

Internal Assessment Test 1 – Jan-2023

(b) Define corrosion penetration rate. A thick steel sheet of area 60 inch² is exposed to air near the ocean and after 6 year it was found to experience a weight loss pf 455 gm due to corrosion. If the density of the metal is 7.9 gm/cm^3 calculate CPR in mpy and mmy. Given $K(mpy) = 534$ and $K (mm/y) = 87.6$.

(Chief Course Instructor)

 $\boxed{6}$ $\boxed{\text{CO3} \mid \text{L3}}$

Answer 1(a) :

Photovoltaic Cells:

Photovoltaic cells or solar cells are semiconductor device that converts sunlight into direct current (DC) electricity. As long as light is shining on the solar cell, it generates electrical power. When light stops, electricity stops.

Figure Photovoltaic cells

Construction & Working of PhotoVoltaic Cells

Construction:

- PhotoVoltaic Cells consist of a semiconductor diode (p-n junction) made of a silicon.
- Silicon wafer or very thin silicon slices are made by silicon blocks and they are doped by p-type and n-type dopents to make p-n junction.
- It has two electrical contact, on one of its sides, a mettalic grid is used and on the other side a layer of noble metal (such as Ag) is used.
- The metal grid permits the light to fall on the diode between the grid lines.
- The part between the metallic grid is coated with antireflective compound. eg $TiO₂$

Working:

 Electromagnetic radiation consists of particle called photon (hv). They carry a certain amount of energy given by the Plank quantum equation.

$E = hc/\lambda$

Where, h = Planck's constant, c = velocity of light, λ = wavelength of the radiation

- The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed.
- The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

Advantage of PhotoVoltaic cells -

- 1. It is unlimited, inexhaustible and renewable source of energy.
- 2. The solar cell operates reliably for a long period of time with no maintenance.
- 3. A photovoltaic system can be constructed to any size based on energy requirement.
- 4. Easy to operate
- 5. Quick installation.
- 6. Can be integrated into new or existing building structure.
- 7. Completely pollution free during its use.

Disadvantage of PhotoVoltaic cells –

- 1. High installation cost.
- 2. Energy can be produced only during the day-time.
- 3. The efficiency of solar cells depends on the seasonal variations, latitude and climate.
- 4. Space required to generate unit power output is relatively more.
- 5. Solar cell generates DC current. It needs to be converted to AC for use.

Answer 1b: Definition: Corrosion is defined as the **destruction of metal or alloys from its surface by the surrounding environment through chemical or electrochemical changes**.

Eg. 1. Rusting of Fe- A reddish brown scale formation on iron. It is due to the formation of hydrated ferric oxide.

Electrochemical theory of corrosion: Most of the corrosion problems are best

explained on the basis of electrochemical theory.

(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

(ii) At the anodic region oxidation reaction takes place and the **metal gets converted into its ions by liberating electrons**. Consequently, **metal undergoes corrosion at the anodic region**.

 $M \longrightarrow M^+ + ne^-$ **Ex:** Fe \longrightarrow Fe $^{2+}$ + 2e⁻

(iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further**, metal atoms at the cathodic region are unaffected by the cathodic reaction**. Some constitutions of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

(i) If the solution is aerated and almost neutral, oxygen is reduced in presence of water to OHions according to the equation.

 $\frac{1}{2}$ O₂ + H₂O + 2e⁻ \longrightarrow 2OH⁻

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

2H2O +2e**-** H² + 2OH**-**

(iii) If the solution is deaerated and acidic, the H^+ ions are reduced to H₂

 $2H^+ + 2e^ \longrightarrow H_2$

(iv) The electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards each other through the conducting medium-range and form a corrosion products.

Corrosion of iron produced Fe²⁺ ions and OH⁻ ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble Fe (OH)2.

 $\text{Fe} \,^{2+}$ + 2 OH \rightarrow Fe (OH) 2 (Ferrous hydroxide)

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

 $2Fe(OH) 2 + O2 + (n-2) H2O \longrightarrow [Fe2O3.nH2O] [Rust]$

Corrosion of metal continues as long as both anodic and cathodic reactions take place simultaneously.

Answer 2a: Classification of Batteries

Batteries are classified under the following categories:

● **Primary battery:** In primary batteries, chemical energy stored in the battery is converted to electrical energy spontaneously as long as active materials are present. This battery cannot be recharged, because cell reaction is irreversible. *Example:* Zn-MnO₂ battery, Li-MnO₂ battery.

● **Secondary battery:** This battery can be recharged by passing electric current, because cell reactions are reversible. The redox reaction is reversed during recharing. Electrical energy is stored in the form of chemical energy in these batteries and used when needed. *Example:* Lead

acid battery, Ni-MH battery, Li-ion battery. Primary cells act only as galvanic cell,

whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy

● **Reserve battery:** In this battery, one of the key component is stored separately, and is incorporated into battery when required. When long storage is required, reserve batteries are often used, since the active component of the cell is separated until needed, thus reducing selfdischarge.

Example: Mg-AgCl battery. They are activated by adding sea water. These batteries have high reliability and long shelf life, hence they find applications in missiles and submarines. Another example is zinc-air batteries where the cell is sealed until use, the seal is removed to admit air and activate the cell when needed.

Answer 2b. Solid state battery: A solid-state battery is essentially battery technology that uses a solid electrolyte instead of liquid electrolytes**.** The solid-state battery uses solid electrolyte, not liquid electrolyte solution, and the solid electrolyte plays a role of a separator as well.

Lithium polymer (LiPo) Batteries

LiPo batteries are composed of a lithium-based cathode and anode separated by a polymer electrolyte. LiPo batteries differ from other lithium-ion (Li-ion) batteries in that they have a solid polymer electrolyte component rather than a liquid electrolyte. Common polymer electrolytes may be dry, porous or a gel, and include poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF), and poly(ethylene oxide) (PEO).

The science behind LiPo batteries is the same as in other Li-ion batteries: chemical energy is converted to electrical energy when electrons travel from the battery's anode to its cathode, creating an electrical current. The cathode contains a lithium metal oxide (such as lithium-cobalt oxide ($LiCoO₂$)), which provides lithium ions, whereas the anode contains a lithium carbon (such as graphite).

The anode and cathode are separated by an electrolyte that interacts with the anode to generate electrons, which creates a charge gradient in the cell. As the anode becomes negatively charged, the electrons travel along a conducting wire to the cathode. The whole system thus undergoes an electrochemical redox reaction (reduction/oxidation): the anode loses electrons and becomes oxidized while the cathode gains electrons and is reduced.

Figure: LiPo Battery

Anode: Lithium intercalated Carbon or graphite

Cathode: lithium transition metal oxides (such as lithium-cobalt oxide (LiCoO2)), **Electrolyte & Separator:** High conductivity semisolid (gel) polymers electrolyte polymer electrolytes and include poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN)

Working:

 Discharge At anode: Li_xC_6 xLi⁺ + xe⁻ + C₆ Charge Discharge At cathode: $LiCoO₂ + xLi⁺ + xe⁻$ Li_{1+x} CoO₂ Charge

Applications: These batteries provide higher specific energy than other lithium battery types and are used in applications where weight is a critical feature, such as mobile devices, radiocontrolled aircraft and some electric vehicles.

Answer 3a. Battery is a device which convert chemical energy into electrical energy on demand through redox titrations. OR

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

Construction:

Anode: Non-graphitic anodes, which consist largely of various carbonaceous materials (such as carbon black, pitch-based carbon-fibers, hard carbons etc)

Cathode: layer and tunnel type transition metal oxides, transition metal sulfides and fluorides etc

Electrolyte: The most common electrolyte formulations for SIBs are NaClO₄ or NaPF₆ salts in carbonate ester solvents (particularly propylene carbonate).

Figure. Na-ion Battery (SIB)

Working principles of SIBs

When the battery is being charged, Na atoms in the cathode release electrons to the external circuit and become ions which migrate through the electrolyte toward the anode, where they combine with electrons from the external circuit while reacting with the layered anode material. This process is reversed during discharge.

Discharge At anode: $\overline{Na_xC_6}$ $\overline{\bullet}$ $\overline{X}Na^+ + xe^- + C_6$ Charge

$$
xNa^{+}+xe^{-}+\ C
$$

At cathode: $NaMO₂ + xNa⁺ + xe⁻$

$$
\overrightarrow{\text{Discharge}} \quad \text{Na}_{1+x} \text{ MO}_2 + \text{C}_6
$$
\nChange

Overall cell reaction: $Na_xC₆ + Na MO₂$ \longrightarrow $Na_{1+x}MO₂ + C₆$

 Discharge Charge

Applications: Sodium-ion batteries can be used for a broad range of battery applications, including renewable energy storage for homes and businesses, grid storage, and backup power for data and telecom companies.

Answer 3b. Construction, working and applications of methanol–oxygen fuel cell.

It is good example for liquid fuel cell. They use either acidic or alkaline medium. The preferred electrolyte is the acidic. Methanol is an efficient active organic fuel at low temperature.

Construction: Methanol – oxygen fuel cell consist of

- 1. Anode It is a porous Nickel (Ni) electrode impregnated with Pt/Pd catalyst.
- 2. Cathode It is a porous Nickel (Ni) electrode coated with silver (Ag) catalyst.
- 3. Electrolyte Aqueous sulphuric acid (H_2SO_4) , 3.7 M.
- 4. Active components: (a) Fuel Methanol mixed with sulphuric acid supplied at anode. (b) Oxidant – Pure oxygen is supplied at cathode.

Figure: Methanol – oxygen fuel cell

Working:

Cell reaction; Anode Reaction: $CH_3OH + H_2O \quad \longrightarrow \quad CO_2 + 6H^+ + 6e$ Cathode Reaction: $3/2$ O₂ + 6 H⁺ + 6e- \longrightarrow 3 H₂O Overall Cell Reaction: $CH_3OH + 3/2 O_2 \longrightarrow CO_2 + 2 H_2O$

 $H₂O$ and $CO₂$ are formed as by-products but they do not harm the cell functioning because they are removed as and when they are formed.

Cell Potential : 1.2 V

Applications:

- 1. used in automobiles, military applications.
- 2. Power backup and portable instruments.
- 3. In large scale power production.

Answer 4a.

Definition: 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.

Construction, working and applications of polymer electrolyte fuel cell.

Polymer electrolyte fuel cells (PEFC) are electrochemical devices, converting the chemical energy of fuel directly into electrical energy. They are also known as Polymer electrolyte membrane (PEM) fuel cells or proton exchange membrane fuel cells. They deliver high power density and offer the advantages of low weight and volume compared with other fuel cells.

Construction: A PEFC comprising a proton-conductive solid polymer electrolyte membrane of thickness 50–180 μm and porous carbon electrodes containing a platinum or platinum alloy catalyst (Figure). The most typical polymer electrolyte membrane is the perfluorosulfonic-acidtype ion exchange membrane such as Nafion®, which has a molecular structure based on a main polytetrafluoroethylene chain with side chains containing sulfonic acid. Pure hydrogen or hydrogen reformed from methanol or natural gas is used as fuel.

Figure: Polymer electrolyte fuel cell

Working:

Hydrogen supplied to the anode side is oxidized, and produced $H⁺$ moves through the membrane to the cathode side. This H^+ is used in the reaction in which water is formed by the reduction of oxygen supplied to the cathode side. As the electrons generated at the anode flow through the external circuit to arrive at the cathode, an electric current can be retrieved. The reactions at the anode and cathode, and the overall reaction, are given as follows.

Applications: Polymer electrolyte fuel cells (PEFCs) are of interest as power sources in vehicles and portable applications because of their high energy efficiency and environmentally friendly qualities.

Answer: 4b. Flow battery: A flow battery, or redox flow battery, is a type of electrochemical cell where chemical energy is provided by two chemical components dissolved in liquids that are pumped through the system on separate sides of a membrane. Example: **Vanadium redox flow battery**

Vanadium redox flow battery: The vanadium redox battery (VRB), also known

as the vanadium flow battery (VFB) or vanadium redox flow battery (VRFB), is a type of rechargeable flow battery. It employs vanadium ions as charge carriers.

Construction: A vanadium redox battery consists of an assembly of power cells in which two electrolytes are separated by a proton exchange membrane.

Electrodes: The electrodes in a VRB cell are carbon based. The most common types are carbon felt, carbon paper, carbon cloth, and graphite felt. Recently, carbon nanotube-based electrodes have attracted interest from the scientific community.

Electrolytes: Both electrolytes are vanadium-based. The electrolyte in the positive half-cells contains VO_2^+ and VO^{2+} ions, while the electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions. The electrolytes can be prepared by several processes, including electrolytically dissolving vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4) . The solution remains strongly acidic in use.

Membrane: The most common membrane material is perfluorinated sulfonic acid (PFSA) (Nafion). polytetrafluoroethylene (Teflon).

Figure. A diagram of a vanadium redox flow battery

Figure. Vanadium redox flow battery: (a) charge reaction and (b) discharge reaction.

Working:

Discharge

Negative electrode: V^{2+}

$$
\longleftrightarrow \quad V^{3+} + e^-
$$

Discharge

Positive electrode: $VO_2^+ + e^- + 2H^+$ $\leftrightarrow \quad \text{VO}^{2+} + \text{H}_2\text{O}$ Charge

Discharge

Overall reaction: $VO_2^+ + V^{2+} + 2H^+$ $\longleftrightarrow \quad \text{VO}^{2+} + \text{V}^{3+} + \text{H}_2\text{O} \quad \text{(E}^{0} = 1.26 \text{ V)}$ Charge

Application: Vanadium batteries are typically used for grid energy storage, i.e., attached to power plants/electrical grids.

Answer 5a The type of corrosion which takes place when iron is in contact with Cu is Differential metal corrosion (Galvanic corrosion)

- Differentian metal corrosion arises when two dissimilar metals are in contact with each other. Under this condition a potential difference is set up resulting in a galvanic current.
- A metal placed high in the electrochemical series is said to be anodic to the one placed below it.
- Eg: Fe is anodic to Cu but cathodic to Zn, Mg.
- Thus, Fe corrodes when it is in contact with Cu and Ni; But Zn and Mg gets corroded when they are in contact with Fe.
- 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.

 Consider a galvanic cell, in this cell, iron and copper in contact with an aerated solution of NaCl. A current flows between the two electrodes spontaneously and electrons flow from Fe to Cu, indicating that Fe is the anode and Cu is the cathode. The reaction that take place as follows-

Fig. Differential metal corossion

" When two metals are in contact with each other, a galvanic cell is set up and a current flows.

The metal acting as anode undergoes corrosion and the metal acting as cathode remains unaffected.

Fig. Corrosion in Bimetallic couple

Answer 5b GALVANIZATION: The **process of coating Zn on iron by hot dipping is called galvanizing.** It is an example of anodic metal coating.

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. H_2SO_4 to remove rust or oxide layer present on it.
- (iii) The metal is then treated with flux of $ZnCl₂$ and NH₄Cl fort best adhesion property.
- (iv)Finally the base metal is dipped into the zinc at $430-470^{\circ}$ C.
- (v) The excess zinc is removed from the surface by rolling or wiping etc.

These steps are diagrammatically shown in Fig below….

Answer 6a

CATHODIC PROTECTION: Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode. This can be achieved by providing electrons from an external source.

Principle: Metals normally undergo corrosion by electrochemical process with the formation of anodic and cathodic regions in contact with each other. The corrosion of metal takes place at the anodic region whereas at the cathodic region the metal is unaffected. Therefore, corrosion can be prevented by eliminating the anode sites and converting the entire metal into cathodic area.

There are two methods of cathodic protection.

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

(i) Sacrificial anodic method:

In this method, the base metal structure is converted into a cathode by connected 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. Eg: A Mg/ Zn block connected to buried oil storage tank, Mg/Zn base areas fixed to the side of ocean going ships, Mg/ Zn blocks area connected to the buried pipe lines.

Fig: Cathodic Protection by sacrificial anode

Advantage:

(i)The method is simple.

- (ii) low installation cost.
- (iii) minimum maintenance cost.
- (iv) Doesn't require power supply.

Disadvantages: Involves recurring expenditure for Replacement of consumed anodes.

Answer 6b Methods of disposal of E-waste:

To avoid the toxic effects of e-waste, it is crucial to dispose them in proper manner, so that items can be recycled, refurbished, resold, or reused.

Following methods are used to dispose e-waste:

Landfills: This is the most commonly used method of disposing e-waste. In this method, large trenches are made in the soil to bury e-waste. But this is not a good method to dispose e-waste because e-waste contains toxic substances like lead, mercury, etc., that leak into the earth and harm the underground water and soil. Incineration: It is also the most commonly used method to dispose of e-waste. In this method, the e-waste is burned at high temperatures in specially designed incinerators. Due to which the volume of e-waste is reduced and the energy produced by this method is also utilized separately. But this is also not a good method because when the e-waste burns, it releases harmful gases which harm our environment.

Acid Bath: In this method, the e-waste is soaked in powerful sulphuric, hydrochloric, nitric acid solutions that remove the metal from the e-waste. The recovered metal is further reused to create other products. This method also has drawbacks, like the acid solutions sometimes dumped into the water resources which is harmful for living things.

Recycling: This is the most efficient method and also environmentally friendly. Recycling involves dismantling, processing and end processing. In this method, separation is done to recover used circuit boards, ICs, motherboard, etc from the e-waste and recycle them. Precious metals like copper, lead, etc., are separated from the e-waste using a PCB recycling machine without harming the environment.

Re-use: It includes direct second hand use or use after slight modifications to the original functioning equipment like Inkjet cartridge is used after refilling. Old working computers can be donated to schools or organization working in the field of education. Computers beyond repairs can be returned back to the manufacturers. This can considerably reduce the volume of E-Waste generation converted into less hazardous compounds.

Answer 7a: Extraction of copper and gold from e-waste: The electronic waste also contains fair percentage of precious metals like Cu, Ag, Au, Pd, Rh etc. These metals can be recovered from Ewaste at cheaper cost than from the usual ores. The recycling of metals such as gold and copper from discarded e-waste is an important aspect to develop the environmental friendly manufacturing processes. Techniques such as Pyrometallurgy, Hydrometallurgy and Biohydrometallurgy are used to recover precious metals like copper, silver and gold.

The extraction of copper and gold from e-waste using hydrometallurgical route comprises the liberation of the metallic fractions from downsized PCBs, a two-stage acid leaching process to provide a bulk separation of copper and gold from the other metals present, and subsequent purification of the copper and gold-containing solutions by solvent extraction using highly selective phenolic oxime and amide extractants, respectively.

Following steps are involved in the process.

1. Pre-procesing: After collection of e-waste, it is segregated, delaminated, cleaned with water and acetone and treated with N,N-dimethylacetamind (DMA) to remove the orgamic components (epoxy resins) present in the e-waste. This pretreated e-waste is shredded into small pieces and powdered, further it is subjected to recovery of precious metals. The metals were dissolved in acid and non-metallic component such as plastic and ceramic is separated by filtration.

2. Leaching: The liberated metallic fraction collected from the pre-processing step was leached in two stages to provide a bulk separation of copper and gold from the other metals present.

(i) First stage leaching process involves the selective dissolution of copper over gold. The samples were dissolved in dilute nitric acid, which almost exclusively leached the copper.

(ii) The filtered residue was then subjected to a second stage leaching process using sulfuric acid and halide salts (NaCl, NaBr) to selectively dissolve, silver and tin.

3. Solvent extraction:

(i) Recovery of Cu: Distilled water and ammonia solution was added to the leach solutions obtained after stage-one leaching process. To selectively recover the copper, the phenolic oxime dissolved in kerosene was used as the extractant. The Cu metal loaded organic phase was separated from the acidic aqueous leach liquor and washed with either sulfuric acid or nitric acid.

(ii) Recovery of Au: In the second-stage solvent extraction, an organic amide diluted in toluene was used as the extractant. The gold-loaded organic phase was then separated from the aqueous phase and stripped of the metal using either water or sodium hydroxide.

Answer 7b: Corrosion Penetration Rate (CPR) is defined in three ways: (1) the speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment, (2) the amount of corrosion lost per year in thickness, (3) the speed at which corrosion spreads to the inner portions of a material.

The CPR is calculated as follows: $CPR = (k \times W) / (D \times A \times T)$ where $k = a$ constant depends on unit used. when $K = 534$ the mpy will be used. when $K = 87.6$, mm/yr will be used. W = total weight lost $(m_0 - m)$ m = weight after corroded m_0 = weight before corroded $T =$ time taken for the loss of metal $A =$ the surface area of the exposed metal D = the metal density in $g/cm³$

Corrosion penetrating rate in mpy $CPR = KW/DAT$ Weight loss, $W = 455 \times 10^3$ mg Density, $D = 7.9g/cm^3$; Time, $T = 6 \times 24 \times 365$ hours Area $A = 60$ in² CPR = $534 \times 455 \times 10^3$ 7.9×60×6×24×365 **CPR = 9.75 mpy**

Corrosion penetrating rate mm/y $CPR = KW/DAT$ Weight loss, $W=455\times10^3$ mg Density, $D = 7.9g/cm3$; Time, $T = 6 \times 24 \times 365$ Area A = 60 in² = 60×6.45 cm² = 387 cm² $CPR = 87.6 \times 455 \times 10^3$ 7.9×387×6×24×365 **CPR = 0.248 mm/y**