Corrosion in Materials

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Syllabus

Corrosion process: Corrosion, Cause of corrosion, Types of corrosion, Protection against corrosion.

CLO: Propose a solution to prevent corrosion.

Corrosion

Corrosion is the deterioration and loss of metal, or material by chemical or electrochemical reactions with its environments.

❑ It is a very natural process.

❑ Most of metallic elements (except noble metals) present in the most stable state having low energy, normally oxides (as metallic ores)

Reason for corrosion

The tendency to decrease the energy of the system as a result of the corrosion reactions.

❑ Metals get oxidized
❑ Polymers react with oxygen and degrade
❑ Ceramic refractories may dissolved in contact with molten materials

Corrosion

Example: Formation of rust on the surface of iron, formation of green film on the surface of copper

The responsible factors for the corrosion of a metal are the metal itself, the environmental chemicals, temperature and the design.

Electro-Chemical Corrosion

Electro-chemical reaction: most common mechanism by which corrosion occur at or near room temperature as a result of a chemical reaction metals with water, o aqueous solutions of salts, acids or bases. It is named electro-chemical corrosion as a chemical reaction accompanied the passage of electric-current takes place.

Metal atoms characteristically lose or give up electrons in what is called an oxidation reaction.

$$M \rightarrow M^{n+} + ne^-$$
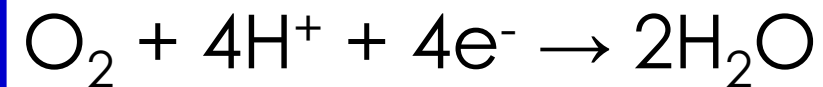$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Al \rightarrow Al^{3+} + 3e^-$$

The electrons generated from each metal atom that is oxidized are transferred to and become a part of another chemical species. This is a reduction reaction.
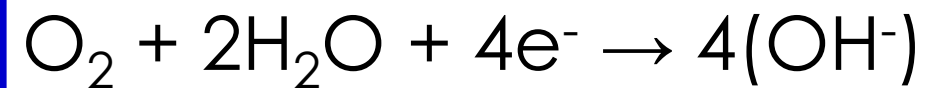
Examples

$2H^+ + 2e^- \rightarrow H_2$

Reduction of hydrogen ions in an acid solution

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Reduction reaction in an acid solution containing dissolved oxygen

$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$

Reduction reaction in a neutral or basic solution containing dissolved oxygen

❑When an electrode (e.g. Zn) is immersed in an aqueous solvent containing its own ions. Some of Zn^{2+} metal ions leave the electrode by giving their valence electrons to the metal electrode and go into the solvent. The negative charge builds up in the electrode.

❑The solvent becomes +ve and the opposing electrical layers leads to a dynamic equilibrium wherein there is no further (net) dissolution of the electrode.

❑If the metal-in concentration in the solution is kept fixed, normally one mole of ions per litre (having unit activity) at a constant temperature (25°C) the electric potential of the metal now becomes the property of the metal. It gives the tendency of a metal to go into solution i.e. to corrode, or to get plated.

❑The electrode potential is measured with the electrode in contact with a solution containing an unit concentration of ions of the same metal with the standard hydrogen electrode as the counter electrode (whose potential is taken to be zero).
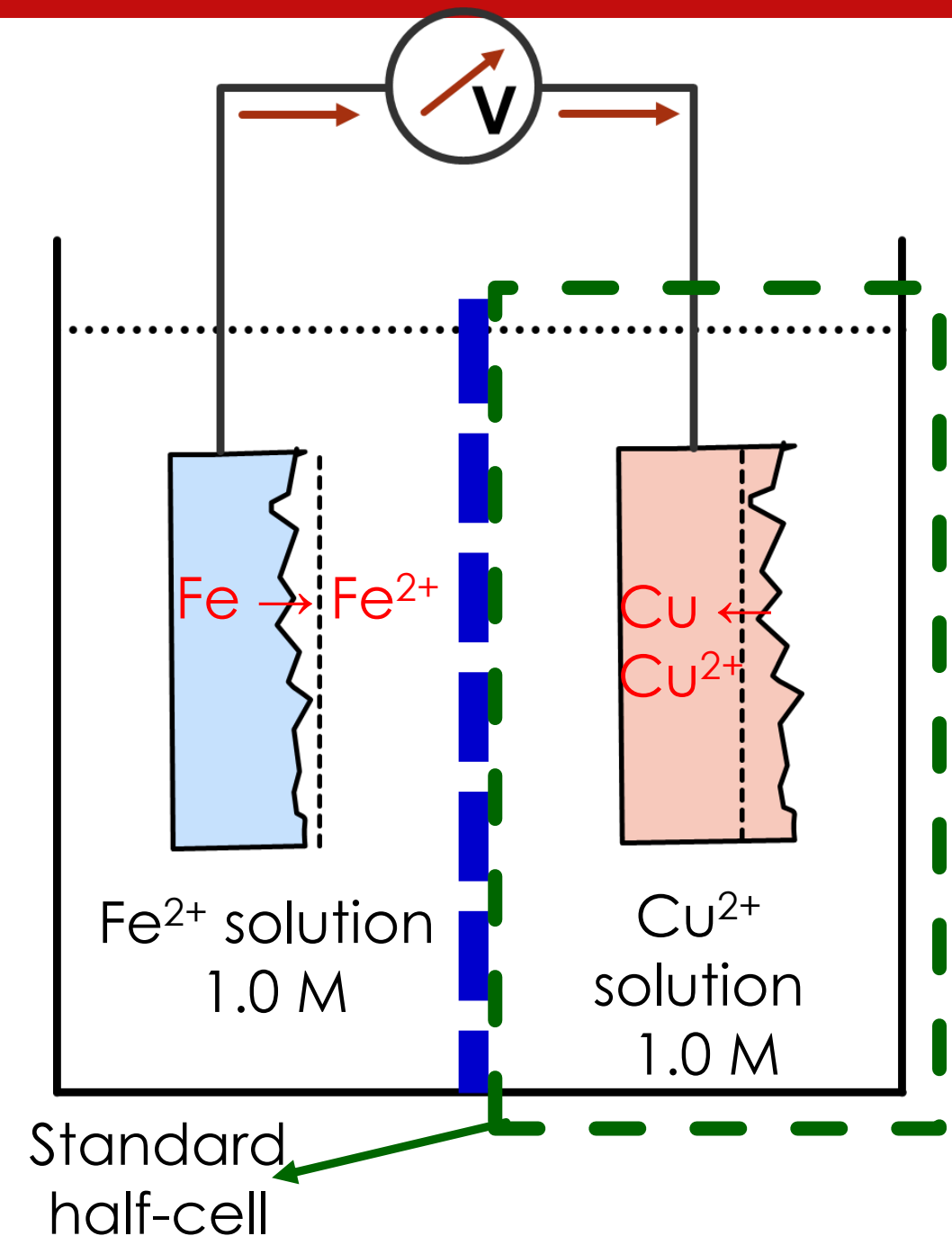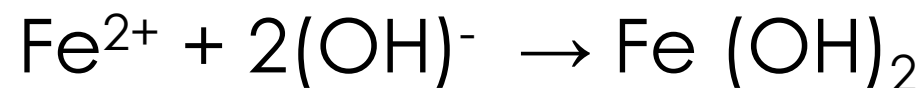
Liberated electrons are move from anode to the higher potential area the cathode (copper side), where they consumed in the cathodic reaction:

$Cu^{2+} + 2e^- \rightarrow Cu$

The cations Fe^{2+} migrate through the electrolyte towards the cathode and the anions $(OH)^-$ migrate towards the anode. Both combine and produce an insoluble compound by the reaction:

$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2$

Fe → Fe²⁺

Cu ←
Cu²⁺

Fe²⁺ solution
1.0 M

Cu²⁺ solution
1.0 M

Standard half-cell

Simple Galvanic Cell

Standard potential at 25°C

	System	Potential in V
Noble end	Au / Au^{3+}	+1.5
	Ag / Ag^+	+0.80
	Cu / Cu^{2+}	+0.34
	H_2 / H^+	0.0
	Pb / Pb^{2+}	-0.13
	Ni / Ni^{2+}	-0.25
	Fe / Fe^{2+}	-0.44
	Cr / Cr^{3+}	-0.74
	Zn / Zn^{2+}	-0.76
	Al / Al^{3+}	- 1.66
Active end	Li / Li^+	-3.05

Increasing propensity to dissolve

Not all metallic materials oxidize to form ions with same degree of ease.

Two dissimilar metals Fe and Cu are placed in electrical contact in the presence of an electrolyte (e.g. salt solution having dissolved oxygen). The potential of each metal is related to its relative tendency to dissolved .

Fe (OH)$_2$

Rust forms

(OH)$^-$

$H_2O + 2e^- + ½ O_2 \rightarrow 2$ (OH)$^-$

Fe^{2+}

Cathodic reaction

Anodic reaction

Fe$\rightarrow$ Fe^{2+} + 2e-

Fe (anode)

Electric current

Fast attack

Cu (cathode)

Anode and cathode
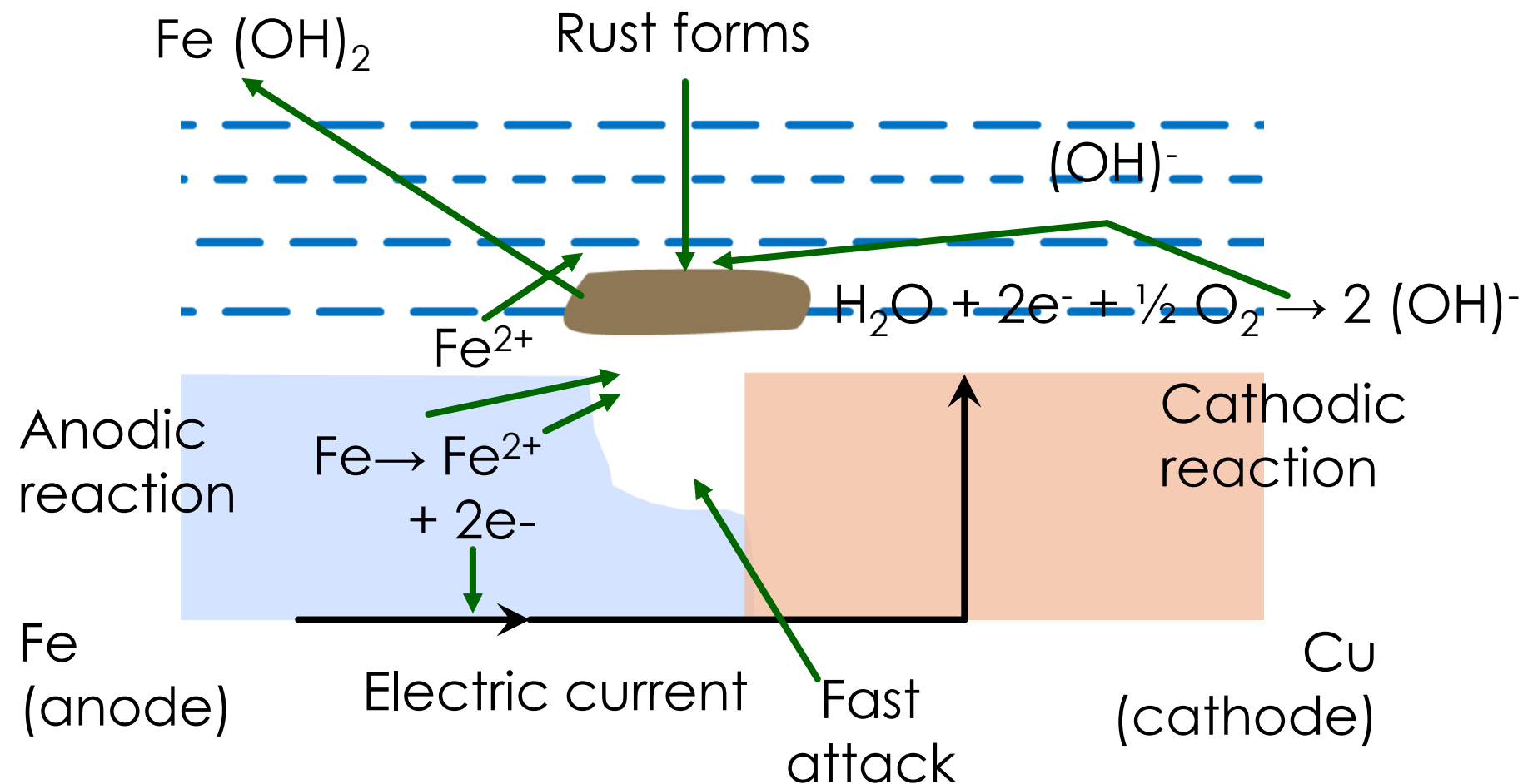
Two dissimilar metals Fe and Cu are placed in electrical contact in the presence of an electrolyte (e.g. salt solution having dissolved oxygen). The potential of each metal is related to its relative tendency to dissolved .

Fe has lower potential acts as anode and dissolved (i.e. corrode) by reaction,

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Anodic reactions are oxidation reaction.

Cathodic reaction, $H_2O + 2e^- + \frac{1}{2} O_2$ (dissolved oxygen) $\rightarrow 2 (OH)^-$
Cathodic reactions are reduction reactions.

More anodic metal corrodes.

Galvanic Cell

When externally connected, electrons generated from the oxidation of iron flow to the copper cell in order that Cu^{2+} be reduced.

In addition, there will be some net ion motion from each cell to the other across the membrane.

This is called a *galvanic couple* - two metals electrically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

An electric potential or voltage will exist between the two cell halves.
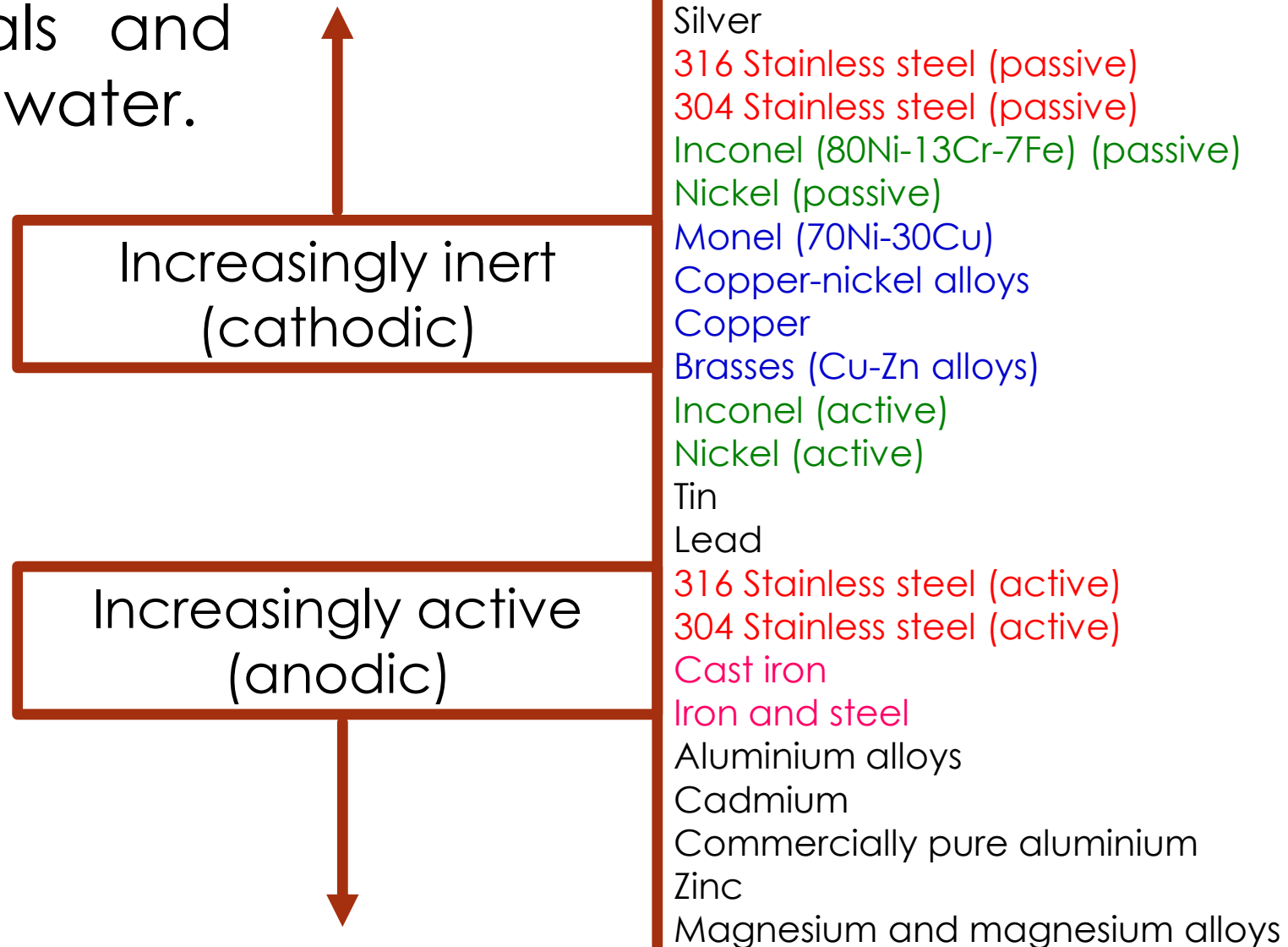
For example:

$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$ Potential: 0.780 V

$Fe^{2+} + Zn \rightarrow Fe + Zn^{2+}$ Potential: 0.323 V
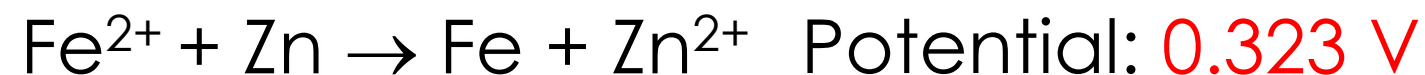
Various electrode pairs have different voltages !

Galvanic Cell

Galvanic series: This represents the relative reactivity of a number of metals and commercial alloys in seawater.

Platinum
Gold
Graphite
Titanium
Silver
316 Stainless steel (passive)
304 Stainless steel (passive)
Inconel (80Ni-13Cr-7Fe) (passive)
Nickel (passive)
Monel (70Ni-30Cu)
Copper-nickel alloys
Copper
Brasses (Cu-Zn alloys)
Inconel (active)
Nickel (active)
Tin
Lead
316 Stainless steel (active)
304 Stainless steel (active)
Cast iron
Iron and steel
Aluminium alloys
Cadmium
Commercially pure aluminium
Zinc
Magnesium and magnesium alloys

Increasingly inert (cathodic)

Increasingly active (anodic)

Corrosion penetration rate

The corrosion rate, or the rate of material removal as a consequence of the chemical action, is an important corrosion parameter.
It is the thickness loss of material per unit of time.

$$CPR = \frac{KW}{\rho A t}$$

where W = weight loss after exposure time t; ρ = density, and A = exposed specimen area, K is a constant.

There is an electric current associated with electrochemical corrosion reactions.

$$r = \frac{i}{nF}$$

where

i = current density (the current per unit surface area of material corroding)

n = number of electrons associated with the ionization of each metal atom

F = 96,500 C/mol.

Galvanic Cell : Passivation

o Some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become extremely inert. E.g., chromium, iron, nickel, titanium, and many of their alloys.

o This passive behaviour results from the formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier to further corrosion.

o e.g. Ashoka Pillar, Delhi

Summary

1. Corrosion is a loss due to electrochemical reactions in the environment.

2. Electrochemical reaction between two different metals gives rise to corrosion.

3. The corrosion in galvanic series is more when the potential difference is more.

4. Passivation is loss of chemical reactivity of the material.