Chapter 3

Principles of corrosion

Corrosion

- Corrosion may be defined as destruction of a material due to the contact with its surrounding environment.

- **Types of Corrosion**

1. Direct or Chemical Corrosion.
2. Indirect or Electrochemical Corrosion.

Direct or Chemical Corrosion

- In this type of corrosion, direct chemical reaction occurs between metal or alloy surface and environment and the corrosion product is deposited there.
- **Example**

  The chemical reaction between zinc metal and acid which lead to the dissolution of aluminum metal.

Indirect or Electrochemical Corrosion.

- It is an electrochemical reaction between metals and the environment.

Electrochemical reaction

- It's known as redox reaction (reduction – oxidation reaction)

Oxidation Reactions

- LOSS of electrons
- Removal of H_2 OR gain of O_2
- Take place at anode
- Oxidation Reaction ≅ Anodic Reaction
- Oxidized metal carry positive charge
- Metal → Positive Ion + Electron(s)
- $\mathbf{M \rightarrow M^{n+} + ne^-}$ (n=1,2,3,…)
- $\mathbf{Na \rightarrow Na^{+} + e^-}$ **&** $\mathbf{Fe \rightarrow Fe^{2+} + 2e^-}$ **&** $\mathbf{Al \rightarrow Al^{3+} + 3e^-}$

Reduction Reactions

- GAIN of electrons
- Removal of O_2 OR gain of H_2
- Take place at cathode
- Reduction Reaction ≅ Cathodic Reaction
- Reduced species carried negative charge.
- For strong acidic medium (pH<4)

  $2H^+ + 2e^- \rightarrow H_2$
- For neutral or basic medium (pH= 4-10)

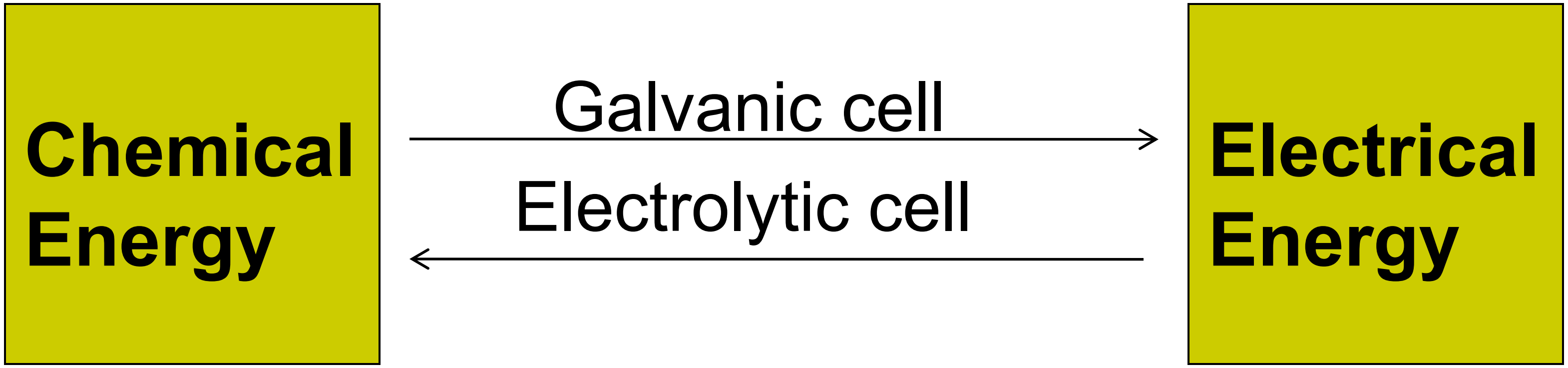
  $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$

PH-scale

It’s a scale to determine the acidity or alkalinity strength.

0 → 4	4 → 7	7 → 10	10 → 14
Strong acid	Weak acid	Weak base	Strong base
Sulfuric acid Hydrochloric acid Phosphoric acid	Acetic acid Oxalic acid Citric acid	Ammonia	Sodium hydroxide Potassium hydroxide

Electrochemical cells



Chemical Energy

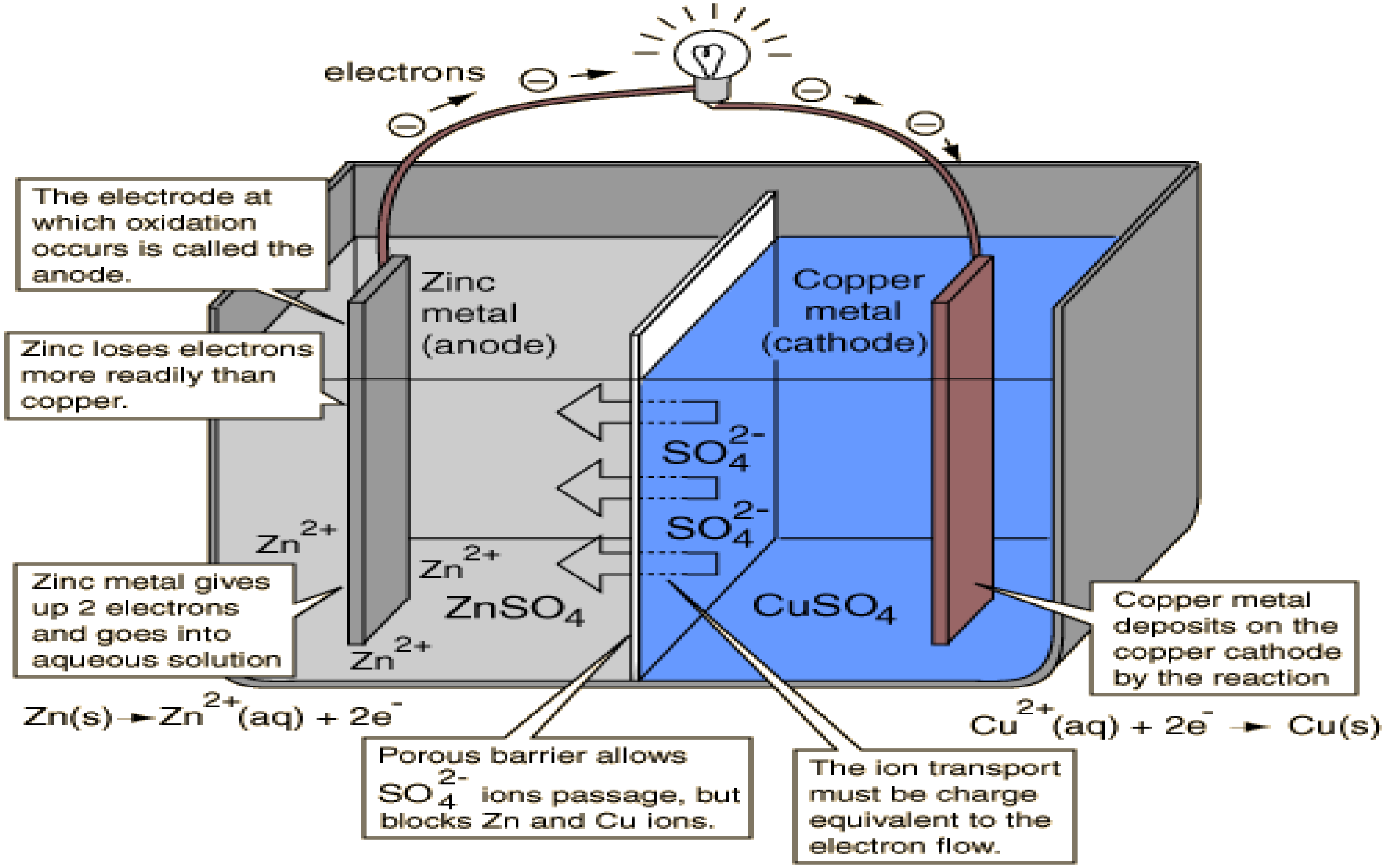
Galvanic cell →

← Electrolytic cell

Electrical Energy

Corrosion cell ≅ Galvanic cell

Galvanic cell



The electrode at which oxidation occurs is called the anode.

Zinc loses electrons more readily than copper.

Zinc metal gives up 2 electrons and goes into aqueous solution

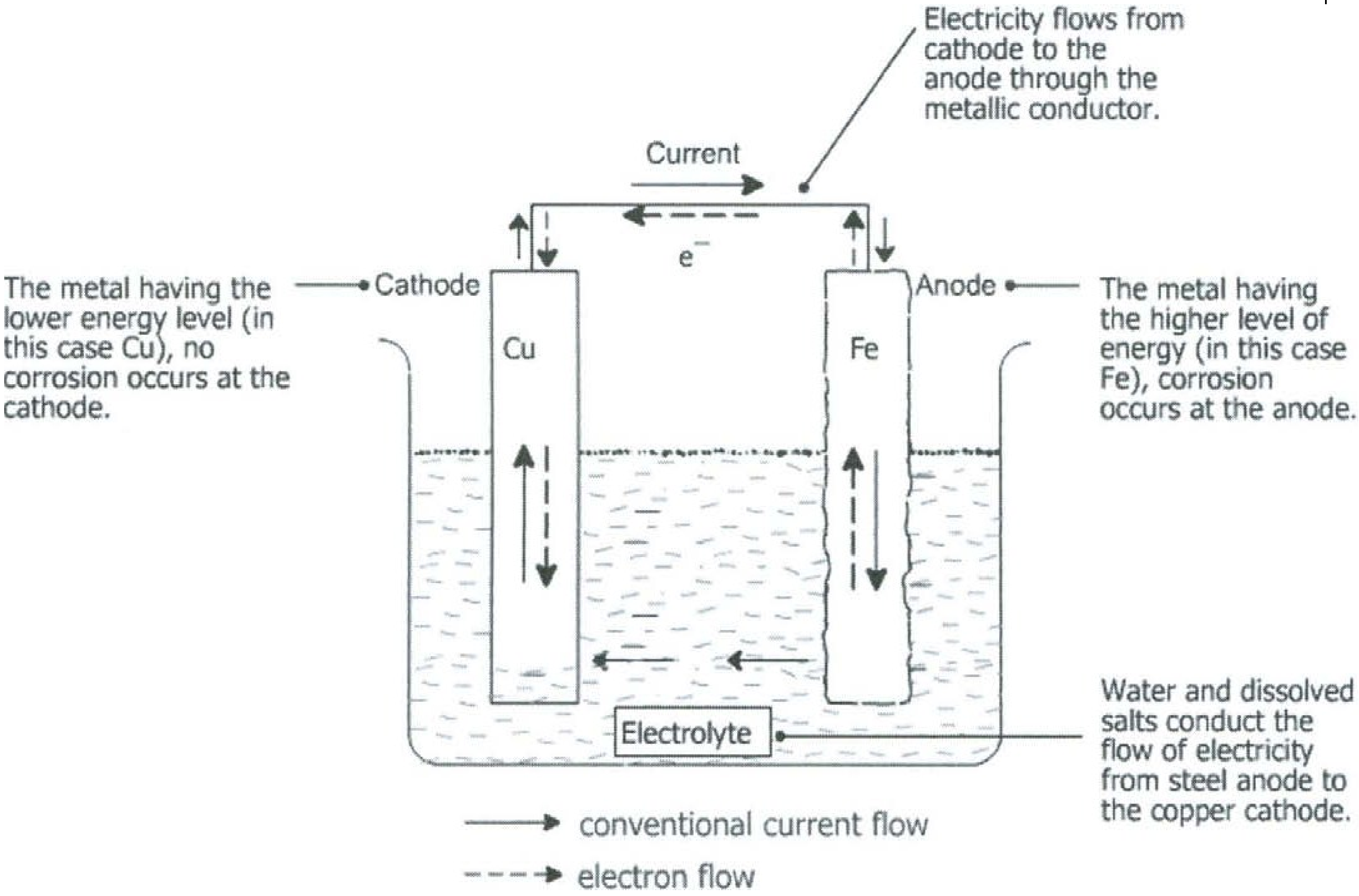
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Porous barrier allows SO_4^{2-} ions passage, but blocks Zn and Cu ions.

The ion transport must be charge equivalent to the electron flow.

Copper metal deposits on the copper cathode by the reaction

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$



Electricity flows from cathode to the anode through the metallic conductor.

The metal having the lower energy level (in this case Cu), no corrosion occurs at the cathode.

The metal having the higher level of energy (in this case Fe), corrosion occurs at the anode.

Water and dissolved salts conduct the flow of electricity from steel anode to the copper cathode.

Galvanic cell reactions.

Cell formula

Anode // Electrolyte // Cathode

(Corroded Area)

At the Anode (+)	At the Cathode (-)
Oxidation Reaction	**Reduction Reaction**
$Zn \rightarrow Zn^{2+} + 2e^-$ Two electrons will flow from the Zinc (anode) to the copper (cathode)	**$2H^+ + 2e^- \rightarrow H_2$** ($H_2$ Reduction at pH<4) **$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$** ($O_2$ Reduction pH= 4-10)

The component of Galvanic Cell

- Potential difference between anode and cathode.
- External conductor between anode and cathode (wire).
- Electrolyte solution between anode and cathode.

  Electrolyte solution is source of ions dissolved in water.

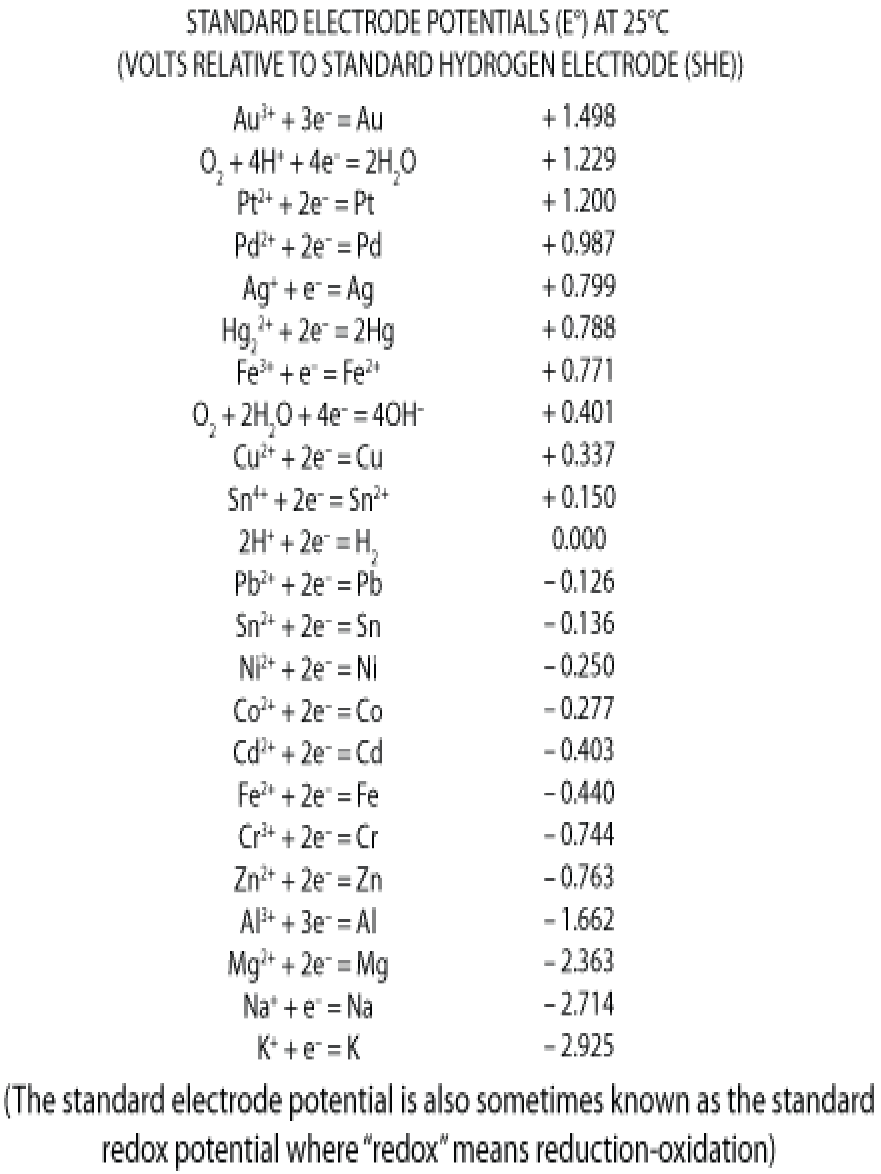
  The source of ions may be acid, base or salt.

<u>Examples:</u>

Zn / electrolyte / Cu
Fe / electrolyte / Pb

Al / electrolyte / Cu

The Electrochemical Series



STANDARD ELECTRODE POTENTIALS (E°) AT 25°C
(VOLTS RELATIVE TO STANDARD HYDROGEN ELECTRODE (SHE))

$Au^{3+} + 3e^- = Au$	+ 1.498
$O_2 + 4H^+ + 4e^- = 2H_2O$	+ 1.229
$Pt^{2+} + 2e^- = Pt$	+ 1.200
$Pd^{2+} + 2e^- = Pd$	+ 0.987
$Ag^+ + e^- = Ag$	+ 0.799
$Hg_2^{2+} + 2e^- = 2Hg$	+ 0.788
$Fe^{3+} + e^- = Fe^{2+}$	+ 0.771
$O_2 + 2H_2O + 4e^- = 4OH^-$	+ 0.401
$Cu^{2+} + 2e^- = Cu$	+ 0.337
$Sn^{4+} + 2e^- = Sn^{2+}$	+ 0.150
$2H^+ + 2e^- = H_2$	0.000
$Pb^{2+} + 2e^- = Pb$	− 0.126
$Sn^{2+} + 2e^- = Sn$	− 0.136
$Ni^{2+} + 2e^- = Ni$	− 0.250
$Co^{2+} + 2e^- = Co$	− 0.277
$Cd^{2+} + 2e^- = Cd$	− 0.403
$Fe^{2+} + 2e^- = Fe$	− 0.440
$Cr^{3+} + 2e^- = Cr$	− 0.744
$Zn^{2+} + 2e^- = Zn$	− 0.763
$Al^{3+} + 3e^- = Al$	− 1.662
$Mg^{2+} + 2e^- = Mg$	− 2.363
$Na^+ + e^- = Na$	− 2.714
$K^+ + e^- = K$	− 2.925

(The standard electrode potential is also sometimes known as the standard redox potential where "redox" means reduction-oxidation)

Polarization

The rate of electrochemical reaction is limited by various physical and chemical factors.

The electrochemical reaction is retarded by several physical and chemical factors.

Polarization is inversely proportional to the corrosion rate.

Steps of electrochemical reaction:

1. Ion transfer from the bulk of solution to the surface through the diffusion layer (charge transfer step or mass transfer step)
2. Chemical reaction between ions and electrons. (Oxidation or reduction)
3. Material transfer from the surface of metal to the bulk of solution through the diffusion layer. (Mass transfer step).

Reduction of hydrogen:

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

-the first and third steps are mass transfer steps.

-the second step is chemical reaction step.

Polarization can be conveniently divided into two type's concentration and activation polarization.

Concentration polarization

It is refers to electrochemical reaction which are controlled by the mass transfer (diffusion) step in the electrolyte.

Condition: the transfer is <u>slower</u> than the chemical reaction.

Activation polarization

It is refers to electrochemical reaction which are controlled by the chemical reaction sequence at the metal surface.

Condition: the chemical reaction is <u>slower</u> than the mass transfer.

<u>Examples:</u>

Corrosion rate in concentrated electrolyte is chemical reaction controlled.

Corrosion rate in diluted electrolyte is diffusion controlled.

Passivity

Some metals and alloys under particular environmental condition loss their chemical reactivity and become inert.

Environment	Iron	Aluminum
Air	Non passive	passive
Nitric acid (HNO_3)	passive	Non passive

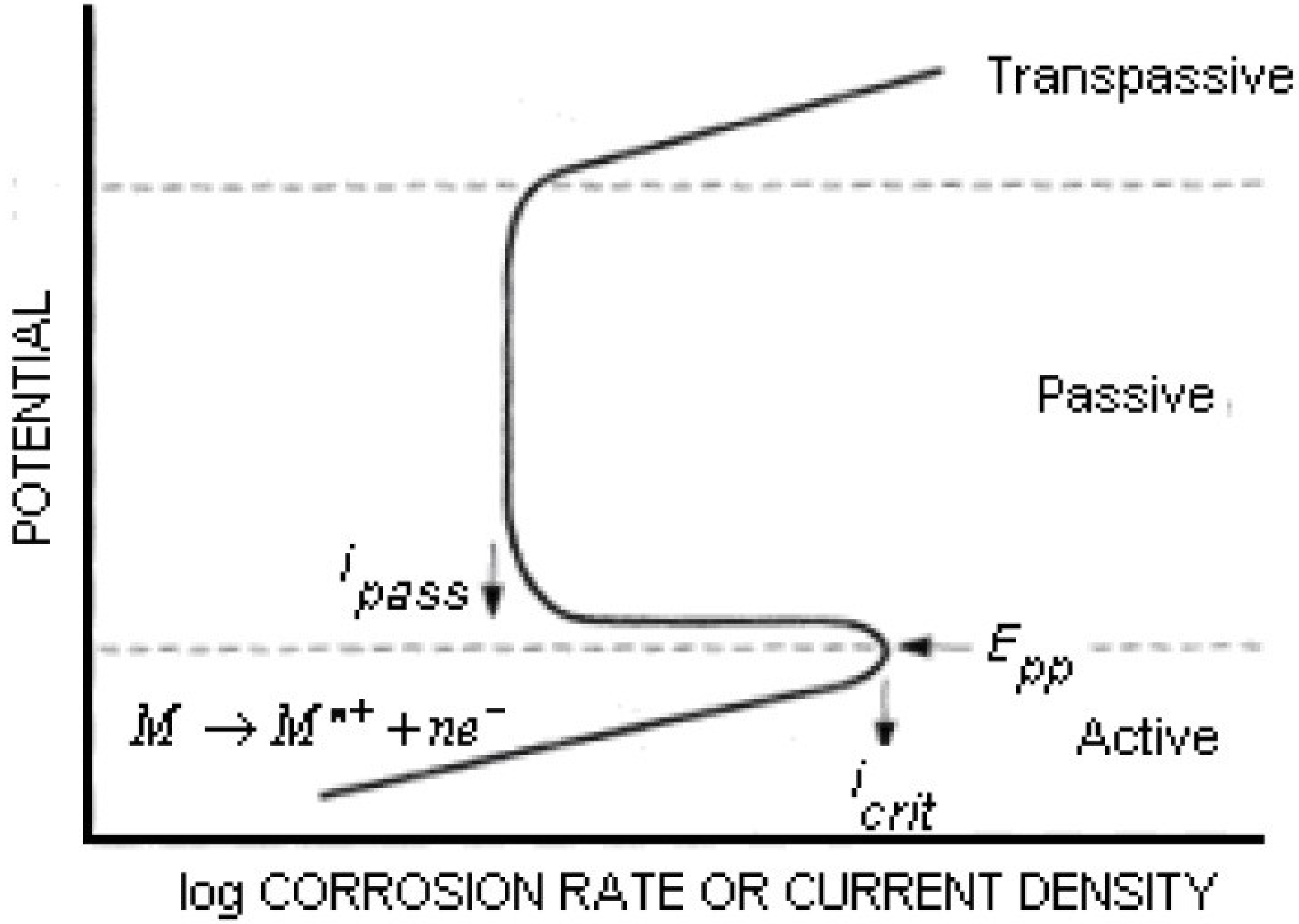
Passivity

Passivity may be defined as the metal or alloy under particular environmental condition form protective layer due to the reaction between the metal and environment.

Passivity depends mainly on:

- The nature of the metal or alloy.
- Type of the environment.

Passivity curve



- Active region: the behavior of metal is identical to that of normal metal where slight increase in the oxidizing power of the solution cause rapid increase in the corrosion rate.

- Passive region: by increasing the oxidizing power the corrosion rate show sudden decrease and further increase in the oxidizing power produce no change(rate is constant).

- Trans passive region: at very high values of oxidizing power, the corrosion rate again increase as oxidizing power increase.

Corrosive environment

Air, water, soil, gases, and acids may acts as corrosive environment.

Types of corrosive environment:

- **Air**:
  - Moist and humid air is more corrosive than dry air.
  - Hot air is more corrosive than cold air.
  - Polluted air is more corrosive than fresh air.

- **Water**:
  - Hot water is more corrosive than cold water.
  - Salty water is more corrosive than fresh water.
  - Polluted water is more corrosive than pure water.

- **Gases**: Acidic gases (SO_x, NO_x, and H_2S.) are more corrosive than Basic gases (NH_3).

Acids:

Acid	Mineral	Organic	Fatty
Strength	Very strong	Weak	Very weak
Examples	H_2SO_4, HNO_3, H_3PO_4, HCL……	Acetic and Formic acid	Animals and plant oils

- Bases: Strong bases (sodium hydroxide, potassium hydroxide) are more corrosive than weak bases (ammonia solution).

- Note: acids is the most corrosive environment.
- Soil:

  Presence of water, salts, gases, stray current, pollutants, affects the corrosion rate greatly.