cr_2O_7$ was added in the increments of 0.25 ml from the semi micro burette and corresponding emf was recorded. This process was continued till there was a sudden rise in the potential and additional five more readings were recorded after sudden rise in potential. A graph was plotted by taking $\frac{\Delta E}{\Delta V}$ along y-axis and volume of $K_2Cr_2O_7$ along X-axis. Amount of FAS was calculated using equivalent point.

Vol. of $K_2Cr_2O_7$ (V) ml	Emf E (mv)	ΔV ($V_2 - V_1$) ml	ΔE ($E_2 - E_1$)	$\Delta E / \Delta V$ (mv/ml)

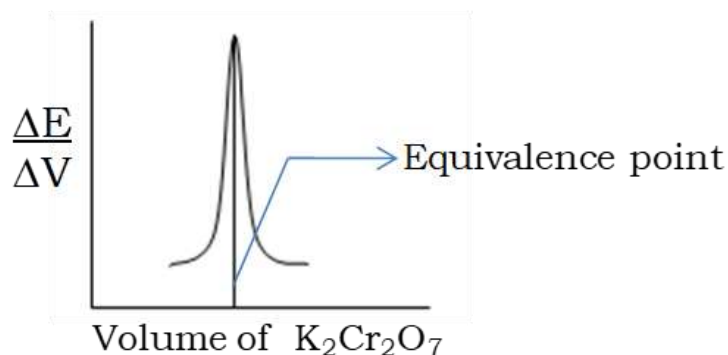


Fig:3. 20 Graph of potentiometry

$$N_{\text{FAS}} = \frac{(NV)_{\text{K}_2\text{Cr}_2\text{O}_7}}{V_{\text{FAS}}}$$

Amount of FAS per liter = $N_{\text{FAS}} \times \text{Eq. Wt. of FAS (392)}$

=g (say 'a')

392 g of FAS contains 55.85 g Fe

a g of FAS contains $\frac{55.85 \times a}{392} = \dots\dots\dots g$ of Iron

b Advantages of Potentiometric titration

- i) The method is inexpensive.
- ii) The technique can be used for colored, turbid or fluorescent solution.
- iii) The technique can be used in the titration of mixture of acids or mixture of bases.
- iv) It provides very accurate results.

MODULE 4

POLYMERS AND GREEN FUELS

“A polymer is defined as a macromolecule formed by the repeated combination of several simple molecules (Monomers) through covalent bonds”

Example: Polyethylene, nylon, PVC, Teflon, polyester, bakelite, etc.

Monomers

The word monomer comes from mono-(one) and -mer (part). Monomer is defined as a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecules to form the macromolecule.

Examples: Alkenes, vinyl chloride, adipic acid, and glycol with two bonding sites act as monomers.

CH₃OH has one functional group and one functionality (Not a true monomer)

CH₂=CH₂ has one functional group and two functionalities (A true monomer)

HO-CH₂-CH₂-OH has two functional groups and two functionalities (A true monomer)

Polymerization, any process in which relatively small molecules, called monomers, combine chemically to produce a very large chainlike or network molecule, called a polymer.

Degree of polymerization (DP): - The no of repeating units or monomer units in the chain of a polymer is called degree of polymerization (DP). The molecular weight of an addition polymer is the product of the molecular weight of the repeating unit and the degree of polymerization (DP).

$$DP = \frac{\text{Molecular weight of the polymer}}{\text{Molecular weight of the monomer}}$$

Molecular weight of a Polymer

“Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer”

Different molecular weights

1. Number – average molecular mass (\bar{M}_n)
2. Weight average molecular weight (\bar{M}_w)

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni}$$

Weight – average molecular mass: (\overline{Mw})

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \dots}{N_1M_1 + N_2M_2 + N_3M_3 + \dots}$$

$$\overline{Mw} = \frac{\sum Ni Mi^2}{\sum Ni Mi}$$

Poly Dispersity index [PDI]: Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

$$PDI = \frac{\overline{Mw}}{\overline{Mn}}$$

If PDI = 1 polymer is mono disperse & Homogeneous.

PDI > 1 polymer is poly disperse & less Homogeneous.

Example 1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 250 molecules have molecular mass 10^4 g/mol, and 300 molecules have molecular mass 10^5 g/mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

Solution:

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	$N_1 = 100$	$M_1 = 10^3$
2	$N_2 = 250$	$M_2 = 10^4$
3	$N_3 = 300$	$M_3 = 10^5$

Number average molecular mass (\overline{Mn}) is given by:

$$\overline{Mn} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\overline{Mn} = \frac{100 \times 10^3 + 250 \times 10^4 + 300 \times 10^5}{100 + 250 + 300} = 50153 \text{ g/l}$$

Weight average molecular mass (\overline{Mw}) is given by:

$$\overline{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \dots}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}$$

$$\overline{M}_w = \frac{100*(10^3)*(10^3) + 250*(10^4)*(10^4) + 300*(10^5)*(10^5)}{100*10^3 + 250*10^4 + 300*10^5} = 92794 \text{ g/l}$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{92794}{50153} = 1.85$$

PDI > 1, the given polymer is less homogeneous and poly disperse in nature.

2. A polymer sample contains 1, 2, 3 and 4 molecules having molecular weights 10^5 , $2*10^5$, $3*10^5$ and $4*10^5$, respectively. Calculate the number average and weight average molecular weight of the polymer.

Solution:

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	$N_1 = 1$	$M_1 = 10^5$
2	$N_2 = 2$	$M_2 = 2*10^5$
3	$N_3 = 3$	$M_3 = 3*10^5$
4	$N_4 = 4$	$M_4 = 4*10^5$

Number average molecular mass (\overline{M}_n) is given by:

$$\overline{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + N_4 M_4}{N_1 + N_2 + N_3 + N_4}$$

$$\overline{M}_n = \frac{1*(1*10^5) + 2*(2*10^5) + 3*(3*10^5) + 4*(4*10^5)}{1+2+3+4}$$

$$\overline{M}_n = \frac{30*10^5}{10} \quad \boxed{\overline{M}_n = 3.0 * 10^5 \text{ g/L}}$$

$$\overline{M}_w = \frac{(1*10^5)*(1*10^5) + 2*(2*10^5)*(2*10^5) + 3*(3*10^5)*(3*10^5) + 4*(4*10^5)*(4*10^5)}{1*(1*10^5) + 2*(2*10^5) + 3*(3*10^5) + 4*(4*10^5)}$$

$$\bar{M}_w = \frac{(1+8+27+64) * 10^{10}}{(1+4+9+16) * 10^5}$$

$$\bar{M}_w = 3.3 * 10^5 \text{ g/L}$$

3 . In a sample of a polymer, 20% molecules have molecular mass 15000 g/mol, 35% molecules have molecular mass 25000 g/mol, and remaining molecules have molecular mass 20000 g/mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

Solution. It is given that,

$N_1 = 20$ & $M_1 = 15000 \text{ g/mol}$,

$N_2 = 35$ & $M_2 = 25000 \text{ g/mol}$,

$N_3 = 45$ & $M_3 = 20000 \text{ g/mol}$.

The number average molecular mass of the polymer is given by

$$\begin{aligned} \bar{M}_n &= \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\ &= \frac{20 \times 15000 + 35 \times 25000 + 45 \times 20000}{20 + 35 + 45} = 20750 \text{ g/mol} \end{aligned}$$

The weight average molecular mass of the polymer is given by

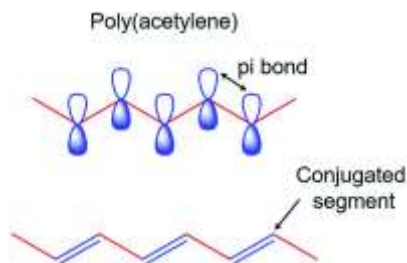
$$\begin{aligned} \bar{M}_w &= \frac{\sum N_i M_i^2}{\sum N_i M_i} \\ \bar{M}_w &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\ \bar{M}_w &= \frac{20 \times (15000)^2 + 35 \times (25000)^2 + 45 \times (20000)^2}{20 \times 15000 + 35 \times 25000 + 45 \times 20000} = 21385 \text{ g/mol} \end{aligned}$$

$$\text{Poly dispersity index, PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{21385}{20750} = 1.03$$

$\text{PDI} > 1$, the given polymer is less homogeneous and

Conducting polymers

Conductive polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π -bonds.

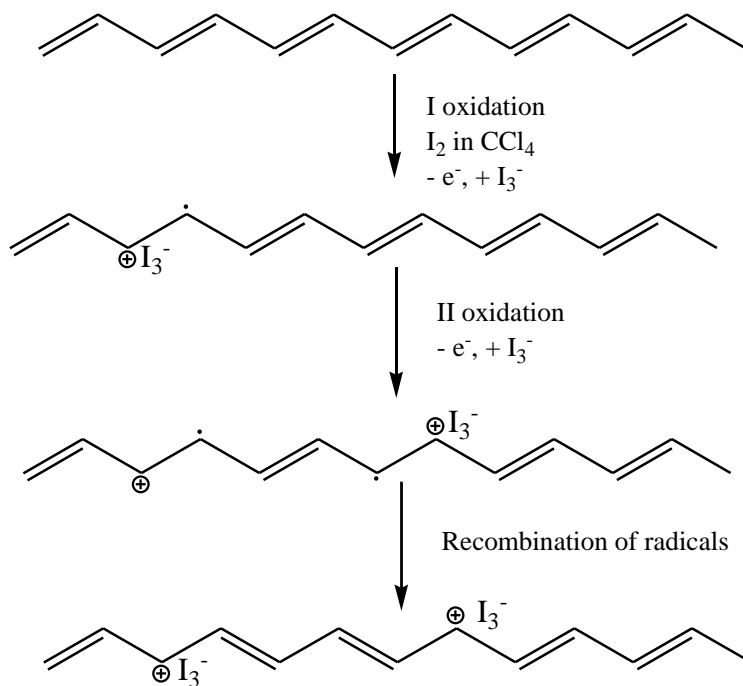


The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-back bone. The important doping reactions are;

1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping)

1. Oxidative doping (p-doping):

In this process, an appropriate oxidizing agent is added to bring partial oxidation of polymer pi-backbone. Thus, positively charged sites are generated on the polymer backbone and facilitates the movement of charge carriers in the chain. Most commonly used oxidative doping or p-doping agents are iodine vapor, iodine in CCl_4 , HBF_4 , perchloric acid and benzoquinone.



Reactions of p- doping of polyacetylene

Mechanism of conduction:

- The removal of an electron from the polymer pi-back bone using a suitable oxidizing agents leads to the formation of delocalized radical ion called polaron.
- A second oxidation of a chain containing polaron followed by radical recombination yields two charge carriers on each chain.
- The positive charges sites on the polymer chains are compensated by anions I_3^- formed by the oxidizing agent during doping.
- The delocalized positive charges on the polymer chain are mobile, not the dopant anions.
- Thus, these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction.

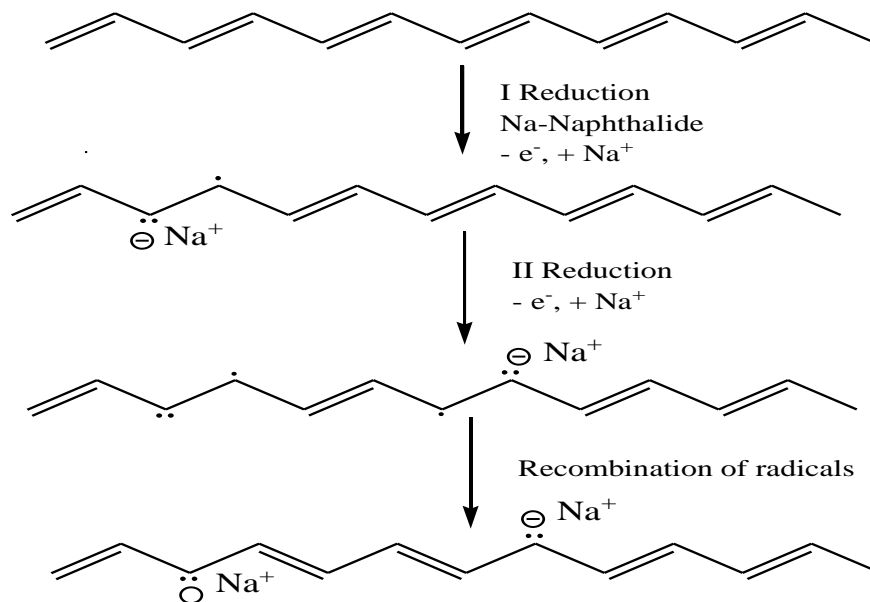
- On doping polyacetylene using iodine in CCl_4 , for partial oxidation, the conductivity increases from $10^{-5} \text{ S.cm}^{-1}$ to $10^3\text{-}10^5 \text{ S.cm}^{-1}$.

2. Reductive doping (n-doping):

In reductive doping technique, pi-backbone of a polymer is partially reduced by a suitable reducing agent. This facilitates the formation of negative charged sites on the pi-backbone and are responsible for conduction. The most commonly used reducing agents are: sodium naphthalide in tetrahydrofuran.

Mechanism of conduction:

- The addition of an electron to the polymer back bone by using a reducing agent generates a radical ion polaron.
- A second reduction of chain containing polaron, followed by the recombination of radicals yields two charged (-ve) carriers on each chain.
- These charge sites on the polymer chains are compensated by cations (Na^+ ions) formed by the reducing agent.



Reactions of n- doping of polyacetylene

Applications of Polyacetylene

- Doped polyacetylene offers a particularly high electrical conductivity therefore it can be used in electric wiring or electrode material in lightweight rechargeable batteries.
- Tri-iodide oxidized polyacetylene can be used as a sensor to measure glucose concentration.

Graphene Oxide

Graphene oxide(GO) is a product of graphene obtained by oxidizing graphene. It has a single monomolecular layer containing oxygen functionalities such as carboxyl, carbonyl, epoxide, or

hydroxyl groups. These added functionalities expand the separation between the layers and make the material hydrophilic.

Preparation of graphene oxide by a hummer's method

1. Graphite flakes (2 g) and NaNO_3 (2 g) were mixed in 50 mL of H_2SO_4 (98%) in a 1000 mL volumetric flask kept under an ice bath ($0-5^\circ\text{C}$) with continuous stirring.

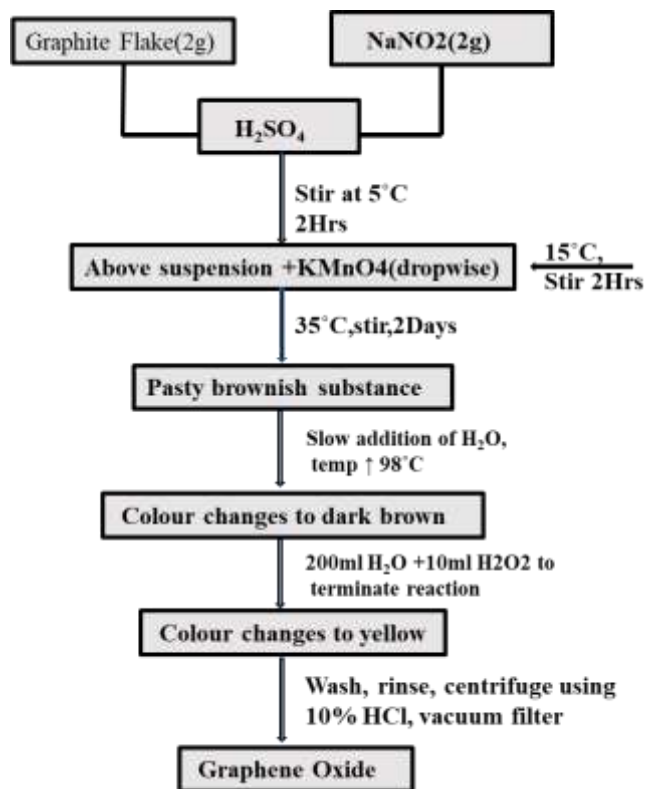
2. The mixture was stirred for 2 hrs, potassium permanganate (6 g) was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C .

3. The ice bath was then removed, and the mixture was stirred at 35°C until it became pasty brownish and kept under stirring for 2 days.

4. It is then diluted with slow addition of 100 mL water. The reaction temperature was rapidly increased to 98°C with effervescence, and the color changed to brown color.

5. Further this solution was diluted by adding additional 200 mL of water stirred continuously.

6. The solution is finally treated with 10 mL H_2O_2 to terminate the reaction by appearance of yellow color.



7. For purification, the mixture was washed by rinsing and centrifugation with 10% HCl and then deionized (DI) water several times.

8. After filtration and drying under vacuum at room temperature, the graphene oxide (GO) was obtained as a powder.

Structure of Graphene



Properties of Graphene Oxide

Monolayer GO (produced by a modified Hummer's method) with a Young's modulus of 207.6 ± 23.4 GPa, possess very good mechanical properties.

Graphene Oxide is hydrophilic, can easily disperse in organic solvents, water, and different matrixes. This is a major benefit when combining the material with polymer or ceramic matrixes to enhance their mechanical and electrical properties.

Graphene oxide functions as an electrical insulator, because of the disturbance of its sp^2 bonding networks. It is important to reduce the graphene oxide so as to recover the honeycomb hexagonal lattice of graphene, in order to restore electrical conductivity.

Applications of Graphene Oxide

Go has led to its emergence as a precursor for fabricating transparent conductive films (TFCs)

Functionalized GO can be used as fluorescence and photo luminescent means in cellular imaging.

Chemically-altered graphene oxide disperse easily in organic solvents makes the material better suited to production of bio devices and optoelectronics, and for use in drug delivery.

KEVLAR FIBER

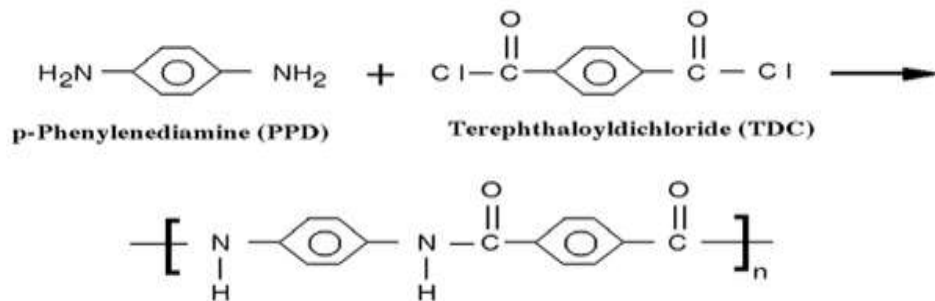
Polymer Composite: A polymer composite is a material made of two or more types of polymers with different physical and chemical properties that, when combined, produce a material with characteristics different from the individual components.

Polymer composites are usually made of two components, Fiber and Matrix

Synthesis, Properties and Applications of Kevlar Fibre:

Kevlar is a polyamide, in which all the amide groups are separated by para-phenylene groups. The Chemical composition of Kevlar is poly para phenylene terephthalamide.

Synthesis:



Kevlar is fiber embedded in an epoxy resin polymer matrix is called Polymer Composite.

Properties of Kevlar

1. Kevlar is crystalline, lightweight and non-flammable
2. Resistant to heat, impact, scratch
3. Withstands harsh environmental conditions
4. Abrasion and corrosion resistant
5. High tensile strength
6. Resistant to Chemicals

Applications

1. It is used in lightweight boat hulls. Aircraft panels, Racecars
2. Bulletproof vests and combat helmets
3. Reinforce material for car tires, bicycle tires, which reduces puncture rate
4. Marine current turbine and wind turbine
5. Ropes and cables
6. Fiber-optic cables for communication, data transmission and ignition

Green Fuels

Green fuel provides real benefits for the environment since the power comes from natural resources such as sunlight, wind and water. Green hydrogen is effectively produced from energy sources that are renewable in nature and also maintains the process of electrolysis by effectively splitting water.

Advantages of green fuel:

The usage of green fuels has successively reduced the emission of greenhouse gasses by around 30 per cent of the combustion rate.

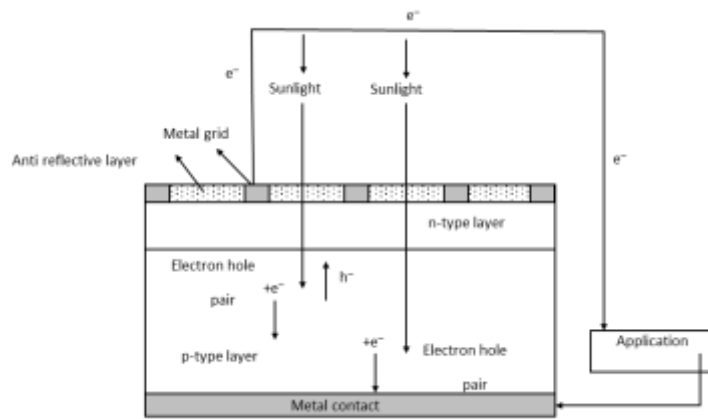
A proper balance is maintained by effectively focusing on fuel sensitivity with respect to the environment.

Furthermore, it is also noted that the application of green energy is responsible for producing more energy referred to as “energy bounce”

Photovoltaic Cells:

Photovoltaic cells are semiconductor device which convert solar energy into electrical energy. (Photovoltaic cell is based on the principle of photoelectric effect).

Construction and working of photovoltaic cells



A typical silicon photovoltaic cell is composed of a thin polycrystalline silicon wafer consisting of an ultra-thin layer of phosphorus doped (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction is formed. A metallic grid forms one of the electrical current contacts of the diode and allows light to fall on the semiconductor between the grid lines as shown in Fig. An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contact is formed by a metallic layer on the back of the solar cell.

PV cell works on the principle of photoelectric effect $E=hf$. When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced.

Applications:

PV can meet the need for electricity for parking meters, temporary traffic signs, emergency phones, radio transmitters, water irrigation pumps, stream-flow gauges, remote guard posts, lighting for roadways, and more.

Advantages of PV cells:

Fuel source is vast and infinite.

No emissions, no combustion or radioactive residues for disposal.

Does not contribute to global warming or pollution.

Low operating cost and high reliability.

No moving parts and so no wear and tear.

No recharging is required.

They do not corrode.

Disadvantages of PV cells:

Sunlight is relatively low density energy.

High installation cost.

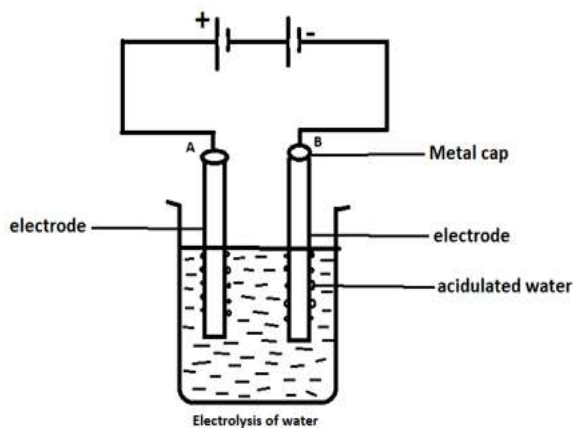
Energy can be produced only during daytime.

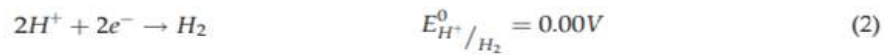
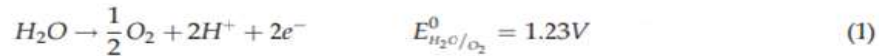
Generation of energy (green hydrogen) by electrolysis of water and its advantages

Green hydrogen is defined as hydrogen produced by splitting water into hydrogen and oxygen using renewable electricity.

Principle of water electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy. Typically, a water electrolysis unit consists of an anode, a cathode separated with an electrolyte, and a power supply. The electrolyte can be made of an aqueous solution containing ions, a proton exchange membrane (PEM) or an oxygen ion exchange ceramic membrane. A direct current (DC) is applied from the negative terminal of the DC source to the cathode (seat of the reduction reaction), where the hydrogen is produced. At the anode, the electrons produced by the electrochemical reaction return to the positive terminal of the DC source. For the case of water electrolysis in an acid aqueous electrolyte, the processes that occur at the anode and the cathode are described, respectively, by Eqs. 1 and 2:

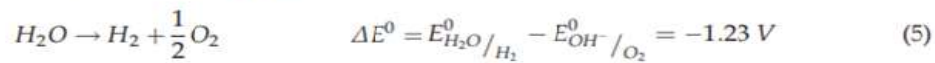




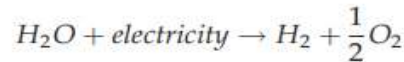
The half reactions occurring on the cathode and anode, respectively, can be written as:



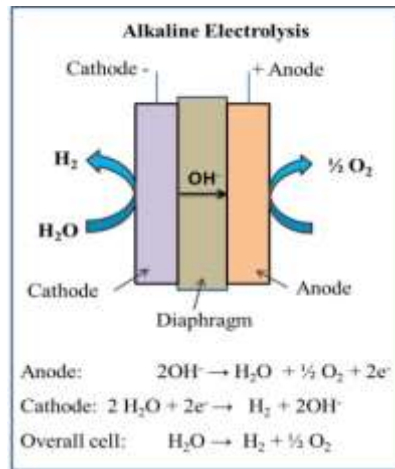
The global reaction for the two cases is:



Electrolysis of water is not a spontaneous phenomenon because the standard global reaction potential is negative. Therefore, it needs an external intervention (power source) and the global reaction can be written as:



Alkaline electrolysis



The conductivity of the solution is enhanced by the use of strong electrolytes that deliver ions with high mobility, such as sodium, potassium for positive ions, and hydroxide or chlorides as negative ions. During electrolysis, the water molecules move to the cathode by diffusion as they are consumed, and the hydroxide ions move to the anode by migration because they have an opposite charge and diffusion because they are consumed. A diaphragm separates the two anode and cathode compartments and the gases formed are thus collected: hydrogen at the cathode and oxygen at the anode as shown in Figure

Alkaline electrolysis operates at lower temperatures such as 30–80 °C with aqueous solution (KOH/NaOH) as the electrolyte, the concentration of the electrolyte is ~20% to 30%.

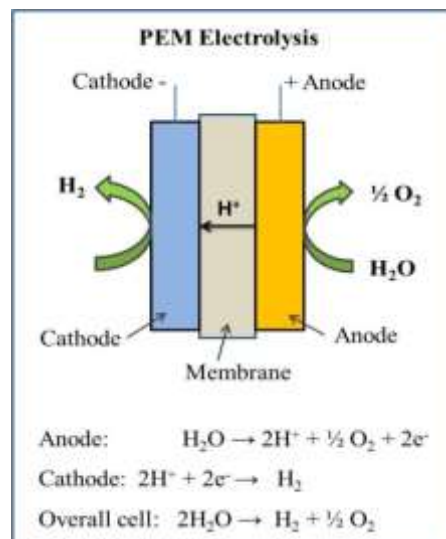
In alkaline water electrolysis process, asbestos diaphragm and nickel materials are used as the electrodes.

The diaphragm having in the middle of the cell and it separates the cathode and anode also separates the produced gases from their respective electrodes and avoiding the mixing of produced gases electrolysis process.

Limitations:

- limited current densities (below 400 mA/cm²),
- low operating pressure and
- low energy efficiency

PEM electrolyzer (Polymer electrolyte Membrane)



(Polysulfonated membranes was used as a electrolyte or Proton Exchange Membrane)

PEM electrolyzers are characterized by their very simple construction and their compactness. The operating principle of electrolysis of water with an electrolyte protons exchange membrane (PEM) is simple. When operating in electrolysis, the water decomposes at the anode into protons and molecular oxygen. The oxygen is evacuated by the water circulation, and the protons migrate to the cathode under the effect of the electric field. There, they are reduced to molecular H_2

These proton exchange membranes having many advantages such as

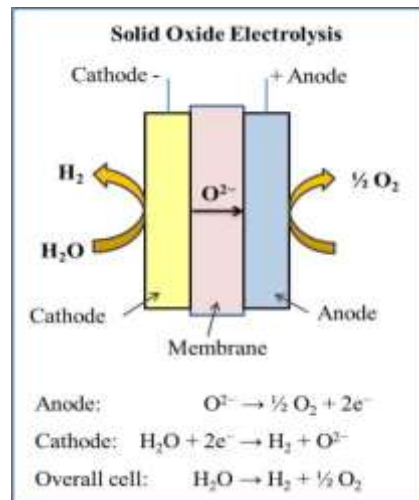
- Lower gas permeability,

- High proton conductivity
- Lower thickness ($\Sigma 20\text{--}300\ \mu\text{m}$)
- High-pressure operations.

Limitations

- Cost of electrodes is too high
- Maintenance cost is high

Solid oxide electrolyzer



Solid oxide electrolysis operates at high pressure and high temperatures 500–850 °C and utilizes the water in the form of steam. Solid oxide electrolysis process conventionally uses the O²⁻ conductors which are mostly from nickel/yttria stabilized zirconia

Solid oxide electrolyzers, which use a solid ceramic material as the electrolyte (YSZ) that selectively conducts negatively charged oxygen ions (O²⁻) at elevated temperatures, generate hydrogen in a slightly different way.

- Steam at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions.
- The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

The main characteristics of solid oxide electrolysis (SOE) technology is higher operating temperature which makes advantageous compared to low temperature electrolysis.

Limitation:

SOE having some issues related to lack of stability and degradation

The advantages of using hydrogen as a fuel in fuel cells are:

- It has high electrochemical reactivity,
- It has high theoretical energy density,
- Unlimited availability (as long as you can break down the water),
- It produces harmless combustion product (H_2O) for the environment.

Disadvantages

It has low density under normal conditions, the difficulty of storage, and the risk of explosion can summarize the major drawbacks of the use of pure hydrogen in fuel cells.

Sources of e-Waste

A generic word E-waste is globally used for waste created this waste stream. It has been defined as **“E-waste is any electrical or electronic equipment that’s been discarded”**.

Major Sources of E-Waste is comprised of

- a) Large Household appliances such as Refrigerator, Freezers, Microwaves, Electric heating appliances, Electric radiators and conditioning equipment. CD players, TVs, radios, drillers. , air-conditioner, grinder, iron, heater, military and laboratory electronic equipment’s, etc.
- b) Informal communications and technology equipment such as Computers, Laptops, Computer accessories, Printers, Copying equipment. Fax machines, photocopiers, printers, toners, ink cartridges, batteries, re-chargeable batteries, digital calculators and clocks, CRT monitors, electric solders, computer mother boards, key board. Televisions, Mobiles, Ipods etc
- c) Consumer electronics include Toasters, Coffee machines, Clocks, Watches, Hair dryer, Sharvers.

Constituents of e-waste

COMPONENTS	CONSTITUENTS
Printed circuit boards	Lead & cadmium
Cathode ray tubes (CRTs)	Lead oxide & Cadmium
Switches & flat screen monitors	Mercury
Computer batteries	Cadmium
Capacitors and transformers	Poly Chlorinated Bi-phenyls (PCB)
Printed circuit boards, plastic	Brominated Flame Retardant casings cable
Cable insulation/coating	Poly Vinyl Chloride (PVC)

Characteristics of e-waste

E-waste contains both hazardous and non-hazardous substances in their components.

- a) Partly hazardous: e-waste contains different substances, some of which can pose serious risk due to wrong handling. Substances like plastic, lead, cadmium, bismuth and arsenic pose health hazards on humankind. The people engaged in the recycling and recovery from the e-waste is severely affected with chronic and acute diseases like cancer etc. The presence of heavy metals in e-waste made it indifferent to the municipal biodegradable waste as they not only hamper the bio-degradation process but harms the human health and environment also. These, heavy metals enters in to food chain and causes Bio-magnification.

b) Partly valuable: Mother boards, PCB's and connectors which are coated with gold and other noble metals are valuable, which can be recycled. A significant amount of valuable materials contained in waste printed circuit boards make them worth being recycled. Below listed table gives the information n valuable metals that can be recycled and extracted from waste motherboards and printed circuit boards. The precious metals gold, Palladium and Silver make up more than 70% of the value of PCB that could be recovered.

Need for e-waste management concerning global perspective

The new challenge of e-waste management system is to shift the paradigm for a toxic pollution source to available resource in the context of sustainable development. Waste hierarchy concept focuses on waste prevention and 3R policy (reduce, reuse and recycle) and give less attention to landfill.

Following are the challenges for E-waste management:

1. Lack of awareness and financial incentives
2. Less information on E-waste generation rates
3. Mismanagement in end of life products
4. Environmentally unsustainable informal sector practices
5. Inadequate regulatory design and enforcement

Consequently, they bear the greatest burden of adverse health hazards and ecosystem degradation, prolonging their achievement of sustainable development goals.

The Negative effect on human health

E-Waste is much more hazardous than many other municipal wastes because electronic gadgets contain thousands of components made of deadly chemicals and metals like lead, cadmium, chromium, mercury, polyvinyl chlorides (PVC), brominated flame retardants, beryllium, antimony and phthalates. Long-term exposure to these substances damages the nervous systems, kidneys, bones, reproductive and endocrine systems. Some of them are carcinogenic and neurotoxic.

The Negative Effects on Air

Contamination in the air occurs when e-waste is informally disposed by dismantling, shredding or melting the materials, releasing dust particles or toxins, such as dioxins, into the environment that cause air pollution and damage respiratory health.

The Negative Effects on Soil

When improper disposal of e-waste in regular landfills, the heavy metals and flame retardants can seep directly from the e-waste into the soil, causing contamination of groundwater or contamination of crops that may be planted nearby. When the soil is contaminated by heavy metals,

the crops become vulnerable to absorbing these toxins, which can cause many illnesses and doesn't allow the farmland to be as productive as possible.

The Negative effect on water bodies

The heavy metals from e-waste, such as mercury, lithium, lead and barium, then leak through the earth and reach groundwater. When these heavy metals reach groundwater, they eventually make their way into ponds, streams, rivers and lakes. The pH of the water bodies changes due to the presence of these heavy metals and affect the pond-eco system.

The infrastructure to deal with abundant e-waste in the developing countries is insufficient in terms of technology, techniques is the root cause of concern as more than 90% e-waste is treated with rudimentary and primitive techniques adopted by informal agencies. The presence of these pollutants in the atmosphere creates various kinds of diseases. To prevent the human being and environment from contamination of these pollutants, it is desirable to manage e-waste scientifically and to follow reuse and recycle methodologies.

Toxic materials used in manufacturing electronic and electrical products; health hazards due to exposure to e-waste.

Electrical and electronic equipment contain different hazardous materials which are harmful to human health and the environment if not disposed off carefully. While some naturally occurring substances are harmless in nature, their use in the manufacture of electronic equipment often results in compounds which are hazardous (Chromium becomes Chromium VI). The following list gives a selection of the mostly found toxic substances in e-waste.

Health hazards of e-waste

Solder: Solder contains lead that damages the nervous system, blood system, and kidney and also affect the development of brain in children.

Relays, Switches and Printed Circuit Boards

Mercury present in these elements leads to brain damage, disorders in the respiratory system and skin diseases.

Corrosion Protectors

Asthmatic bronchitis and DNA damage are caused due to the Hexavalent Chromium present.

Cabling and Computer Housing

When burn these produce dioxin, which causes problems of reproduction, destruction of the immune system, and regulatory hormones are damaged too.

Brominated Flame Retardants: BFRs increases contamination of the environment, wildlife, and people. These do not decompose easily in the environment, and long term exposure can cause impaired memory function and learning. Pregnant women exposed

to brominated flame retardants have been shown to give birth to babies with behavioral problems as it interferes with estrogen and thyroid functioning.

Arsenic: Arsenic is a poisonous metallic element which is present in dust and soluble substances. Chronic exposure to arsenic can lead to various diseases of skin and decrease nerve conduction velocity. Chronic exposure to arsenic can also cause lung cancer and can often be fatal.

Barium: Barium forms toxic oxides when reacted with air. Short term exposure to barium could lead to brain swelling, damage to heart, liver and spleen.

Beryllium: Exposure to Beryllium causes lung cancer. People working in beryllium atmosphere will suffer from Beryllicosis, a disease primarily affects lungs.

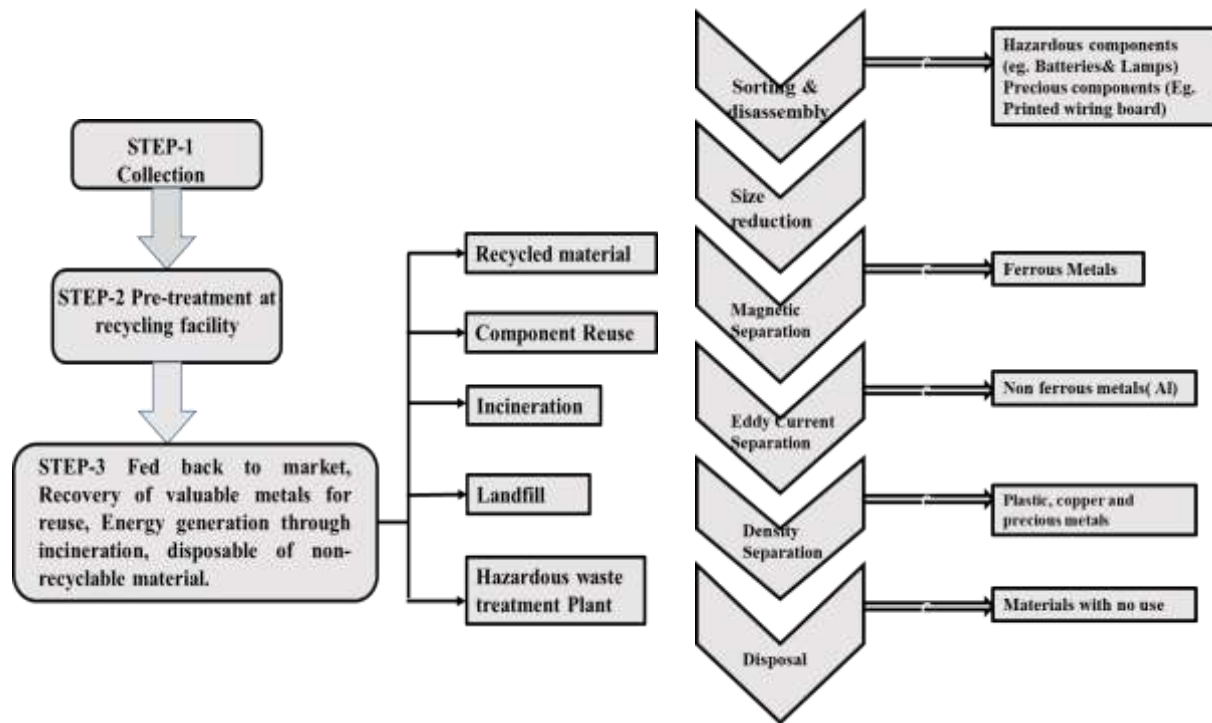
Cadmium: Cadmium can easily be accumulated in human body. Acute exposure to cadmium fumes causes flu-like symptoms of weakness, fever, headache, chills, sweating and muscular pain. Long exposure to Cadmium causes lung cancer and kidney damage. It also causes pulmonary emphysema and one disease(osteomalacia and osteoporosis)

Recycling and Recovery (Direct recycling)

The recycling of e-waste serves a lot of useful purposes. For instance, include protecting human and environmental health by keeping those devices out of landfills. Or recovering the parts within the devices that still have value, and providing manufacturers with recycled metals that can be used to make new products.

E-waste recycling is **the process of extracting valuable materials after shredding the e-waste into tiny pieces that could be reused in a new electronic appliance.**

After having reached the end of its life, the total recycling process of a product can be subdivided into three steps (Fig), each of which requires different management methods and technical approaches for its optimization.



STEP 1: The first step comprises the collection and consolidation of waste, the so-called take-back. For products containing more than about 250 ppm gold and 150 ppm palladium, separate collection is always more eco-efficient than mixing these products with others containing smaller amounts of precious metals.

STEP 2: In the second step, pretreatment of the electronic scrap is carried out by specialized recycling companies. In the pre-treatment phase, different technological processes are utilized for separating the integrated material content in the product so that different material fractions can be directed to the appropriate recycling processes.

- a) **Sorting & Disassembly:** Disassembly of complex electronic equipment is done only if either the equipment contains valuable parts which must not be diluted with less valuable ones and that will render profit when being separately recycled, like printed wiring boards, or it does contain hazardous materials that need to be separated for special hazardous waste treatment, such as mercury-containing lamps.
- b) **Shredding or size reduction:** The next phase in the pre-treatment process is typically size reduction by using shredders.
- c) **Magnetic separation:** The next steps in the process aim at separating ferrous metals, aluminum and plastic from the shredded material.
- d) **Eddy current separation:** Non-ferrous metals such as aluminium is extracted in this step.

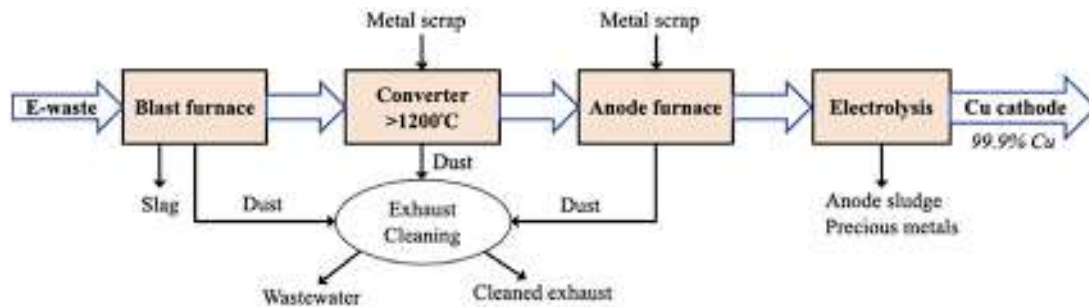
- e) Density separation: Lightweight materials such as plastic, copper and precious metals are extracted in this step. With regard to recovering the most precious material content, i.e. precious metals and copper, integrated copper smelters report high recovery yields of more than 95%.
- f) Disposal: Organic materials are utilized in this process as substitutes for coke as a reducing agent and as fuel (energy source). Iron and aluminum are transferred into the slag in the integrated copper smelting, and are thus not recovered as metals; rather, they are disposed of, e.g. in landfills.

STEP 3: In the third step, feeding back into the market, recycled materials are often mixed with materials coming from other sources. The third step will yield profit through the sale of material recovered from the recycling process for reuse in new products.

- a) Recycled Material: The material fractions separated by the pre-treatment which have the potential to be fed back into the market, i.e. for reuse in new products.
- b) Component reuse: Recycled products will be sold to the same companies which are producing those materials both from primary raw material sources and secondary sources resulting from recycling.
- c) Incineration (Thermal treatment): Non-recyclable material can be used for energy generation through incineration. Incineration of residual material for energy generation is typically a zero sum activity.
- d) Land fill: Non-recyclable material cannot be used for any purpose will finally be disposed of in landfills.
- e) Hazardous waste treatment Plant: Hazardous waste can be treated by chemical, thermal, and physical methods.

Pyrometallurgy is the predominantly used technology for industrial e-waste treatment. In industrial pyro metallurgical processes for e-waste recycling, the scrap is usually fed into furnaces, where the load is smelted via flash or bath smelting. Subsequently, the conversion process takes place. Because preprocessed e-waste is primarily made of Fe, Al, Cu, Pb, and PM, either copper or lead converters may be used during secondary treatment of WEEE. Scraps containing high contents of Cu follow the Cu smelting route.

Pyrometallurgy is the most traditional and commonly used route for metal separation and recovery.



Steps involved in the Pyrometallurgical e-waste management are incineration, smelting in plasma arc or blast furnaces, drossing, sintering, melting, and gas-phase reactions at high temperatures. Essentially, the electronic scraps, PCBs, etc., are first fed into a blast furnace, upgraded in a converter and anode furnace, and then electro-refined through electrolysis or electro winning for metal recovery.

Incineration: Samples of the printed circuit board were heated for 3 minutes at 840–850°C and at 6.2 vol.% of oxygen. Weight losses of the incinerated material were equal to approximately 21 wt.%. Product of incineration was a brittle substance, suitable for chemical and mechanical processing. It was pulverized below 0.2 mm and was leached with sulfuric acid with concentrations from 30 to 95%. With 95% concentration of sulfuric acid is possible to obtain almost complete leaching of copper (99.95%) and precious metals (e.g. 97% for Ag)

Smelting: The plasma arc or blast furnace is fed from the top. The air, enriched in oxygen up to 90 vol.%, is blown into the furnace also from the top. In the process, the melt is intensively mixed by the process gases – this mixing is essential for fast equilibration of the melt. Smelting is carried out at temperature of 1200°C (approximately.) Molten metal and slag are tapped from the furnace bottom. Precious metals are dissolved in molten copper. Further processing is typical for copper metallurgy: the copper is refined, electrolyzed and precious metals are recovered from anode slimes.

Drossing: The dross residues generated from melting of e-waste separation of metal can be re-processed to produce alum. Aluminium metal is recovered from alum by leaching.

Sintering: Extraction of the iron metal from the melt obtained from blast furnace. Here, a large quantity of loose aggregate material is subjected to a sufficiently high temperature and pressure to cause the loose materials to become compact solid piece. The temperature applied for the process is lesser than the melting point of the metal.

Gasification: Gasification, not pyrolysis, is the process that enables complete elimination of organic fractions to the gaseous phase at low oxygen potential of the system. Typical gasifying reagents are: steam, oxygen. This is method developed methods for metals recovery from electronic waste.

Electrolysis: The anode sludge contains valuable metal like copper can be obtained by electro refining process.

Disadvantages of Pyrometallurgy

- Risk of toxic material release and high concentration of dioxin formation
- Smelting is undesirable as it leads to the formation of slag and more industrial wastes
- Integrated smelters cannot recover Al and Fe, helps to recover only copper and Al and Fe becomes concentrated in the slag.
- Only partial separation of the metals is achieved, resulting in limited upgrading of metal value.
- Subsequent processing, such as electro refining, is thus needed for complete separation of metals.
- The ceramics and glass components in PCB (refractory) contribute to more slag formation and higher losses of precious and base metals from PCB.

Extraction of precious metals by Hydro metallurgy:

The hydrometallurgical process have been utilized for the recovery of metals from E-waste using acid or caustic leaching of selective dissolutions of the targeted metals from the solid E-waste. Then the solution with the targeted metal and a few impurities is refined further for concentrating the metal via solvent extraction, adsorption, or ion exchange processes. Finally, the metal is fully recovered through electro refining or through electrochemical reduction reactions to regain the solid metals from the E-waste.

Hydrometallurgical process involve a series of acid and caustic leaches of solid material.

1. Leaching:

Chemicals are used to dissolve solder mask (sodium hydroxide), dissolve solder (using acids such as methanesulfuric acid, hydrochloric acid or dilute nitric acid), dissolve resin or other purpose.

Leaching is carried out by dissolving crushed e-waste in mineral acid like HCl, H₂SO₄, and aqua regia for leaching metals like Zinc, Tin, Iron and Aluminium.

Cyanide based solutions are used for leaching precious metals like Copper and gold.

2. Precipitation:

Recovery of metals by precipitation of the dissolved metals and their recovery in solid form. In Chemical precipitation more reactive metals displace less active metals by displacement reaction. Gold metal present in the acid leach or cyanide leach is extracted by displacement reaction using reactive metal such as Zinc.



3. Cementation : Zinc shavings are added to the leached solution to precipitate Copper metal at a definite pH.



4. Solvent extraction:

The aqueous leachate is mixed with organic solution such as chelating agents at desirable acidic pH of 1 to form Copper-Chelate complex.



5. Activated carbon adsorption - Au and Ag recovery from cyanide leaching solutions.

6. Ion exchange by resin – comparable to adsorption with activated carbon often with higher adsorption and recovery rates.

7. Electrodeposition – utilization of simple electric device with minimal chemicals input – environmental point of view.

Advantages

1. More exact
2. More predictable
3. Easily Controllable
4. Precocious Metal recovery is high

Disadvantages

1. Choice of solution is difficult
2. Solution required in high quantity leading to additional expenses.

Extraction of gold from e-waste

E-waste has been a major segment of the waste produced in the past decades. Second-hand computers, mobile phones, and televisions made up an estimated 9.8 million tons of e-waste in 2015. Scientific reports have shown that developing countries will produce twice the amount of e-waste of developed countries by 2030. Recovering precious metals from e-waste through hydrometallurgical processes is more attractive economically than other methods.

Process:

Step 1: CPUs are ground well, (grinding of the CPUs): First, any dust or other particles were removed from the CPUs. The size of the grind pieces was 1 mm so that good contact between the sample and acid.

Step 2: Leaching with Nitric acid

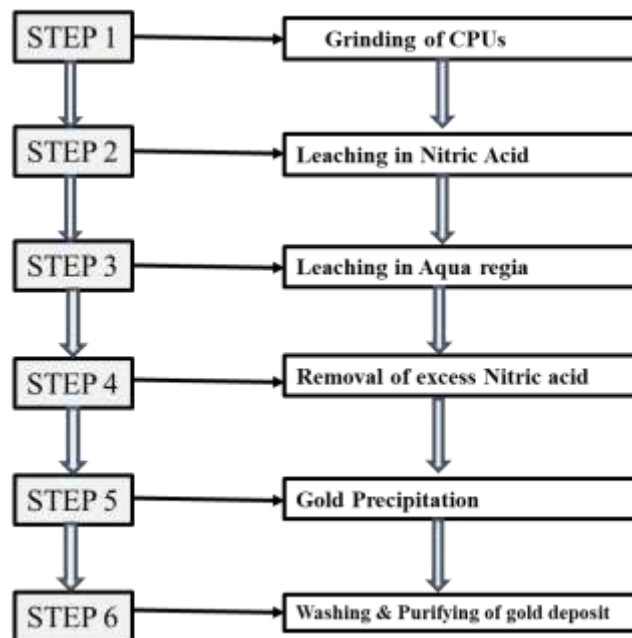
Powdered sample was digested with Conc.HNO₃ for 1 Hr and loss of gold can be prevented by carrying out digestion at room temperature and amount of acid consumed is directly proportional to CPU powder.

Step 3 (leaching in aqua regia): The aqua regia solution was obtained using three volumes of HCl plus one volume of HNO₃ (under the hood). Typically, the gold of composite CPU-containing boards is easily dissolved in **4-to-1** aqua regia. The reaction releases bubbles and is followed by sublimation of NO₂ brown gas. The solution was decanted, and the pieces were subsequently washed with 10 mL of concentrated HCl so that all of the gold content was fed into the solution.

Step 4 (removing the excess nitric acid): Sulfuric acid was added to the solution to accelerate the removal of nitric acid and sedimentation of the lead as lead sulfate (if present). The time required for the complete removal of nitric acid from this solution was 45 minutes. At this stage, the solution's color was golden yellow and the solution's pH was around 0.5. If any deposit was observed (possibly related to silver chloride), it was separated by a filter.

Step 5 (precipitation of gold): A certain amount of iron sulfate (per one gram of gold: 4.2 g of iron sulfate) was dissolved in warm water and gradually added to the gold-containing solution. For better dissolution of iron sulfate, some drops of HCl can be used.

Step 6 (washing and purifying gold deposits): The deposit was coated with HCl and then boiled (to dissolve the excess copper sulfate). Following boiling, the acid was removed and the deposit was re-washed in HCl to ensure the cleanness of the gold powder. Eventually, the deposit was filtered and washed with large amounts of warm water. At this stage, the deposit was placed in an oven at a temperature of 100°C to dry. Gold powder obtained was weighed.



Role of stake holders in environmental management of e-waste (producers, consumers, recyclers, and statutory bodies).

India generates about 350,000 tonnes of electronic waste every year and imports another 50,000 tonnes. With the annual growth rate of e-Waste generation of ten to fifteen percent, government Institutions & Businesses account for seventy percent of e-waste. Of the e-Waste generated in India internally and through imports, only three percent of the e-Waste is captured by authorized e-waste recycling facilities. The amount of e-waste being produced - including mobile phones and computers - could rise by as much as 500 percent over the next decade.

E-waste recycling system bears the following characteristics:

- 1) Individual consumers sell their e-waste to collector, which is contrary to the practice in developed countries;
- 2) Collectors consist of distributors, manufactures, repair shops, after sale service companies, and operators engaged in collections; Large part of the e-waste volume flows into the non-professional e-waste recyclers;
- 3) Producers contribute to the e-waste treatment fund, which is managed by the foundation center.
- 4) E-waste recycler can get governmental subsidies;
- 5) Management authorities, including local municipal level, provincial level, and state council level, share the responsibility.

Within the recycling network, multiple stakeholders are involved. Each stakeholder shares its specific responsibilities in terms of information, material and financial flows.

Financial flow: Producers pay the recycling fee, which is managed by the authority or the e-waste fund management center, which further distribute the money to the recyclers according to the volume of treated e-waster.

Material flow: Collectors bring together e-waste from consumer and sell them to qualified primary recyclers, where the e-wastes are sorted, dismantled and treated. The useful materials are further recovered by secondary recyclers, while the waste and hazardous material are disposed by incineration or land-filling.

Information flow: Producer should information about the material used in the product and treatment advice, which help recyclers to treat the e-waste properly.

Role of stake holders in environmental management of e-waste (producers, consumers, recyclers, and statutory bodies) is listed in the below table:

Stakeholder		Responsibility
Management authorities	E-Waste recycling Fund Management Center	Operation of the system
	State Council	Release of Regulation
	Authorities from local municipal level, and state council level	Planning, Technical policy, environmental inspection, etc
Collectors	Retailers	Collection of the e-waste and submit them to qualified recyclers
	Professional Collectors	
	Repair shops	
Third party Service Providers	Logistic Providers	Transportation
	Quality Inspector	Environmental inspection

	IT service provider	IT services
Producers		Pay the e-waste recycling fee according to market share
Recyclers		Sorting: dismantling: treatment of e-waste
Waste disposers		Landfill or incineration of hazardous material & waste
Consumers		Submit(or sell) the e-waste to the qualified collectors