Unit 2

Electrolytic Process

Definition of Electrolysis

An electrolyte is such a chemical that's atoms are normally closely bonded together but when it is dissolved in water, its molecules split up into positive and negative ions. The positively charged ions are referred as cations whereas negatively charged ions are referred as anions. Both cations and anions move freely in the solution.

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. 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, electric current continues to circulate around the closed loop created by battery, electrolytic and electrodes. This is the most basic **principle of electrolysis**

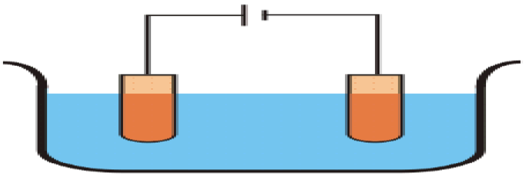

Fig:2.1: Electrolysis process

Electrolysis of Copper Sulfate

Whenever copper sulfate or $CuSO_4$ is added to water, it gets dissolved in the water. As the $CuSO_4$ is an electrolyte, it splits into Cu^{++} (cation) and SO_4^{--} (anion) ions 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 i.e. the electrode connected to the negative terminal of the battery. 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 i.e. the electrode connected to the positive terminal of the battery. So SO_4^{--} ions will move towards anode where they give up two electrons and become SO_4 radical but since SO_4 radical can not 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 can not 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.

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2$$

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_4reacts with copper anode and becomes $CuSO_4$ but in water it can not 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.

Faraday's Laws of Electrolysis

Before understanding **Faraday's laws of electrolysis**, we have to recall the process of electrolysis of a metal sulfate.

Whenever an electrolyte like metal sulfate is diluted in water, its molecules split into positive and negative ions. The positive ions or metal ions move to the electrodes connected with negative terminal of the battery where these positive ions take electrons from it, become pure metal atom and get deposited on the electrode. Whereas negative ions or sulphions move to the electrode connected with positive terminal of the battery where these negative ions give up their extra electrons and become SO_4 radical. Since SO_4 cannot exist in electrically neutral state, it will attack metallic positive electrode and form metallic sulfate which will again dissolve in the water. **Faraday’s laws of electrolysis** combine two laws and these are,

Faraday's First Law of Electrolysis

From the brief explanation above, it is clear that the flow of current through the external battery circuit fully depends upon how many electrons get transferred from negative electrode or cathode to positivemetallic ion or cations. If the cations have valency of two like Cu^{++} then for every cation, there would be two electrons transferred from cathode to cation. We know that every electron has negative electrical charge -1.602×10^{-19} Coulombs and say it is - e. So for disposition of every Cu atom on the cathode, there would be - 2.e charge transfers from cathode to cation. Now say for t time there would be total n number of copper atoms deposited on the cathode, so total charge transferred, would be - 2.n.e Coulombs. Mass m of the deposited copper is obviously function of number of atoms deposited. So, it can be concluded that the mass of the deposited copper is directly proportional to the quantity of electrical charge that passes through the electrolyte. Hence mass of deposited copper $m \propto Q$ quantity of electrical charge passes through the electrolyte.

Faraday's First Law of Electrolysis states that only,

According to this law, the chemical deposition due to flow of electric current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it.

i.e. mass of chemical deposition,

$$m \propto Quantity\,of\;electricity,\;Q \Rightarrow m = Z \cdot Q$$

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.

Faraday's Second Law of Electrolysis

So far we have learned that the mass of the chemical, deposited due to electrolysis is proportional to the quantity of electricity that passes through the electrolyte. The mass of the chemical, deposited due to electrolysis is not only proportional to the quantity of electricity passes through the electrolyte, but it also depends upon some other factor. Every substance will have its own atomic weight. So for same number of atoms, different substances will have different masses. Again, how many atoms deposited on the electrodes also depends upon their number of valency. If valency is more, then for same amount of electricity, number of deposited atoms will be less whereas if valency is less, then for same quantity of electricity, more number of atoms to be deposited. So, for same quantity of electricity or charge passes through different electrolytes, the mass of deposited chemical is directly proportional to its atomic weight and inversely proportional to its valency.

Faraday's second law of electrolysis states that, when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

Applications of Electrolysis:

Electrolytic Refining of Metals

The process of **electrolytic refining of metals** is used to extract impurities from crude metals. Here in this process, a block of crude metal is used as anode, a diluted salt of that metal is used as electrolyte and plates of that pure metal is used as cathode.

Electrolytic Refining of Copper

For understanding the process of **electrolytic refining of metals**, we will discuss about an example of **electrolytic refining of copper**. Copper extracted from its ore, known as blister copper, is 98 to 99 % pure but it can easily be made up to 99.95% pure for electrical application by the process of **electrorefining**.

In this process of electrolysis, we use a block of impure copper as anode or positive electrode, copper sulfate acidified with sulfuric acid, electrolyte and pure copper plates coated with graphite, as cathode or negative electrode.

The copper sulfate splits into positive copper ion (Cu^{++}) and negative sulfate ion (SO_4^{--}). The positive copper ion (Cu^{++}) or cations will move towards negative electrode made of pure copper where it takes electrons from cathode, becomes Cu atom and is deposited on the graphite surface of the cathode.

On the other hand, the SO_4^{--} will move towards positive electrode or anode where it will receive electrons from anode and become radical SO_4 but as radical SO_4 can not exist alone, it will attack copper of anode and form $CuSO_4$. This $CuSO_4$ will then dissolve and split in the solution as positive copper ion (Cu^{++}) and negative sulfate ion (SO_4^{--}). These positive copper ions (Cu^{++}) will then move towards negative electrode where it takes electrons from cathode, become Cu atoms and are deposited on the graphite surface of the cathode. In this way, the copper of impure crude will be transferred and deposited on the graphite surface of the cathode. The metallic impurities of anode are also merged with SO_4, form metallic sulfate and dissolve in the electrolyte solution. The impurities like silver and gold, which are not effected by sulfuric acid-copper sulfate solution, will settle down as the anode sludge or mud. At a regular interval of electrolytic refining of copper, the deposited copper is stripped out from the cathode and anode is replaced by a new block of crude copper.

Electroplating

The process of **electroplating** is theoretically same as electrorefining - only difference is that, in place of graphite coated cathode we have to place an object on which the **electroplating**has to be done. Let's take an example of brass key which is to be copper-platted by using**copper electroplating**.

Copper Electroplating

We have already stated that copper sulfate splits into positive copper ion (Cu^{++}) and negative sulfate ion (SO_4^{--}) in its solution. For **copper electroplating**, we use copper sulfate solution as electrolyte, pure copper as anode and an object (a brass key) as cathode. The pure copper rod is connected with positive terminal and the brass key is connected with negative terminal of a battery. While these copper rod and key are immersed into copper-sulfate solution, the copper rod will behave as anode and the key will behave as cathode. As the cathode or the brass key is connected with negative terminal of battery, it will attract the positive cations or Cu^{++} ions and on reaching of Cu^{++} ions on the surface of the brass key, they will receive electrons from it, become neutral copper atom and are about to be deposited on the surface of the brass key as uniform layer. The sulfate or SO_4^{--} ions move to the anode and extract copper from it into the solution as mentioned in the process of electro-refining. For proper and uniform copper plating, the object (here it is brass key) is being rotated slowly into the solution.

Electroforming

Reproduction of objects by electro-deposition on some sort of mould is known as**electroforming**. This is another very useful example among many applications of electrolysis. For that, first we have to take the impression of objects on wax or on other wax like material. The surface of the wax mold which bears exact impression of the object, is coated with graphite powder in order to make it conducting. Then the mold is dipped into the electrolyte solution as cathode. During electrolysis process, the electrolyte metal will be deposited on the graphite coated impressed surface of the mold. After obtaining a layer of desired thickness, the article is removed and the wax is melted to get the reproduced object in form of metal shell.

A popular use of **electroforming** is reproduction of gramophone record dices. The original recording is done on a record of wax composition. This wax mold is then coated with gold powder to make it conducting. Then this mold is dipped into a blue vitriol electrolyte as cathode. The solution is kept saturated by using a copper anode. The copper electroforming on the wax mold produces master plate which is used to stamp a large number of shellac discs.

Factors affecting Electro deposition Process

Electrophoretic deposition (**EPD**), is a term for a broad range of industrial processes which includes**electrocoating**, **e-coating**, **cathodic electrodeposition**, **anodic electrodeposition**, and **electrophoretic coating**, or **electrophoretic painting**. A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes materials such as polymers, pigments, dyes, ceramics and metals.

The process is useful for applying materials to any electrically conductive surface. The materials which are being deposited are the major determining factor in the actual processing conditions and equipment which may be used.

Due to the wide utilization of electrophoretic painting processes in many industries, aqueous EPD is the most common commercially used EPD process. However, non-aqueous electrophoretic deposition applications are known. Applications of non-aqueous EPD are currently being explored for use in the fabrication of electronic components and the production of ceramic coatings. Non-aqueous processes have the advantage of avoiding the electrolysis of water and the oxygen evolution which accompanies electrolysis.

Uses of EPD

This process is industrially used for applying coatings to metal fabricated products. It has been widely used to coat automobile bodies and parts, tractors and heavy equipment, electrical switch gear, appliances, metal furniture, beverage containers, fasteners, and many other industrial products.

EPD processes are often applied for the fabrication of supported titanium dioxide (TiO_2) photocatalysts for water purification applications, using precursor powders which can be immobilised using EPD methods onto various support materials. Thick films produced this way allow cheaper and more rapid synthesis relative to sol-gel thin-films, along with higher levels of photocatalyst surface area.

EPD processed have a number of advantages which have made such methods widely used

1. The process applies coatings which generally have a very uniform coating thickness without porosity.
2. Complex fabricated objects can easily be coated, both inside cavities as well as on the outside surfaces.
3. Relatively high speed of coating.
4. Relatively high purity.
5. Applicability to wide range of materials (metals, ceramics, polymers, etc.)
6. Easy control of the coating composition.
7. The process is normally automated and requires less human labor than other coating processes.
8. Highly efficient utilization of the coating materials result in lower costs relative to other processes.
9. The aqueous process which is commonly used has less risk of fire relative to the solvent-borne coatings that they have replaced.
10. Modern electrophoretic paint products are significantly more environmentally friendly than many other painting technologies.

Process of electrophoretic painting

The overall industrial process of electrophoretic deposition consists of several sub-processes:

1. The object to be coated needs to be prepared for coating. This normally consists of some kind of cleaning process and may include the application of a conversion coating, typically an inorganic phosphate coating.
2. The coating process itself. This normally involves submerging the part into a container or vessel which holds the coating bath or solution and applying direct current electricity through the EPD bath using electrodes. Typically voltages of 25 - 400 volts DC are used in electrocoating or electrophoretic painting applications. The object to be coated is one of the electrodes, and a set of "counter-electrodes" are used to complete the circuit.
3. After deposition, the object is normally rinsed to remove the undeposited bath. The rinsing process may utilize an ultrafilter to dewater a portion of the bath from the coating vessel to be used as rinse material. If an ultrafilter is used, all of the rinsed off materials can be returned to the coating vessel, allowing for high utilization efficiency of the coating materials, as well as reducing the amount of waste discharged into the environment.
4. A baking or curing process is normally used following the rinse. This will crosslink the polymer and allows the coating, which will be porous due to the evolution of gas during the deposition process, to flow out and become smooth and continuous.

Power Supply for electrolytic process

Electrolysis is a method of using a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially highly important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell. The voltage that is needed for electrolysis to occur is called decomposition potential.

Electrolysis is the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

The main components required to achieve electrolysis are:

An electrolyte : a substance containing free ions which are the carriers of electric current in the electrolyte. If the ions are not mobile, as in a solid salt then electrolysis cannot occur.

A direct current (DC) supply : provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.

Two electrodes : an electrical conductor which provides the physical interface between the electrical circuit providing the energy and the electrolyte

Electrodes of metal, graphite and semiconductor material are widely used. Choice of suitable electrode depends on chemical reactivity between the electrode and electrolyte and the cost of manufacture.

Energy changes during electrolysis

The amount of electrical energy that must be added equals the change in Gibbs free energy of the reaction plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum thermodynamic efficiency equals the enthalpy change divided by the free energy change of the reaction. In most cases, the electric input is larger than the enthalpy change of the reaction, so some energy is released in the form of heat. In some cases, for instance, in the electrolysis of steam into hydrogen and oxygen at high temperature, the opposite is true. Heat is absorbed from the surroundings, and the heating value of the produced hydrogen is higher than the electric input.