

Lecture 11

Mixed Potentials – Concepts and Basics

Keywords: Mixed Potential, Charge Conservation, Corrosion Potential

Principle of charge conservation:

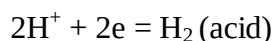
Total rate of oxidation must be equal to total rate of reduction.

i.e. Sum of anodic oxidation currents must be equal to sum of cathodic reduction currents.

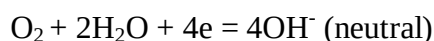
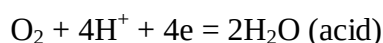
General Anodic reaction $M = M^{++} + 2e$

Cathodic reactions can be different depending on environmental conditions.

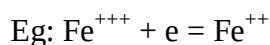
a) Evolution of hydrogen from acid or neutral solution



b) Reduction of dissolved oxygen in acid or neutral solution.



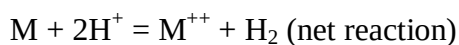
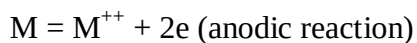
e) Reduction of dissolved oxidizers such as ferric ions



To understand the combined effect of various reducible species on the corrosion of a metal (M), it is essential to use the zero current criterion, $\sum i_a = \sum i_c$

$$i_a^M = i_c^{H(M)} + i_c^{O_2(M)} + i_c^{Fe^{+++}(M)}$$

Take for example, the case of an active divalent metal, M corroding in an acid electrolyte.



The metal corrodes with the evolution of hydrogen. There are two half-reactions as shown above and they cannot coexist as separate entities on the same metal surface. Each half reaction has its own electrode potential and exchange current density (see Fig. 11.1).

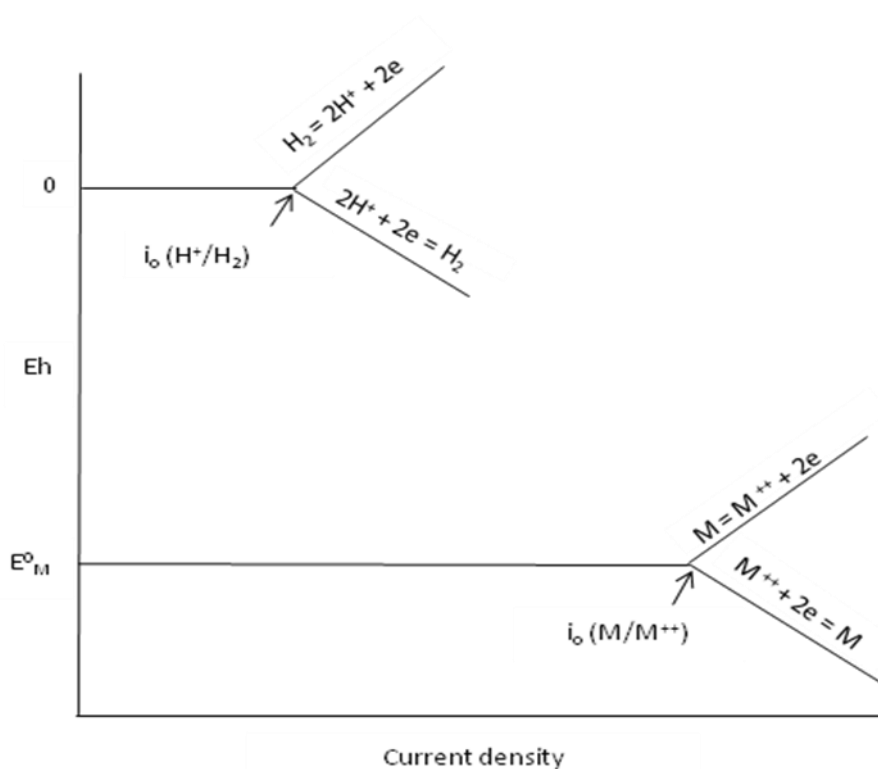


Fig 11.1 Anodic and cathodic half – cell reactions occurring simultaneously on a corroding metal, M.

Each electrode polarizes (shifts in potentials in anodic and cathodic directions) to an intermediate value (between the two half-cell potentials).

Since such a polarized potential is a mixture of the two half – cell potentials, it is referred to as MIXED POTENTIAL (See Fig. 11.2).

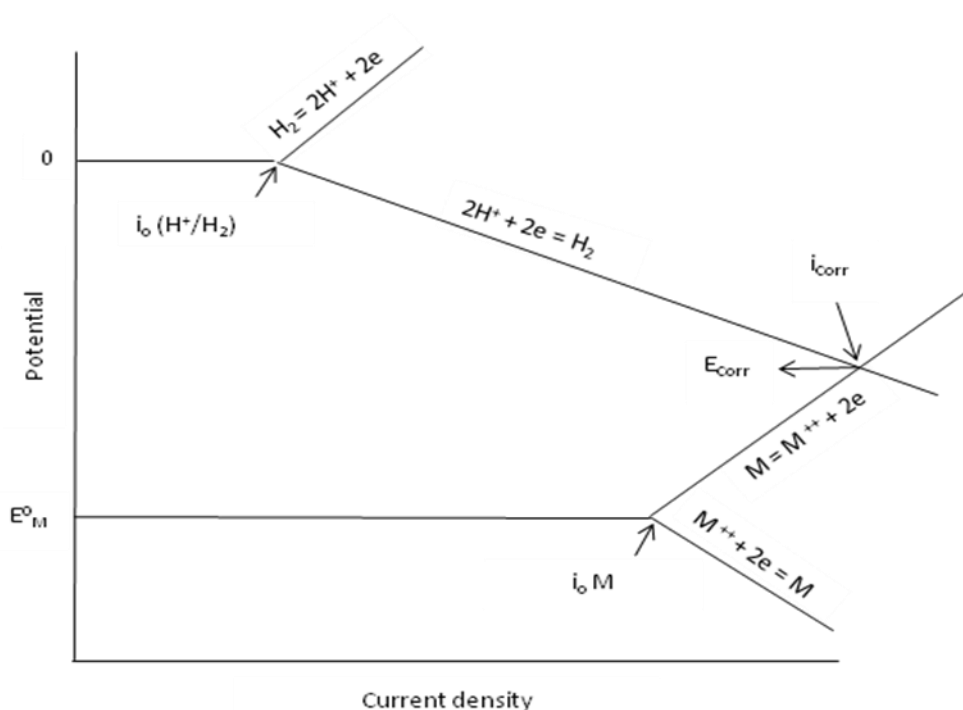


Fig 11.2 Polarization of anodic and cathodic reactions to yield a mixed potential

E_{corr} is corrosion potential which is a mixed potential.

At E_{corr} , rates of anodic and cathodic reactions are equal.

$$i_c = i_a = i_{\text{corr}}, \text{ at } E_{\text{corr}}$$

i_{corr} is the corrosion rate of the metal in the acid, and also represents the rate of hydrogen liberation at the metal surface.

With a knowledge of β and i_0 for the system, corrosion rate of the metal in the acid solution can be estimated.

From actual practice, corrosion of zinc or iron in hydrochloric acid can be represented as detailed above. A mixed potential due to anodic oxidation of zinc (or iron) and reduction of hydrogen ions from the acid (with liberation of hydrogen gas on the metal surface) could be realized.

However, kinetic parameters including the exchange current density for the redox reaction at the given metal surface need be considered in assessing the corrosion behavior (and rate) of the metal in the corrosive medium.

Comparing the corrosion rates for zinc and iron (when present separately) in dilute hydrochloric acid solutions, zinc dissolution is expected to be higher than that of iron from a thermodynamic view point ($E^0_{\text{zn}/\text{zn}^{++}} = -0.76\text{V}$ compared to E^0 for $\text{Fe} | \text{Fe}^{++} = -0.44\text{V}$). The corrosion rate of iron will however be higher than that of pure zinc, when immersed in similar concentrations of hydrochloric acid due to differences in their exchange current densities for hydrogen liberation reaction. Exchange current density for hydrogen reduction on zinc is lower than that on iron (see Table 9.1).

Engineering systems are heterogeneous and complex. The zero current criterion ($\sum i_a = \sum i_c$) in such multi-electrode systems in a corrosive environment becomes all the more relevant.

Consider two electrodes X and Y with one reduction reaction in an acid solution.

$$i_a^X + i_a^Y = i_c^{H(X)} + i_c^{H(Y)}$$

Relative areas of the anode and cathode are important in the prediction of anodic corrosion rates and current density (current / unit area) need be considered.

Corrosion rates need to be estimated based on kinetic parameters such as overpotential and exchange current density.

Driving force for corrosion in fact depends on the overpotential and not essentially on their electrode potential differences.