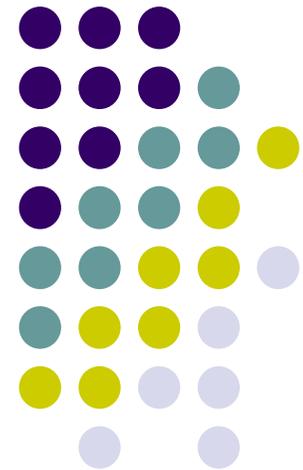
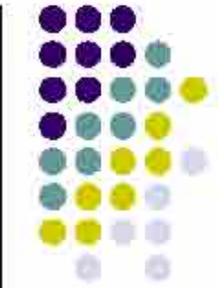


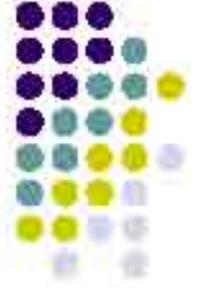
Chapter 3

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**
Dissolution of metals in contact with non-conducting organic media.

Indirect or Electrochemical Corrosion.



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

Electrochemical reaction

- It's the oxidation–reduction type of chemical reactions which is known as redox reaction

CLASSIFICATION OF CORROSION



There is not a unique classification of the types of corrosion, but the following classification is adapted hereafter.

Chemical corrosion (dry corrosion)

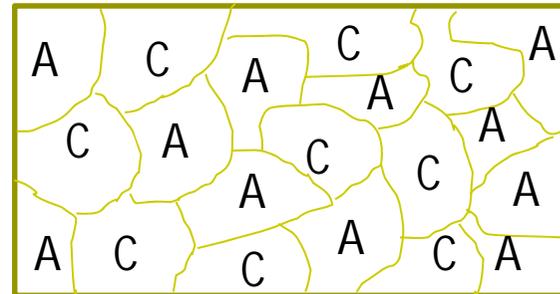
Takes place by direct combination of metal and its environment . There is no transport of electric charge.

ex:

- Dissolution of metals in contact with non-conducting organic media.
- Destruction of metals attacked at high temperatures by aggressive gases.

Electrochemical corrosion (wet corrosion)

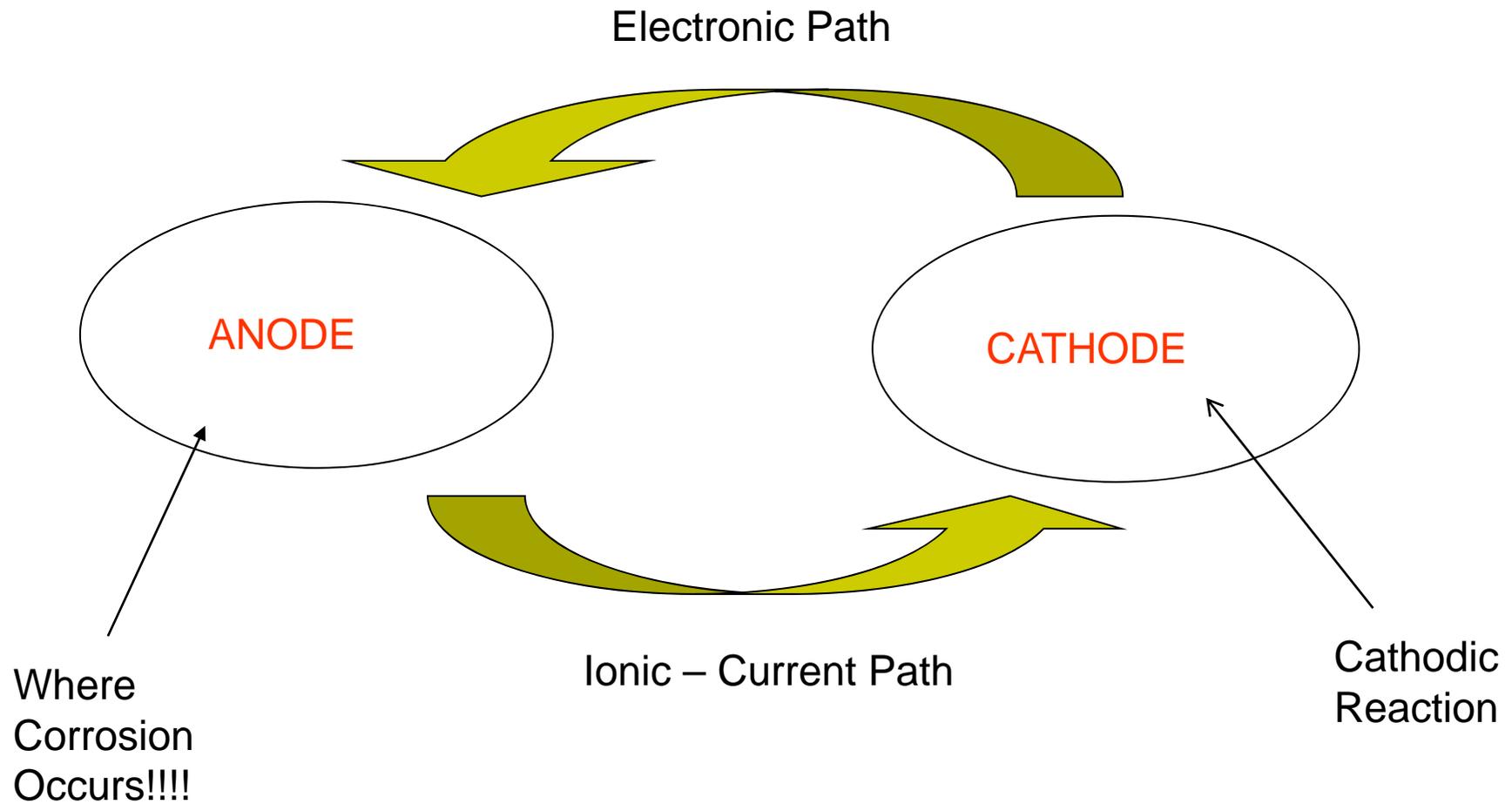
Takes place at the anodes of the micro electrochemical corrosion cells formed on the metal surface



The five essential components of the corrosion cell are:

- 1- Anodic zones (A)
- 2-Cathodic zones (C)
- 3-electrical contact between them
- 4-an (ionically) conducting solution
- 5- cathodic reactant

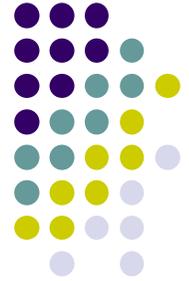
Requirements for Electrochemical Corrosion:





Oxidation Reactions

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



Reduction Reactions

- GAIN of electrons
- Removal of Oxygen OR gain of Hydrogen
- Take place at cathode
- Reduction Reaction \cong Cathodic Reaction
- Reduced species carried negative charge.
- For strong acidic medium (pH<4)
$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$
- For neutral or basic medium (pH= 4-10)
$$1/2 \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$$

The corrosion cell reactions



- ***The anodic reaction is:***



- ***The most common cathodic reactions are:***



OR



OR



OR



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



Galvanic (Voltaic) Cell

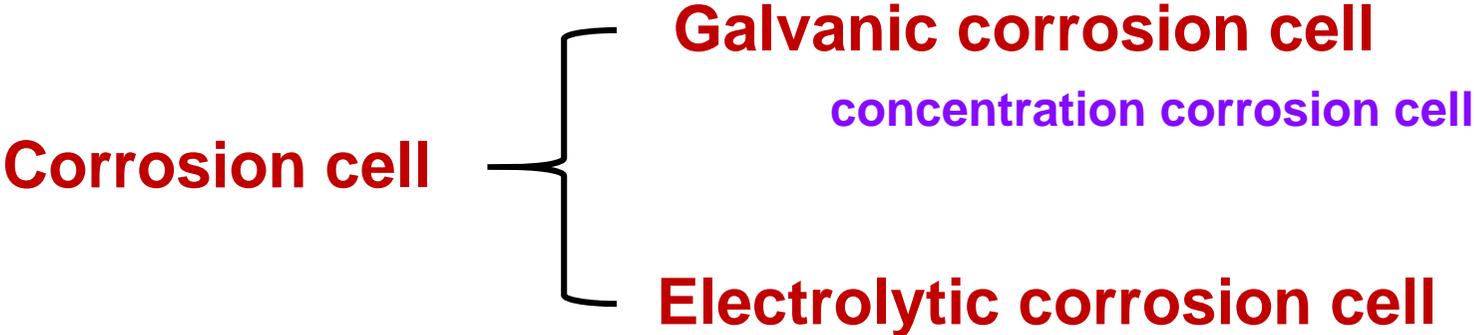
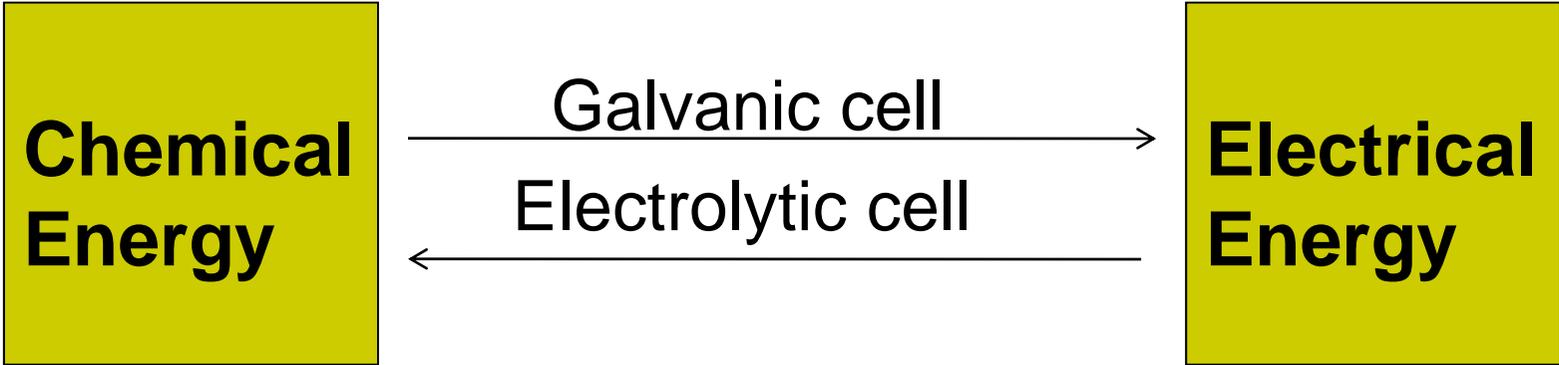
generating electricity by using a spontaneous chemical reaction (one with $\Delta G = -ve$)

Electrolytic Cell

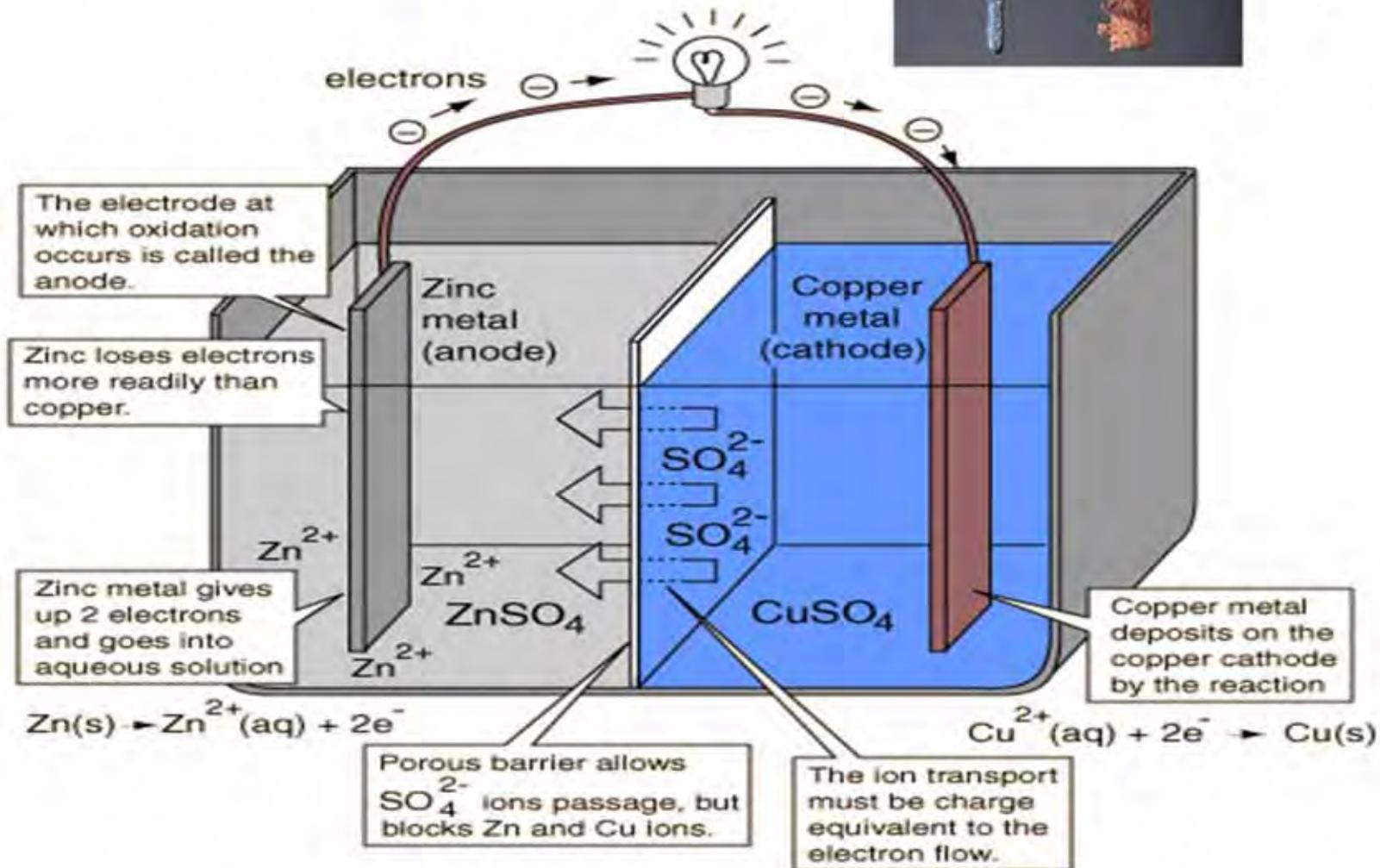
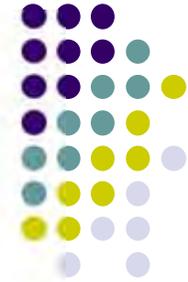
using electricity to force a chemical reaction to occur (one that is *non-spontaneous*, $\Delta G = +ve$).

The two electrodes are connected with an external source of potential..

Electrochemical cells

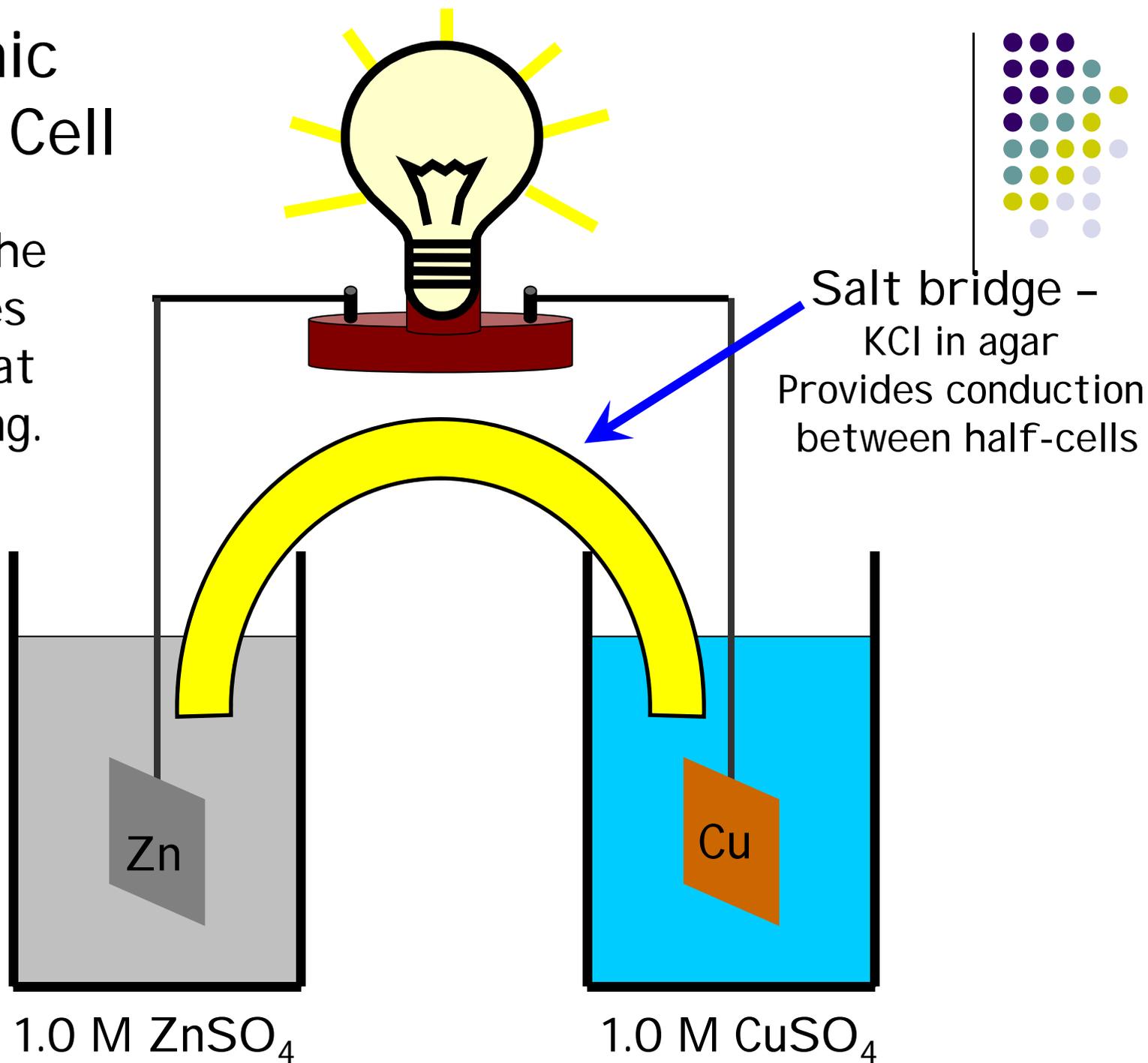


Galvanic cell



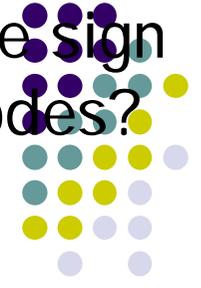
I - Galvanic (Voltaic) Cell

Observe the electrodes to see what is occurring.



What about half-cell reactions?

What about the sign of the electrodes?



Why?

anode half-cell
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$

cathode half-cell
 $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$

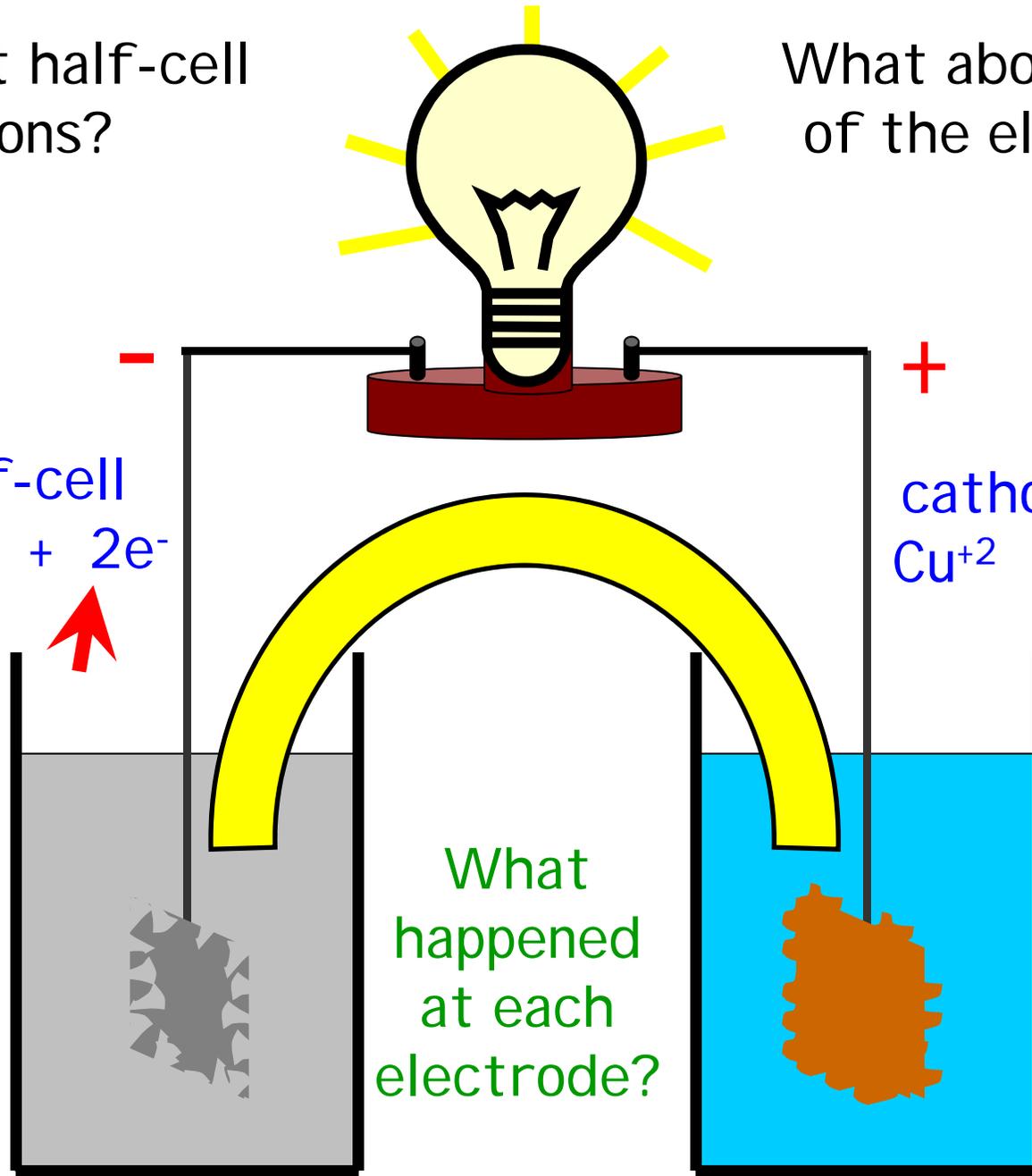
Zn electrode corrodes or dissolves

Cu plates out or deposits on electrode

What happened at each electrode?

1.0 M ZnSO_4

1.0 M CuSO_4



Galvanic cell



- cathode half-cell (+)
REDUCTION



- anode half-cell (-)
OXIDATION



- overall cell reaction



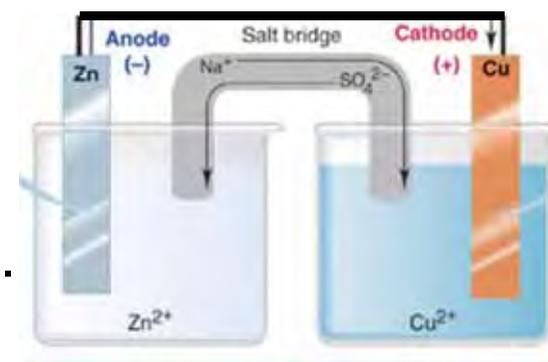
Spontaneous reaction that produces electrical current!

Line Notation of a Galvanic Cell



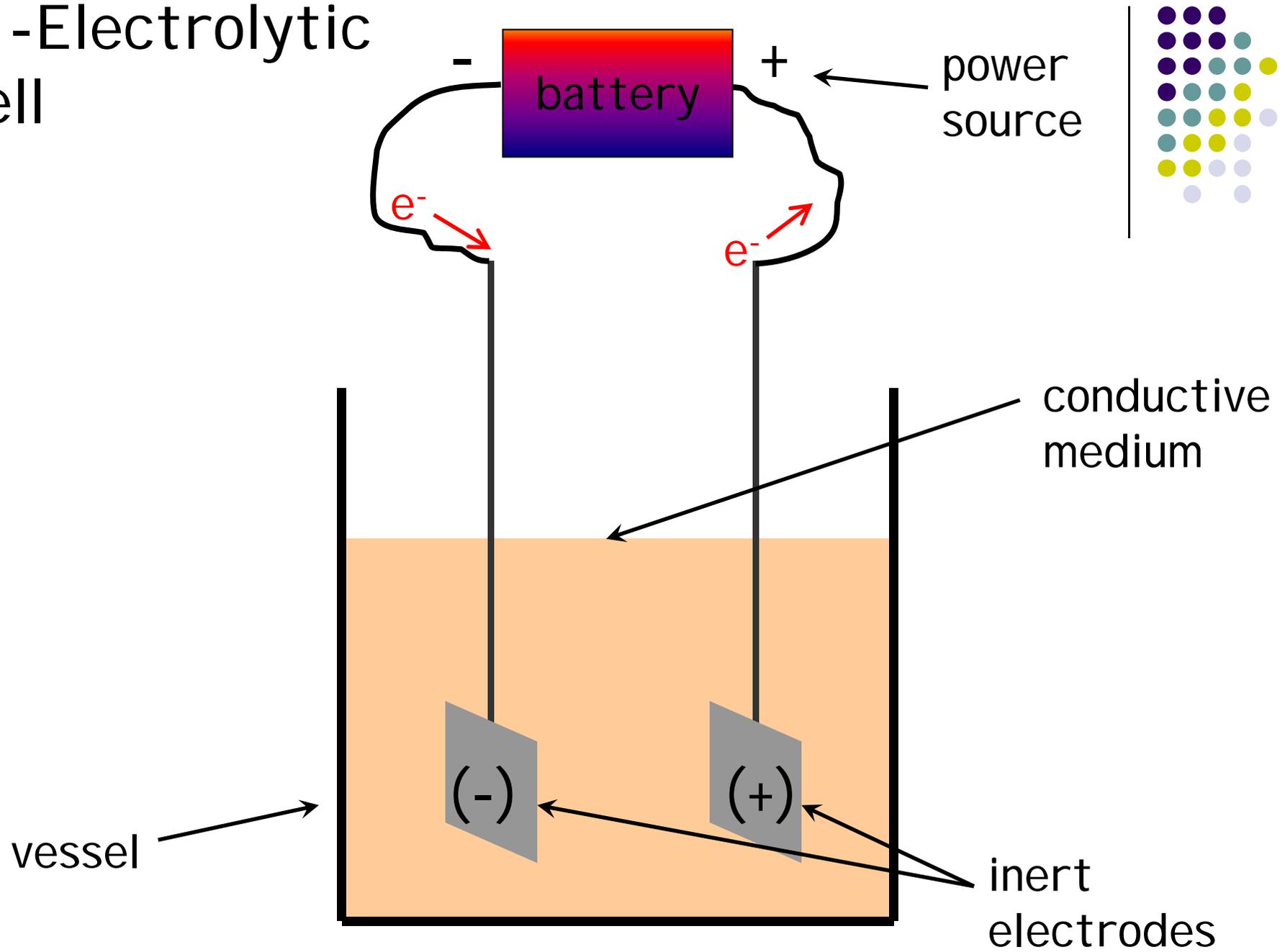
An electrochemical cell needs to be described in a more convenient way than drawing a diagram!

We use “line notation” to describe a cell. The zinc-copper standard cell is described:



- The ANODE is described before the CATHODE.
Reduction (cathode) at Right
- Concentrations of ions are indicated in brackets.
- A vertical line (|) represents a phase boundary.
- A double vertical line (||) represents the salt bridge.
- Comma (,) separates two components in the same phase
- A dashed line (⋮) represent the separation of two liquids by a semi-permeable membrane (liquid junction pot. is significant)

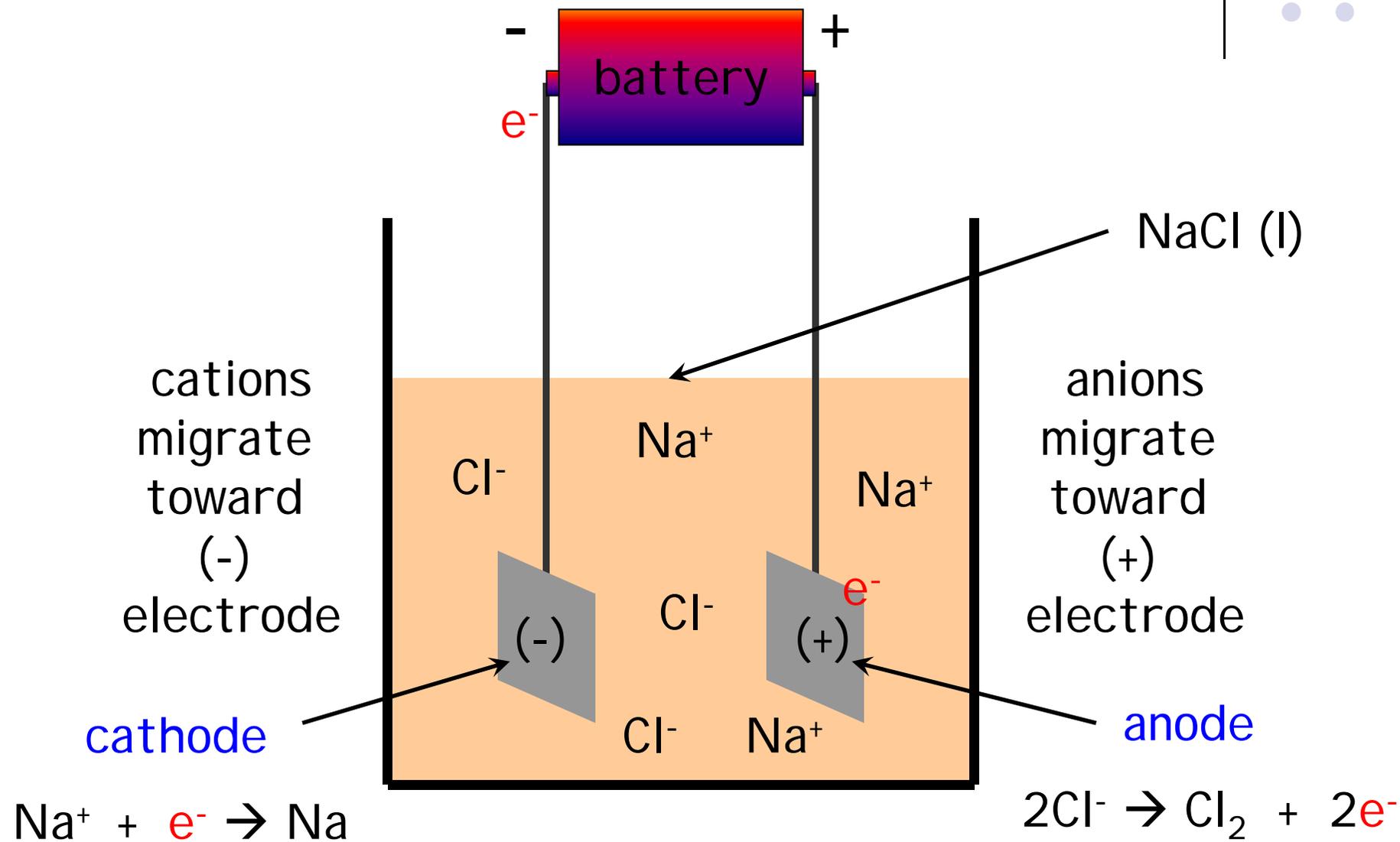
II - Electrolytic Cell



Sign or polarity of electrodes

Ex: Molten NaCl Electrolysis

At the microscopic level



Molten NaCl Electrolytic Cell



cathode half-cell (-)

REDUCTION



X 2

anode half-cell (+)

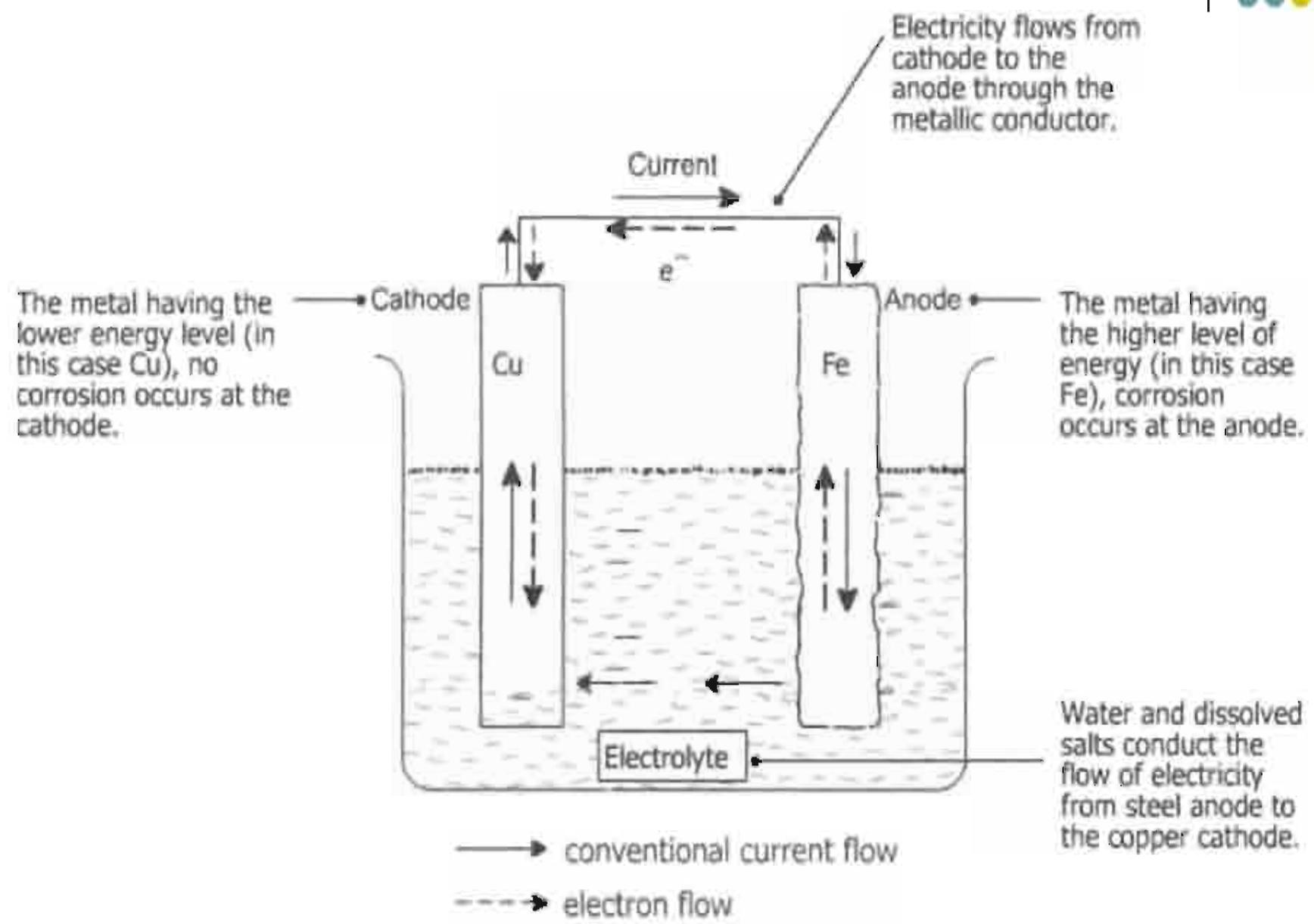
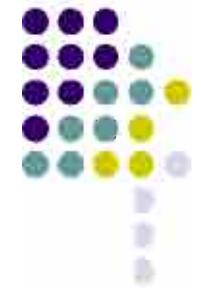
OXIDATION



overall cell reaction



Non-spontaneous reaction!



The corrosion cell reactions



- ***The anodic reaction is:***



- ***The most common cathodic reactions are:***



OR



OR



OR





The component of Galvanic Cell

- Potential difference between anode and cathode.
- External electronic conductor between anode and cathode (wire).
- Electrolyte solution between anode and cathode.
Electrolyte is a solution containing ions dissolved in water. The source of ions may be acid, base or salt.

Examples:

Zn | electrolyte | Cu

Fe | electrolyte | Pb

Al | electrolyte | Cu

The five essential components of the corrosion cell are:

1- Anodic zones (A)

2-Cathodic zones (C)

3-electrical contact between them

4-an (ionically) conducting solution

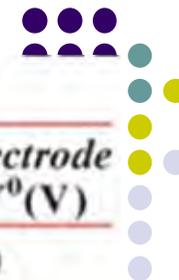
5- cathodic reactant

Table 16.1 The Standard emf Series The Electrochemical Series

	<i>Electrode Reaction</i>	<i>Standard Electrode Potential, V^0 (V)</i>
	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^- \longrightarrow \text{Pt}$	~+1.2
	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4(\text{OH}^-)$	+0.401
	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.340
	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.744
	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
	$2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	-0.828
	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.363
	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.924

↑
Increasingly inert
(cathodic)

↓
Increasingly active
(anodic)

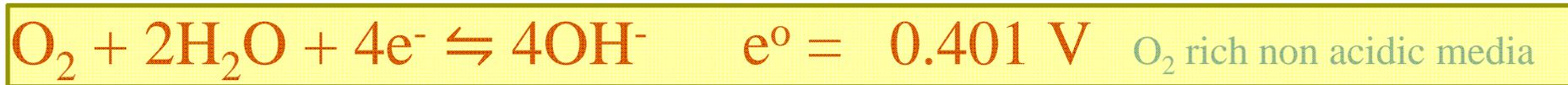
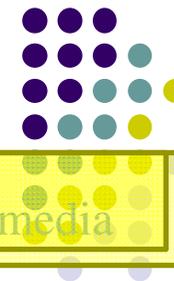




Strong tendency to occur as a reduction
(i.e. as written $\text{Au}^{3+} + 3\text{e}^{-} \rightarrow \text{Au}$)



Strong tendency to occur as an oxidation
(i.e. $\text{Na} \rightarrow \text{Na}^{+} + \text{e}^{-}$)



Polarization

*the shift of the electrode potential
from its equilibrium value*

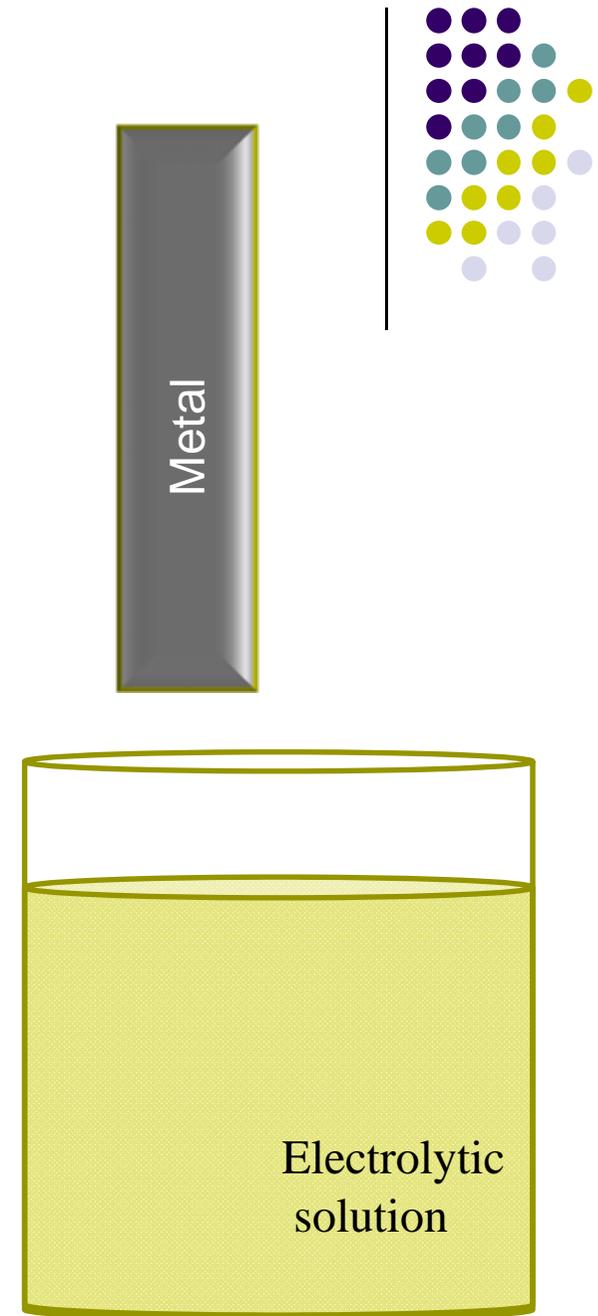


The rate of electrochemical reaction is limited by various physical and chemical factors.

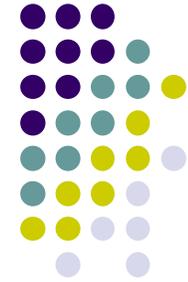
The electrochemical reaction is retarded by several physical and chemical factors.

Polarization is inversely proportional to the corrosion rate.

Why the electrode potential shifts from its equilibrium value as a result of passing an electric current in the cell?

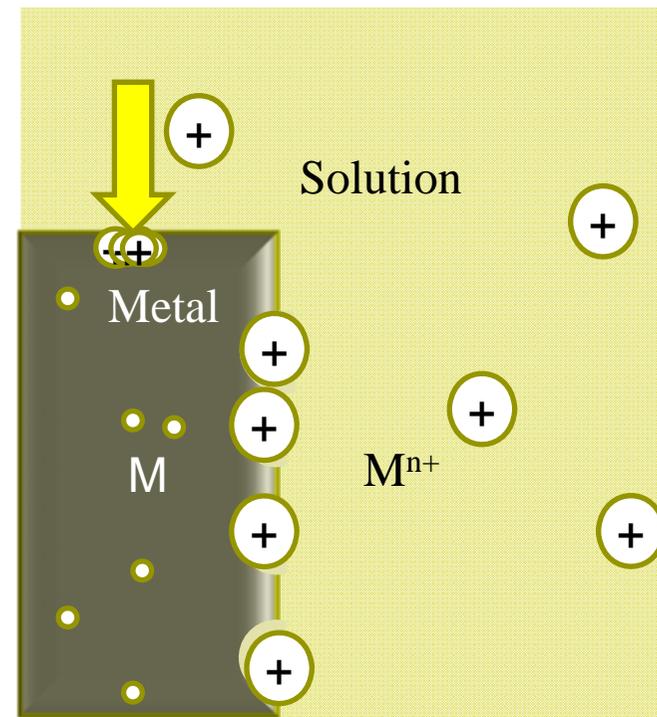


Adopting the consideration that the electrode is an electric potential reservoir.



Polarizable electrode
Slow electrode reactions accumulate
the excess charge

Non-polarizable electrode
Fast electrode reactions release
the excess charge

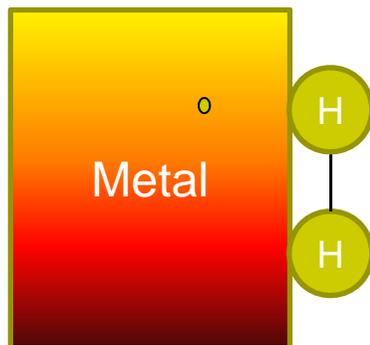


Steps of electrochemical reaction:

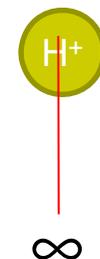


1. Ion transfer from the bulk of solution to the surface through the diffusion layer (mass transfer step)
1. 2. Chemical reaction between ions and electrons. (Oxidation or reduction) (charge transfer step)
2. 3. Material transfer from the surface of metal to the bulk of solution through the diffusion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

Example: Reduction of hydrogen:



- (1) mass transfer step
- (2) Charge (electron) transfer step
Chemical reaction
- (3) mass transfer step



- the first and third steps are mass transfer steps.
- the second step is chemical reaction step.

Polarization can be conveniently divided into two types:



Concentration polarization

Refers to electrochemical reaction that's controlled by the mass transfer (diffusion) step in the electrolyte.

Condition: the mass transfer step is slower than the chemical reaction.

Activation polarization

Refers to electrochemical reaction that's controlled by the chemical reaction sequence at the metal surface.

Condition: the chemical reaction is slower than the mass transfer.

Examples:

Corrosion rate in concentrated electrolyte is chemical reaction controlled.

Corrosion rate in diluted electrolyte is diffusion controlled.

Passivity



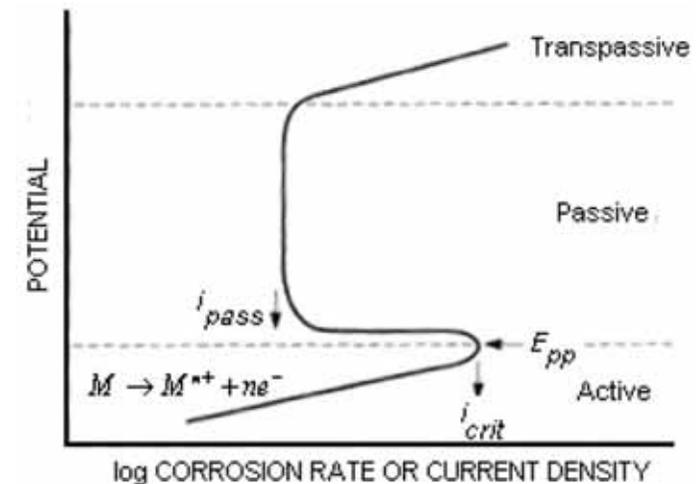
Some metals and alloys under particular environmental condition loss their chemical reactivity and become inert.

Environment	Iron	Aluminum
Air	Non passive	passive
Nitric acid (HNO ₃)	passive	Non passive

Passivity *may be defined as the formation of a thin protective film (1-10 nm thickness) on a metal surface due to its reaction with the surrounding environment under oxidizing conditions. (Passive film is protective only if: (1) adherent (2) non-porous, dense and compact)., e.g., the formation of oxide layers of Al₂O₃, TiO₂, Cr₂O₃. this is why Cr is added to Fe to prepare stainless steel*

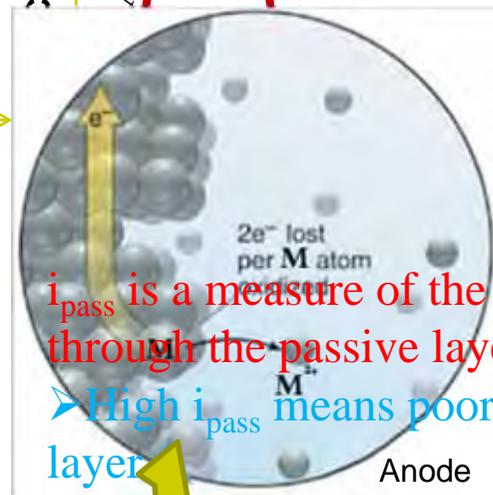
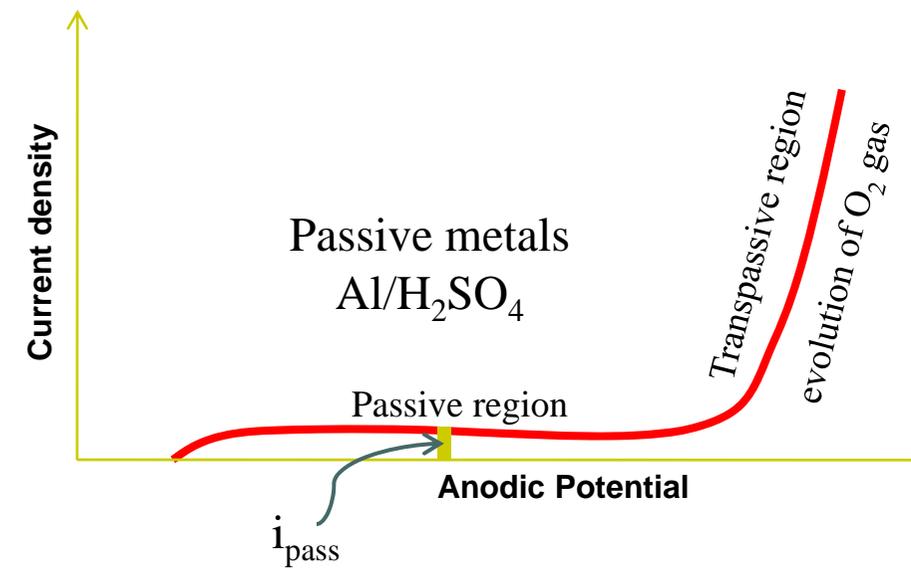
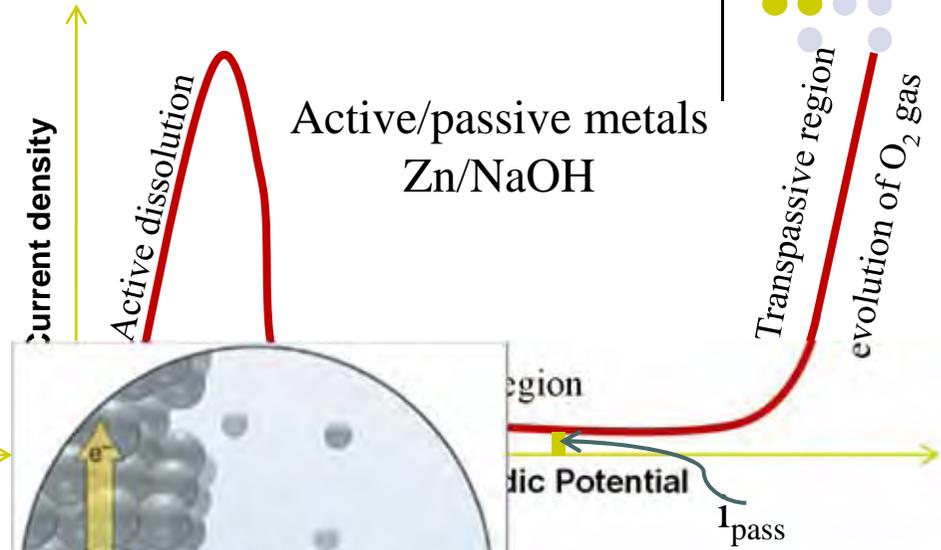
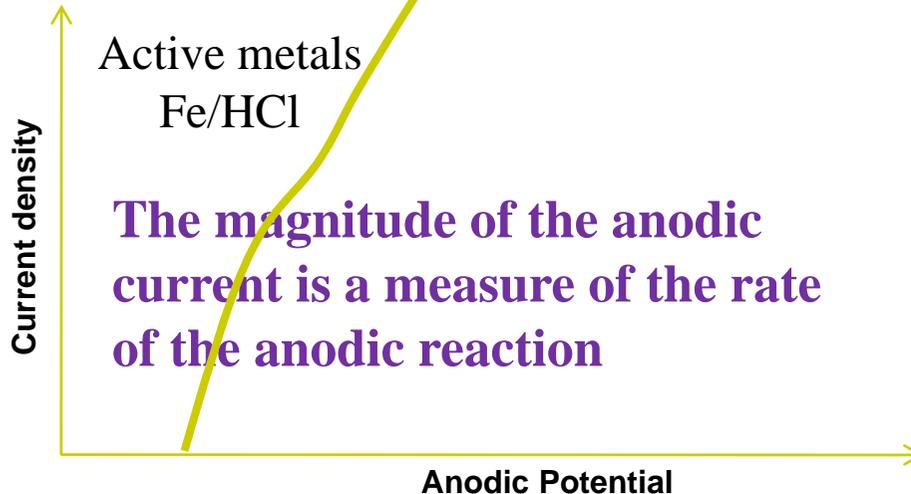
Passivity depends mainly on:

- The nature of the metal or alloy.
- Type of the environment (composition, temp., humidity,).



Potentiodynamic polarization Passivity curve

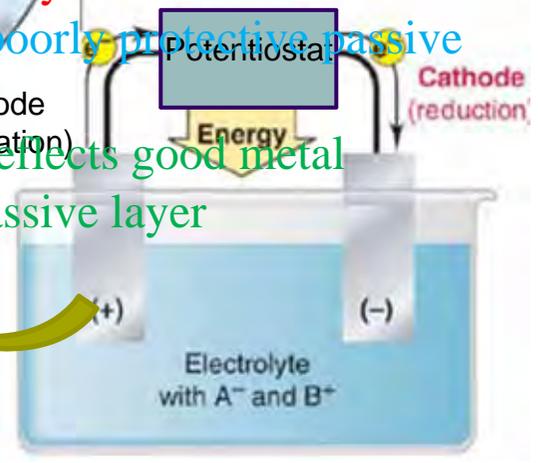
Potentiodynamic polarization

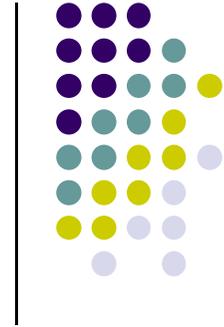
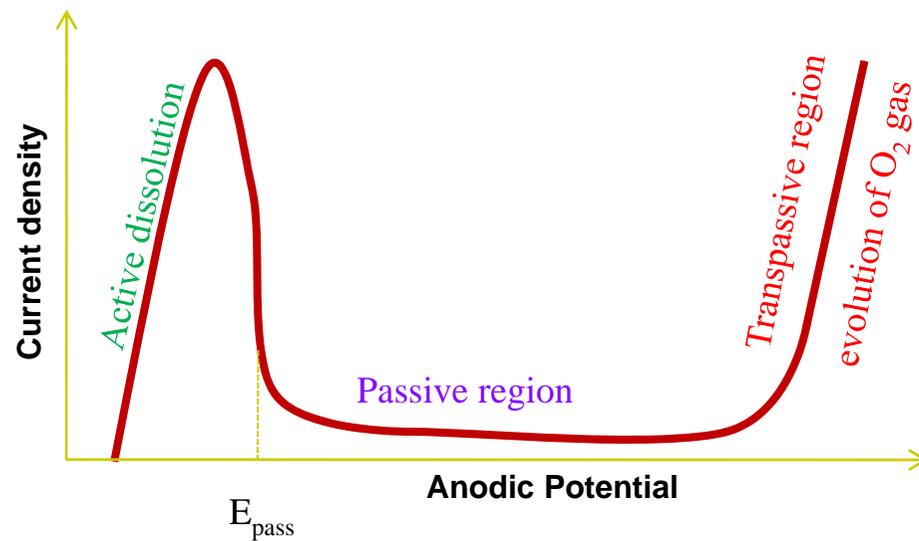


i_{pass} is a measure of the rate of dissolution through the passive layer

➤ High i_{pass} means poorly protective passive layer

➤ Small i_{pass} value reflects good metal protection by the passive layer





Active region: in this region, a slight increase in the potential or oxidizing power of the solution causes 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 or the rate of another oxidation process again increases 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).

➤ Soil:

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





➤ **Acids:**

Acids are very corrosive environment.

Acid	Mineral	Organic	Fatty
Strength	Very strong	Weak	Very weak
Examples	H ₂ SO ₄ , HNO ₃ , H ₃ PO 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).