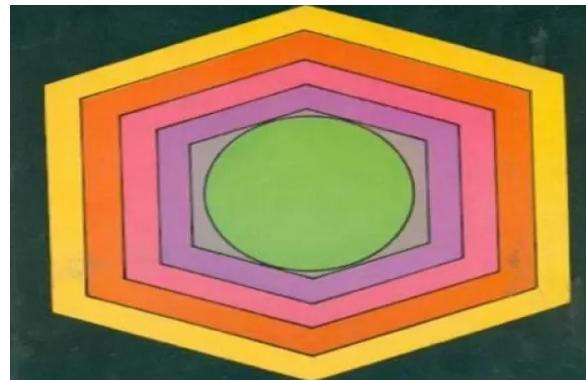




ENGINEERING CHEMISTRY –A Simplified Approach

[MODULE 3,4&5 for CAT II syllabus]

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[FOR INTERNAL CIRCULATION ONLY]



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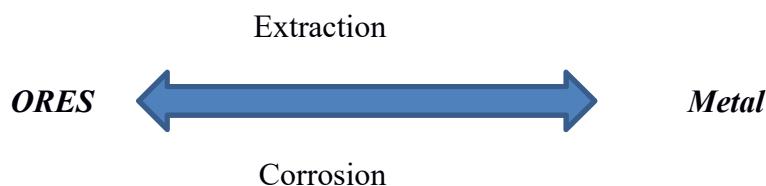
Department of Chemistry,SAS

CHY1701 Engineering Chemistry

**Module 3
CORROSION**

Introduction: - Many metals exist in nature in combined form as their ores. Metals are extracted from their ores. During extraction process , they go to the uncombined form as metallic state. It is the natural tendency of the metal to go back to the combined form [Ore] from the uncombined form [Metallic state].

Thus, Corrosion is the reverse process of extraction.



Definition: - Corrosion is defined as a gradual process of deterioration of a metal by chemical or electrochemical reaction with its environment.

Examples:-

- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.
- ii) Formation of green film of basic carbonate- $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of copper when exposed to moist air containing CO_2 .

Disadvantages of corrosion: The process of corrosion is slow and takes place only at surface of metals but the losses experienced are huge. Destruction of machines, equipment, building materials and different types of metallic products, structures etc. Thus the losses incurred are very enormous and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over

the world.

Theories of corrosion: - Corrosion can be described by the following two theories .

1. Dry or chemical corrosion.
2. Wet or electrochemical corrosion.

I) Dry or Chemical corrosion: -

This corrosion occurs due to the direct chemical attack of atmospheric gases such as O₂, halogens, H₂S, SO₂, N₂ or anhydrous inorganic liquids on the metal surface .No moisture is present.

This type of corrosion is due to adsorption, and the corrosion products accumulate in the same spot where corrosion occurs.

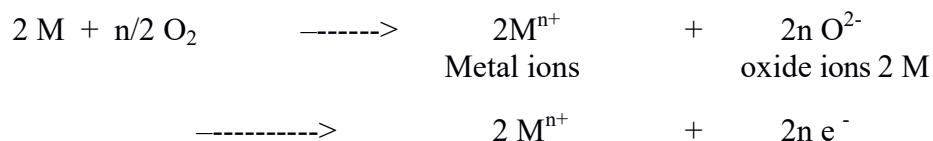
Main types of this corrosion are

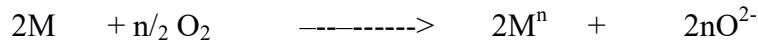
- 1) Corrosion by oxygen (or) oxidation corrosion.
- 2) Corrosion by other gases like SO₂, CO₂, H₂S and F₂ etc.
- 3) Liquid metal corrosion (or) Erosion Corrosion.

Oxidation corrosion:-

- It is brought about by direct action of oxygen at low (or) high temperatures, usually in the absence of moisture.
- At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, and Pt.
- At ordinary temperature generally all the metals are slightly attacked. However alkali metals – Li, Na, K, Rb etc. and alkaline earth metals – Be, Ca, Sr etc. are attacked very rapidly and get oxidized readily.

The reactions in the oxidation corrosion are





Mechanism of oxidation corrosion: - Oxidation takes place first at the surface of the metal and the resulting metal oxide (scale) forms a barrier, that tends to restrict further oxidation.

For oxidation to continue, either the **metal must diffuse outwards** through the scale to the surface or the **oxygen must diffuse inwards** through the scale to the underlying metal. Both transfers occur, but the outward diffusion of the metal is generally much more rapid than the inward diffusion of oxygen. Since the **metal ion is appreciably smaller than the oxide ion, therefore the metal ion has much higher mobility** and undergoes corrosion.

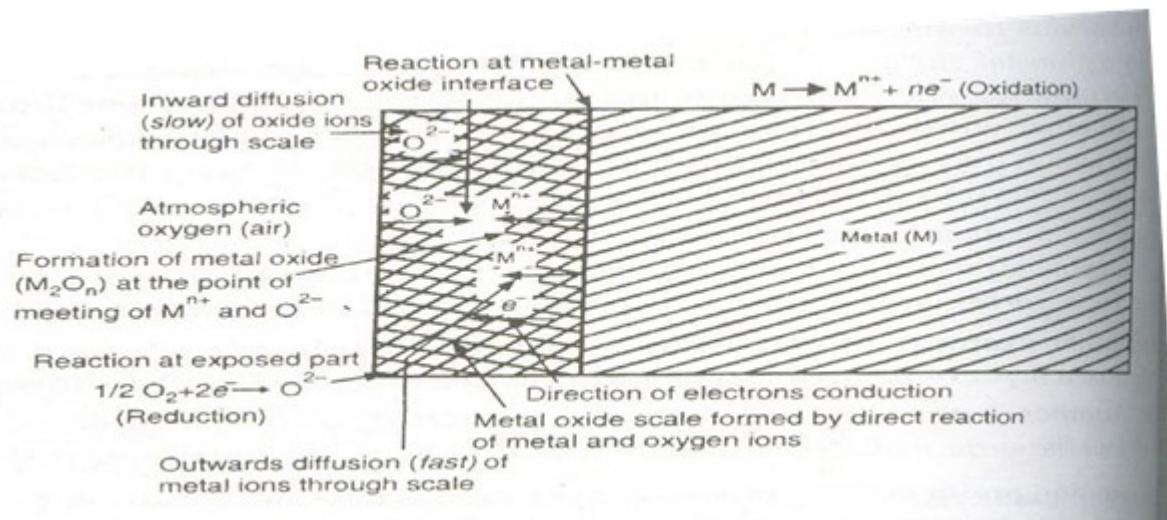
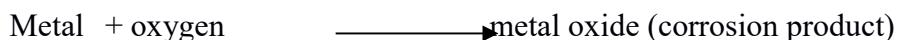


Fig. 1. Oxidation mechanism of metals.

Nature of the oxide formed plays an important part in oxidation corrosion process.



When the oxide film formed is

- i) **Stable layer:** - A stable layer is of impervious in nature. Such a film behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

E.g.: Oxides of Al, Sn, Pb, Cu, etc. are this type.

- ii) **Unstable Layer:** - The oxide layer formed decomposes back into metal and oxygen



Consequently oxidation corrosion is not possible in such cases. Eg:

Ag, Au and Pt do not undergo oxidation corrosion.

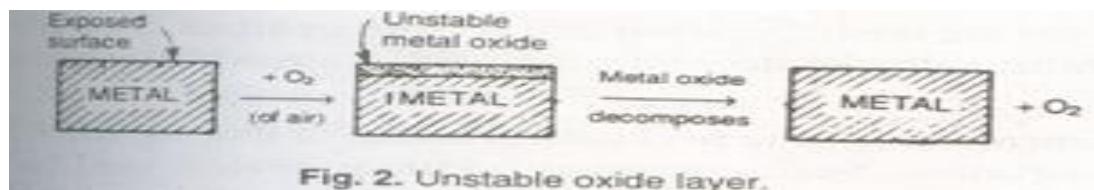


Fig. 2. Unstable oxide layer.

- iii) **Volatile Layer:** It volatilizes as soon as they are formed thereby leading to rapid and continuous corrosion . Example : Mo- molybdenum forms volatile MoO₃ layer.

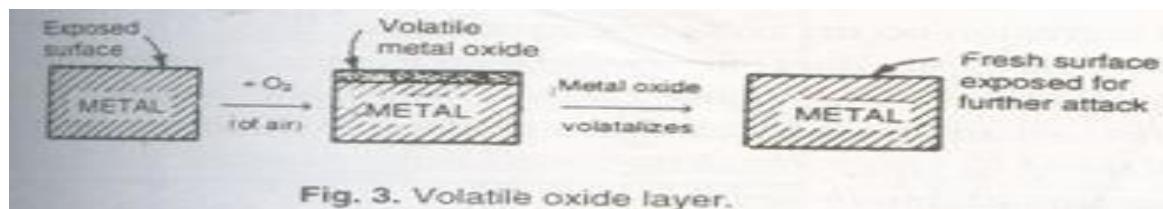


Fig. 3. Volatile oxide layer.

- iv) **Porous Layer:** The atmospheric oxygen has access to the underlying surface of the metal through the pores or cracks of the layer, there by corrosion continues till the entire metal is converted into its oxide.

Eg: Iron when attacked by H₂S at high temperature forms porous FeS layer.

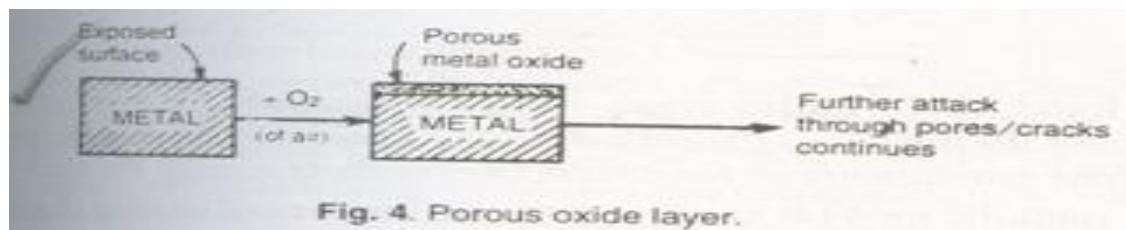


Fig. 4. Porous oxide layer.

Pilling – Bedworth rule (P-B ratio): The protective or non-protective nature of the oxide film is determined by a rule known as the Pilling-Bedworth rule. **The ratio of the volume of the oxide formed to the volume of the metal consumed is called as Pilling-Bedworth rule or P-B ratio.** According to it, if the volume of the oxide layer is greater than the volume of the metal, the oxide layer is protective and non-porous.

Example: Metals like Al forms Aluminium oxide whose volume is greater than the volume of the metal (Al) . Hence these do not undergo corrosion more rapidly.

On other hand, if the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is non protective and porous.

Example : alkali and alkaline earth metals like Li, Na, K, Mg forms oxides of volume less than volume of metals. Hence these undergo corrosion more rapidly.

The P–B ratio is defined as:

$$PBR = V_{\text{oxide}}/V_{\text{metal}} = M_{\text{oxide}} \cdot \rho_{\text{metal}} / n \cdot M_{\text{metal}} \cdot \rho_{\text{oxide}}$$

where:

- RPB is the Pilling–Bedworth ratio,
- M – the atomic or molecular mass,
- n – number of atoms of metal per one molecule of the oxide
- ρ – density, and
- V – volume.

Usually for oxides:

$PBR < 1$: oxide coating layer is too thin, likely broken and provides no protective effect (Mg)

$RPB > 2$: oxide coating chips off and provides no protective effect (Fe)

$1 > RPB < 2$: oxide coating is passivating and provides a protecting effect against further surface oxidation (Al, Ti, Cr-containing steels)

Corrosion by other gases (by hydrogen):

Hydrogen Embrittlement: It leads to loss in ductility of a material in the presence of hydrogen.

- 1) When metals are in contact with H_2S , **at ordinary temperature** causes evolution of atomic hydrogen.



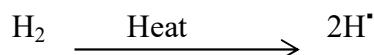
- 2) This atomic hydrogen diffuses readily into the metal and collects in the voids, where it recombines to form molecular hydrogen



- 3) Collection of these hydrogen gases in the voids develops very high pressure, which causes cracks and blisters on metal. Thus, the process of formation of cracks and blisters on the metal surface, due to high pressure of hydrogen gas is called hydrogen embrittlement.

Decarburization:

At higher temperature, atomic hydrogen is formed by the thermal dissociation of molecular hydrogen.



When steel is exposed to this environment, the atomic hydrogen readily combines with carbon of steel and produces methane gas. Thus the formation of methane gas reduces the strength of steel and this process is known as decarburization.

Liquid -Metal corrosion or Erosion- corrosion:

This type of corrosion is experienced in pipe lines used in oil and refineries. In metallic pipelines, the fast flow of corrosive liquid or aggressive fluid completely removes the underlying layer of metal in the pipeline due to **mechanical abrasion (like Friction)**. This is known as Liquid-metal corrosion or Erosion- corrosion.

2) Wet or Electrochemical Corrosion

Criteria for Electrochemical Corrosion

1. Formation of galvanic cells on the surface of metal generating anodic and cathodic areas.
2. Presence of conducting liquid with the formation of electrochemical cells.
3. At anode of metal surface, oxidation [Corrosion] takes place liberating electrons.
4. At cathode, reduction [No corrosion] takes place.

Hence, corrosion is an electrochemical process.

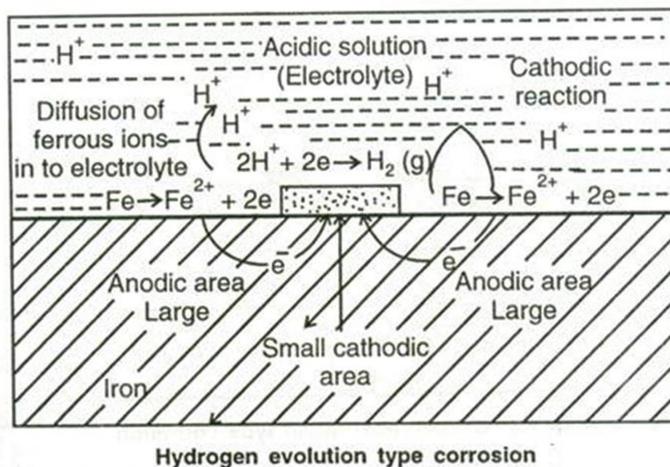
Wet corrosion takes place in two ways.

1. Evolution of Hydrogen.
2. Absorption of Oxygen.

Evolution of Hydrogen:

This type of corrosion occurs in acidic medium.

Eg: Rusting of iron metal in acidic environment takes place in the following way:



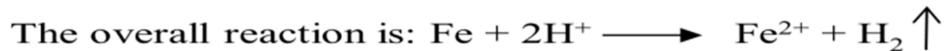
At Anode:

The oxidation of Iron takes place and forms Fe^{2+} ions



The electrons released at anode flow through the metal from anode to cathode.

At Cathode : H^+ ions of acidic solution consume these electrons and liberate as hydrogen gas.



This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.

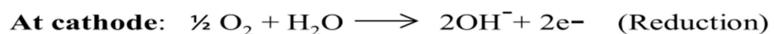
In hydrogen evolution type corrosion, the anodic areas are large and cathodic areas are small.

Absorption of Oxygen

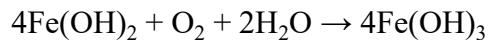
- ✓ This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- ✓ For example, rusting of iron in neutral or basic aqueous solution of electrolyte in presence of atmospheric oxygen.
- ✓ Usually the surface of iron is coated with a thin film of iron oxide.
- ✓ If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
- ✓ It shows that anodic areas are small and the cathodic areas are large.

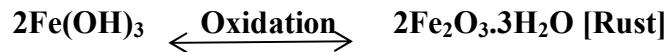


The released electrons flow from anode to cathode through iron metal.



If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide and then to hydrated ferric oxide which is known as rust.





Difference between Dry Corrosion and Wet Corrosion

	Dry corrosion	Wet corrosion
1	It occurs in dry condition.	It occurs in wet condition.
2	If the corrosion takes place due to direct chemical attack (in the absence of moisture), corrosion is known as dry corrosion.	If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium ,corrosion is known as wet corrosion
3	Explained by absorption mechanism	Explained by electrochemical mechanism
4	It occurs on both heterogeneous and homogeneous surfaces.	It occurs only on heterogeneous metal surfaces.
5	Corrosion is uniform.	Corrosion is not uniform.
6	It is a slow process.	It is a fast process.
7	Corrosion products accumulate at the place where corrosion occurs.	Corrosion take place at anode but products accumulate near the cathode.

Differential metal corrosion (galvanic corrosion) or Bi-Metallic Corrosion

When two dissimilar metals are in contact with each other and exposed to aqueous environment, the metal with lower reduction potential (anode) undergoes oxidation and the metal with higher reduction potential (cathode) undergoes reduction. The potential difference between the metals causes driving force for corrosion. The greater the electrode potential difference, the higher is the corrosion rate. Thus anodic area always undergoes corrosion and cathodic area remains unaffected.

For example, if aluminium and carbon steel are connected and immersed in seawater, the aluminium (-1.66V) will corrode more quickly, whilst the steel (-0.44 V) will receive protection.

Galvanic corrosion can be prevented by:

1. Selecting materials with similar electrode potentials. [e.g., Joining Cu metal and Bronze]
2. Breaking the electrical connection by insulating [plastic washer, Paint] the two metals from each other.
3. Applying coatings to both materials. The coating on the cathode is the most important and must be in good condition, otherwise the galvanic corrosion could be worsened.
4. Separating the two materials by inserting a suitably sized spacer.
5. Installing a sacrificial anode that is anodic to both metals.
6. Adding corrosion inhibitor to the environment. The inhibitor will adsorb on the metal surface thereby preventing the contacts of anode and cathode surface with electrolyte or aqueous medium.

If these measures are not practical, the rate of attack can be minimised by keeping the anode to cathode area larger, i.e. over 10 times . Alternatively, the anode could be designed with an appropriate corrosion allowances.

Galvanic action can cause **preferential corrosion of welds** in certain environments. For example, in sea water, carbon steel weld metal can be susceptible to severe corrosion, whilst the adjacent parent material is unattacked.

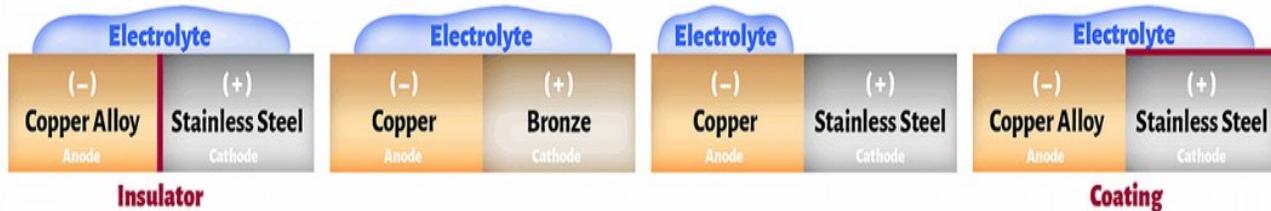
Ways to prevent Galvanic Corrosion.

Disconnect the electrical joint between metals.

Use similar metals with little differential of potential

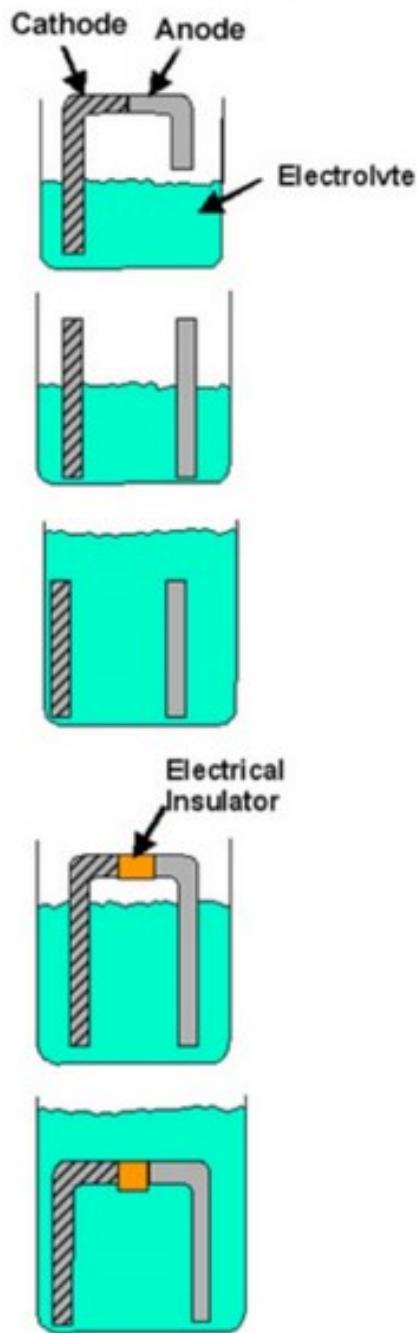
Control moisture from connecting the two metals

Coat either the anode or the cathode to prevent electrical connection



Courtesy: NACE International Hand book(2007), 13th edition

No Galvanic Corrosion



Courtesy:

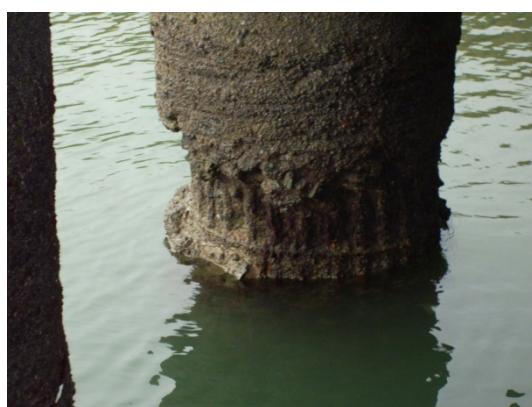
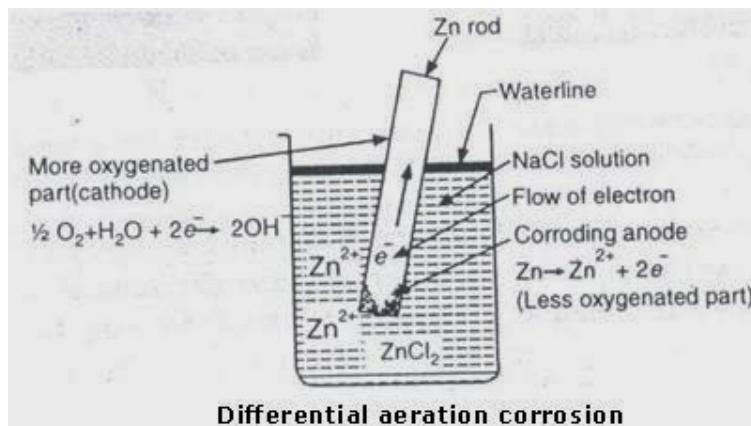
Corrosion Engineering Handbook (2006), Second Edition. Author : Philip A. Schweitzer, P.E

Differential aeration (cell) corrosion

- The difference in the availability of air or oxygen over a metallic surface leads to formation of oxygen concentration cells.
- The less aerated or less oxygenated part behaves anodic while the more oxygenated part cathodic. Since cathodic reactions involve consumption of oxygen, the more oxygenated part behaves cathodic and less oxygenated part behaves anodic.
- The corruptions which are caused due to formation of such oxygen concentration cells are known as differential aeration corrosion.
- It is believed that aeration causes the formation of an oxide film on the metal surface resulting in the development of a metal metal-oxide cell or even oxygen electrode-metal electrode system.
- Most of the common types of corrosion are due to differential aeration. The following is the examples

(a) Corrosion of metals partly immersed in solution or Water line Corrosion

When a metal piece is partly immersed in a solution or water, the part of the metal piece above the surface of the solution is more aerated and behaves cathodic while the metal piece immersed in interior has less accessibility to oxygen [only with Dissolved oxygen] and behaves anodic. The difference of potential thus created causes the flow of current between the two regions which results in corrosion.

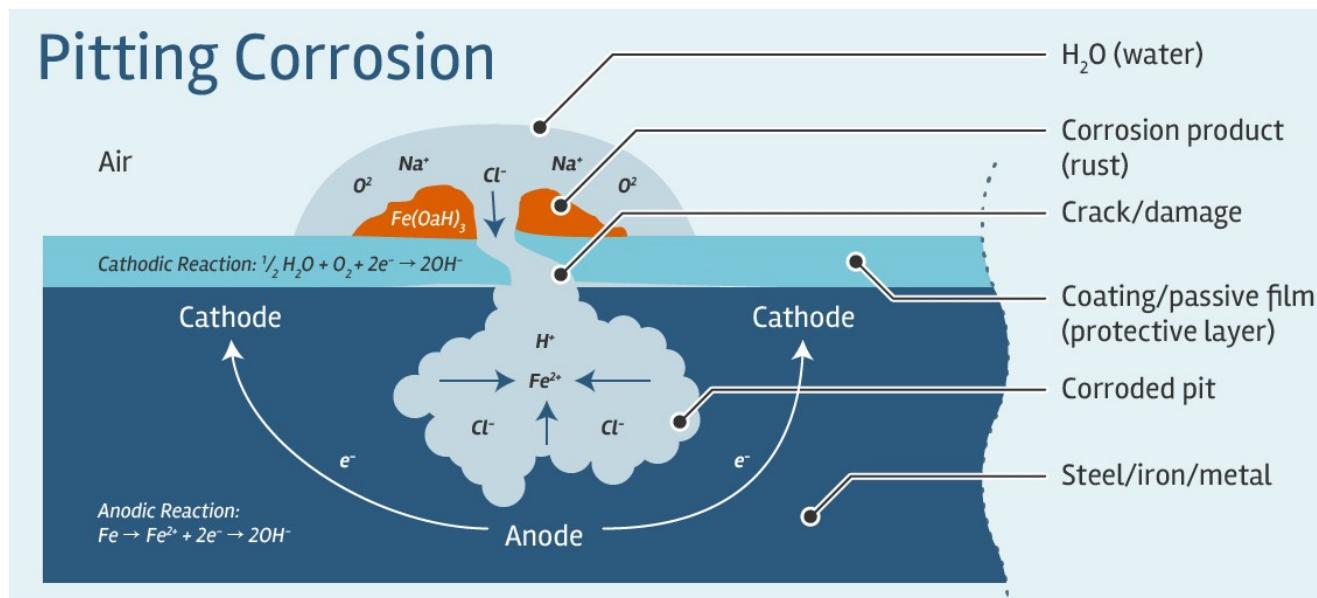


(b) Pitting Corrosion

Pitting is a type of corrosion that occurs in materials that have protective films. It is an attack with localized (Selective) holes on the metal's surface. The attack can penetrate the metal very rapidly, while some parts of the metal surface remain free from corrosion.

Explanation:

- ✓ Let us consider a drop of water or aqueous NaCl is resting on a metal surface.
- ✓ The area covered by the drop of water acts as an anode due to less oxygen concentration and suffers corrosion. The uncovered area (freely exposed to air) acts as a cathode due to high oxygen concentration.
- ✓ This causes the creation of differential aeration cell on the metal surface.



- ✓ Since the cathodic area is larger than the anodic area, the demand of electrons will be more by cathode and hence more metal will be removed from the same spot wherein the water drop is resting (anodic area).
- ✓ **The removal more metal from the same spot (anodic area) leads to the formation of pits and hence this is known as pitting corrosion.**

Pitting corrosion can be controlled by:

- Use of a coating that will prevent pitting on metal surfaces.
- Using more corrosion resistant materials [e.g alloys containing Ti,Cr.Mo].
- Ensuring that the fluids in contact with the material is washed away regularly.

Pitting Corrosion



Stress corrosion Cracking [SCC]

- ✓ It is the combined action of static (without movement) tensile stress and corrosive environment on metal surface.
- ✓ SCC leads to the formation of cracks on the internal portion of metal without affecting the surface of metal [*rarely visualized through outer surface*].
- ✓ The creation of stresses on metal is imposed by mechanical conditions such as Welding, Forging or by applying un- tolerable load on metal.

[*e.g., in a 7 seater car, if 10+ persons are loaded with heavy luggage's, the car body which is made of steel will be facing unbearable load and undergoes stress*]

- ✓ The metal atoms under stress are always at higher energy level so acts as anode and stress free parts of metal acts as cathode under specific corrosive environmental conditions, corrosion process starts.
- ✓ The corrosion medium is highly selective and specific in their action.

For example,

- (1) *Season cracking of brass* - Brass undergoes stress corrosion in the presence of ammonia.
- (2) *Caustic embrittlement of Steel* - Stainless steel in the presence of Chloride ions and caustic substances.

Control measures:

1. By laser shot peening, the tensile stress is eliminated.
2. Applying coatings with high thickness of above 150 microns will protect the attack of metal by corrosive environment.

This titanium tank, is one of four propellant tanks in the Vega upper stage. It ruptured during burst testing, having been weakened by stress corrosion cracking.



Courtesy: European space Agency

Factors influencing the rate of Corrosion:

The rate and extent of corrosion mainly depends on

- (i) Nature of the metal.
- (ii) Nature of the environment.

(i) Nature of the Metal:

1. **Position in EMF Series:** The extent of corrosion depends on the position of the metal in the emf series. Metals above the hydrogen in emf series get corroded vigorously. Lower the reduction potential, greater is the rate of corrosion. When two metals are in electrical contact, the more active metal (or the metal having high negative reduction potential) undergoes corrosion.
 2. **Relative Areas of the Anode and Cathode:** The rate of corrosion will be more, when the cathodic area is larger. When the cathodic area is larger, the demand for electrons will be more and this results in an increased rate of corrosion (dissolution) of metals at anodic area.
 3. **Purity of the Metal:** The 100% pure metal will not undergo any type of corrosion. This is known as homogeneity on metal. But, the presence of impurities in a metal creates heterogeneity and thus galvanic cells are set up with distinct anodic and cathodic area in the metal. Higher the percentage of impurity, faster is the rate of corrosion of the anodic metal.
-
4. **Over voltage :**

Over potential or over voltage is the deviation of electrode potential from its equilibrium potential. When a metal or electrode is put into a solution such as water, the solution presumes a potential. If the metal begins to undergo corrosion, the metal's potential alters in value. The difference in this value of potential is referred to as over potential.

The same thing applies to hydrogen, since hydrogen overvoltage can be described as the difference between the hydrogen's equilibrium reactions in a solution and the hydrogen itself present in the solution when it begins to form a corrosive reaction with metal. In order to reduce the corrosion of metal, more potential is applied. The addition of metals and inhibitors enhance the potential values thereby reducing the corrosion.

Explanation:

When a metal, which occupies a high position in galvanic series (say Zinc), is placed in H_2SO_4 , it undergoes corrosion forming a film and hydrogen gas. The initial rate of reaction is quite slow, because of high over voltage (0.70 V) of the zinc metal, which reduces the effective electrode potential to a small value. However, if few drops of copper sulphate (CuSO_4) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal forming minute cathodes, where the hydrogen over voltage is now 0.33 V, thus, reduction in over voltage of the corroding metal/ alloy accelerates the corrosion rate.

Thus, the over voltage (potential) of a metal in the corrosive environment is inversely proportional to corrosion rate.

5. Nature of surface oxide film:

The nature of the oxide film formed on the metal surface decides the extent of corrosion which can be decided by Pilling-Bed worth rule.

6. Nature of the corrosion product:

If the corrosion product is soluble in the corroding medium; the corrosion rate will be faster.

Similarly, if the corrosion product is volatile (like MoO_3 on Mo surface), the corrosion rate will be faster.

(ii) Nature of Environment:

1. Temperature :

The rate of corrosion is directly proportional to temperature. This is because, the rate of chemical reaction and the rate of diffusion of the ions increases with rise in temperature. Hence the rate of corrosion increases with temperature.

2. Humidity:

The rate of corrosion will be more, when the humidity in the environment is high. The moisture acts as a solvent for the oxygen in the air to produce the electrolyte, which is essential for setting up a corrosion cell.

3. Presence of Corrosive Gases:

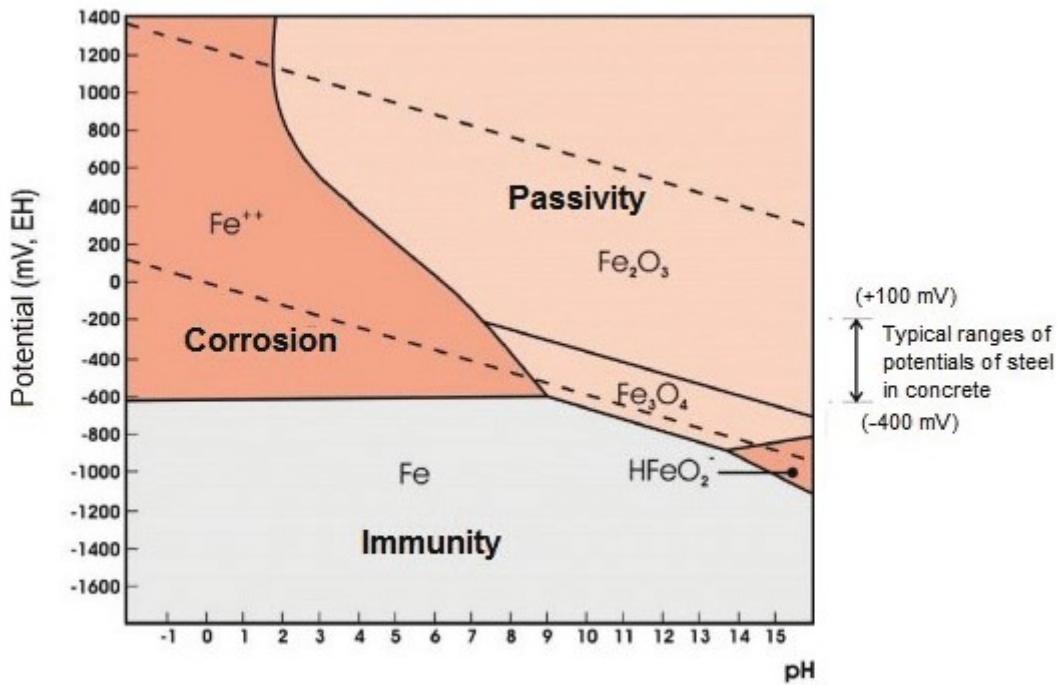
The acidic gases like, CO_2 , SO_2 , H_2S and fumes of HCl , H_2SO_4 , etc., produce electrolytes, which are acidic and increases the electrochemical corrosion.

4. Presence of Suspended Particles: Particles like, NaCl , $(\text{NH}_4)_2\text{SO}_4$ along with moisture act as powerful electrolytes and thus accelerate the electrochemical corrosion.

5. Effect of pH:

The possibility of corrosion with respect to pH of the electrolytic solution and the electrode potential of the metal is correlated with the help of a Pourbaix diagram.

From the diagram it is clear that the rate of corrosion can be altered by shifting the point 'Z' into immunity or passivity regions. The iron will be immune to corrosion, if the potential is changed to about - 800 mV by applying an external current. On the other hand, the rate of corrosion of iron can also be reduced by moving into the passivity region by applying positive potential.



The diagram clearly indicates that the rate of corrosion can also be reduced by increasing the pH of the solution by adding alkali. Thus the rate of corrosion will be maximum , when the corrosive environment is acidic. i.e. pH is less than 7.

References:

1. Corrosion Engineering, M.G.Fontana, McGraw-Hill Book Company; 3rd edition , (November 1, 1985) ISBN-10: 0070214638.
2. Uhlig's Corrosion Handbook, Willey on line publisher (2011) ,Third Edition.

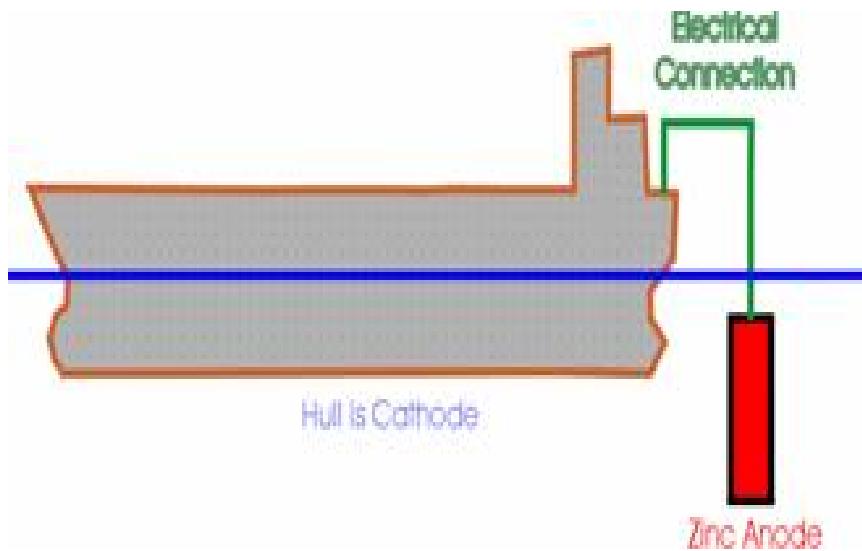
Module 4

CORROSION CONTROL

1) **Cathodic protection** : The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur. There are two types of cathodic protection.

(i) **Sacrificial anodic protection method (SAP): -**

- In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal sacrifices itself and gets corroded slowly. While the parent structure which is cathodic is protected .The more active metal so employed is called “sacrificial anode” .
- Whenever the sacrificial anode is consumed completely, it is replaced by a fresh one. Metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc.



- The anode consisted of a back fill which will be having the following materials, if the protection of buried pipe-pines are required.

Coal coke breeze

Petroleum coke breeze

Bentonite clay

Gypsum

Sodium sulfate

Advantages:

1. It is a simple method.
2. It does not require external power.
3. It has low maintenance and installation cost
4. Cathodic interferences are minimum.

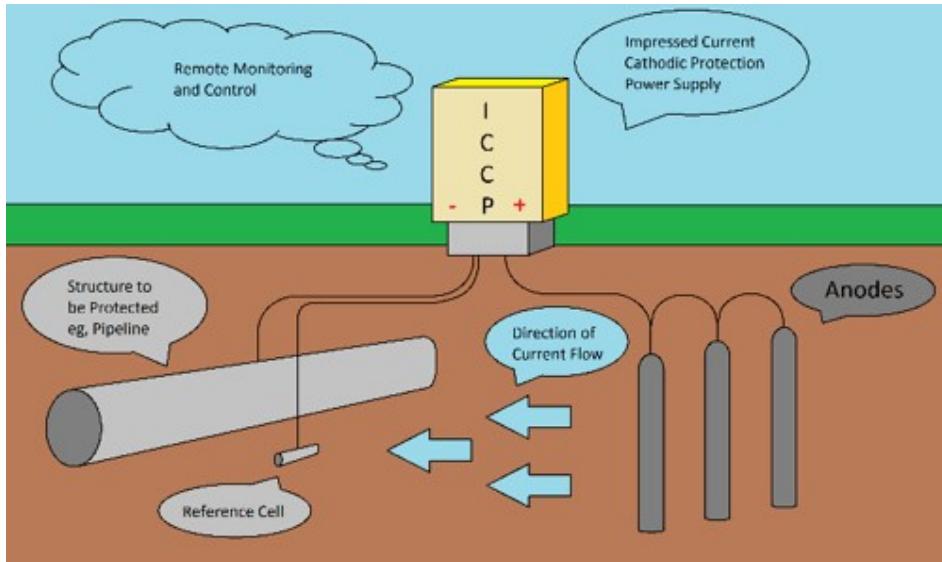
Disadvantages:

1. More than one anode is required some times.
2. It does not work properly in high corrosive environment.
3. Sacrificial anode must be replaced periodically as and when it is consumed.

(ii) *Impressed current – cathodic protection(ICCP)*

- ✓ In this method an impressed current is applied in opposite direction to nullify the corrosion current and converting the corroding metal from anode to cathode.
- ✓ Usually the impressed current is derived from a direct current source (like battery or rectifier on ac line) with an insoluble anode, like graphite, high silica iron, scrap iron, stainless steel or platinum.
- ✓ A sufficient direct current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected.

- ✓ The anode is a backfill composed of materials such as coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.
- ✓ In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and does not get oxidized.



- ✓ A reference cell is used to measure the potential of cathode. There are several types of reference cells, but the most common types are saturated copper/copper sulfate (CSE) electrode, silver/silver chloride (SSC) electrode, and saturated calomel electrode (SCE).

Applications

1. The impressed current cathodic protection is used for the protection of water tanks, water & oil pipe lines, transmission line towers etc.

Advantages:

The method is mainly employed to protect large structures for long term operations.

Disadvantage:

1. The method is expensive as it requires high current.
2. Capital investment and maintenance costs are more.
3. It is difficult to maintain uniform current over the entire metal surface as a result localized corrosion may occur.

4. The metal should not be over protected, ie, use of much high potential is avoided otherwise problems related to cathodic reactions like evolution of H₂ and formation of OH⁻ Ions takes place leading to corrosion of base metal.

Metallic Coatings

The surface of the base metal coated with another metal (coating metal) is called metallic coatings. Metallic coatings are broadly classified into anodic and cathodic coatings.

1. Anodic coatings:

- The metal used for the surface coating will be more anodic than the base metal which is to be protected.

For example, coating of Al, Cd and Zn on steel surface are anodic, because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.

- The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

2. Cathodic Coatings:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings:

1. HOT DIPPING

- ✓ Hot dipping process is applicable to the metals (Base metal) having higher melting point than the coating metal.
- ✓ It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.
- ✓ The flux cleans the surface of the base metal and prevents the oxidation of the molten

coating metal. Eg: Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are

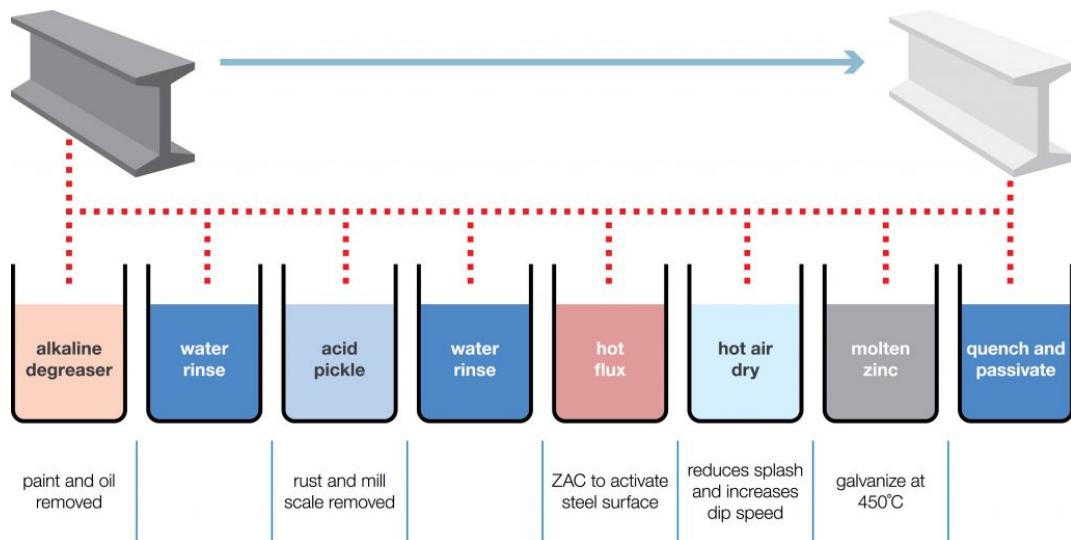
- (a) Galvanizing
- (b) Tinning

(i) GALVANIZING

- a. Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- b. It is the anodic protection offered by the zinc.
- c. In this process, at first iron or steel is cleaned by pickling with dil. H_2SO_4 solution for 15- 20 minutes at $60-90^{\circ}C$. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface.
- d. The article is washed well and then dried.
- e. It is then dipped in bath of molten zinc maintained at $425-430^{\circ}C$.
- f. The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath.
- g. It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness
- h. Then it is annealed and finally cooled slowly.

Applications:

Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized Iron [GI] sheets are not used for keeping eatables because of the solubility of zinc is higher in acidic pH's.



(iii) TINNING

The process of coating **tin metal** over the iron or steel articles to protect them from undergoing corrosion is known as **tinning**.

- Tin is a noble metal and therefore it possess more resistance to chemical attack. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath of $ZnCl_2$ molten flux followed by **molten tin** and finally through a suitable vegetable oil. The $ZnCl_2$ flux helps the molten metal to adhere to the base metallic surface. A cathodic protection on iron sheets are offered by the tin coatings.
- Palm oil protects the tin coated surface against oxidation.
- Finally the sheet is passed through rollers to remove excess of tin and produce thin layer of tin coatings with uniform thickness.

Applications:

1. Tin metal possess good resistance against atmospheric corrosion. Tin is non-toxic and widely used for coating steel, copper and brass sheets
2. The containers coated with tin are used for storing food stuffs, ghee, oil etc and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

(iv) Electroplating:

- It is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.
- The base metal to be plated is made cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity.

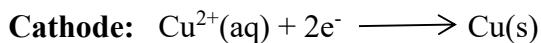
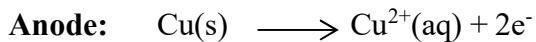
Theory:

- ✓ If the anode is made of coating metal itself in the electrolytic cell, during electrolysis, the concentration of electrolytic bath remains unaltered.
- ✓ Since the metal ions deposited from the bath on cathode (Base metal) are replenished continuously by the reaction of free anions with the anode.
- ✓ If the anode is made of an inert material like graphite, electrolyte should be added continuously to maintain the concentration of the coating metal ions in the bath.

Process:

Let us consider the electroplating of Copper.

- a. Base metal (object) is treated with dil. HCl or dil. H_2SO_4 to remove oxide layers.
- b. Object to be coated acts as cathode. Copper foil is taken as the anode. Copper sulphate is used as an electrolyte.
- c. When a direct current is passed from an external source, the copper ions migrate towards cathode and get deposited over the surface of base metal (object) in the form of a thin layer.



- d. Low temperature, medium current density, low metal ion concentration are maintained for better electro-plating.

Temperature: 20-40°C (low temp for brighter and smooth surface)

Current density: 20-30 mA/cm²

Copper sulphate : 0.44 Molar solution

Objectives:

1. To increase resistance to corrosion, chemical attack and wear resistance of the plated metal.
2. To improve physical appearance and hardness.
3. To increase the decorative and commercial values of metals.
4. To increase the strength of non-metals like plastics, wood and glass etc.
5. To make surface conductive by using light weight non-metallic materials like wood and plastics.

(v) Electroless plating

- a. The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating.
- b. This process is also called autocatalytic plating, since it takes place on catalytic surface.
- c. The metallic ions (M^+) are reduced to the metal with the help of reducing agents(R^-). When the metal(M) is formed, it gets plated over a catalytic surface.



Pretreatment and activation of the surface:

The surface to be plated is activated by treatment with organic solvents or alkali, followed by acid treatment.

Advantages :

1. Electrical energy is not required.
2. Even intricate parts (of irregular shapes) can be plated uniformly.
3. There is flexibility in plating volume and thickness.
4. The process can plate recesses and blind holes with stable thickness.
5. Chemical replenishment can be monitored automatically.
6. Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.
7. It is a pore free coatings with very high hardness , corrosion resistance and wear resistance values.

Thin film coatings:

It is the technology of applying a very thin film of material – between a few nanometers and about 100 micrometers.

Thin Film Deposition is usually divided into two broad categories – Physical Vapor Deposition (PVD) and Chemical vapour Deposition (CVD) Coating Systems.

Physical vapour deposition (PVD)

- ❖ It is a thin-film coating process which produces coatings of pure metals, metallic alloys and ceramics with a thickness usually in the range 1 to 10 μm .
- ❖ Physical vapour deposition, as its name implies, involves physically depositing atoms, ions or molecules of a coating species on to a substrate.
- ❖ The surface of substrate and target should have accessibility [line of sight] to receive coatings.

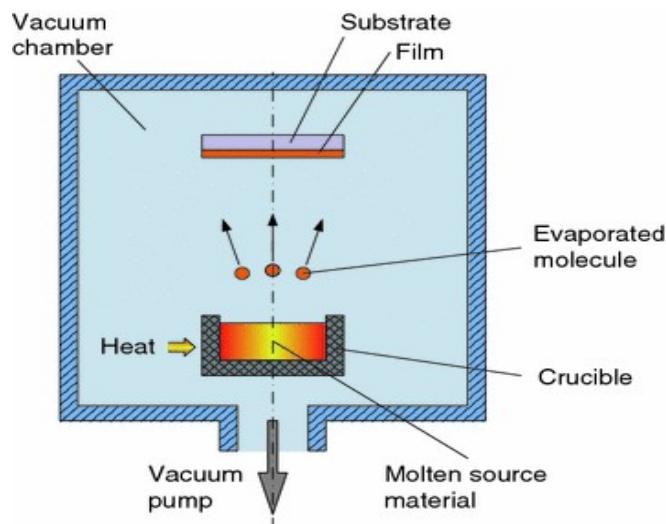
There are three main types of PVD, all of which are undertaken in a chamber containing a controlled atmosphere at reduced pressure (0.1 to 1 N/m²):

a. **Thermal evaporation**

b. **Sputtering**

c. **ion plating**

a. **Thermal Evaporation**



- ❖ It uses the heating of a material to form a vapour which condenses on a substrate to form the coating. Heating is achieved by various methods including hot filament, electrical resistance, electron or laser beam and electric arc.
- ❖ The surface to be coated needs to have a higher melting temperature than the coating metal and this limits the choice and make more complicated to mix the components.
- ❖ There is no chemical bonding between the coatings and substrates is established.
- ❖ When the coating materials hit the substrate, it is physically deposited as layers or atom by atom or molecules by molecules.

{ e.g., *peelable Layers in cabbages or Onions*}

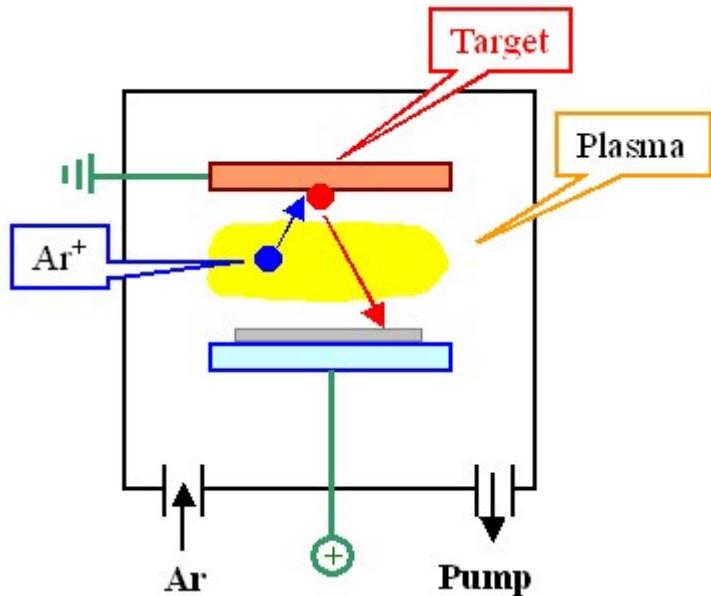
- ❖ The other common heat source is an electron beam or **E-Beam Evaporation** where an electron beam is aimed at the source material to evaporate it and enter the gas phase.

b. Sputtering

- ✓ If the surface of a target (contains coating materials) is bombarded by atomic particles of sufficiently high energy, individual atoms of the target materials may acquire enough power due to the collision that they are ejected from the target's surface by transfer of momentum. This is the process of dislodging atoms from the target material is known as sputtering.
- ✓ The most convenient form of high energy particle is an ionized gas, such as argon, energized means of an electric field to form a plasma.
- ✓ **The dislodged atoms will have substantial kinetic energies, and some will fly to the substrate to be coated and stick there.**
- ✓ As a PVD process, sputtering involves bombardment of the cathodic coating material with argon ions (Ar^+), causing surface atoms to escape and then be deposited onto a substrate, forming a thin film on the substrate surface. The ionized form of inert gas (Ar^+) is known as plasma.

✓ Example : **TaSi_{2-x} coatings for electro-magnetic applications. [x = 0.01 - 0.1]**

✓ The simple set-up of sputtering is given below:



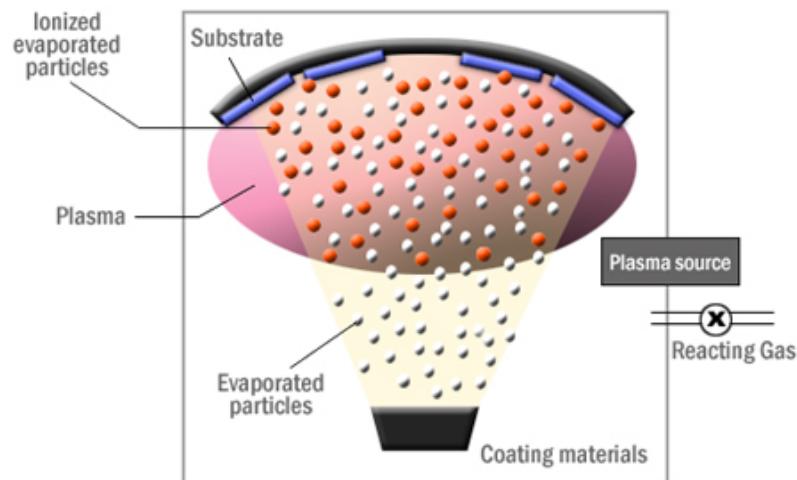
✓ The target atoms hit the substrate coming from *all directions*.

Disadvantages:

- The coatings are having very poor crystallinity.
- Formation of holes inside the coating matrix due to very energetic hitting of target atoms.

(c). Ion plating

- ✓ It is the combination of thermal evaporation and sputtering process.
- ✓ The heating methods used here are similar to those used in vacuum evaporation, resistance heating, electron beam bombardment, and so on.
- ✓ The substrate has to be prepared by sputtering cleaning in order to prepare the surface to receive the coating particles, and this can be done by shooting a stream of ions of the target material on the substrate.

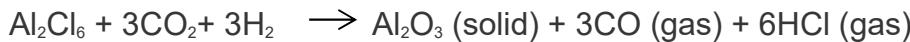


Chemical vapour deposition [CVD]

- ✓ Chemical vapour deposition (CVD) is a coating process that uses thermally induced chemical reactions at the surface of a heated substrate, with reagents supplied in gaseous form.
- ✓ Here, the reactants used are gases, thereby taking advantage of the many characteristics of gases.
 - ✓ It is not a line-of-sight process.
 - ✓ The simplest CVD process involves the pyrolytic decomposition of a gaseous compound on the substrate to provide a coating of a solid reaction product.

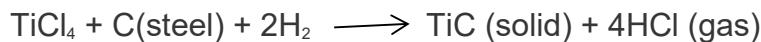
Example : The the following reactions are used to produce solid coatings of tungsten metal (W), titanium carbide (TiC) and titanium nitride (TiN) respectively:

- ✓ $\text{WF}_6 + 3\text{H}_2 \longrightarrow \text{W} \text{ (solid)} + 6\text{HF} \text{ (gas)}$
- ✓ $\text{TiCl}_4 + \text{CH}_4 \longrightarrow \text{TiC} \text{ (solid)} + 4\text{HCl} \text{ (gas)}$
- ✓ $\text{TiCl}_4 + \frac{1}{2} \text{N}_2 + 2\text{H}_2 \longrightarrow \text{TiN} \text{ (solid)} + 4\text{HCl} \text{ (gas)}$
- ✓ Alumina may be deposited by the reaction:



However, the reactions listed above involve only gaseous reagents, the substrate material in some cases also plays a significant role.

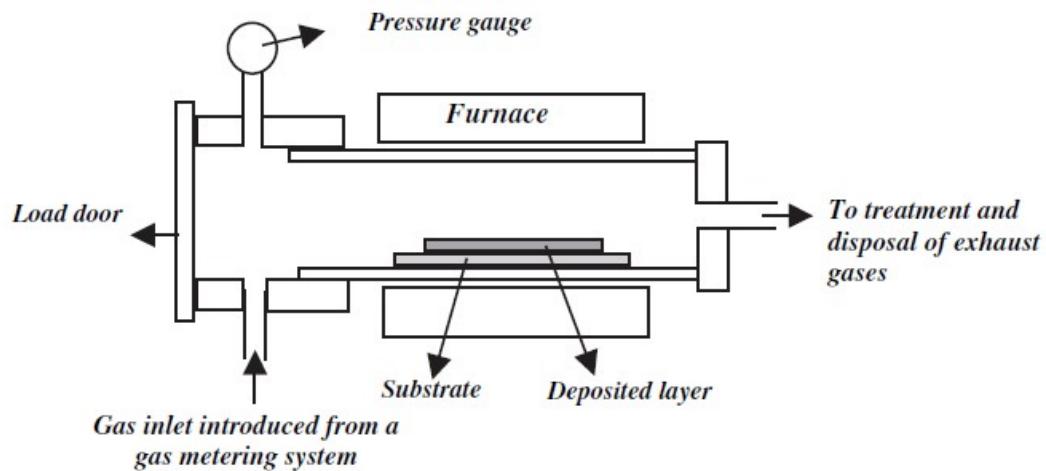
For example, the formation TiC layer on carbon steels



- ✓ This reaction can lead to decarburisation of the substrate
- ✓ CVD coating processes employ temperatures typically in the range 600 to 1100°C. At these temperatures, significant thermal effects may occur in the substrate material. Steels, for example, will often be heated into the austenite phase region and the coating process may need to be followed by suitable heat treatment to optimise the properties of the substrate.
- ✓ Other types of CVD processes include plasma assisted CVD[PACVD].

- ✓ In this process, an electrical discharge in a low pressure (<100 Pa) gas is used to accelerate the kinetics of the CVD reaction. This can lower the reaction temperatures by several hundreds of degrees Celsius.
- ✓ PACVD coating rates are generally lower than CVD as a consequence of the lower gas pressure.

Example: PACVD of Diamond like coatings with very high hardness and wear resistance.



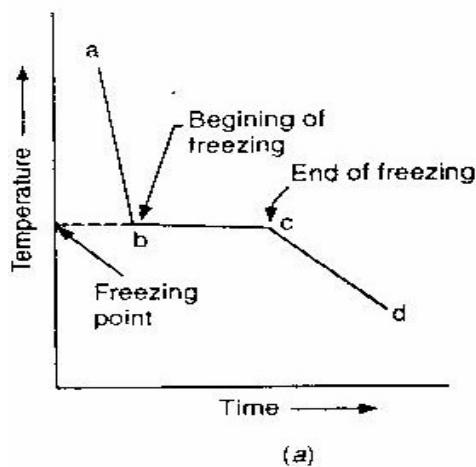
- Uniform coating layer
- Thickness: 2–100 μm

References:

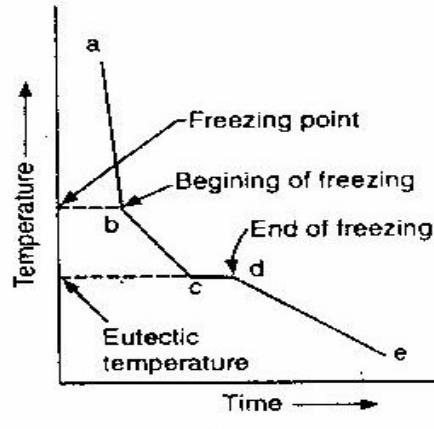
1. Advanced Techniques for Surface Engineering, W. Gissler, H.A. Jehn, 3rd Edition, 2012.
2. Electrochemistry, P.H. Rieger, 2nd Edition, Chapman&Hall, 1995

Thermal analysis:

Thermal analysis is the study of the cooling curves of various compositions of a system during solidification. It is used for finding the shape of the freezing – point curves of any system especially those involving metals. For any mixture of a definite composition, it is possible to find out freezing point and eutectic point from the cooling curves.



(a)



(b)

Figure: (a). When a pure substance in the fused state is allowed to cool slowly and the temperature noted at definite intervals. The graph of rate of cooling will be continuous curve. When the freezing point is reached and the solid makes its appearances [Point b] by the break in the continuity of the cooling curve and the temperature remains constant, until the liquid is fully solidified [point c]. There after, the fall in temperature will again become continuous.

Figure: (b). When a mixture of two solids in the fused state is allowed to cool slowly and the temperature noted at definite intervals. The graph of rate of cooling will be continuous curve. When a solid phase begins

to form, the rate of cooling curve exhibits a break [point B]. However, the temperature does not remain constant as in the previous case of cooling of a pure substance. The temperature decreases continuously until the eutectic point reached [point C] . Now the temperature remains constant, till the completion of solidification [Point D] . There after, the fall of temperature becomes uniform, but the rate of fall is quite different from the previous one.

Applications:

1. The melting point and eutectic temperature of various solids can be obtained.
2. The percentage of the compounds can be found out.
3. The behavior of the compound can be understood from the cooling curve.
4. The procedure of thermal analysis can be used to derive the phase diagram of any two component system.

Eutectic system:

Eutectic – Easy to melt. Let us Consider a binary system in which two components are miscible in all proportions in the liquid (molten) state. They do not react chemically and each component has the property of lowering each other's freezing point. Such a binary system is called Eutectic system.

Eutectic mixture:

A solid solution of two component system which has the lowest freezing point of all the possible mixtures of the components is called eutectic mixture.

[example : Point 'c' in figure (b) of Thermal analysis]

Eutectic point:

Minimum freezing point attainable corresponding to the eutectic mixture is called **eutectic point** (means lowest melting point). The eutectic mixture has a definite composition and a sharp melting point. In this respect it resembles a compound. However, it is not a compound for the components are not present in **stoichiometric proportions**.

When the solid was examined under a powerful microscope, both the constituents were seen to lie as separate crystals. Moreover, physical properties such as density and heat of solution of eutectic solid were almost equal to the mean values of the constituents. Hence it is a mixture and not a chemical compound.

Applications:

1. Alloys which are known to form eutectic mixture's are used as 'fail – safe' device in boilers, as plugs in automobiles, fire – sprinklers and other such safety devices.
2. Eutectic systems, because of their low melting points are also used for joining two metal pieces together. Example: Pb – Sn solders.

Phase rule:

It was introduced by Williams Gibbs in 1874. It is stated as, “*When an equilibrium between any number of phases is influenced only by temperature, pressure and concentration, but not influenced by gravity, or electrical or magnetic forces or by surface tension then the number of degree of freedom (F) of the system is related to the number of components (C) and of phases (P) by the phase rule equation*”

$$\underline{F = C - P + 2}$$

Condensed (reduced) phase rule

The phase rule equation is $F = C - P + 2$

For a two component system, $C = 2$ then $F = 2 - P + 2 = 4 - P$

The minimum number of phase at equilibrium is one. Then $F = 4 - 1 = 3$.

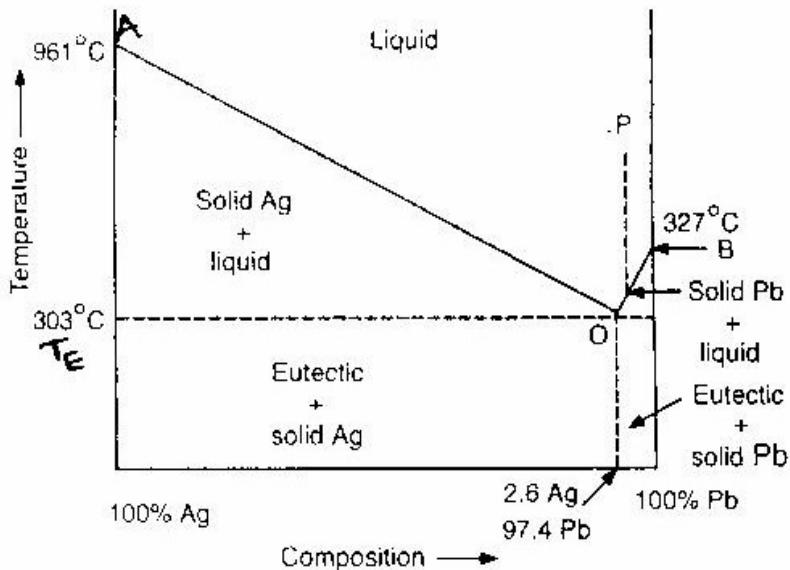
Hence the maximum number of degree of freedom is three and temperature, pressure and composition are required to define the system. This leads to 3 dimensional figures which cannot be explained on a paper. Hence one of the three variable to be kept constant.

$F = C - P + 1$ (Two component system)

$F = 2 - P + 1 = 3 - P$. This is the reduced / condensed form of the phase rule.

Lead – Silver system [Non-ferrous alloys]

It is a two – component system with four possible phases – solid Ag, solid Pb, solution of Ag + Pb and its vapour. The two metals are completely miscible with each other in liquid state and do not form any chemical compound. There is almost no effect of pressure on equilibrium, the temperature and composition are considered to construct the phase diagram at constant atmospheric pressure.



Phase diagram of Pb – Ag system.

It consists of (1) Curves AO and BO.

- (2) Eutectic point – “O” .
- (3) Areas: Above AOB / Below AO / Below BO.

Curves AO & BO:

CURVE AO	CURVE BO
It is the freezing point curve of Ag (961°C)	It is the freezing point curve of Pb (327°C)
It shows decrease in freezing point / melting point of Ag due to the addition of Pb to Ag	It shows decrease in freezing point / melting point of Pb due to the addition of Ag to Pb.
Solid Ag is equilibrium with solution of Pb in Ag.	Solid Pb is equilibrium with solution of Ag in Pb.

Here C = 2 and P = 2, then the reduced phase rule is $F = C - P + 1 = 2 - 2 + 1 = 1$.

Hence the system is **univariant**. The point O (303°C) represents a fixed composition of 97.4 % Pb and 2.6 % Ag, and is called **eutectic composition**. On cooling, the whole mass crystallizes out as such.

Eutectic point 'O':

The curves AO & BO meet at the point O is called eutectic point. Here, solid Ag, Solid Pb and solution of Ag & Pb are in equilibrium. Thus, C = 2 and P = 3.

Hence the reduced phase rule is $F = C - P + 1 = 2 - 3 + 1 = 0$ and the system is **invariant**. The point O (303°C) represents a fixed composition of 97.4 % Pb and 2.6 % Ag, and is called **eutectic composition**.

Area above AOB:

The components Ag and Pb are exist as solution. Thus, C = 2 and P = 1.

Hence $f = C - P + 1 = 2 - 1 + 1 = 2$, the system is bivariant. The system will exist when the temperature $T > 303^{\circ}\text{C}$, Pb $< 97.4\%$ and Ag $> 2.6\%$.

AREA	EXISTENCE	P	C	F
Below AO	Ag + Solution of Pb / Ag	2	2	1
Below BO	Pb + solution of Ag / Pb	2	2	1
Below T_E line	Solid Ag + Solid Pb	2	2	1

All these areas have P = 2 and F = 1. The system is **univariant**.

Pattinson's process:

The recovery of Ag from argenti ferrous lead is explained in the process with the help of phase diagram. Argentiferrous lead contain 0.1 % Ag and 99.9 % Pb. This alloy on heating above 327°C , then it is allowed to cool. The melted alloy reaches P on the curve BO, solid Pb separates out and solution having more Ag. On further cooling, more of Pb separated till the eutectic point reached. At "O" an alloy containing 2.6 % Ag and 97.5 % Pb is obtained.

Ferrous alloys:

Alloys containing iron as one of their main component are called ferrous alloys.

Example: Nichrome and stainless steel, etc

Nichrome:

It contains 60% Ni, 1.2% Cr and rest Fe. It can be used at 1000 to 1100°C . The presence Ni improves tensile-strength, ductility, toughness, elasticity, heat and corrosion – resistances and the presence of Cr imparts high corrosion – resistance, hardness and toughness simultaneously.

References:

- Physical chemistry, Peter Atkins, 9th Edition, ISBN-10: 1429218126.

The Iron–Iron Carbide (Fe–Fe₃C) Phase Diagram

This is one of the most important alloys for structural applications. Concentrations of carbon are usually given in weight percent. The possible phases are:

- α -ferrite (BCC) Fe-C solution
- γ -austenite (FCC) Fe-C solution
- δ -ferrite (BCC) Fe-C solution
- liquid Fe-C solution
- Fe₃C (iron carbide) or cementite. An intermetallic compound.

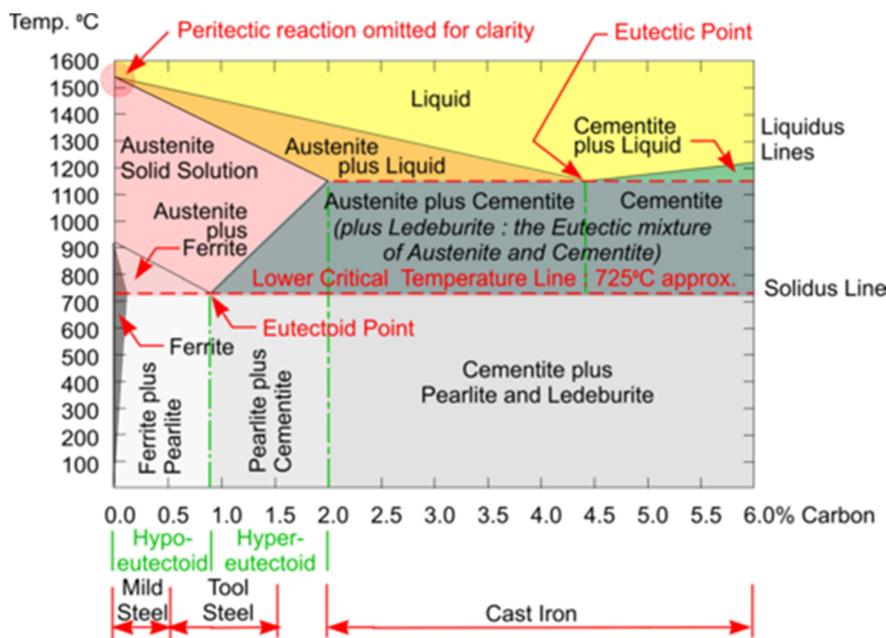
The maximum solubility of C in α - ferrite is 0.022 wt%. δ -ferrite is only stable at high temperatures. It is not important in practice. Austenite has a maximum C concentration of 2.14 wt %. It is not stable below the eutectic temperature (727° C) unless cooled rapidly. Cementite is in reality metastable, decomposing into α -Fe and C when heated for several years between 650°C and 770°C.

For their role in mechanical properties of the alloy, it is important to note that:

Ferrite is soft and ductile

Cementite is hard and brittle

Thus, combining these two phases in solution an alloy can be obtained with intermediate properties. (Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.)



Phases Observed in Fe-C Diagram

1. Ferrite

Ferrite is the interstitial solid solution of carbon in alpha iron. It has B.C.C. Structure. It has very limited solubility for carbon (maximum 0.022% at 727°C and 0.008% at room temperature). Ferrite is soft and ductile.

2. Austenite

Austenite is the interstitial solid solution of carbon in gamma (γ) iron. It has FCC structure. Austenite can have maximum 2.14% carbon at 1143°C. Austenite is normally not stable at room temperature. Austenite is non-magnetic and soft.

3. Cementite

Cementite or iron carbide (Fe_3C) is an intermetallic compound of iron and carbon. It contains 6.67% carbon. It is very hard and brittle. This intermetallic compound is a metastable phase and it remains as a compound indefinitely at room temperature.

4. δ -ferrite

It is a solid solution of carbon in δ -iron. It is stable at high temperatures. It has BCC structure.

Phase Mixtures Observed in Fe-C Diagram

- **1. Pearlite**

The pearlite consists of alternate layers of ferrite and cementite. It has properties somewhere between ferrite and cementite. The average carbon content in pearlite is 0.76%

- **2. Ledeburite**

Ledeburite is an eutectic mixture of austenite and cementite in the form of alternate layers. The average carbon content in ledeburite is 4.3%.

Important Reactions in Fe-C System

- There are three important reactions taking place in Fe-C system

1. Eutectic reaction

2. Eutectoid reaction

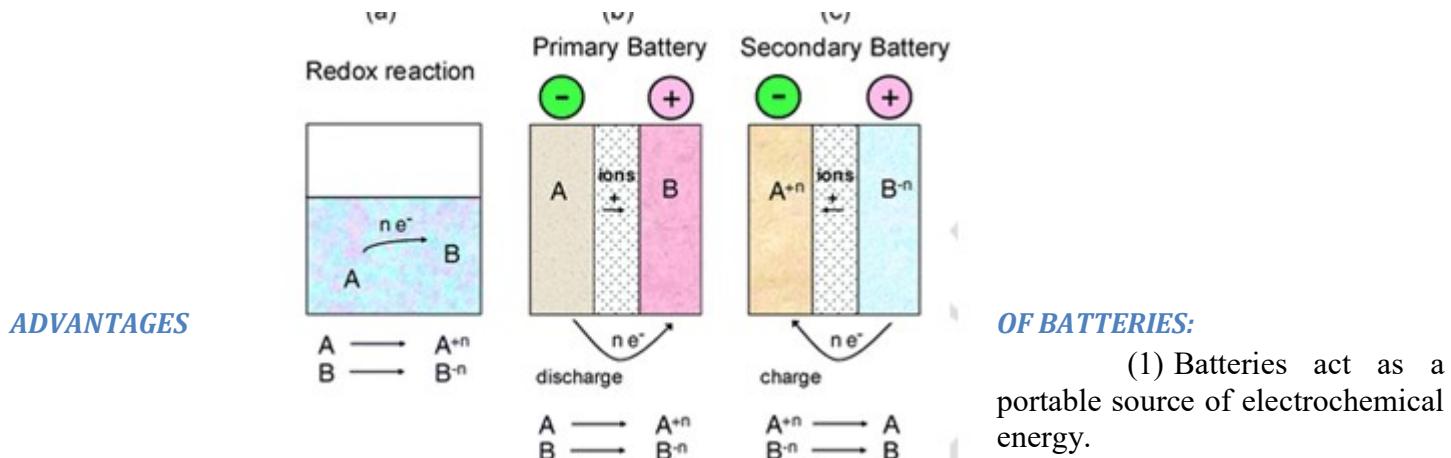
3. Peritectic Reaction

- Eutectic reaction
- Eutectic: 4.30 wt% C, 1147 °C
- $L(4.30\% C) \leftrightarrow \gamma(2.14\% C) + Fe_3C$
- Eutectoid reaction
- Eutectoid: 0.76 wt% C, 727 °C
- $\gamma(0.76\% C) \leftrightarrow \alpha(0.022\% C) + Fe_3C$
- Peritectic Reaction
- Peritectic: 0.16% C, 1493°C
- $\delta(0.11\% C) + L(0.51\% C) \leftrightarrow \gamma(0.16\% C)$

MODULE 5

Electrochemical Energy Systems

Battery is an electrochemical cell connected in series that can be used as a source of direct electric current at constant voltages. A device which converts chemical energy to electrical energy is called battery connected together electrically in series. Batteries are commercial electrochemical cells.



ADVANTAGES

- (1) Batteries act as a portable source of electrochemical energy.
- (2) The portability of electronic equipment in the form of handsets has been made possible by batteries.
- (3) A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.
- (4) For all commercial applications, batteries are constructed for their service. For example batteries for automotives and aircrafts, stand by batteries etc.

OF BATTERIES:

Requirements of Battery:

A useful battery should fulfill the following requirements

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. The voltage of the battery should not vary appreciably during its use.

Differences between Primary, Secondary and Fuel cells:

Distinction between Primary, Secondary & Fuel cells

Primary	Secondary	Fuel cells
1) It only acts as galvanic or voltaic cell. i.e., produces electricity	1) It acts as galvanic or voltaic cell while discharging (produces electricity) and acts as electrolytic cell (consumes electricity)	1) It is a simple galvanic or voltaic cell. i.e., produces electricity
2) Cell reaction is not reversible.	2) Cell reaction is reversible.	2) Cell reaction is reversible.
3) Can't be recharged.	3) Can be recharged	3) Energy can be withdrawn continuously
4) Can be used as long as the active materials are present	4) Can be used again and again by recharging.	4) Reactants should be replenished continuously. it does not store energy.
eg: Leclanche cell or Dry cell, Lithium cell.	eg: Lead storage battery, Ni-Cd battery, Lithium ion cell	eg: H ₂ &O ₂ Fuel cell CH ₃ OH &O ₂ Fuel cell
<u>Uses:</u> In Pace makers watches, Transistors, radios ect.	<u>Uses:</u> In electronic equipments, automobile equipments, digital cameras, laptops, flash light.	<u>Uses:</u> Great use in space vehicles due to its light weight (product of is source of fresh water for astronauts)

PRIMARY CELLS

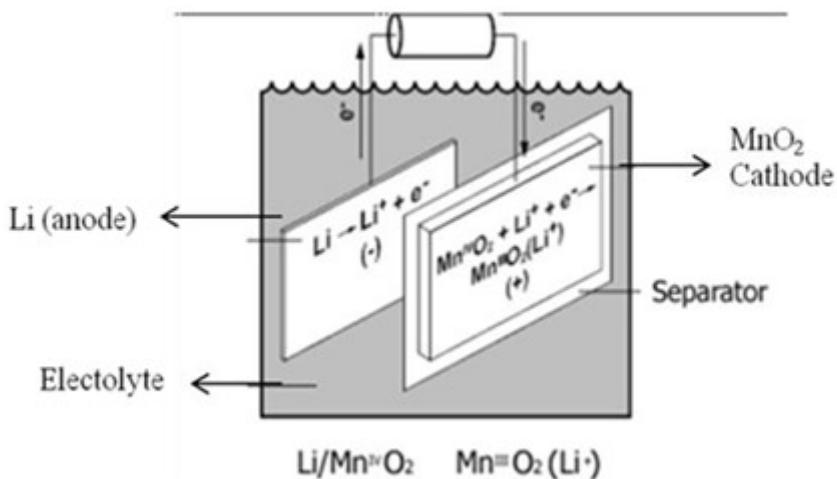
Lithium cells:

Lithium cells are primary cells in which lithium acts as anode and the cathode may differ. Lithium metal **is** used as anode because of its light weight, high standard oxidation potential ($\geq 3V$) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

Lithium cells are classified into two categories:

(a) Lithium cells with solid cathode:

The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium – manganese dioxide cell (3V). MnO₂ should be heated to over 300°C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.

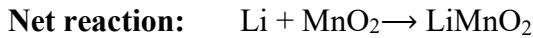
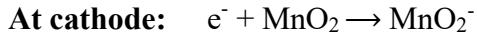


Anode: Lithium Metal,

Cathode: MnO_2 as an active material.

Electrolyte: LiBF_4 salt in a solution of propylene carbonate and dimethoxy ethane.

Reactions:



Applications:

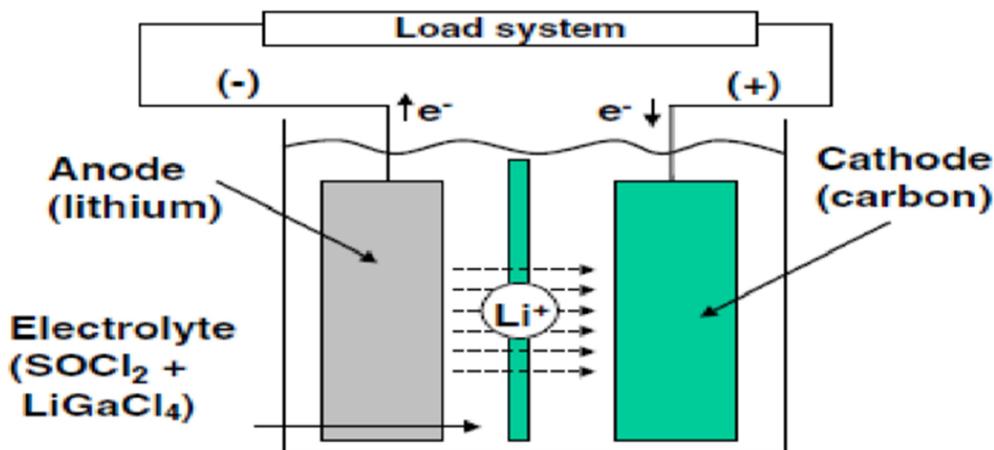
1. The coin type cells are used in watches and calculators.
2. Cylindrical cells are used in fully automatic cameras

(b). Lithium cells with liquid cathode: Lithium–sulphur dioxide cell is an example of liquid cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of the two with SO_2 in 50% by volume.

Cell reaction: $2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$

Lithium thionyl chloride cell is another example of liquid cathode. It consists of high surface area carbon cathode, a non – woven glass separator. Thionyl chloride acts as an electrolyte and as a cathode. Sometimes it is mixed with LiGaCl_4 to avoid its decomposition.

Cell reaction:



USES:

1. They are used for military and space applications.
2. In medicinal devices such as neuro-stimulators, drug delivery system, lithium batteries are widely used.
3. They are also used in electric circuit boards for supplying fixed voltage for memory protection and standby functions.

Advantages

1. The energy output of a lithium cell is 2-4 times better than that of conventional zinc anode batteries.
2. Lithium batteries can work over temperature range of 40-70°C.
3. They have higher voltages of about 4V when compared to other primary cells with 1.5 V only.

Secondary cells

Lithium-ion batteries (or) Lithium-ion cells:

Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode. As the name suggests, the movement of lithium ions are responsible for charging '& discharging. Lithium-ion cell has the following three components.

1. A positive electrode (Layers of lithium-metal oxide) (cathode).
2. A negative electrode (Layers of porous carbon) (anode).
3. An electrolyte (Polymer gel) (separator)

Construction:

The positive electrode is typically made from a layers of chemical compound called lithium- cobalt oxide (LiCoO_2).

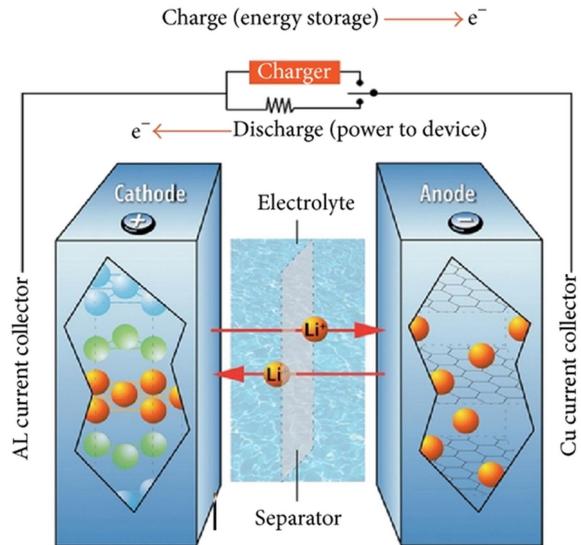
The negative electrode is made from layers of porous carbon (C) (graphite).

Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the Li^+ ions to pass through.

Working

Charging Reaction:

During charging, Li^+ ions flow from the positive electrode (LiCoO_2) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.



Discharging Reaction:

During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.



Advantages (or) Characteristics:

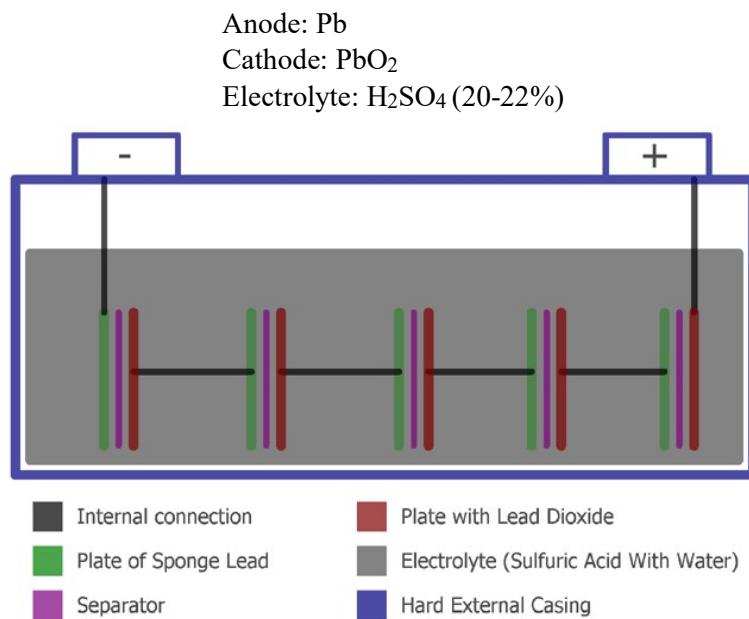
1. Lithium-ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three time the voltage of Ni-Cd batteries.
4. It has none of the memory effect seen in Ni-Cd batteries.

Uses:

It is used in cell phone, note PC, portable LCD TV, semiconductor driven audio, etc.

Lead-Acid cells

The lead storage battery is one of the most common **secondary batteries** that are used in the automobiles. A 12 V lead storage battery is generally used, which consists of six cells, each providing 2V. Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode. These electrodes are arranged alternately, separated by a thin wooden piece and suspended in dil. H_2SO_4 (38%), which acts as an electrolyte. Hence, it is called lead acid battery.



Lead storage cells: To increase the current output of each cell, the cathode and the anode plates are joined together, keeping them in alternate positions. The cells are connected parallel to each other.

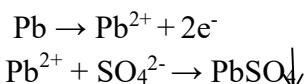
The cell is represented as



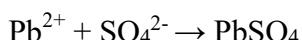
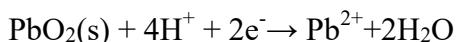
In the process of discharging, i.e., when the battery produces current, the reactions at the electrodes are as follows:

Discharging

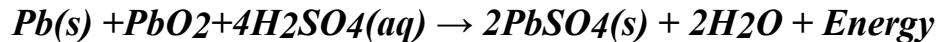
At anode:



At cathode:



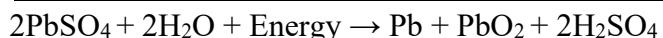
Therefore, the overall reaction is:



During discharging the battery, H_2SO_4 is consumed, and as a result, the density of H_2SO_4 falls. When it falls below 1.20 g/cm³, the battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs.

Charging

During recharging, the cell is operated like an electrolytic cell, i.e. electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge.



During this process, lead is deposited at the cathode, PbO_2 is formed at the anode and H_2SO_4 is regenerated in the cell.

Advantages

Lead-acid batteries are used for supplying current to railways, mines, laboratories, hospitals, automobiles, power stations, telephone exchange, gas engine ignition, UPS. Other advantages are its recharge ability, portability, and relatively constant potential and low cost. **Disadvantages:** Use of conc. H_2SO_4 is dangerous. Use of lead battery is fragile.

FUEL CELL

A fuel cell is an electrochemical which converts chemical energy contained in readily available fuel oxidant system into electrical energy.

Principle:

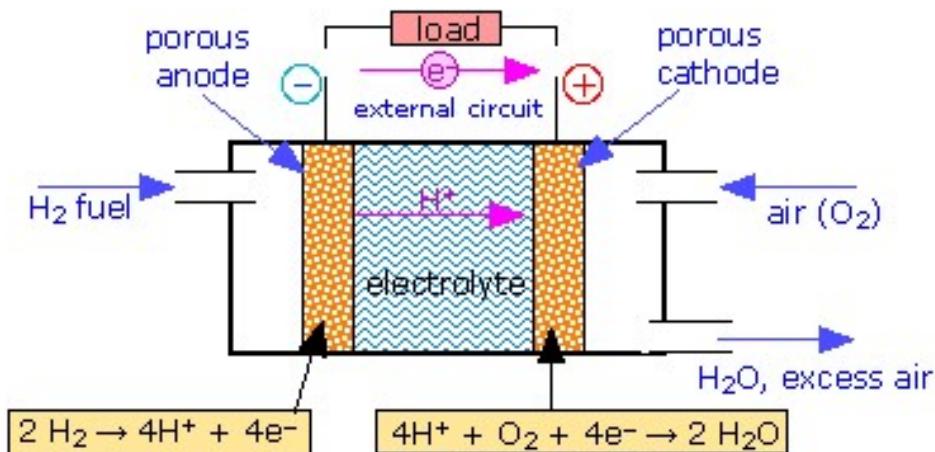
The fuel cell operates like a galvanic cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel and oxidant are supplied continuously and separately to the electrodes at which they undergo redox reaction. Fuel cells are capable of supplying current as long as reactants are replenished.

Fuel + Oxidant → Oxidation products + Electric Energy

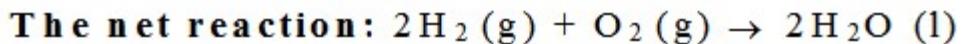
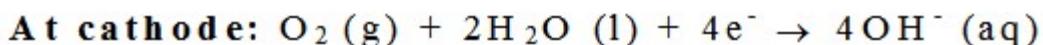
- Examples:** 1. H₂-O₂ fuel cell
2. CH₃OH-O₂ fuel cell

Hydrogen-Oxygen fuel cells:

- ✓ This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cell also have two half cells.
- ✓ Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide).
- ✓ The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte.
- ✓ Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes.
- ✓ The two half-cell reactions are as follows;



- ✓ The EMF of this cell is measured to be 1.23V.
- ✓ A number of such fuel cell are stacked together in series to make a battery.



Advantages

1. The energy conversion is very high (75-82%).
2. Fuel cell minimizes expensive transmission lines and transmission losses.
3. It has high reliability in electricity generation.
4. The byproducts are environmentally acceptable.

5. Maintenance cost is low for these fuels.
6. They save fossil fuels.
7. Noise and thermal pollution are very low

Disadvantages:

1. The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
2. The accurate life time is also not known.

APPLICATIONS:

1. The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
2. The product H_2O is valuable source of fresh water by the astronauts.
3. Fuel cell batteries for automotive will be a great boom for the future.

Limitations:

1. The life time of fuel cells is not accurately known
 2. It cannot store electricity
 3. Electrodes are expensive ad short lived.
 4. Storage and handling of H_2 gas is dangerous because it is inflammable.
-

Proton exchange membrane fuel cell (PEMFC)

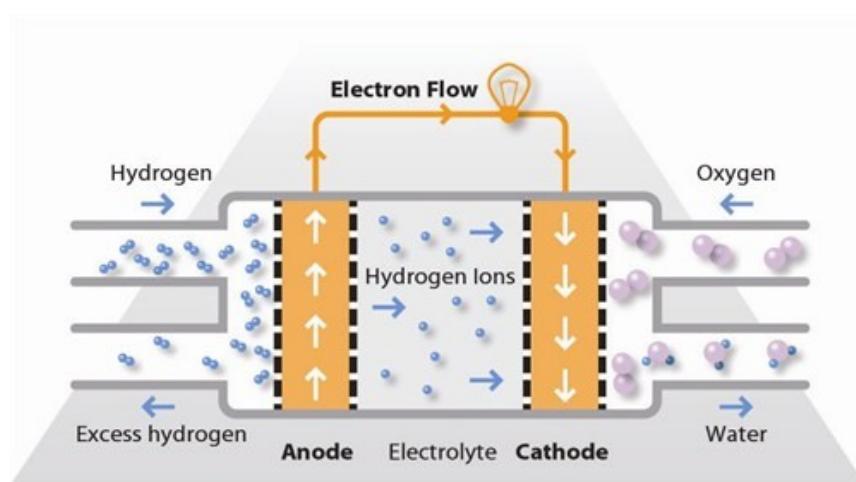
- ✓ It uses a water-based, acidic polymer membrane as its electrolyte, with platinum-based electrodes.
- ✓ PEMFC cells operate at relatively low temperatures (below 100 degrees Celsius) and can tailor electrical output to meet dynamic power requirements.
- ✓ Due to the relatively low temperatures and the use of precious metal-based electrodes, these cells must operate on pure hydrogen.
- ✓ PEMFC cells are currently the leading technology for light duty vehicles and materials handling vehicles, and to a lesser extent for stationary and other applications.
- ✓ The PEMFC fuel cell is also sometimes called a polymer electrolyte membrane fuel cell (also PEMFC).

Process:

- a. Hydrogen fuel is processed at the anode where electrons are separated from protons on the surface of a platinum-based catalyst.
- b. The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell.
- c. On the cathode side, another precious metal electrode combines the protons and electrons with oxygen to produce water, which is expelled as the only waste product; oxygen can be provided in a purified form, or extracted at the electrode directly from the air.

Advanced PEMFC:

- A variant of the PEMFC which operates at elevated temperatures is known as the **high temperature PEMFC (HT PEMFC)**.
- By changing the electrolyte from being water-based to a mineral acid-based system, HT PEMFCs can operate up to 200 °C.
- This overcomes some of the current limitations with regard to fuel purity .



Solid oxide fuel cells

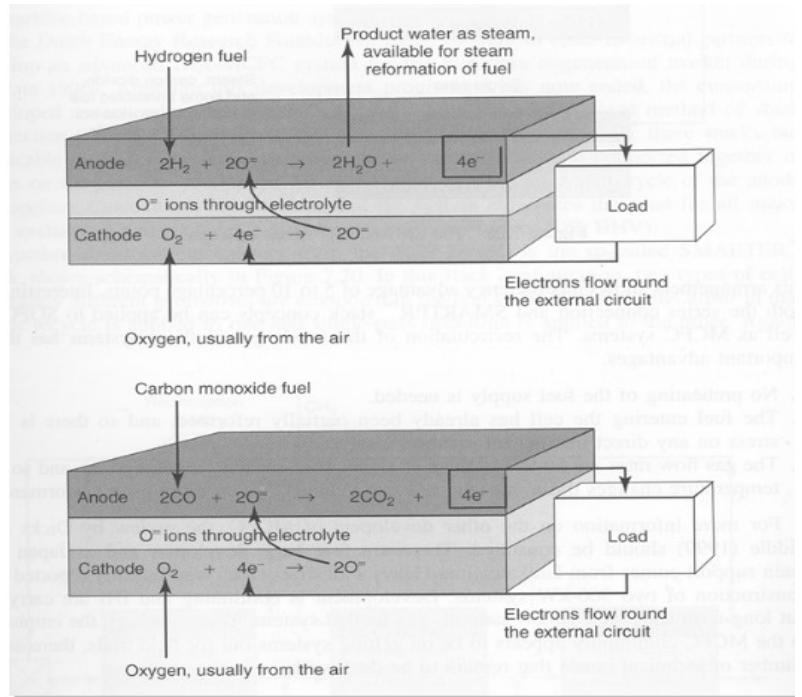
- ✓ It involves two phases i.e solid and gas.
- ✓ SOFCs use a solid ceramic electrolyte, such as zirconium oxide stabilised with yttrium oxide, instead of a liquid or membrane.
- ✓ Both hydrogen and carbon monoxide are used as fuels.
- ✓ Solid oxide fuel cells work at very high temperatures, the highest of all the fuel cell types at around 800°C to 1,000°C.

The **anode** is usually a **zirconia cermet** (an intimate mixture of ceramic and metal). The metallic component is usually Ni (nickel chosen amongst other things because of its high electronic conductivity and stability under chemically reducing and part reducing conditions; it can also be used as

- ✓ catalyst for direct internal reforming on the anode!);

At present most cathodes are made from electronically conducting oxides or mixed electronically conducting and ion-conducting ceramics. The most common cathode material of the latter type is strontium-doped-lanthanum manganite (**SLM**).

- ✓ Efficiency : over 60% when converting fuel to electricity
- ✓ In this cells, fuels can be reformed within the fuel cell itself, eliminating the need for external reforming and allowing the units to be used with a variety of hydrocarbon fuels.
- ✓ This cell relatively resistant to small quantities of sulphur in the fuel, compared to other types of fuel cell, and can hence be used with coal gas.



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