ELECTROLYTIC CELLS AND ELECTROLYSIS

Electrolysis

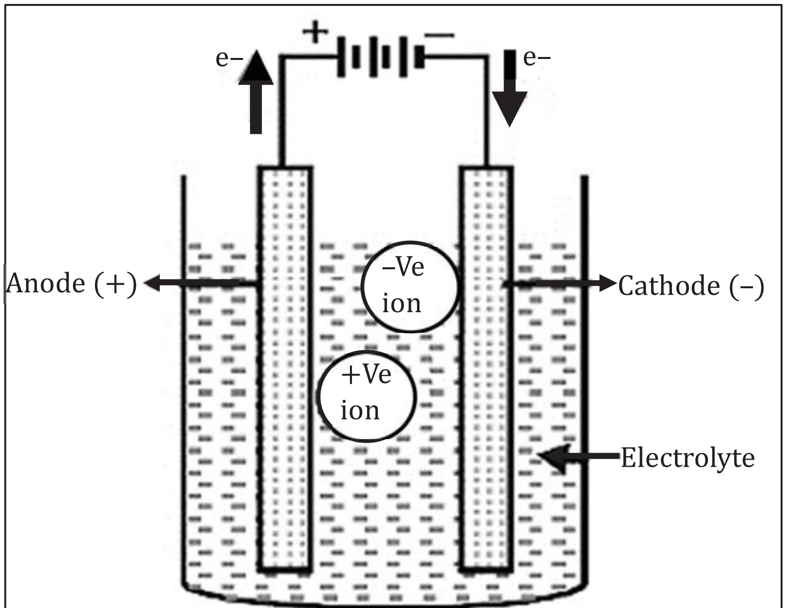
1. An electrolyte consists of fused cations and anions, allowing it to conduct electricity.
2. The conductivity is enabled by the movement of ions within the electrolyte.
3. Electrolysis refers to the application of an electric current to induce chemical changes.
4. The electrolysis process involves oxidation and reduction reactions driven by the electric current in the electrolyte.

   The product obtained during electrolysis depends on following factors.
   - The characteristics of the electrolyte
   - The electrolyte concentration
   - The charge density during electrolysis
   - The electrode's nature

Electrolytic Cell and Electrolysis and Faraday's law

Electrolytic Cell

This cell converts electric energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell.



Electrolytic cell

Cell reaction

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

Representation of Galvanic cell.

$$Zn/Zn^{+2}//Cu^{+2}/Cu$$

(C_1) Anode | (C_2) Cathode

salt bridge

Faraday's Laws of Electrolysis

Michael Faraday deduced two important laws:

(a) Faraday's First Law of Electrolysis

This principle asserts that "The quantity of a substance deposited or dissolved at an electrode is directly correlated with the charge that traverses through the electrolytes. If a current of I amperes flows for t seconds, resulting in a charge of Q in coulombs, and if W grams of a substance is deposited by Q coulombs of electricity, then..."

$$W \propto Q \propto It$$

$$W = Z\,It = \frac{E}{96500}It$$

Where Z is constant of proportionality and is known as electrochemical equivalent.

➢ When $Q = 1$ coulomb, $W = Z$

thus, electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity

Ex. How many cc of chlorine will be deposited by 100 amp. current flowing for 5 hours through melted NaCl.

Sol. $Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5$

$$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = \frac{18 \times 35.5}{965} \times 10^3 = 662.2\text{g}$$

$\because$ Volume of 71g Cl_2 at NTP $= 22.4$L

$\because$ Volume of 662.2 g Cl_2 at NTP $= \frac{22.4}{71} \times 662.2 = 208.9$L

Ex. The time required to coat a metal surface of 80 cm^2 with 0.005mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3A current through silver nitrate solution is –

Sol. Volume of layer of silver $= 0.005 \times 10^{-1} \times 80 = 0.04$ cm^3

$\therefore$ Mass = Density × volume $= 10.5 \times 0.04 = 0.42$ g

So,

$$w = \frac{E}{96500} \times It \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

(b) Faraday's Second Law

This principle asserts that the quantities of distinct substances deposited at electrodes, through the passage of an identical amount of electricity, are directly proportional to their respective chemical equivalents (E).

$$W \propto E$$

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights then –

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

combining the two laws

$$W \propto It\,E \quad W = \frac{ItE}{F}$$

Where $\frac{1}{F}$ is proportionality constant and F is called faraday.

When, $It = F$ then $W = E$

Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance. The Faraday (F) is also the quantity of charge carried by one mole of electrons.

$$F = e \times N = 1.6 \times 10^{-19} \times 6.023 \times 10^{23} = 96500 \text{ coulombs.}$$

Products of Electrolysis

During the process of electrolysis, the reactions taking place at the electrodes involve oxidation and reduction reactions. The outcome of electrolysis is influenced by the nature of the material undergoing electrolysis and the types of electrodes utilized. In the case of inert electrodes like gold or platinum, they remain uninvolved in the chemical reaction and serve solely as sources or sinks for electrons. Conversely, if the electrode is reactive, it actively participates in the electrode reaction, resulting in potential variations in the products of electrolysis between inert and reactive electrodes.

1. The products of electrolysis primarily hinge on the diverse oxidizing and reducing species present in the electrolytic cell and their respective standard electrode potentials.
2. Certain electrochemical processes, while theoretically feasible, may be kinetically slow, and at lower voltages, they may not seem to occur. The sluggishness of the electrode reaction introduces electrical resistance at the electrode surface. Hence, for these reactions to transpire, an additional potential or voltage beyond the theoretical value of their standard electrode potential is necessary. This additional voltage requirement is termed overvoltage.