

## Solutions

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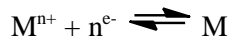


Sub:	<b>Engineering Chemistry</b>	Code:	17CHE22
Date: <u>12/03/2018</u>	Duration: <u>90</u> mins	Marks: <u>50</u>	Sem: <u>II</u>
			Branch: <u>All</u>

### Internal Assessment Test I – September 2017

**1. (a) Derive Nernst equation for a single electrode potential. (05 Marks) (CO1, L3)**

**Solution:** Consider an electrode assembly undergoing a spontaneous reaction.



The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

$$\Delta G = \Delta G^{\circ} + RT \ln Kc \text{ -----(1)}$$

For above reaction  $Kc = \frac{[M]}{[M^{n+}]} \text{ -----(2)}$

According to thermodynamics, decrease in free energy ( $-\Delta G$ ) represents maximum amount of work that can be obtained from a chemical reaction.

$$-\Delta G = W_{\max} \text{ ----- (3)}$$

Work done in electrochemical reaction depends on

(i) Number of coulombs of electricity that flow and (ii) Energy available per coulomb.

Number of coulombs =  $n \times F$  (Where  $n$  = number of electrons involved in the cell reaction and  $F$  = Faraday constant)

Energy available per coulomb =  $E_{\text{cell}}$  (V) or  $J C^{-1}$

When  $E_{\text{cell}}$  = maximum, work derived from cell is maximum.

$$\text{Thus, } W_{\max} = n \times F \times E \text{ ----- (4)}$$

$n$  = moles of electrons,  $F = C \text{mol}^{-1}$ ,  $E = J C^{-1}$

Equating equations (3) & (4)

$$-\Delta G = n \times F \times E \text{ or}$$

$$\Delta G = - n \times F \times E \text{ ----- (5)}$$

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$$\Delta G^{\circ} = - n \times F \times E^{\circ} \text{ -----(6)}$$

Where  $E^{\circ}$  is a constant called **standard electrode potential**.  $E^{\circ}$  is the potential when a metal is dipped in 1M solution of its ions or when an inert electrode is in contact with a gas at a pressure of 1 atm at 298 K.

Therefore by substituting values of  $\Delta G$ ,  $\Delta G^{\circ}$  and  $Kc$  from equation (2), (5) and (6) into equation (1), we get

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nFE^\circ + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by  $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^\circ}{-nF} + \frac{RT \ln [M]}{-nF} - \frac{RT \ln [M^{n+}]}{-nF}$$

$$E = E^\circ - \frac{RT \ln [M]}{nF} + \frac{RT \ln [M^{n+}]}{nF}$$

Under standard condition  $[M] = 1$ ,

$$\therefore E = E^\circ + \frac{RT \ln [M^{n+}]}{nF} \text{----- (7)}$$

Converting natural log to base 10 in eqn (7) we get

$$E = E^\circ + \frac{RT \log [M^{n+}]}{nF} \text{----- (8)}$$

Substituting the values for R (8.314 JK<sup>-1</sup>mol<sup>-1</sup>), F (96500Cmol<sup>-1</sup>) and T (298K) in eqn (8) we get

$$E = E^\circ + \frac{0.0591 \log [M^{n+}]}{n}$$

**(b) Define Fuel cell. What are the differences between Fuel cell and Conventional cell? (05 Marks) (CO1, L1, L4)**

**Solution:** Fuel cells are the galvanic cells which convert chemical energy of a fuel- oxidant system directly into electrical energy by oxidation of fuel at anode and reduction of oxidant at cathode”.

**Or**

A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity. Eg: Methanol-Oxygen fuel cell.

	<b>Conventional batteries</b>		<b>Fuel Cells</b>
1.	Anodic and cathodic compartments are preloaded and reaction products are retained in the battery.	1.	Permit continuous movement of fuel, oxidant and reaction products in and out of battery.
2.	They have definite amount of stored energy.	2.	They are only energy conversion devices, do not store any energy.
3.	As long as active components exist, battery continues delivering energy.	3.	As long as fuel and oxidant are supplied at respective electrodes, energy is available.
4.	Generally function at ambient temperatures without an active catalyst being employed.	4.	Generally work at higher temperature or in presence of an electrocatalyst.

**2. (a) What is electrolyte concentration cell? The EMF of the cell Cu(s)/CuSO<sub>4</sub> (0.001M)// CuSO<sub>4</sub> (XM)/Cu(s) is 0.0595 V at 25°C. Find the value of X and write cell reaction. (06 Marks) (CO1, L3)**

**Solution:** Electrolyte Concentration Cell: It is an electrochemical cell in which two identical electrodes immersed in same ionic solution but of different concentration. Ex: Copper concentration cell

**Cell Reaction:**  $\text{Cu} \longrightarrow \text{Cu}^{2+} (0.001\text{M}) + 2\text{e}^-$  (ANODE)

$\text{Cu}^{2+} (\text{XM}) + 2\text{e}^- \longrightarrow \text{Cu}$  (CATHODE)

$n=2$ ,  $E_{\text{cell}} = 0.0595\text{V}$ ,  $T=25^\circ\text{C}=25+273= 298\text{K}$ ,  $C_1=0.001\text{M}$ ,  $C_2=\text{XM}$

**Formula:**  $E_{\text{cell}} = 2.303RT/nF \log [C_2]/[C_1]$

**Substitution:**  $0.0595 = 2.303 \times 8.314 \times 298 / 2 \times 96500 \log [X]/[0.001]$

Or,  $0.0595 = 0.0295 \{ \log [X] - \log [0.001] \}$

Or,  $2.017 = \log [X] - \log [0.001]$

Or  $2.017 = \log [X] + 3$

Or,  $\log [X] = -0.983$

Or,  $X = 0.103\text{M}$

**(b) Which type of corrosion control mechanism could be deployed to protect the underground crude oil pipeline and explain the method in detail? (04 Marks) (CO2, L4)**

**Solution:** Cathodic protection can be deployed to protect the underground crude oil pipeline. These can be done either by:

(i) Sacrificial anodic method. Or (ii) Impressed current method.

**(i) Sacrificial anodic method:**

In this method, the base metal structure is converted into a cathode by connecting it to a more active [higher up in galvanic series or less noble] metal. This active metal actually acts as an auxiliary anode. Mostly Zn, Mg, Al are the common auxiliary anodes used in this method. These metals being more active, acts as anode and undergo destruction and protect the metal structure.

Since the anode material sacrifice to protect the metal structure, the method is known as sacrificial anode method. After continuous use exhausted sacrificial anodes are replaced by new ones as and when required.

Advantages: (i)The method is simple. (ii) Low installation cost. (iii) Minimum maintenance cost.

(iv) Doesn't require power supply.

Disadvantage (i) Involves recurring expenditure for replacement of consumed anodes.

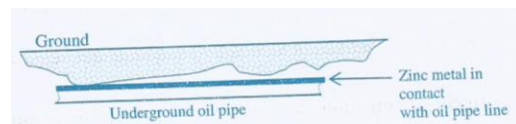
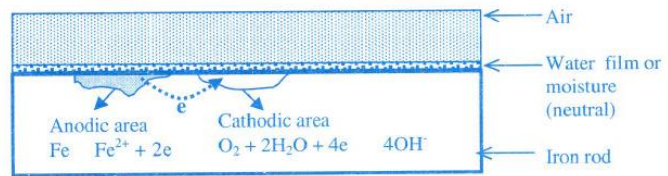


Fig: Cathodic Protection by sacrificial anode

**3. (a) Define corrosion. Explain the electrochemical theory of corrosion by taking iron as an example. (06 Marks) (CO2, L4)**

**Definition:** It's defined as the destruction of metal or alloys by the surrounding environment through chemical or electrochemical changes.

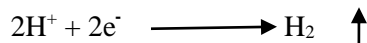
According to electrochemical theory, corrosion of metals takes place due to the formation of anodic and cathodic regions on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.



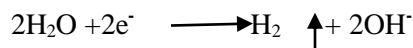
AT ANODE:  $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$

At CATHODE: Since metal cannot be reduced further, metal atoms at the cathodic region are not affected. Therefore, cathodic reaction depends on the nature of the electrolyte. There are three possible ways in which the reduction can take place.

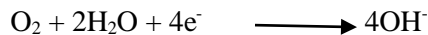
(a) If the solution is deaerated and acidic, the cathodic reaction involves evolution of hydrogen.



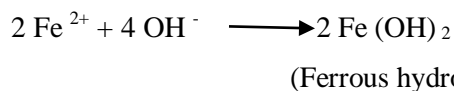
(b) If the solution is deaerated and almost neutral the cathodic reaction involves evolution of hydrogen gas and hydroxyl ions.



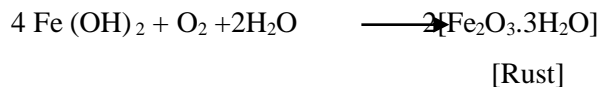
(c) If the solution is aerated and almost neutral the alkaline oxygen or water are reduced to  $\text{OH}^-$  ions.



Corrosion of iron produced  $\text{Fe}^{2+}$  ions and  $\text{OH}^-$  ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since small  $\text{Fe}^{2+}$  ions diffuse more rapidly than  $\text{OH}^-$  ions. Their combination occurs more commonly near cathodic region.



In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.



**(b) Explain the following characteristics of a battery: (i) Cell potential (ii) Cycle Life. (04 Marks) (CO1, L3)**

Solution: (i) **Cell Potential:** The cell potential of a battery is given by the equation,

$$E_{\text{cell}} = (E_c - E_A) - |\eta_A| - |\eta_C| - iR_{\text{cell}}$$

Where,  $E_c$  and  $E_A$  are the electrode (reduction) potential of cathode and the anode respectively,  $\eta_A$ ,  $\eta_C$  are the over-potentials at the anode and the cathode respectively and  $iR_{\text{cell}}$  is the internal resistance.

To derive maximum voltage from a battery

- The difference in the electrode potentials must be high.
- The electrode reactions must be fast so as to minimize the overpotential.
- The internal resistance of cell must be low.

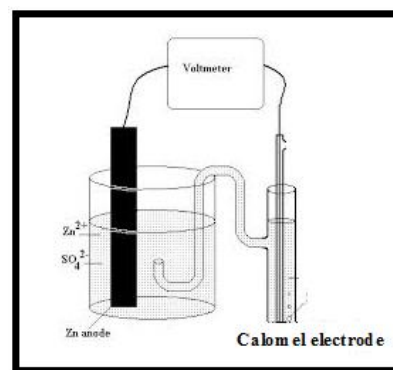
The electrode system should be such that the active mass at the positive electrode depletes readily and that at the negative electrode increase easily. This minimize the overpotential at the cathode and anode. The cell should be appropriately designed so as to minimize internal resistance. This can be achieved by keeping the electrodes close to each other and also by using an electrolyte of high conductivity.

**(ii) Cycle Life:** An important feature of secondary batteries is the rechargeability. The number of times a battery can be discharged/ recharged before occurrence of failure is called cycle life. Cycle life depends on chemical composition, morphological changes and distribution of active materials in the cell. Reasons which lower the cycle life of battery are as listed:

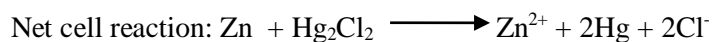
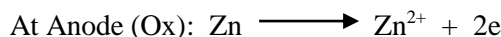
- Corrosion at contact points.
- Shedding of active materials from plates.
- Short circuiting between electrodes due to irregular crystal growth and changes in morphology.

**4. (a) Explain the measurement of unknown electrode potential using calomel electrode as secondary reference electrode. (05 Marks) (CO1, L4)**

**Solution:** The given electrode, say zinc electrode, is coupled with saturated calomel electrode as in the figure. Since the reduction potential of zinc electrode less than that of calomel electrode, zinc acts as anode and calomel as cathode. The cell assembly is represented as,  $Zn / ZnSO_4 (1 M) // KCl (saturated) / Hg_2Cl_2 / Hg$



**Cell reactions:**



The EMF of the cell assembly is,  $E_{cell} = E_{right} - E_{left}$   
 $= E_{cal} - E_{Zn/Zn^{2+}}$

$$1.002 = 0.242 - E_{\text{Zn}/\text{Zn}^{2+}}$$

$$E_{\text{Zn}/\text{Zn}^{2+}} = 0.242 - 1.002$$

$$E_{\text{Zn}/\text{Zn}^{2+}} = -0.76 \text{ volt.}$$

**(b) Describe construction and working of Li-ion battery. Mention its applications. (05 Marks) (CO1, L2)**

Solution: A lithium-ion battery is a member of a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging.

Anode : Li-metal oxide , like lithium cobalt oxide , Cathode: Carbon (graphite)

Electrolyte: lithium salts ( $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ) in organic carbonate solvents (ethylene carbonate)

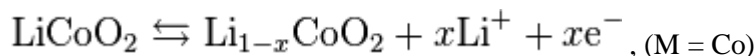
Separator : polypropylene separator

Type and Cell representation: Li-ion battery is a secondary battery.

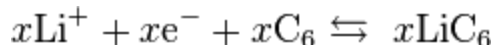
$\text{LiCoO}_2$  / electrolyte (lithium salt in an organic solvent) / C(graphite)

Working:

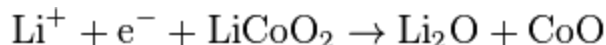
The positive electrode half-reaction is:



The negative electrode half reaction is:



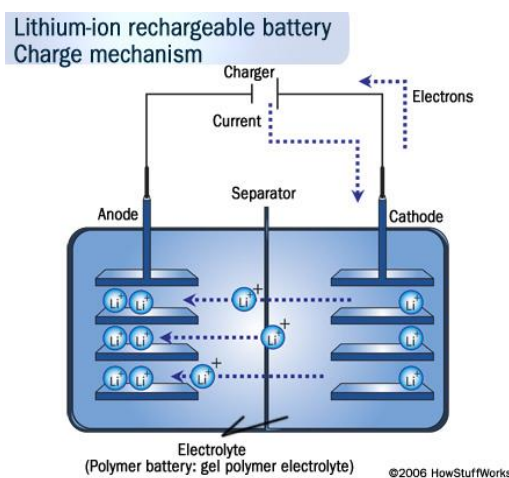
The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:



Use : It is used in mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights). Li-ion batteries are used in tools such as cordless drills, sanders, saws. Electric vehicles, in telecommunications applications.

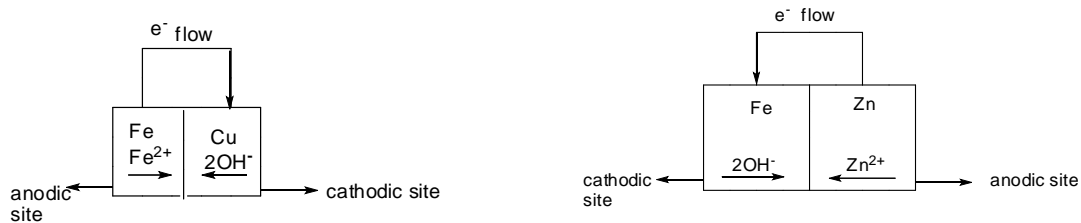
**5. (a) Discuss the differential metal corrosion with an example. (04 Marks) (CO2, L2)**

Solution: When two dissimilar metals are in contact with each other, a potential difference is setup resulting in a galvanic current. A metal placed high in the electrochemical series is said to be anodic with



respect to the one placed below it. The rate of differential metal corrosion depends primarily on the amount of the current passing from anode to cathode i.e.; on the difference in electrochemical potential, higher the difference faster is the rate of corrosion.

When iron is in contact with copper, iron behaves as anode owing to lower reduction potential and thereby undergoes corrosion. While copper being cathode, remains unaffected. On the other hand, zinc is anodic to iron since it has lower reduction potential and thus corrodes while iron remains unaffected.



**(b) Explain the following factors affecting corrosion: (i) pH of the medium (ii) Nature of corrosion product (iii) Ratio of anodic to cathodic areas. (06 Marks) (CO2, L4)**

Solution: (i) **pH** : In general, the rate of corrosion is high when the nature of the environment is acidic.

(a) If the  $\text{pH} < 3$ , severe corrosion occurs even in the absence of air due to the continuous evolution of hydrogen at the cathodic region.

(b) If the  $\text{pH} > 10$ , corrosion of the metal practically ceases, due to the formation of a protective coating of hydrogen oxide of iron.

(ii) **Nature of the corrosion product**: The nature of the corrosion product largely decides the rate of further corrosion. The corrosion product formed on the surface of the metal may or may not act as a protective layer.

(a) The nature of the oxide layer largely decides the rate of further corrosion. If its composition is stoichiometric, highly insoluble and non-porous with low ionic and electrical conductivity, the layer acts as a protective film and prevents further corrosion. For eg. Al, Ti and Cr develop such a layer on their surface and become passive to further corrosion. Stainless steel (18% Cr, 8% Ni) builds up a thin but a highly protective film of  $\text{Cr}_2\text{O}_3$  which resists attack in a highly corrosive environment. Metals such as Zr and Mo not only form such a protective layer but are also capable of self-repairing the oxide films when it is damaged. Hence these metals are extremely resistant to corrosion.

(b) If the oxide layer is non-stoichiometric, highly porous, soluble, unstable, it cannot control further corrosion. In such cases the fresh metal surface is continuously exposed to the corrosion environment and corrosion takes place continuously. Eg. Fe and Zn

**iv) The ratio of anodic and cathodic areas:** The rate of corrosion largely depends on the relative size of anode and a cathode.

(a) If the metal has a small anodic and large cathodic area (i.e; the ratio of anode to cathode is small) then the corrosion is more intensive and faster in rate. This is explained as follows:

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed when the anode is smaller and cathode region is large, the electrons liberated at the anode, are rapidly consumed, at the cathode region. This process makes the anodic reaction to take place faster .thus increasing the corrosion rate.

(b) If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.

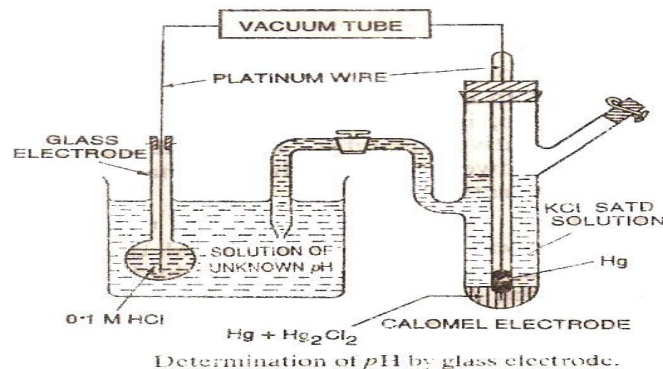
Ex: A broken coating of tin on iron surface, tin is cathodic to iron and the small exposed part of iron acts as anodic region and rest of the large tin coated surface acts as cathodic region. Because of small ratio of anodic to cathodic area, the corrosion rate is very high, on the other hand Zn plating on Fe gives an anodic coating to iron (Zn is above Fe in electrochemical series). Thus even if Zn plating peels off at some point, Fe does not get corroded.

**6. (a) What are ion selective electrodes? Explain the determination of pH of unknown solution using glass electrode. (05 Marks) (CO1, L4).**

Solution: These are the electrodes, which responds to specific ions only and develops a potential against that ions while ignoring the other ions present in the solution.

**Determination of pH using glass electrode or calomel electrode**

To determine the pH of given solution, glass electrode is dipped in a solution whose pH has to be determined. It is combined with a saturated calomel electrode through a salt bridge.



Cell assembly representation:

$\text{Hg} / \text{Hg}_2\text{Cl}_2 / \text{Cl}^- // \text{Unknown solution} / \text{glass membrane} / 0.1\text{N HCl} / \text{AgCl} / \text{Ag}$

From the emf, the pH of the solution is calculated as below:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{cal}}$$

$$E_{\text{cell}} = (E_{\text{G}^+} + 0.0591 \text{ pH}) - E_{\text{cal}}$$



$$E_{\text{cell}} = E_G^\ominus - E_{\text{cal}} - 0.0591 \text{ pH}$$

$$\text{pH} = (E_G^\ominus - E_{\text{cal}} - E_{\text{cell}})/0.0591$$

$$\text{pH} = (K' - E_{\text{cell}})/0.0591$$

**(b) What is galvanization and tinning? Explain galvanization process by hot dipping method. (05 Marks) (CO2, L1,L2)**

Solution: Galvanization is the corrosion control technique where Zn is coated on top of base metal. It is a type of anodic metal coating.

Tinning is the corrosion control technique where Sn is coated on top of base metal. It is a type of cathodic metal coating.

**GALVANIZATION:** the process of galvanization is carried out as follows,

- (i) The base metal is first treated with organic solvent to remove grease or oil material present on it.
- (ii) It is further treated with dil.  $\text{H}_2\text{SO}_4$  to remove rust or oxide layer present on it.
- (iii) The metal is then treated with flux of  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  for best adhesion property.
- (iv) Finally the base metal is dipped into the zinc at  $430\text{--}470^\circ\text{C}$ .
- (v) The excess zinc is removed from the surface by rolling or wiping etc.

These steps are diagrammatically shown in Fig below:

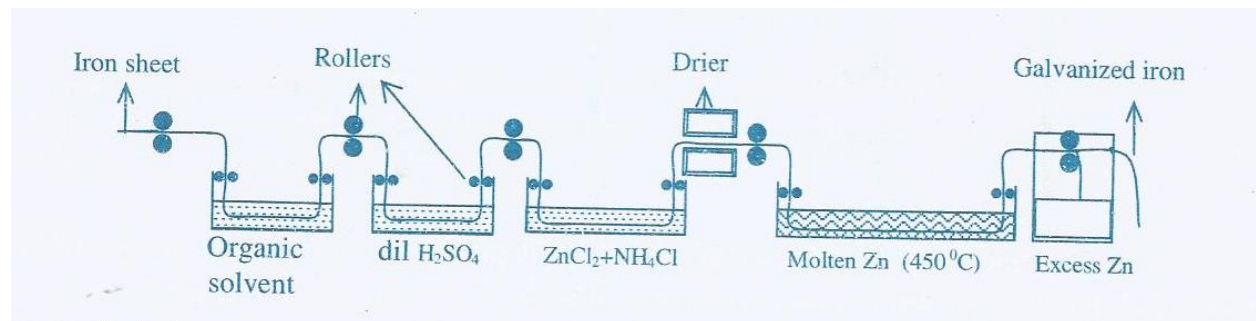


Fig: Galvanisation of Iron

**7. (a) Define battery. Explain the construction, working and applications of Zn-Air battery. (06 Marks) (CO2, L1,L3)**

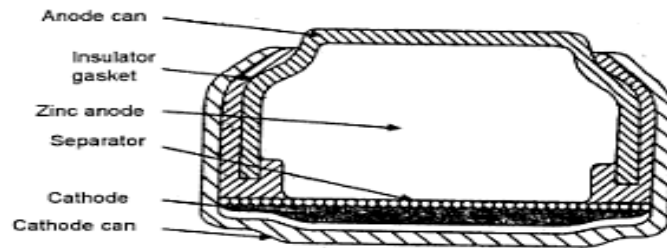
Solution: Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Zinc Air Battery:

This is a type of metal-air batteries which use oxygen directly from the atmosphere to produce electrochemical energy.  $\text{O}_2$  diffuses into the cell and is used as the cathode reactant. The air cathode catalytically promotes the reaction of  $\text{O}_2$  with an alkaline electrolyte and is not consumed during discharge.

**Construction:**

1. Anodic material – Loose granulated zinc powder mixed with aqueous alkaline electrolyte (20% NaOH) and a gelling agent (to immobilize the composite).
2. Cathodic material – Carbon, catalyst mixture (oxides of Mn, La) with a wet proofing agent. Beneath Carbon electrode, oxygen permeable membrane Teflon is used. Oxygen is allowed into cell through air access holes to the cathode can.
3. Electrolyte – 20% NaOH absorbed in a porous separator is placed in between anodic zinc and cathodic carbon.



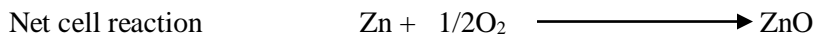
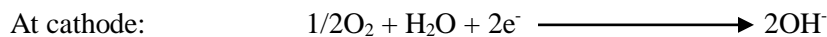
**Fig. 2.6** *Zinc – Air Battery*

**Cell representation;**

The battery is representation as,  $\text{Zn} / \text{NaOH (aq, 20\%)} / \text{air (O}_2\text{)}$ ,

**Working:**

Electrode reactions (discharging and charging) are:



During discharging process at, anode Zn oxidizes to  $\text{Zn}^{2+}$  in  $\text{ZnO}_2$ . similarly, at cathode  $\text{O}_2$  reduces to  $\text{O}^{2-}$  forming  $\text{OH}^-$ . Finally the battery produces a potential of 1.7V

**Advantages:**

1. High energy density as cathodic compartment is not there in cell.
2. Low cost with long shelf life in sealed condition.

**Applications:**

1. Used in hearing aids and medical devices.
2. Used in telecommunication devices such as pagers and wireless headsets.

3. Zinc-air batteries are often used to power a number of medical devices, such as patient monitors and recorders, nerve and muscle stimulators, and drug infusion pumps.

**(b) What is metal finishing? Mention the technological importance of metal finishing. (04 Marks)**  
**(CO3, L1)**

Solution: Process of surface modification by way of deposition of another metal or metal alloy or polymer or ceramic or oxide layer to bring about intended better surface characteristics is known as metal finishing.

Technological Importance:

Technological significance of metal finishing refers to imparting following different characteristics:

- (i) Better corrosion resistance,
- (ii) Better hardness, strength, wear / abrasion resistance, etc.
- (iii) Better thermal conductance or resistance or reflectance, etc.
- (iv) Better optical reflectance,
- (v) Better electrical conductance or insulation, etc.
- (vi) Building up material or restoration
- (vii) Manufacturing printed circuit boards, capacitors, contacts, etc.
- (viii) Electrotyping (e.g., gramophone records)
- (ix) Electroforming or reforming of articles,
- (x) Electrochemical machining, electropolishing and electrochemical etching, etc.