
Lecture 4

EMF and Galvanic Series - Bimetallic Couples

Keywords: EMF Series, Galvanic Series, Galvanic Corrosion.

EMF Series

- a) EMF series lists only metals (little engineering application). Alloys not included
- b) Electrode potentials listed calculated from thermodynamic principles (corrosion potentials are more relevant).
- c) Equilibrium potentials with concentrations at unit activity (Exact prediction of galvanic coupling not possible).
- d) Predicts only tendency to corrode (Role of passive films and oxidation kinetics not predicted).
- e) Effect of environment not predicted (Eg: Sn – Fe couple as in Tin cans)

Galvanic series

- a) Instead of standard electrode potentials, actually measured rest potentials of metals and alloys in a given environment arranged with respect to nobility and activity.
- b) Practically measured potentials vs reference electrode.
- c) Effect of coupling of metals and alloys on corrosion rate can be predicted.

Certain anomalies Eg: Stainless steels (active and passive)

Galvanic series is generally good for stagnant conditions and not for turbulent conditions.

EMF and galvanic series are illustrated in tables 4.1 and 4.2.

Table 4.1 EMF Series

Reaction	$E^0, V(SHE)$	
$Au^{+++} + 3e = Au$	+1.42	Noble
$Pt^{++} + 2e = Pt$	+ 1.2	↑
$O_2 + 4H^+ + 4e = 2H_2O$	+1.23	
$Pd^{++} + 2e = Pd$	+0.83	
$Ag^+ + e = Ag$	+0.799	
$O_2 + 2H_2O + 4e = 4OH^-$	+0.401	↑
$Cu^{++} + 2e = Cu$	+0.34	
$Sn^{+++} + 2e = Sn^{++}$	+0.154	
$2H^+ + 2e = H_2$	0.00	Reference
$Pb^{++} + 2e = Pb$	-0.126	↓
$Sn^{++} + 2e = Sn$	-0.140	
$Ni^{++} + 2e = Ni$	-0.23	
$Co^{++} + 2e = Co$	-0.27	
$Cd^{++} + 2e = Cd$	-0.402	
$Fe^{++} + 2e = Fe$	-0.44	
$Cr^{+++} + 3e = Cr$	-0.71	
$Zn^{++} + 2e = Zn$	-0.763	
$Al^{+++} + 3e = Al$	-1.66	
$Mg^{++} + 2e = Mg$	-2.38	
$Na^+ + e = Na$	-2.71	
$K^+ + e = K$	-2.92	Active

Table 4.2 Galvanic Series in Seawater

Platinum	↑ Noble
Gold	
Graphite	
Silver	
Hastelloy C	
18 – 8 stainless steel (passive)	
Chromium steel > 11% Cr (passive)	
Inconel (passive)	
Nickel (passive)	
Monel	
Bronzes	↓ Active
Copper	
Brasses	
Inconel (active)	
Nickel (active)	
Tin	
Lead	
Lead-tin solder	
18-8 Mo stainless steel (active)	
18-8 stainless steel (active)	
Ni-resist	
Chromium steel < 11% Cr (active)	
Cast iron	
Steel or iron	
2024 aluminium	
Cadmium	
Commercially pure aluminium	
Zinc	
Magnesium and its alloys.	

The EMF series is an arrangement of various metals in the order of their electrochemical activities based on their standard oxidation-reduction potentials (E^0). The most active metal in the series will be having a high negative standard potential while nobler metals possess relatively less negative (or more positive) standard potential (E^0). If we consider a couple of two metals in the EMF series, the one with higher negative E^0 will act as anode (and will corrode) compared to the other with a relatively less negative E^0 value (cathode).

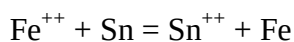
There are several exceptions to the predicted activity of a metal (or couple) as arranged in the EMF series.

Eg: Aluminium exhibits higher corrosion resistance due to Al_2O_3 layer present on surface.

Chromium exhibits stable Cr_2O_3 layer and is used as alloying element for corrosion resistance in stainless steels.

Many metals alter their potentials depending on the environment. Reversal in polarity can occur in some environments, leading to changes in anodic (and cathodic) behaviour.

Tin (Sn) is nobler to iron (Fe) in the EMF series. Internally tinned (tin-coated) steel cans are used to preserve vegetable and fruit juices. Such a cathodic protection of iron by tin is however only limited since many food constituents such as organic acids can combine with Sn^{++} to form soluble tin complexes, resulting in lowering the activity of stannous ions. The polarity of Fe – Sn couple can reverse under these conditions.



The cell polarity reverses when $E_{\text{cell}} = 0$

$\log \frac{[\text{Sn}^{++}]}{[\text{Fe}^{++}]}$ can be calculated and works out to be -10.30

Ratio of $\frac{[Sn^{++}]}{[Fe^{++}]}$ must be $< 5 \times 10^{-11}$ for tin to become more active than iron.

$\left[\frac{[Sn^{++}]}{[Fe^{++}]}\right]$ ratio within the can must be very small for the reversal of polarity to occur.

Amenability of galvanic corrosion in bimetallic contacts can be predicted by the EMF and galvanic series.

Bimetallic and Concentration cells are mainly responsible for galvanic corrosion. Typical example is rusting of iron in a moist environment where oxygen concentration gradients come into play.

Galvanic corrosion rates are influenced by two factors, namely **distance** and **area effects**. Severity of corrosion is the highest near the junction of the bimetal contacts.

Area effect refers to ratio of anodic to cathodic areas and a larger cathode in contact with a small anode is considered 'unfavourable area ratio'. For a given current flow in a galvanic cell, the current density is higher for a smaller electrode than for a larger anode. Higher current density results in larger rates of anodic corrosion.

Examples demonstrating the area effect:

- Copper plates (larger cathodes) connected by steel rivets (smaller anodes) exposed to sea water.
- Steel plates (larger anode) connected with copper rivets (smaller cathode) exposed to sea water.

Case (a) represents unfavourable area effect leading to severe corrosion of steel rivets. Case (b) represents favourable area effect. Larger anode and smaller cathode results in negligible galvanic corrosion.

A graphical representation of area effect with respect to anodic corrosion rate is illustrated in Fig 4.1.

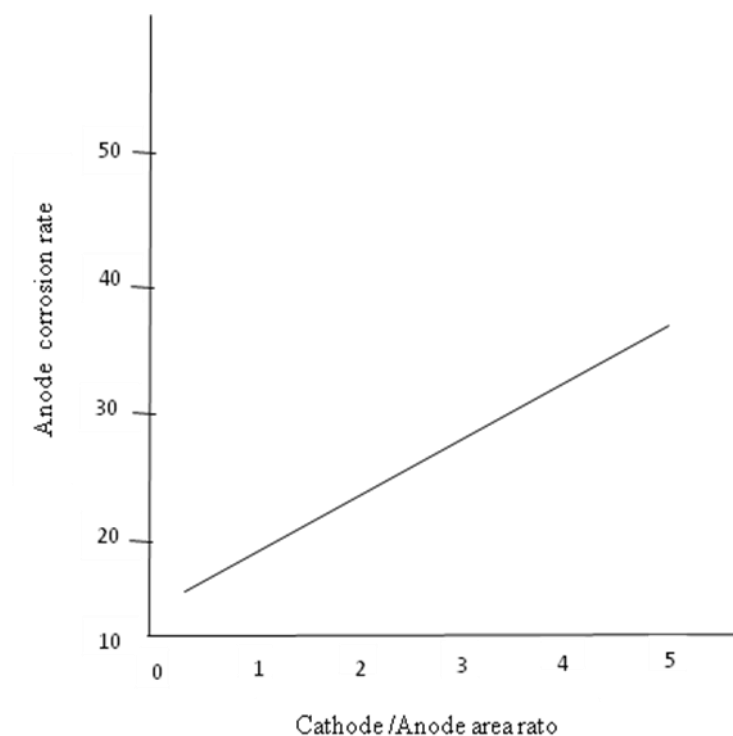


Fig 4.1 Graphical representation of area effect

Galvanising of steels for corrosion protection is a classic example of corrosion protection through proper galvanic (sacrificial) method.

Zinc is anodic to iron and hence corrodes away protecting the steel base metal surfaces.

Consider a uniformly zinc coated steel surface exposed to a corrosive environment. Even if portions of zinc coating are abraded away, the base steel will still be protected! (Due to favourable area effect). See Fig 4.2.

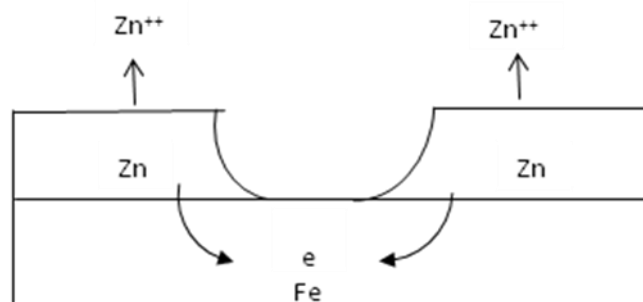


Fig 4.2 Pictorial representation of zinc coated steel surface in a corrosive environment

All coatings have defects in the form of pinholes and mechanical damage. Corrosion of steels can be concentrated at coating defects (small anodes). For example, in a carbon steel (anode) structure having contact with stainless steel (cathode), surface coating of only the carbon steel could lead to disastrous corrosion due to unfavourable area effect. The best alternative would then be, if one of two dissimilar metals (alloys) in contact is to be coated, the more noble one should be coated (or painted).

The following factors need be considered for prevention of galvanic corrosion.

- Select combinations as close together in the galvanic series.
- Avoid unfavourable area effect.
- Insulate dissimilar metal contacts.

Corrosion currents can be generated due to several reasons in metals and alloys, namely

- Impurities
- Grain orientation and grain boundaries
- Differential thermal treatment
- Surface roughness.
- Alloying elements (Brass, Zn corrodes with respect to Cu)
- Metallographic defects
- Strain/stress

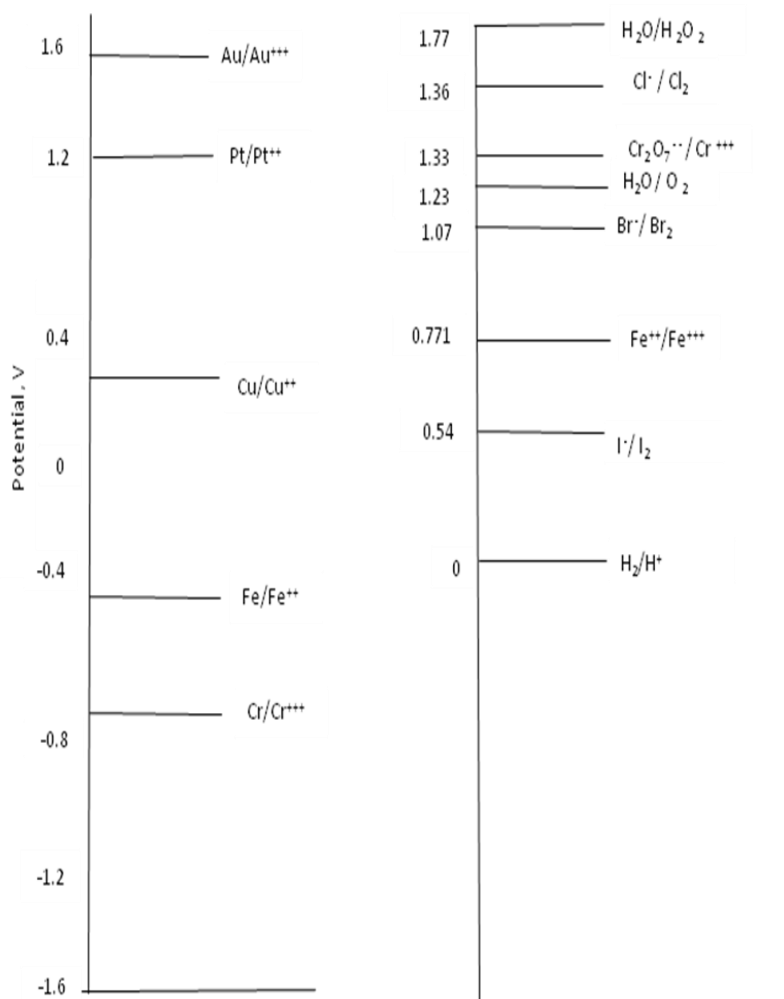


Fig 4.3 Electrode potentials of some metals and oxidising – reducing agents

With respect to arrangement of the electrode potentials for metals on the one hand and those of various oxidising and reducing agents on the other, it becomes easy to predict the relative oxidising or reducing power of various reagents with respect to a desired metal / metal ion reaction (Fig 4.3). A wide selection of strongly oxidizing species is available for oxidation of most of the metals excluding perhaps the nobler metals such as gold and platinum. Similarly, reducing power of hydrogen with respect to precipitation of metal ions can also be predicted. However, it may be borne in mind that not all equilibria are always oxidizing or reducing. Effect of pH and gaseous partial pressures on oxidisability and reducibility need be taken into consideration.