Lecture 8

Electrode-Solution Interface – Definition and Types of Polarization

*Keywords: Electrochemical Interface, Polarization, Anodic Control, Cathodic Control*

Proportionality between current density \( i \) and reacted mass \( m \) in an electrochemical reaction is stated by Faraday’s law.

\[
m = \frac{ita}{nF}
\]

Corrosion rate \( r = \frac{m}{tA} = \frac{ia}{nF} \)

Where \( n \) = number of electrons involved

\( a \) = atomic weight

\( t \) = time

\( F \) = Faraday constant (96500 coulombs / equiv)

Corrosion rate \( r = \frac{m}{tA} = \frac{ia}{nF} \)

Where \( i \) = current density

\( A \) = surface area

Corrosion rate in mpy [mils (0.001 in) per year] is given as

\[
r = 0.129 \frac{ai}{nD}
\]

Where \( i = \mu A/cm^2 \)

\( D \) = density, g/cm\(^3\)
Through above relationship, anodic current density in corrosion can be converted to metal loss in mpy.

When electrode reactions take place, the potential will no longer be at equilibrium due to current flow through an electrochemical cell causing a change in the electrode potential. This electrochemical phenomenon is termed POLARIZATION.

- Polarization of anode – anodic polarization
- Polarization of cathode – cathodic polarization

Corroding systems are not in equilibrium with deviation from thermodynamics. Deviation of the potential from its reversible value is referred to as polarization. A cell or electrode is said to be polarised when there is little or no change in current with larger changes in potential.

An electrode is not in equilibrium when a net current flow from or to its surface. Polarization can result from either a slow step in an electrode process or discharge of ions at an electrode surface.

Distribution of anions and cations at a metal–solution interface is shown as electrical double layer (Fig. 8.1).

A compact layer (Helmholtz) closest to metal surface in which charge distribution and hence potential varies linearly with distance (Fig. 8.2).

A more diffuse inner layer (G. C. layer) where potential changes exponentially.
Processes at an electrochemical interface are schematically represented below:

Fig. 8.3 Transport processes at electrochemical interface
Mass transport to metal surface involves forces such as convection, diffusion and migration, depending on presence or absence of electric field and flow conditions. Concentration polarization is controlled by diffusion gradients (Fick’s law). Activation polarization involves kinetic factors related to charge transfer, such as activation energy barrier and equilibrium current density.

Transport processes at an electrode – electrolyte interface are illustrated in Fig. 8.3.

Consider a solid-solution interface. Diffusion of electro-active ions from bulk to the interface and interaction at electrode resulting from charge transfer.

\[
\eta_{\text{Total}} = \eta_{\text{conc}} + \eta_{\text{act}}
\]

Polarization resulting from concentration gradients is termed concentration polarization; while activation polarization is caused by a slow step in the electrode reaction (electrode reaction requires activation energy in order to reach the final state)
Examples of activation polarization include:

Hydrogen overvoltage (overpotential)

\[ \text{H}^+ + e = \text{H}_{\text{ads}} \]

\[ 2\text{H}_{\text{ads}} = \text{H}_2 \]

\[ 2\text{H}^+ + 2e = \text{H}_2 \quad E^0 = 0.00 \text{ V} \]

For this cathodic reaction, there will be deviation from the reversible value to more negative values and that deviation is the overvoltage.

\[ \Delta E = E_{\text{app}} - E_{\text{rev}} \]

(Overpotential)

Similarly, we come across oxygen overvoltage, chlorine overvoltage etc.

\[ 2\text{OH}^- = \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e \]

The contribution to polarization due to IR drops is referred to as Resistance polarization

So Total polarization \( \eta_T = \eta_{\text{Act}} + \eta_{\text{Conc}} + \eta_{\text{resist}} \)

When polarization occurs mostly at anodes, corrosion reaction is Anodically Controlled - Anodic process at electrode is accelerated by moving the potential in the positive direction.

When polarization occurs mostly at cathodes, it is Cathodically controlled - Cathodic process accelerated by moving the potential in the negative direction.

**Resistance control** when electrolyte / electrode resistance is so high that the current is insufficient to polarise either of the electrodes.
Mixed control refers to the condition where both anode and cathode are polarized.

Schematic illustrations of anodic, cathodic, mixed and resistance controls are given in Fig 8.4.