Chapter three
Electrochemical Kinetics of corrosion

Corrosion is thermodynamically possible for most environmental conditions, but thermodynamic tell us nothing about how it fast (rate of corrosion), while chemical kinetics is a study of the rate of reaction.

Faraday's law

Electrochemical reaction either produce or consume electrons, thus the rate of electron flow to or from a reacting interface is a measure of reaction rate.

Electrons flow conveniently measured as current, I in ampere where 1-ampere is equal to 1- coulomb of charge (6.2×10^{18} electrons) per second

The proportionality between I and mass reacted, m , in electrochemical reaction is given by Faraday's Law :

$$m = \frac{ItM}{zF} \quad \text{........ (1)}$$

Dividing equation (1) through t and surface area, A yields the corrosion rate r:

$$r = \frac{m}{tA} = \frac{iM}{zF} \quad \text{...... (2)}$$

Where i defined as current density, equal I /A, equation (3) shows proportionality between mass loss per unit area per unit time (e.g. , $mg/dm^2/day$) and current density (e.g. , $\mu A/cm^2$) .The proportionality constant includes (M / z F) and any conversion factors for unit.

Current density rather than current is proportional to corrosion rate because the same current concentrated into smaller surface area results in a larger corrosion rate, corrosion rate in inversely proportional to area for same dissolving current.

Units of penetration per unit time result from dividing equation (2) by the density D of metal, for corrosion rate in mils per year (mpy) equation (2) becomes

$$r = 0.129 \frac{Mi}{zD} \quad \text{(unit in mpy) ..... (3)}$$

For units i, $\mu A/cm^2$ and D in g/cm^3 . The proportionality constant becomes 0.00327 and 3.27 for mm/yr and μM /yr respectively .

Example (1) : steel corrodes in an aqueous solution , the corrosion current is measure as $0.1 \ mA/cm^2$, calculate the rate of weight loss per unit area in units of mdd

Solution

For $Fe \rightarrow Fe^{+2} + 2e^-$
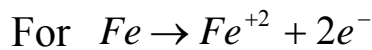
$$\frac{m}{tA} = \frac{iM}{zF}$$

Where M=55.9 g /mol , i = 0.1×10^{-3} A/ cm^2 , and z=2

$$\frac{m}{tA} = 2.897 \times 10^{-8} \quad \text{g.cm}^{-2}.\text{s}^{-1}$$

$= (2.897 \times 10^{-8}) \times (10^3) \times (100) \times (3600 \times 24)$
$= 2.503$ mg.dm^{-2}.day^{-1} (mdd)

Calculation of correspondence between penetration rate and current density for alloy requires a determination of equivalent weight M/z in equations (2) and (3) for the alloy. This alloy equivalent weight is a weighted average of M/z for the major alloying elements in any given alloy. The below equation is used to calculate number of equivalents

$$N_{EQ} = \sum \left(\frac{f_i}{M_i / z_i} \right) = \sum \left(\frac{f_i z_i}{M_i} \right)$$

Where f_i ,z_i , and M_i are mass fraction , electrons exchanged and atomic weight respectively of ith alloying element. Equivalent weight EW , is then reciprocal of N_{EQ} ;i.e. EW=N_{EQ}^{-1}.

Example (2): calculation of equivalent weight for Type 304 stainless steel , is given in the flowing , assuming the following parameters for the alloy :
Cr =19% , z=3
Ni = 9.25 % , z=2
Fe = 71.75 %, z=2
All minor elements below 1 % are neglected

$$N_{EQ} = \frac{(0.19)(3)}{52.00} + \frac{(0.0925)(2)}{58.71} + \frac{(0.7175)(2)}{55.85} = 0.03981$$

EW for 304 stainless steel = 25.12

Double layer theory

A conducting metal containing mobile electrons forms a complex interface in contact with n aqueous solution. un symmetrical polar H_2O molecules (H-atom positive , O-atom negative) are attracted to the conductive surface , forming an oriented solvent layer , which prevents close approach of charged species (ions) from bulk solution. Charged ions also attract their own sheath of polar water-solvent molecules which further insulate them from the conducting metal.

The plane of closest approach of positively charged cations to the negatively charged metal surface is often referred to as the outer Helmholtz plane the result is an interfacial structure of separated change commonly referred to as the electrical double layer which behaves experimentally much like a charged capacitor
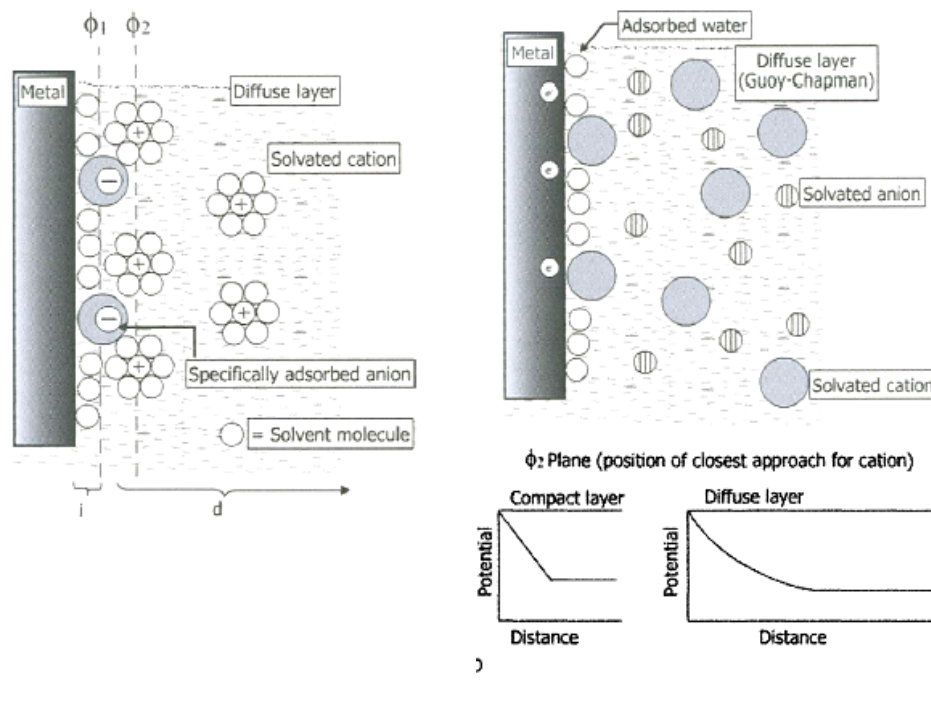
The electrical field of double layer structure prevents easy charge transfer , thereby limiting electrochemical reaction at the surface.

1- An inner layer in which the potential changes linearly with the distance comprises the adsorbed water molecules
2- An outer Holmholtz layer it comprises hydrated (solvated) cations and the potential varies with the distance
3- An outer diffuse layer (Guey-Chapman layer) it contains excess cations or anions distributed in diffuse layer and potential varies exponentially with distance.

Exchange current density
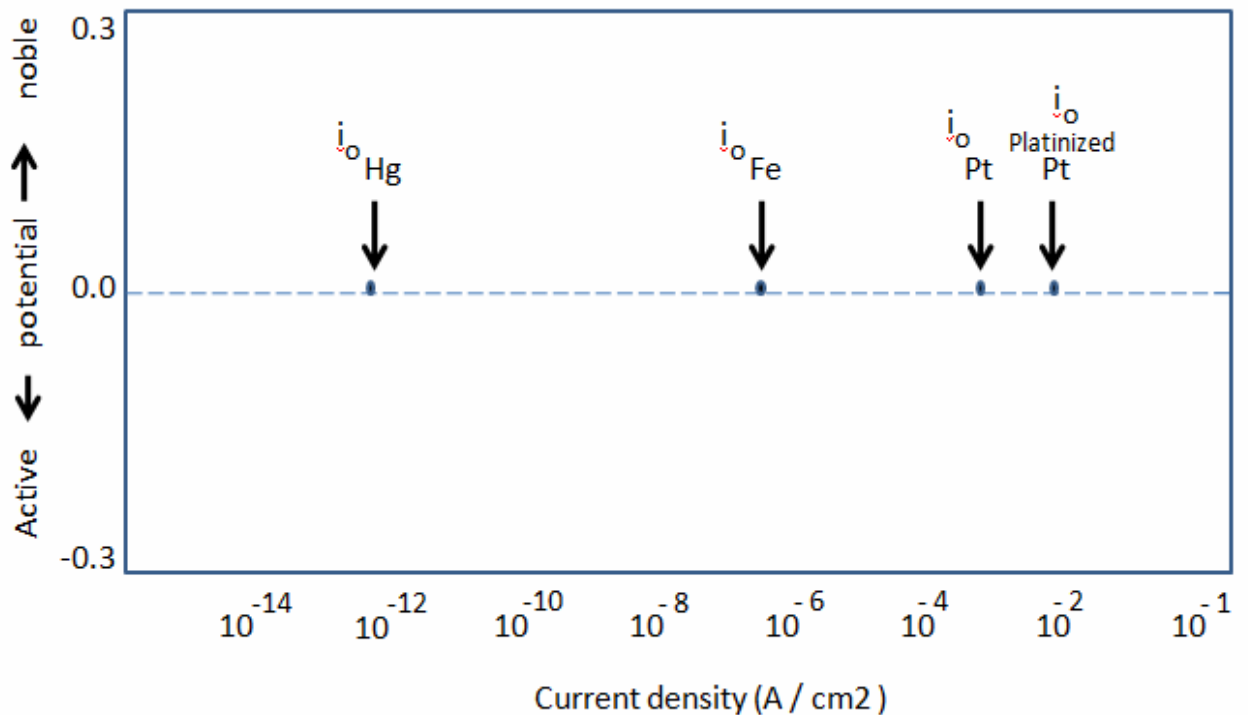
Consider the reaction : $2H^+ + 2e^- \rightarrow H_2$

At the standard half cell or redox potential E H+/H2 , this reaction is in the equilibrium state, at this state the forward rate (left to right) r_f, is equal to reverse rate (right to left) r_r

$$r_f = r_r = \frac{iM}{zF}$$

The value or half cell current density here is termed as exchange current density , io and this lead to

$$r_f = r_r = \frac{i_\circ M}{zF}$$

Exchange current density is analogous to free energy or half cell electrode potential is the fundamental thermodynamic parameter characteristic of an electrochemical reaction. Neither free energy (electrode potential) nor i_o can be calculated from first principles ; both must be determined experimentally .Exchange current density is affected mainly by the nature of the surface on which reaction is occur.

The above figure shows the half cell electrode potential for the hydrogen plotted versus i_o , two facts must be emphasized from this figure , first ,

the surface on which reaction occurs has no effect on electrode potential , second , the i_o , in contrast is strongly affected by the surface
Exchange current density affected by ;forward reaction , electrode composition , surface roughness , and impurities.

Electrochemical Polarization
When a metal is not in equilibrium with a solution of its ions, the electrode potential differs from the equilibrium potential by amount known as polarization or over voltage or over polarization and the symbol is η
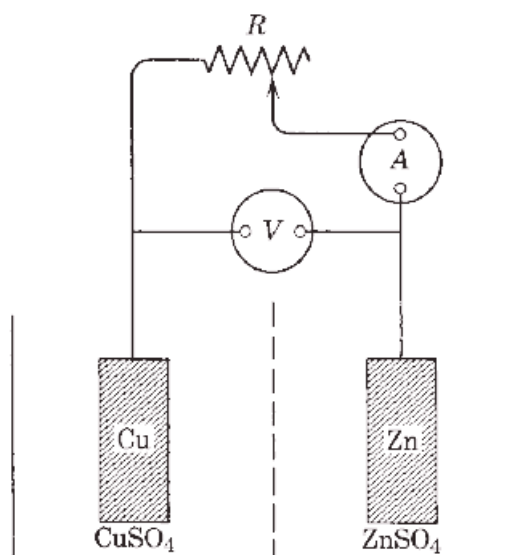
$$\eta = E_{actual} - E_{equ(reverse)}$$

Suppose zinc electrode has a potential -0.621 volt often is has been connected to the platinum electrode , the equilibrium potential is -0.763 volt therefore
$\eta = -0.62 - (-0.763) = 0.142$ volt

- Note: open circuit potential ,the potential for electrode when is no current flow through the cell

The polarized cell

The potential difference (emf) of zinc and copper electrodes of cell without current flow is about 1 volt, if a small current is allowed to flow through the external resistance , the measured potential difference fall below 1 volt because both electrodes polarized. The voltage continues fall as current increases on complete short circuiting (very small external resistance) maximum current flows and the potential difference of copper and zinc electrodes because almost zero.
Zinc polarized along abc while copper polarized along def
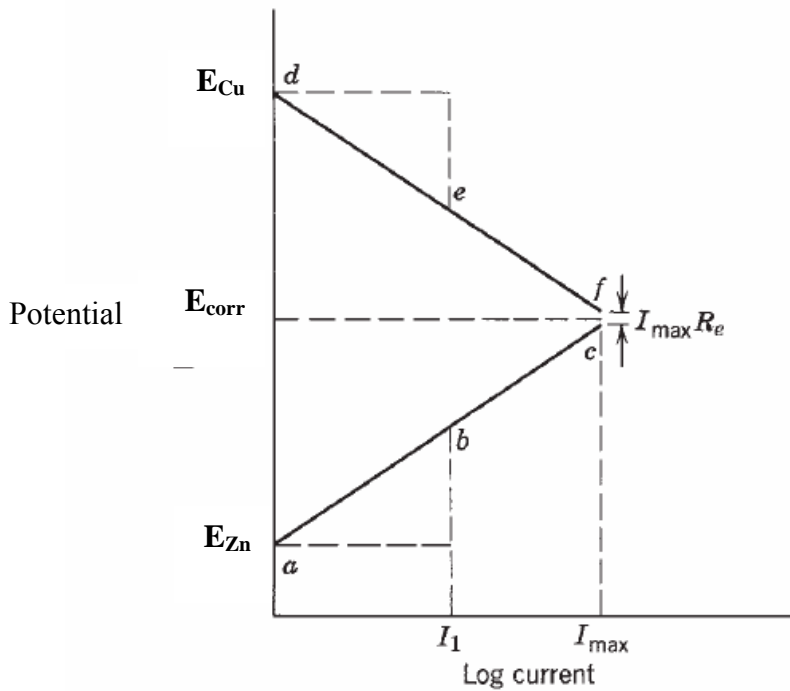
At point which current value through ammeter equal to I_1 , the polarization of zinc in volts is given by difference between the actual potential at b and open circuit potential at point a

Potential difference of polarized electrode b-e is equal to the current I1 multiplied by the total resistance of both external metallic resistance R_m and internal electrolytic resistance R_e

On short circuit the current refer as I_{max} , R_m can be neglected and potential difference of both electrodes decreases to minimum equal to $I_{max}R_e$.

Activation polarization
Activation polarization is caused by a slow electrode reaction step , the reaction at the electrode requires an activation energy in order to proceed , the most important example is the hydrogen ion reduction reaction at a cathode: $2H^+ + e^- \rightarrow H_2$
For this reaction, the polarization is called hydrogen over-potential
Over-potential is defined as the polarization (potential change) of an equilibrium electrode that results from current flow across the electrode-solution interface.
Hydrogen ion reduction is done by the following steps:
1-adsorption of hydrogen ion from solution to metal electrode
2-electron transfer from zinc to form hydrogen atom
3-cobining of two hydrogen atoms to form a molecule of hydrogen

$$2H \rightarrow H_2$$
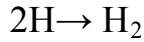
4-the coalescence of many hydrogen molecules to form a bubble
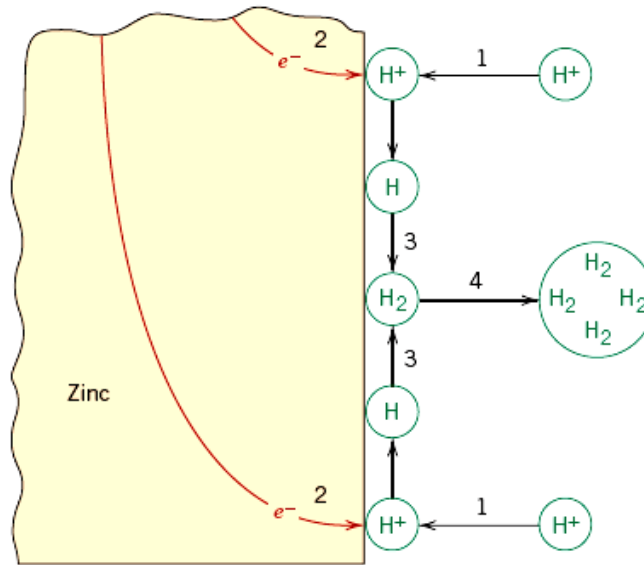
For the reaction $M \xleftarrow{i_a} M^{+z} + ze^-$

Corrosion rate $v = k_{corr}[reac\tan t]$

Where $k_{corr} = A\exp(-\Delta G^* / RT)$

A is constant

$\therefore v = A\exp(-\Delta G^* / RT)[reac\tan t]$

At equilibrium $i_a = i_c = i_\circ$

i_a (at equilibrium) $= i_\circ = A_\circ \exp(-\Delta G^* / RT)$

A∘ = A [reactant] solid material concentration treated as constant

The deviation from the equilibrium potential , polarization is the combination of an anodic polarization and a cathodic polarization of the environment , that mean energy of metal has increased and energy of environment has decreased, if the total polarization $= \eta$

Thus we can define the anodic polarization $= \alpha\eta$

And cathodic polarization $= (1-\alpha)\eta$

The new activation energy for anodic reaction, which can to be $(\Delta G^* - \alpha\eta zF)$ because energy state of metal has increased and activation energy reduced thus we can write the below:

$$i_a = A_\circ \exp(\frac{-\Delta G^* + \alpha\eta zF)}{RT}$$

$$i_a = A_\circ \exp(\frac{\Delta G^*}{RT})\exp(\frac{\alpha\eta zF}{RT})$$
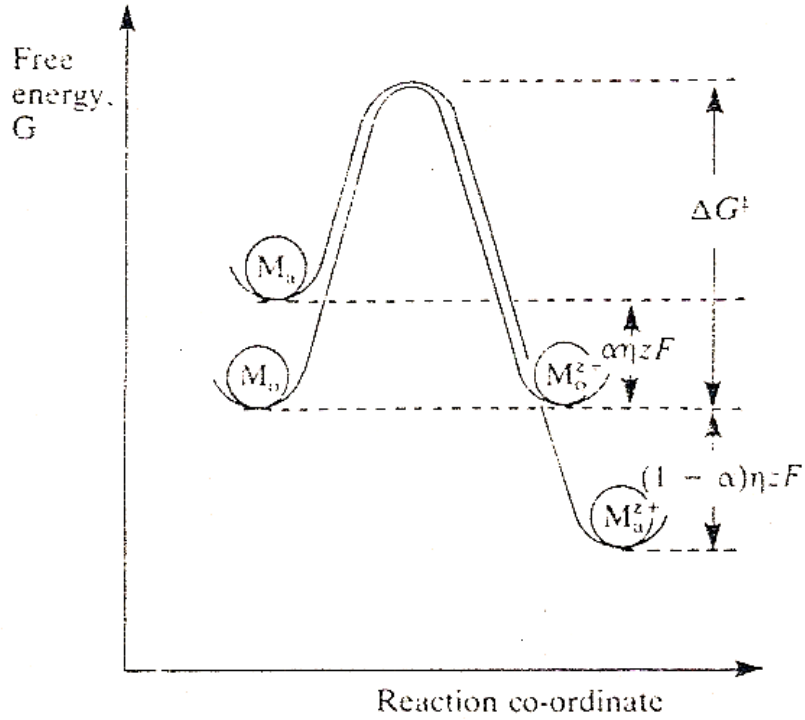
$$i_a = i_\circ \exp(\frac{\alpha\eta zF}{RT})$$

Similarly

$$i_c = i_\circ \exp(\frac{(1-\alpha)\eta zF}{RT})$$

$$i_{mean} = i_a - i_c \quad \text{bulk current flow}$$

$$i_{mean} = i_\circ \left[\exp(\frac{\alpha\eta zF}{RT}) - \exp(\frac{(1-\alpha)\eta zF}{RT}) \right] \qquad \text{-------------- (1)}$$

This equation is known Butler-Volmer equation

Let

$$A^- = \frac{\alpha\eta zF}{RT}$$

∧

$$\therefore i_a = i_{\circ} \exp(A^{-}\eta)$$

$$\ln i_a = \ln i_{\circ} + A^{-}\eta$$

rearranging lead to :

$$\ln(\frac{i_a}{i_{\circ}}) = A^{-}\eta$$

$$\eta = \frac{2.303}{A^{-}} \log(\frac{i_a}{i_{\circ}})$$

Let

$$\beta_a = \frac{2.303}{A^{-}} = \frac{2.303RT}{\alpha zF}$$

$$\therefore \eta_a = \beta_a \log(\frac{i_a}{i_{\circ}}) \qquad \text{------------ (2)}$$

Similarly

$$\therefore \eta_c = \beta_c \log(\frac{i_c}{i_{\circ}}) \qquad \text{----------- (3)}$$

Where

$$\beta_c = \frac{2.303RT}{(1-\alpha)zF}$$

β_a and β_c are the Tafel constants , and the equation 2 and 3 are Tafel equations.

Factors affecting activation polarization

1-current density: where activation polarization increases with current density

2- Materials: Activation polarization varies with one metal to another because of the specific effect of current density.

3- Surface Roughness: Activation polarization is high on a smooth surface compared to a shiny surface.

4- Temperature: Increased temperatures decrease polarization as less activation energy would be needed and the exchange current density would be increased.

5- Pressure: Hydrogen over-voltage increases rapidly with decreasing pressure.

6- pH: Over-voltage increase initially and decreases with increased pH value.

7- Agitation: It has no effect on activation polarization, because it is a charge transfer process involving electrons and not a mass transfer.

8- Adsorption of Ions: The hydrogen overvoltage is decreased by adsorption of anions and increased by adsorption of cations.

Concentration polarization

Consider the hydrogen evolution reaction at low reduction rate the distribution of hydrogen ions in the solution adjacent to the electrode surface is relatively uniform ,while at high reduction rate the region adjacent to the electrode surface will becomes depleted of hydrogen
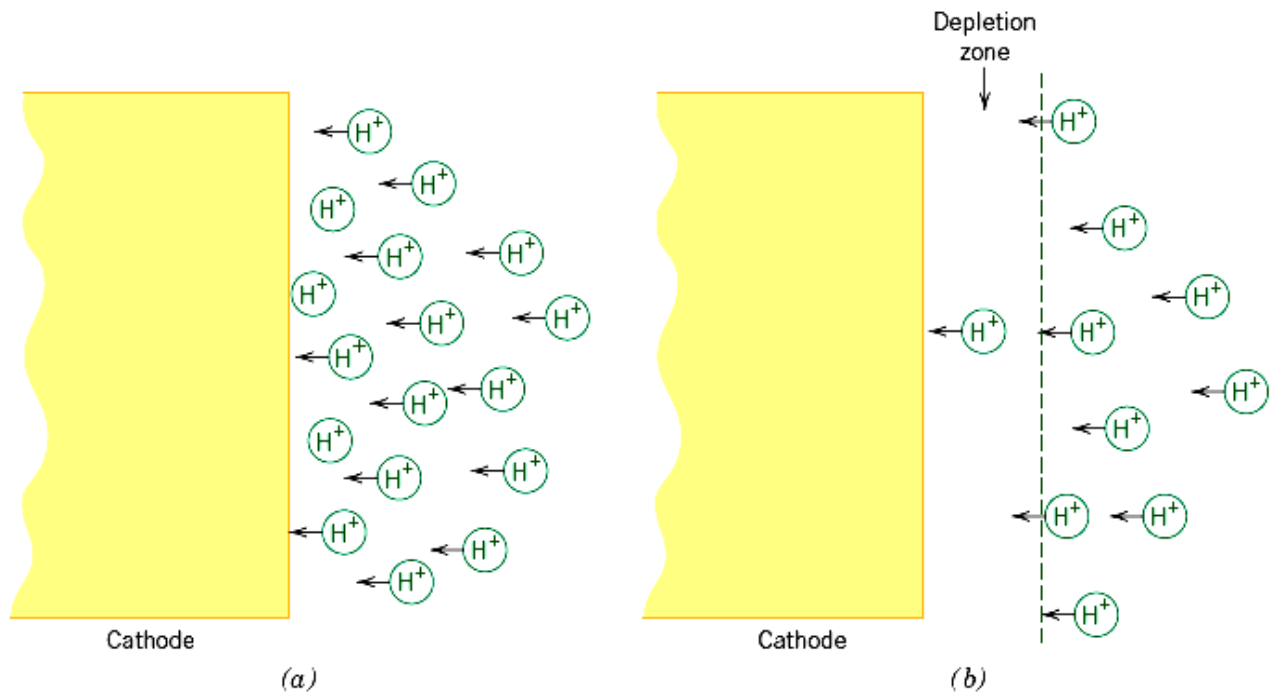
If the reduction rate increased further , a limiting rate will be reached that is determined by diffusion rate of hydrogen ions to the electrode surface .this limiting rate is the limiting current density i_L , it is represents the maximum rate of reduction possible for a given system

$$i_L = \frac{DzFC_B}{\delta}$$

D   is diffusion coefficient of the reacting ions
CB concentration of reacting ions in the bulk solution
δ is the thickness of diffusion layer
Generally observed that there is a linear relationship between the concentration of reaction ions and limiting current density
The diffusion layer thickness is influenced by the shape of particular electrode, geometry of the system and by agitation (agitation tends to g

Limiting current density is usually only significant during metal dissolution reactions because there is an almost unlimited supply of metal atoms for dissolution

Thickness of diffusion layer must be determined by empirical experimental measurement.

$$M \rightarrow M^{+z} + ze^-$$

Under zero current condition concentration is CB

When the cell is connected and current flow the concentration is C

Faraday law for electrolysis

Q= z F M

$$\frac{dQ}{dt} = zF \frac{dM}{dt} \Rightarrow i = zFJ$$

J is flux of substance

But

$$J = -D \frac{dc}{dx} \qquad \text{first Fick's law}$$

$$\therefore i = -zFD \frac{dc}{dx}$$

Assume that the concentration gradient is linear and can be replaced by

$$\frac{C_B - C}{\delta}$$

$$\therefore i = -zFD \frac{C_B - C}{\delta}$$

Negative sign it tell us that the current is being carried away from the cathode

The maximum or limiting current density i_L is given by

$$i_L = -zFD \frac{C_B}{\delta}$$

So potential under no current condition:

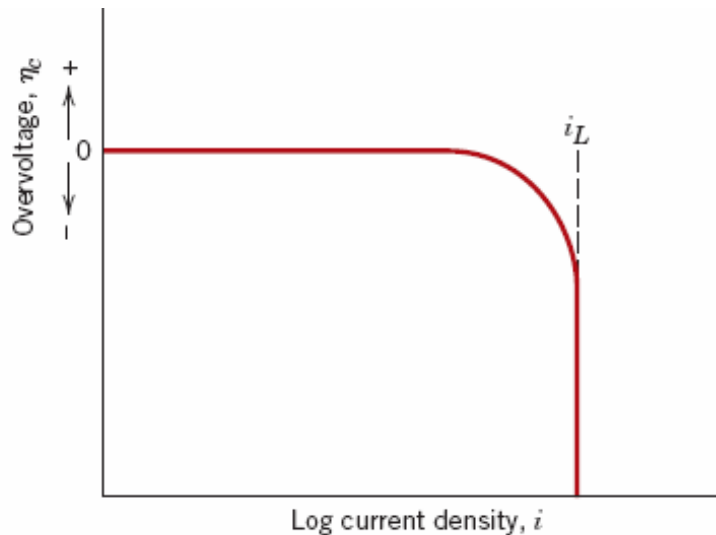$$E_1 = E^\circ + \frac{0.0592}{z} \log C_B$$

When current flow the potential:

$$E_2 = E^\circ + \frac{0.0592}{z} \log C$$

$$\eta_c = E_2 - E_1 = \frac{0.0592}{z} \log \frac{C}{C_B}$$

$$\frac{i}{i_L} = \frac{C_B - C}{C_B} = 1 - \frac{C}{C_B} \Rightarrow \frac{C}{C_B} = 1 - \frac{i}{i_L}$$

$$\therefore \eta_c = \frac{0.0592}{z}\log(1 - \frac{i}{i_L})$$

Effect of various factors on concentration polarization

1-Agitation. By agitation, the thickness of the diffusion layer is decreased, and the rate of diffusion of ions increases. There is no build up of any concentration gradient between the corroding surface and bulk electrolyte. The end result is a decrease in concentration polarization and an increase in the rate of corrosion. As the rate of agitation is increased the corrosion potential shifts in the noble direction because of a decrease in cathodic over-potential caused by concentration polarization.

2-Temperature. As the temperature rises, the thickness of diffusion layer is decreased and the corrosion current is increased.

3-Velocity. The higher the velocity, the less is concentration polarization. At a sufficiently high velocity, concentration polarization becomes zero because the ionic flux is now sufficient to maintain the surface concentration of ions at the electrode/electrolyte surface equal to the bulk concentration.At high velocity, the driving force for the concentration polarization becomes zero. The process at high velocity becomes totally activation controlled and there is no concentration polarization at high velocity
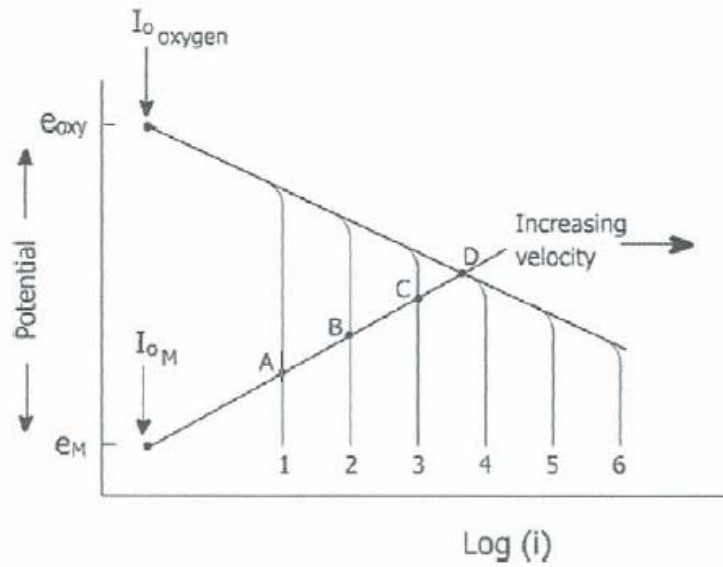
4-Concentration of ionic species. Concentration polarization generally results from the depletion of ions in the vicinity of the cathode. When the concentration of species at the cathode reaches zero, $Q = 0$, the reaction is completely mass transport controlled. The higher is the concentration of species, the greater would be the concentration polarization.

5-Geometry. The geometry of fluid flow and the design of the cell (horizontal or vertical) affects concentration polarization.

Combined polarization
Both activation and concentration polarization usually occur at an electrode, at low reaction rates activation usually controls, whereas at higher concentration becomes controlling .the total polarization of an electrode is the sum of them as below

$$\eta_t = \eta_c + \eta_a$$
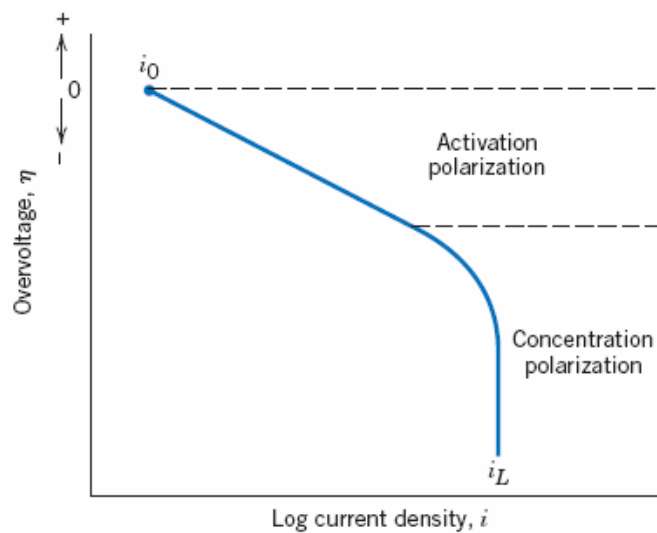
During anodic dissolution, concentration is not a factor

$$\eta_{diss} = \beta \log \frac{i}{i_o}$$

During reduction process such as hydrogen evolution concentration polarization will be considered

$$\eta_{red} = -\beta \log \frac{i}{i_o} + \frac{0.0592}{z} \log(1 - \frac{i}{i_L})$$