Topic: **APPLIED ELECTROCHEMISTRY** **T.Y.B.Sc**

Q.1 **What is polarization? Explain the various type of polarization.**

Ans. The phenomenon of reverse e.m.f. brought about by the presence of product of electrolysis is called polarization. It results mainly due to slowness of one or more processes occurring at the electrode during discharge or formation of ions.

Eg. Consider the electrolysis of dilute H_2SO_4 solution using two platinum electrodes. In the initial stage the external emf applied is such that it just causes the evolution of H_2 gas at cathode and O_2 gas at anode. But after some time, the evolution stops even though the current flows through the cell. This is accounted for the fact that the H_2 and O_2 molecules get adsorbed on the surface of electrodes thereby giving rise to back e.m.f. which opposes the external e.m.f. applied. When the back e.m.f. (ie polarization e.m.f.) becomes equal to external e.m.f., no current flows and the fuel cell is said to be completely polarized.

Polarization at a reversible electrode is mainly due to the disturbance caused in the equilibrium reaction taking place at that electrode. This is observed when the electric current flows through the electrode. Such a phenomenon is called electrolytic polarization and the electrode is said to be polarized.

Platinized electrodes are said to behave irreversibly due to slowness of one or more stages in the electrode process.

There are two types of polarization:

A) Concentration polarization:

It arises mainly due to a concentration change in the vicinity of the electrode.ie due to slowness of diffusion of ions from or to the electrode and the bulk of the solution. It is mostly observed in metals.

Eg. Consider the dissolution of a metal anode giving cations in solution. If the cations formed do not travel rapidly in the solution, then there will be more concentration of the cations around the vicinity of the anode than in the bulk of the solution. This

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	results in an increase in potential at the anode. The increase will be greater for higher current density. At cathode , the conditions are exactly opposite. The discharge of cations result in a decrease in concentration of the ions near the electrode and if this is not made up by diffusion , the concentration in the vicinity of the electrode becomes less than in the bulk of the solution. **<u>B)</u> <u>Over voltages</u>**: Decomposition voltage of electrolytes often differ from the theoretical reversible values due to polarization. For aqueous solutions of acids and bases where H_2 and O_2 are evolved as a result of electrolysis, the extent of polarization is different for different electrodes. The theoretical value of the voltage in each case remains the same. The difference between the voltage actually necessary for gas evolution to take place and that theoretically required is called over voltage. It depends upon the nature of the electrode material.
Q.2	**Explain the term 'decomposition potential'. How is it experimentally measured?**
Ans.	**Decomposition Potential**: The minimum potential that can be applied externally between the two electrodes immersed in an electrolytic solution so as to bring about continuous decomposition of an electrolyte is called decomposition potential. **Explanation** :- The phenomenon of decomposition potential was discovered by Le Blanc. When 1N H_2SO_4 solution is electrolyzed by some Pt electrodes and applying an external potential of 1 volt, it is found that current flows initially and after some time it stops due to polarization at the respective electrodes. The H_2 and O_2 form a layer at the surface of the electrodes thus gives rise to back e.m.f. Now if the applied potential is slowly increase to oppose the back e.m.f., the current slowly increases and at a particular value of applied potential , the current suddenly increases. For this value of applied potential, continuous evolution of H_2 and O_2 gas takes place at the two electrodes.(H_2 at cathode and O_2 at anode). This applied potential necessary for continuous electrolytic decomposition is called decomposition potential and for

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H_2SO_4 its vale is found to be **1.7 volts** at 25^0C.

Experimental measurement of decomposition potential.

The set up for the experiment is as shown in the figure given below.

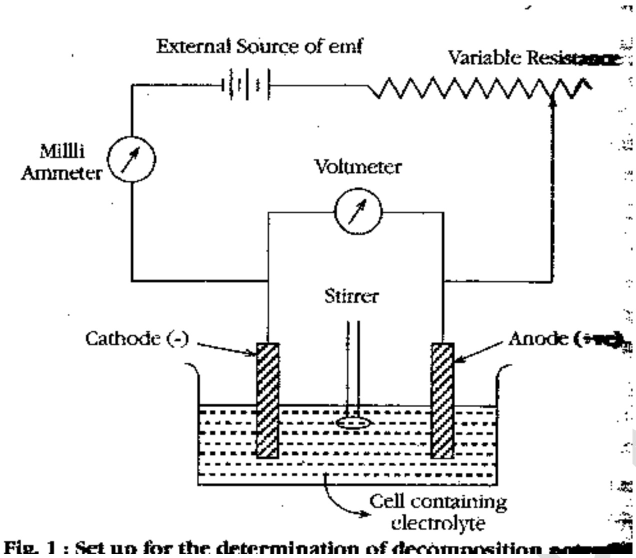

Fig. 1 : Set up for the determination of decomposition

The beaker is filled with the experimental solution. Two electrodes and a stirrer are immersed in the beaker. One electrode is connected through milliammeter to the -ve terminal of the battery and act as cathode. The other electrode through the variable resistance is connected to the +ve terminal of the battery and act as anode. The voltmeter is connected across the anode and cathode. To start with , first the sliding contact is moved slowly on the wire and the value of the applied potential and current flowing are noted down from the voltmeter and mA. This process of recording current and potential is continued till sudden rise in the current is shown by the mA, then a graph of current on Y –axis and applied potential on X-axis is plotted. The curve obtained is as shown below from the graph.

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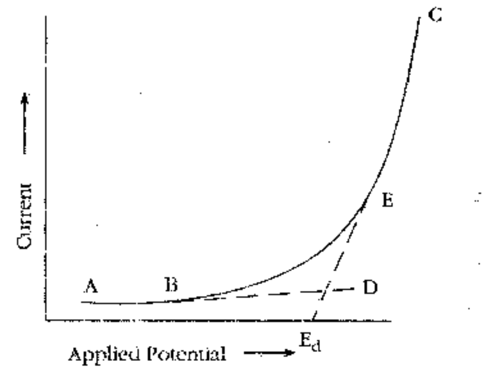

Fig. 2 : Determination of decomposition potential

Q.3)

Ans

Thus we find that current increases slowly with increase in applied potential as shown by AB. However beyond B current increases abruptly and shoots up as shown by CD. Thus by extrapolating AB and CD to meet at E, the corresponding value of applied potential obtained. By further extending CE on X-axis is the decomposition potential of the electrolyte.

On what factors the decomposition potential depends?

Q.4)

Ans;

The magnitude of decomposition potential of the electrolyte depends upon:

1) Nature of electrolytes
2) Nature of electrodes
3) Temperature
4) Concentration of electrolytes
5) Nature of product of electrolysis

How is polarization eliminated?

Methods to eliminate polarization potential:

1) **Mechanical method**:
   In this method, the smooth surface of electrode is coated with rough one for eg. Pt coated with patinic chloride and is every time washed off to remove the thin layer formed on the surface of electrode.

2) **Chemical method**:
   If the products of electrolysis at cathode and anode are hydrogen and oxygen

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respectively then the polarization can be minimized by using strong oxidizing agent such as chromic acid, HNO_3 etc. These substances are therefore called depolrizer. Besides the above method the magnitude of the concentration of polarization can be reduced by agitating the mixture, increase of concentration of electrolyte or by raising components of electrolyte. However it cannot be eliminated completely.

Q.5) **Explain the term 'Over voltage.'**

Ans: **Overvoltage**: It is defined as the difference between the actual potential at which the electrode process occurs and the reversible or theoretical value at which it should have occurred when concentration polarization is eliminated.

Overvoltage is mainly observed with hydrogen evolution at cathode and oxygen evolution at anode.Hence it is also defined as the difference between the potential of the electrode when gas evolution is actually observed and the reversible(theoretical) value for the same solution.

<u>Explanation:</u>

When an aqueous solution of 1N H_2SO_4 is electrolyzed using Pt electrode at 25^0C evolution of H_2 and O_2 takes place at cathode and anode respectively. The reactions taking place at the electrodes are as follows:

At Cathode : $\mathbf{2H^+ + 2e^- \rightarrow H_{2(g)}}$

At Anode : $\mathbf{2OH^- \rightarrow \frac{1}{2} O_{2(g)} + H_2O + 2e^-}$

Net reaction: $\mathbf{2H^+ + 2OH^- \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)} + H_2O(l)}$

For the above electrolytic cell the potential at which continued evolution of H_2 and O_2 gas took place was measured and was found to be 1.7 Volts. This is called decomposition potential of 1N H_2SO_4 which is also the observed value of the potential.

Now if a galvanic cell is set up using H_2 and O_2 as gas electrodes placed in 1N

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H_2SO_4 solution then following reactions takes place at respective electrodes at 1 atm pressure.

L.H.E. = oxidation $H_{2(g)} \rightarrow 2H^+ + 2e^-$

R.H.E. = reduction $\frac{1}{2} O_{2(g)} + H_2O(l) + 2e^- \rightarrow 2OH^-$

$$\mathbf{H_{2(g)} + \tfrac{1}{2} O_{2(g)} + H_2O(l) \rightarrow 2H^+ + 2OH^-}$$

The reversible emf of the above cell is given by Nernst's equation.

This value is called theoretical reversible decomposition potential of the galvanic cell. Thus we find that theoretical reversible potential is greater than the actual decomposition potential by 1.7 – 1.23 = 0.47 Volts.

This excess potential is termed as over voltage.

It is given by the formula

$$\boldsymbol{\eta = E_d - E_r.}$$

where E_d is the decomposition potential of the electrolyte

E_r. = Theoretical reversible potential of the cell

Q.6) What is cathodic and anodic overvoltage?

Ans: **Cathodic overvoltage** : It is the potential which is in excess of the reversible discharge potential cations at cathodic surface. For reversible discharge of cation $E_d >> E_r$.

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<u>**Anodic Over voltage**</u>: It is a potential which is in excess of reversible discharge potential of the anion at the anodic surface. For irreversible discharge of anion $E_d >> E_r$. It is denoted by n_{anodic}.

Q.7) What are the causes of overvoltage?

Ans: Different theories were put forward to explain the phenomenon of over voltage. The main principle involved is as follows:

i) The discharge of the ions from the bulk of the solution to the layer on the electrode surface and diffusion across the layers

ii)Discharge of the ions to form atom on the electrode.

iii)Conversion of atoms to normal start from the deposited substance. It is predicted that any one of the above process may be slow and hence might require excess of voltage.

Q.8) **Explain Tafel's theory of hydrogen over voltage.**

Ans Hydrogen over voltage is defined as the potential which is in excess of the reversible discharge potential of the hydrogen ions at the cathodic surface. The mechanism of continued discharge to take place in the following stages:

1) Discharge of H^+ ions at the electrode surface
2) Discharge of these ions at the electrode surface
3) Neutralization of the charge of the ions or protons by electrons
4) Combination of the resulting hydrogen atom to form molecules
5) Evolution of H_2 molecules as bubble of the gas

According to Tafel's theory, the over voltage is due to slow combination of hydrogen atom at the cathode surface to form H_2 molecules. Hydrogen over voltage depends upon the nature of cathodic surface and current density. The view that combination of H atoms to form H_2 molecules is a slow process , it is supported by the fact that metals (Pt, Pd) that are good catalyst for this reaction, have low over voltage, whereas those metals (Pb , Hg) that are poor catalyst have high over voltage. If the graph of over voltage is plotted against current density then depending upon the

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nature of the cathodic surface, it is found that hydrogen over voltage increases steadily in the form of parabolic curve as shown in the figure. The variation of hydrogen over voltage with current density at constant temperature is given by Tafel's equation:

$$\eta = a + b \log I_d$$

where **a** and **b** are constant and I_d is current density.

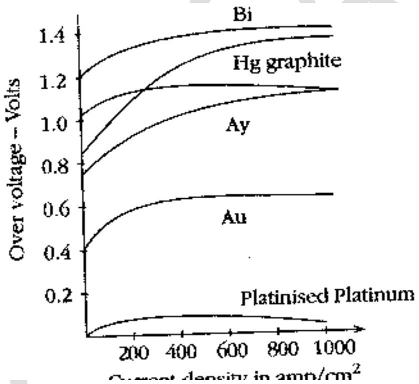
This equation resembles to the linear equation of the curve y = mx + C with slope b and y intercept=a

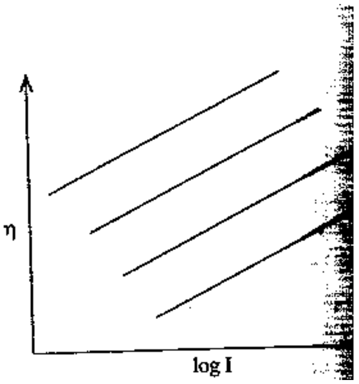
A plot of η against **log** I_d for the most metals found to be a straight lines parallel to each other indicating that their slopes are equal.

The slope b is given by the equation

$$b = \frac{2.303\ RT \times 2}{F} = 0.118 \text{ at } 298K$$

The term a of the Tafel equation is found to be totally dependent on the cathode used.





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Q.9 **How over voltage is determined experimentally?**

Ans. The circuit diagram to determined over voltage is given as follows:

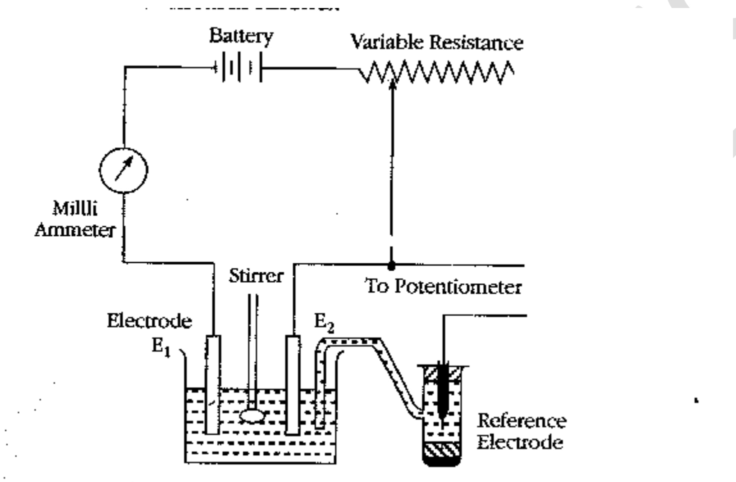

Fig. 3 : Determination of overvoltage

Construction

The apparatus used to measure over voltage consist of 2 electrodes A and B of known cross-sectional area placed in a solution of known concentration. The electrode is generally an inert metal such as Platinum, which does not interfere with the properties of the solution. The electrode A and B are connected to a source of potential C, a high voltage battery through a variable resistance D. A suitable ammeter indicates the strength of the current passing through the solution. The solution is made free from dissolved O_2 by passing N_2 gas through it, which maintains inert atmosphere or by saturating the solution with N_2 at atmospheric pressure. A stirrer in the solution helps to polarization.

Working: The solution is first stirred by means of a stirrer and then a current of known strength (or of known as current density) is passed through the solution by the adjustment of variable resistance D. After the current reaches a steady value, the potential of the cathode say A at a given current density is measured with the help of potentiometer by combining it with a reference electrode such as calomel.

	These measurements are repeated at different current densities. The potential of A at each stage is obtained by subtracting the potential of the Calomel electrode from the total measured emf. The over voltage is then determined by using the relation $\eta_d = E_d – E_r$, where E_d = Electrode decomposition potential , E_r = Reversible electrode potential. E_r for A is determined by using Nernst's equation.

Q.10) What is electroplating? What are its objectives?

Ans:

Electroplating is the process of producing a metallic coating on a surface electrolytically. The process used in electroplating is also termed as electrodeposition.

Objectives of electroplating

I) For decoration purpose or to improve aesthetic qualities e.g. gold silver coating on jewellery made of inferior metals such as plastic

II) For repair or build up thickness on undersized parts. e.g. Welding of broken parts of machinery

III) For protection or corrosion protection e.g. chrome plating metal parts in automobiles to enhance corrosion resistance.

Q.11) Explain the process of electroplating.

Ans: Electroplating is the process of producing a metallic coating on a surface electrolytically. The process used in electroplating is also termed as electrodeposition.

Process: The schematic representation of the electrolytic for electroplating a metal M from aqueous solution of its metal salt is shown below

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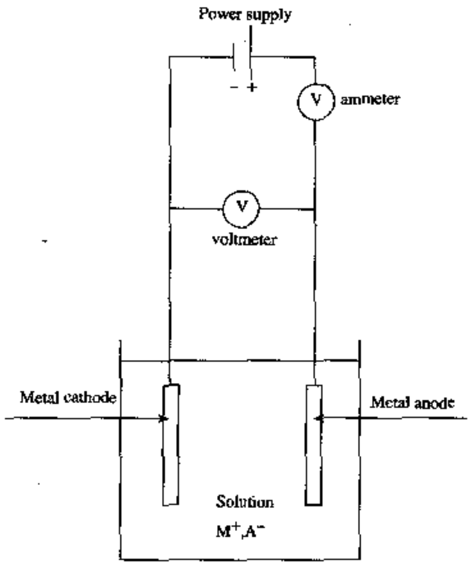

ectrolytic cell for plating metal "M" from a solution of the metal salt 'MA'.

The surface to be coated becomes the cathode.

The anode may be of the metal to be plated or it may be a non- consumable anode such as lead. In the second case, it is necessary to periodically replenish the electrolyte. The anode and cathode are connected to the external source of ditect current as shown. Experimental conditions such as current density, nature and concentration of electrolyte, temperature etc. affect the nature of the deposited metal.

Q.12) What are the factors that influence the nature of deposited metal?

Ans:The factors are

I. Current density

II. Concentration of the electrolyte

LII. Temperature

IV. Presence of colloidal matter

V. Nature of the electrolyte

VI. Nature of the base metal

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