5.1 Introduction

- The fact that electrical energy can produce chemical changes and the processes based on it, called the "electrolytic processes", are widely used for extraction of pure metals from their ores (such as aluminum, zinc, copper, magnesium, sodium etc.), manufacturing of various chemicals (such as caustic soda, potassium permanganate, hydrogen, oxygen, chlorine etc.), electro deposition of metals including electroplating, electrotyping, electroforming, building up of worn-out parts in metallurgical, chemical and other industries.

5.2 Principle of electrolysis

- As discussed in the definition of electrolyte, whenever any electrolyte gets dissolved in water, its molecules split into cations and anions moving freely in the electrolytic solution.
- Now two metal rods are immersed in the solution and an electrical potential difference applied between the rods externally preferably by a battery. These partly immersed rods are technically referred as electrodes.
- The electrode connected with negative terminal of the battery is known as cathode and the electrode connected with positive terminal of the battery is known as anode.
- The freely moving positively charged cations are attracted by cathode and negatively charged anions are attracted by anode.

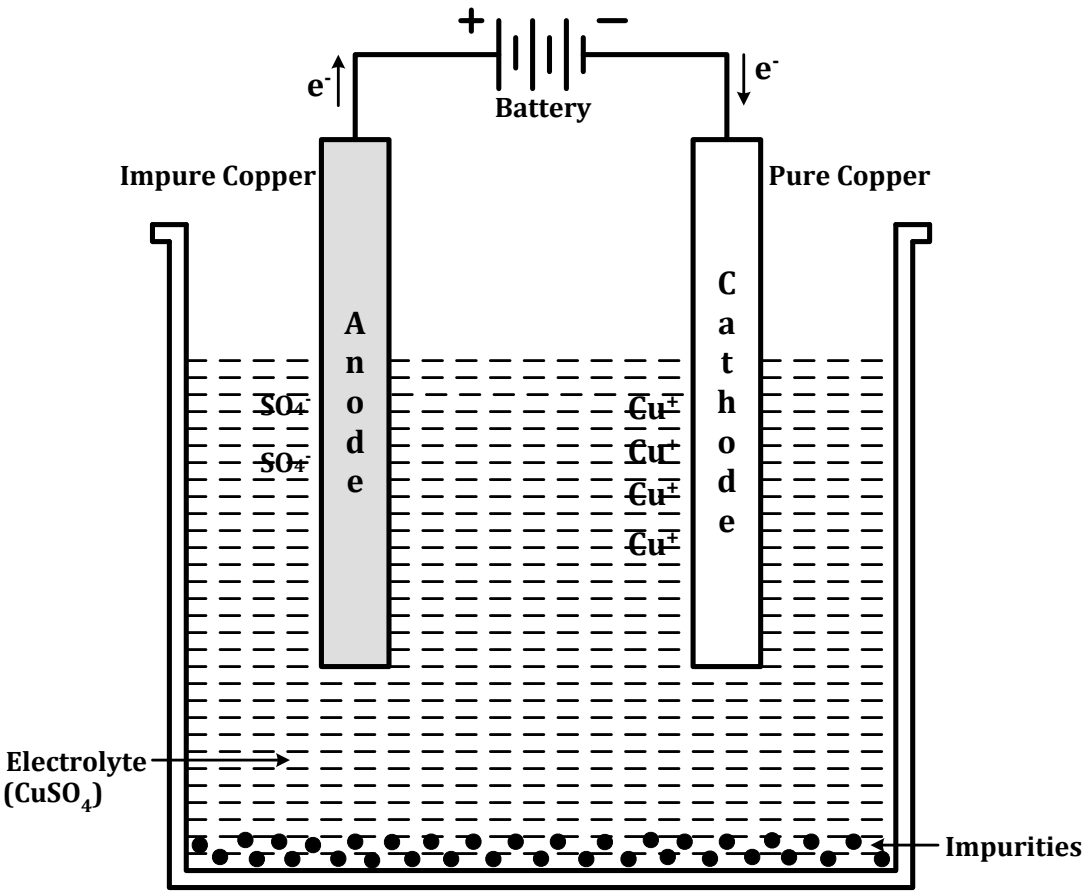

Figure 5.1 Electrolysis

- In cathode, the positive cations take electrons from negative cathode and in anode, negative anions give electrons to the positive anode. For continually taking and giving electrons in cathode and anode respectively, there must be flow of electrons in the external circuit of the electrolytic.
- That means, current continues to circulate around the closed loop created by battery, electrolytic and electrodes. This is the most basic principle of electrolysis.
- Whenever copper sulfate ($CuSO_4$) is added to water, it gets dissolved in the water. As the $CuSO_4$ is an electrolyte, it splits into Cu^{++} (cation) and $SO4^{--}$ (anion) and move freely in the solution.
- Now if two copper electrodes are immersed in that solution, the Cu^{++} ions (cation) will be attracted towards cathode. On reaching on the cathode, each Cu^{++} ion will take electrons from it and becomes neutral copper atoms.
- Similarly the SO_4^{--} (anion) ions will be attracted by anode. So SO_4^{--} ions will move towards anode where they give up two electrons and become SO_4 radical but since SO_4 radical cannot exist in the electrical neutral state, it will attack copper anode and will form copper sulfate.
- If during electrolysis of copper sulfate, we use carbon electrode instead of copper or other metal electrodes, then electrolysis reactions will be little bit different.
- Actually SO_4 cannot react with carbon and in this case the SO_4 will react with water of the solution and will form sulfuric acid and liberate oxygen.
- The process described above is known as electrolysis. In the above process, after taking electrons the neutral copper atoms get deposited on the cathode.
- At the same time, SO_4 reacts with copper anode and becomes $CuSO_4$ but in water it cannot exist as single molecules instead of that $CuSO_4$ will split into Cu^{++}, SO_4^{--} and dissolve in water.
- So it can be concluded that, during electrolysis of copper sulfate with copper electrodes, copper is deposited on cathode and same amount of copper is removed from anode.

5.3 Faraday's first law of electrolysis

- It States that "The chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it".

$$\textit{Mass of chemical deposition}, m \propto \textit{Quantity of Electricity}, Q$$
$$m = Z \cdot Q$$
$$\textit{where}, Q = It$$
$$\textit{so}, m = ZIt$$

- According to this law, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it. i.e. mass of chemical deposition, Where Z is a constant of proportionality and is known as electrochemical equivalent of the substance.
- If we put $Q = 1$ coulombs in the above equation, we will get $Z = m$ which implies that electrochemical equivalent of any substance is the amount of the substance deposited on passing of 1 coulomb through its solution. This constant of passing of

electrochemical equivalent is generally expressed in terms of milligram per coulomb or kilogram per coulomb.

- Where *I*= the steady current in Ampere and *t*= Time (second) for which current I flows through the electrolyte.

5.4 Faraday's second law of electrolysis

- It states that, "When the same quantity of electricity is passed through several electrolytes, the masses of the substances deposited are proportional to their respective chemical equivalents or equivalent weights".

5.5 Chemical equivalent or equivalent weight

- The chemical equivalent or equivalent weight of a substance can be determined by Faraday's laws of electrolysis and it is defined as the weight of that substance which will combine with or displace unit weight of hydrogen.
- The chemical equivalent of hydrogen is unity.
- Since valency of a substance is equal to the number of hydrogen atoms, which it can replace or with which it can combine, the chemical equivalent of a substance, therefore may be defined as the ratio of its atomic weight to its valency.

$$The\ chemical\ equivalent = \frac{atomic\ weight}{valency}$$

5.6 Terms connected with electrolytic processes

- Following terms are used in electrolytic processes:

1. <u>Current Efficiency</u>

- Due to impurities which cause secondary reactions, the quantity of the substance(s) liberated is slightly less than that calculated from Faraday's laws. This is taken into account by employing a factor, called the "Current efficiency".
- The current efficiency is defined as the ratio of the actual quantity of substance liberated or deposited to the theoretical quantity, as calculated from Faraday's laws.

$$Current\ efficiency = \frac{Actual\ quantity\ of\ substance\ liberated\ or\ deposited}{Theoretical\ quantity\ of\ substance\ liberated\ or\ deposited}$$

2. <u>Voltage</u>

- The voltage that is essentially required to pass the current through any electrolytic cell is equal to the sum of voltage drop in the resistance of the electrolyte and the voltage drops at electrodes.
- It is, therefore, desirable that these drops are made as small as possible. This can be achieved, in many cases, by adding special conducting agents to the electrolyte to make it (electrolyte) a good conductor.
- For example dilute sulphuric acid is added to copper sulphate bath in copper plating.
- The normal voltage required to pass current through most electrolytes is 1 to 2 V.

3. <u>Energy efficiency</u>

- Owing to secondary reactions, the voltage actually required for the deposition or liberation of metal is higher than the theoretical value which increases the actual energy required.

- The ratio of theoretical energy required to the actual energy required for depositing a given quantity of metal is known as energy efficiency.

$$Energy\ efficiency = \frac{Theoretical\ energy\ required}{Actual\ enerergy\ requied}$$

5.7 Applications of electrolysis

- The major applications of electrolysis are as under.

1. Electro-deposition
   - Electroplating
   - Electro-deposition of rubber
   - Electro-metallization
   - Electro-facing
   - Electro-forming
   - Electro-typing
2. Manufacture of chemicals
3. Anodizing
4. Electro polishing
5. Electro-cleaning or pickling
6. Electro-parting or electro stripping
7. Electro-metallurgy
   - Electro-extraction
   - Electro-refining

5.8 Electro-deposition

- The process of depositing a coating of one metal over another metal or non-metal electrically is called the electro-deposition.
- It is used for protective, decorative and functional purposes and includes such processes as electro-plating, electro-forming, electro-typing, electro-facing, electro metallization etc.
- As earlier discussed that, the compounds in the solution dissociate into positive and negative ions which when subjected to electric field travel towards respective electrodes then, one of the following events may take place:

  i. In case the ion, after giving off electric charge to electrode, has stable existence and does not have chemical reaction with electrode material, it will be deposited on the electrode. This is the principle of electro-deposition and electro-extraction.

  ii. The ion after giving off electric charge to electrode may undergo chemical reaction with electrode material, the product of reaction in turn is soluble in the electrolyte and the electrode is gradually eaten away. This principle is employed in Electro-refining.

  iii. Ion if after giving off charge to electrode, does not react with the electrode material, or has any independent and stable existence, will react with the water of solution, thereby liberating oxygen or hydrogen.

- Factors on which quality of electro deposition depends.
  1. Nature of electrolyte:
     The electrolyte from which complex ions can be obtained (e.g., cyanides) provides a smooth deposit.
  2. Current density:
     The deposit of metal will be uniform and fine-grained if the current density is used at a rate higher than that at which the nuclei are formed. The deposit will be spongy and porous if the rate of nuclei formation is very high due to very high current density.
  3. Temperature:
     A low temperature of the solution favours formation of small crystals of metal and a high temperature, large crystals.
  4. Conductivity:
     The solution of good conductivity provides economy in power consumption and also reduces the tendency to form trees and rough deposits.
  5. Electrolytic concentration:
     By increasing the concentration of the electrolyte, higher current density can be achieved, which is necessary to obtain uniform and fine grain deposit.
  6. Additional agents:
     The addition of acid or other substances to the electrolyte reduces its resistance. Addition agents like glue, gums, dextrose, dextrin etc. influence the nature of deposit. The crystal nuclei absorb the addition agent added in the electrolyte; this prevents it to have large growth and thus deposition will be fine-grained.
  7. Throwing power:
     It is defined as the ability of the electrolyte to produce uniform deposit on an article of irregular shape and is one of the most important characteristics of plating or deposition bath.
     Due to irregular shape of the cathode the distance between the various portions of the cathode and anode will be different.
     Due to unequal distance, the resistance of the current path through the electrolyte for various portions of the cathode will be different but the potential difference between the anode and any point on the article to be plate (cathode) will, of course be the same and the result will be that the current density will be more on the portion nearer to anode and it will cause uneven deposit of the metal.
     - Copper cyanide bath is better suited for electroplating intricate articles.
     - Zinc cyanide bath has better throwing power than zinc sulphate solution for zinc plating.
  8. Polarization:
     With the increase in the electroplating current density, rate of metal deposition is also increased upto certain limit after which electrolyte surrounding the base metal becomes so much depleted of metal ions that rate of deposition does not increase with increase in current density.
     If current density more than this limit is employed, it will result in electrolysis of water and hydrogen deposition on the cathode. This hydrogen evolved, blankets the

base metal which diminishes the rate of metal deposition. This phenomenon is called "polarization".

5.9 Electroplating

- "Electroplating" is an art of depositing a superior or a more noble metal on an inferior or a base metal by means of electrolysis of an aqueous solution of a suitable electrolyte.

<u>or</u>

- "Electroplating" is defined as the electro-deposition of metal upon metallic surfaces.

- Electroplating is done to accomplish the following:
  a) To protect the metals against corrosion.
  b) To give reflecting properties reflectors.
  c) To give a shiny appearance to articles.
  d) To replace worn out material.
- Various operations involved in electroplating are

1. <u>Cleaning operation</u>

- In case the object to be electroplated is not cleaned, polished and degreased, the deposit formed may not be well adherent to the base metal and is likely to peel off.
- Cleaning operation includes the following:

a) Removal of oil, grease or other organic material etc. To accomplish this, soaps, hot alkali solutions or organic solvents such as gasoline or carbon tetrachloride are used.
b) Removal of rust, scale, oxides, or other inorganic coatings adhering to the base metal/work piece to accomplish this various acids, alkali and salt solutions are employed.
c) Mechanical preparation of the surface of the metal to remove the deposited metal, by polishing, buffing etc to accomplish this mechanical abrasion and polishing are used.

2. <u>Deposition of metal</u>

- In all types of metal deposition processes, article to be electroplated is made cathode, solution is made up of salt4f the metal to be deposited and anode is often of the same metal which is to be deposited.

a) Electra-deposition of rubber

- Rubber latex obtained from the tree consists of very fine colloidal particles of rubber suspended in water. Like other colloidal solutions, particles of rubber are negatively charged.
- On electrolysis of the solution the rubber particles migrate towards the anode and deposit on it.
- Current density of roughly 100 A/m^2.

b) Electro-metallization

- It is the process of depositing metal on conducting base for decoration and for protective purposes. Nonconductive base is made conductive by a coating of graphite which is made the cathode.

c) Electro-facing

- It is a process of coating of metallic surface with a harder metal by electro-deposition in order to increase its durability.

d) Electro-forming

- "Electro-forming" is the reproduction of objects by electro-deposition on some sort of a mould or form. In the reproduction of medals, coins, engravings etc., a mould is first made by impressing the object say in wax.
- The wax surface, which bears exact impressions of the object, is coated by powdered graphite in order to make it conducting. The mould is then dipped in an electro-forming cell as a cathode.
- After obtaining coating of desired thickness, the article is removed and the wax core is melted out of the metal shell.
- Other applications of electro-forming are:
  (i) Manufacture of gramophone records.
  (ii) Production of seamless tube.

e) Electro-typing

- Electro-typing is a special application of electro-forming and it is used to reproduce printing, setup type, engraving and medals etc.
- The process is same as for electro-forming.

5.10 Manufacture of chemicals

- The industrial applications of electrolysis include the manufacture of chemicals like chlorine, caustic soda, potassium permanganate, ammonium per sulphate, hydrogen and oxygen.
- The most important process of production caustic soda by electrolysis of brine and production of hydrogen and oxygen gases by electrolysis of water are explained below.

1. <u>Production of caustic soda.</u>

- The oldest process is Diaphragm process.
- There are a number of variations, but all essentially consist of an anode compartment separated from a cathode compartment by a porous diaphragm which prevents the mechanical mixing of two solutions.
- Chlorine is formed at the anode, and most of it is evolved as a gas, a small part going into solution.
- Sodium is discharged at the cathode and reacts with hydroxyl ions to form sodium hydroxide and hydrogen gas is liberated at the cathode.
- Usually, the brine is fed into the anode compartment to resist the flow of hydroxyl ions towards the anode.

2. <u>Production of hydrogen and oxygen gas by electrolysis of water.</u>

- Gases obtained by this process are of high purity and at a cheap cost because of the low energy consumption.
- The electrolyte consists of 15-20% solution of caustic soda or its equivalent caustic potash and electrodes are of iron.
- Sulphuric acid is no longer used.

- Thus hydrogen and oxygen gases are liberated at cathode and anode respectively and water disappears while the quantity of caustic soda remains constant.
- It is therefore, necessary to add water to the solution periodically.
- The voltage requirement is 2-2.2 V per cell during operation and 2.3-2.5 V per cell during starting period.
- Energy consumption is about 6 kWh per cubic meter of hydrogen and ½ cubic meter of oxygen.

5.11 Anodizing

- An "anodic coating "means an oxide film deposited/created on a metal surface, with the help of an anode and oxidation. The process of providing an oxide film is known as Anodizing.
- The surface of the metal can be anodized to achieve one or more of the following:
  i. To provide a protective coating on the surface.
  ii. To provide a decorative appearance to the surface.
  iii. To provide a specific color base for subsequent painting on the surface.
  iv. To provide a bright and smooth surface on aluminum articles as a prior treatment to electroplating.
  v. To improve the corrosion resistance of aluminum and its products.
- Anodizing process is neither a purely electrical process nor a purely chemical process; it is a combination of both i.e., an electrochemical process. It is completed in the following three stages:
  I. The "first stage" consists of cleaning and preparing the surface through different cleaning methods.
  II. The "second stage" consists of anodizing i.e., converting the metal surface into an oxidized film.
  III. The "third stage" consists of providing desired color and stability to the anodized film, called sealing of oxide film.

5.12 Electro-polishing

- This process, in principle, consists of making the work as anode in a suitable position.
- This produces insoluble compounds, which are broken down by more anodic action on the hills than on valleys of the surface.

5.13 Electro-cleaning or pickling

- Electrolytic solution of sodium phosphate is contained in iron tank which is made anode.
- Work is suspended as cathode. When the current is passed, it produces caustic soda on cathode has cleaning action. This is called cathodic cleansing.
- In anodic cleansing, work is made anode. Dirt particles are positively charged in alkaline by electrophoresis process they migrate to negative pole.

5.14 Electro-parting or Electro-stripping

- Two or more metals may be separated electrolytically.
- As an example if copper is to be stripped Iris Prom steel, the work piece is made anode in a solution of 75 gm of sodium cyanide, 25 gm of caustic n111141 in 1000 c.c. of water.

- Sheet of iron is made cathode and pressure used is 6 V.

5.15 Electro-metallurgy

- Electro-metallurgy includes electro-extraction and electro-refining processes.

5.16 Electro-extraction

- Extraction of metal is an electro-chemical process employed for production of metal with commercially acceptable purity.
- Depending upon the physical state of the ore, following are the two methods of extraction of metals:
  (i) In one of the methods the ore is treated with a strong acid to obtain a salt and the solution of such a salt is electrolyzed to liberate the metal.
  (ii) The second method is used when the ore is available in molten state or can be fused and in this method the ore, which is in a molten state is electrolyzed in a furnace.

5.17 Extraction of magnesium

- Magnesium is obtained by electrolysis of magnesium chloride, employing current density-of 160 to 350 Aim2.
- Energy expenditure is 17 to 20 kWh/kg and operating temperature of 360 to 670°C.

5.18 Extraction of sodium

- Sodium is obtained by the electrolysis of sodium hydroxide, sodium nitrate or sodium chloride requiring expenditure of 10 to 20 kWh/kg of sodium.

5.19 Electro-refining

- Refining is the process whereby a highly concentrated mixture of metals is subjected to electrochemical treatment for recovering not only the principal metal in pure form, but also the precious metals like gold, silver, bismuth etc., which may be present in the form of minute traces.
- By electro-refining, it is possible to get metal of almost 100% purity. This is one of the most important prerequisite expected out of copper and aluminum in order to have high electrical conductivity.
- Electro-refining process in essence is same as electro-plating, anode being made of impure metal and electrolyte being made of the salt of the metal to be refined.
- Pure metal is deposited at the cathode.
- Copper refining requires copper sulphate solution with electric consumption of 150 to 300 kWh/tonne of copper refined.
- Silver is refined requiring solution of nitric acid and silver nitrate with electric consumption of 400 to 420 kWh/tonne.
- Iron is refined by using solution of iron-ammonium sulphate with electric consumption of 1000 to 1600 kWh/tonne.
- Lead is refined by using solution of lead fluorosilicate with electric consumption of 100 to 120 kWh/tonne.
- Gold refining requires gold chloride solution with electric consumption of 300 to 350 kWh/tonne of gold refined.
- Nickel refining requires nickel-ammonium sulphate solution with electric consumption of 2500-4000 kWh/tonne of nickel refined.

5.20 Power supply for electrolytic processes

- For electrolytic process, the power supply required is D. C, and at very low voltage.
- The power required for electro-deposition is usually very small (between 100 and 200A at 10 or 12V) and can be obtained either by employing a motor-generator set consisting of a standard induction motor driving a heavy current low voltage D.C. generator (preferably separately excited) or by employing the copper oxide rectifier.
- The latter is preferred since it has high operating efficiency, occupies less space and its maintenance cost is low.
- For extraction and refining of metals and large scale manufacture of chemicals a very large amount of power is required.
- Since most of the processes are continuous and as such have a 100 percent load factor, these plants are located near hydroelectric power stations or atomic power plants even if extra transportation or raw material is necessitated.