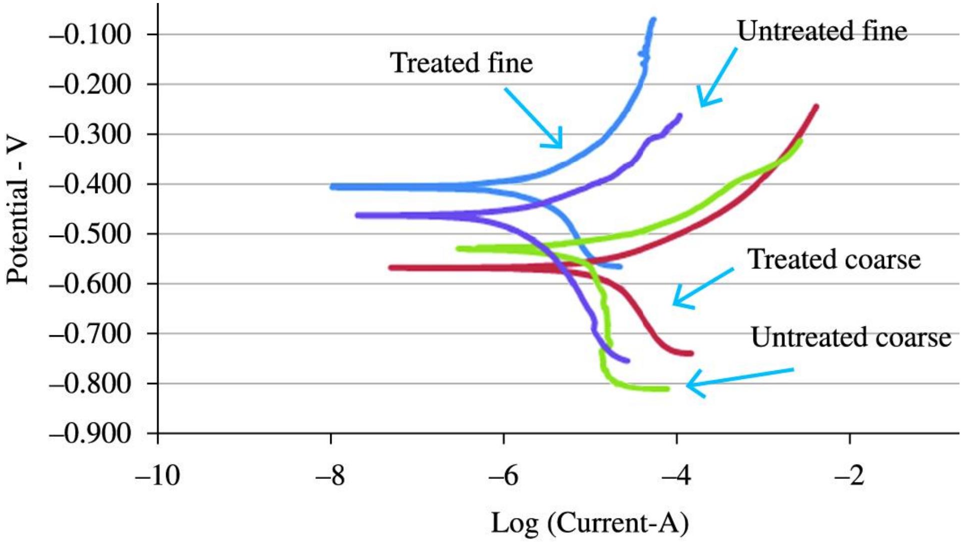
Chapter (4-B)

Corrosion Kinetics- Part (B):

Polarization & Overpotential



Oct. 10th , 2017

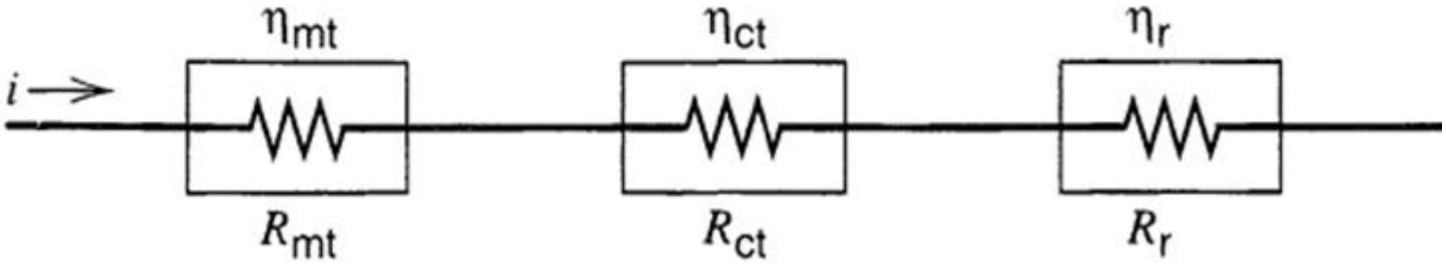
Polarization / Overpotential

1. Electrode reactions are assumed to induce deviations from equilibrium due to the passage of an electrical current through an electrochemical cell causing a change in the electrode potential. This electrochemical phenomenon is referred to as **polarization.**
2. Galvanic (spontaneous cells) operate below their maximum potential (OCP: open circuit potential) due to the electrode polarization required to produce current (anode E is less negative than E°, and cathode E is less positive than E°).
3. The deviation from equilibrium causes an “electrical potential difference” between the polarized and the equilibrium (unpolarized) electrode potential known as **overpotential.**
4. **Overpotential** is an expression of degree of polarization of an electrode. It is equals the difference between actual electrode potential (E) and equilibrium potential (Eeq):

$$\eta = E - E_{eq} \quad \text{where} \quad E < E_{eq}$$

Polarization / Overpotential

- Overpotential is the driving force for an electrochemical reaction is the overpotential. This driving force is used up by all the steps in the electrochemical reaction.
- Thus an applied overpotential may be broken into:
  1. Mass transfer overpotential
  2. Charge transfer overpotential
  3. Other: Reaction, adsorption or barrier-crossing overpotential
- Correspondingly, the resistance offered to the passage of current may be viewed as sum of a series of resistances



Three Components of Polarization

1) Activation overpotential (η_{act}).

Commonly encountered in anodic charge transfer reactions (metal oxidation):

$$\mathbf{M_{surface} = M^{n+}_{surface} + n\, e^{-}}$$

η_{act} occurs when some step in the half-cell reaction controls the rate of charge transfer. It is commonly found in anodic (oxidation) reactions, e.g. metal dissolution. In general, η_{act} can be:

- positive (anodic) if net current is dissolution <u>(oxidation),</u>
- negative (cathodic), if net current is deposition <u>(reduction).</u>

2) Concentration polarization (η_{conc}).

Commonly encountered in cathodic reactions, particularly oxygen and hydrogen reductions.

3) Resistance polarization (η_R) OR Potential drop. If there is a resistance between the anode and the cathode in a cell, then the current flowing through that resistance will cause a potential drop given by <u>Ohm's Law</u>: **V = IR**

This is important for paint films and for high-resistance solutions.

Rate Limiting Step in Corrosion Reactions

I. Activation Control:

- The case when corrosion is controlled by charge transfer reactions. Either the anodic charge transfer OR the cathodic charge can be the controlling (rate limiting) step. Note that anodic reactions and cathodic reactions in a system can be studied individually by electrochemical methods.

II. Mass Transfer Control:

- If the cathodic reagent at the corrosion site (e.g., dissolved O_2 in the O_2 reduction reaction) is in short supply, mass transfer of the reagent can become rate limiting. Then, the cathodic charge-transfer reaction is fast enough to reduce the concentration of the reagent (e.g. O_2) at the surface corrosion site to a value less than that in the bulk solution.

Three Components of Polarization

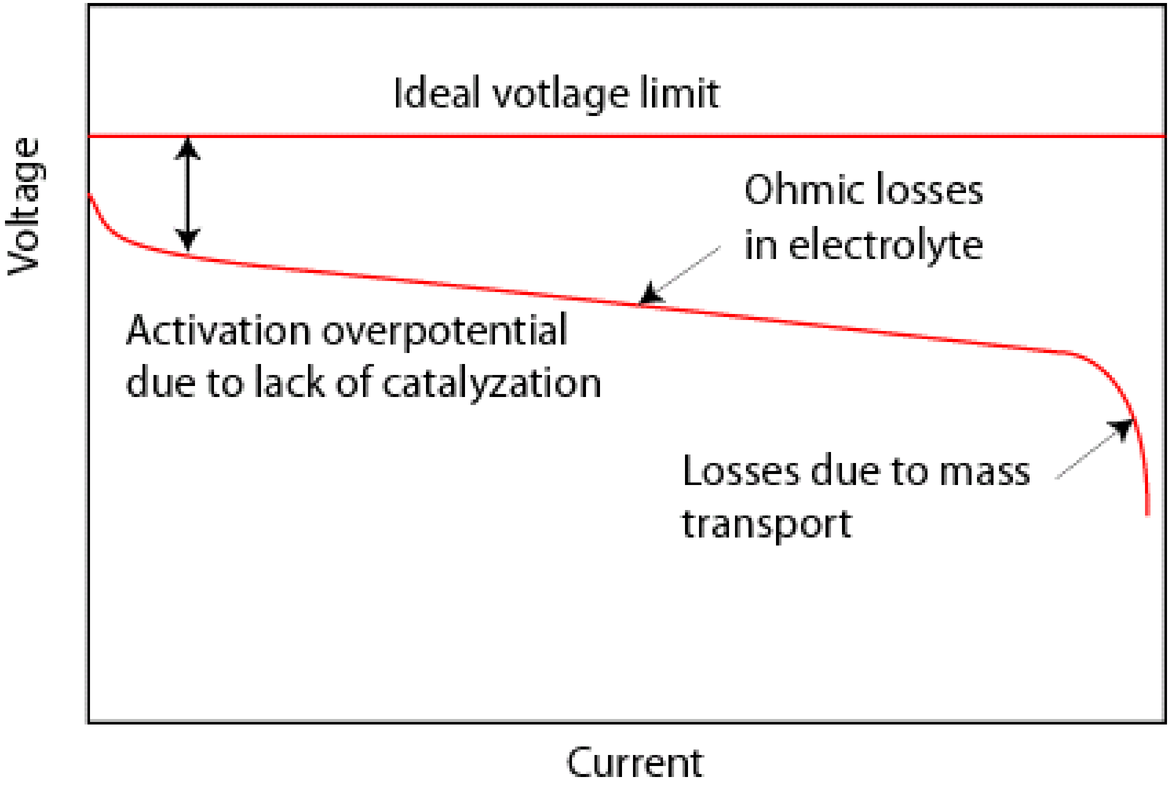
1. Theoretically, total polarization at an electrode is the sum of the three components: activation, concentration and resistance polarizations:

$$\eta_{TOTAL} = \eta_{act} + \eta_{conc} + \eta_{R}$$

1. The actual polarization is normally limited to one or the sum of two components.
2. This is based on the relative amounts of these components which makes an over-potential negligible at a given electrode.
3. In many cases, $\boldsymbol{\eta}_{\mathbf{act}}$ is the only significant polarization component at the anode while $\boldsymbol{\eta}_{\mathbf{Conc}}$ is the only significant polarization component at the cathode.

Three Components of Polarization

- At low current density, charge transfer is low (rate-controlling), thus activation polarization dominates.
- At high current density, consumption of electroactive ions at the electrode surface results in a concentration gradient and slow mass transfer in solution, thus concentration polarization dominates.



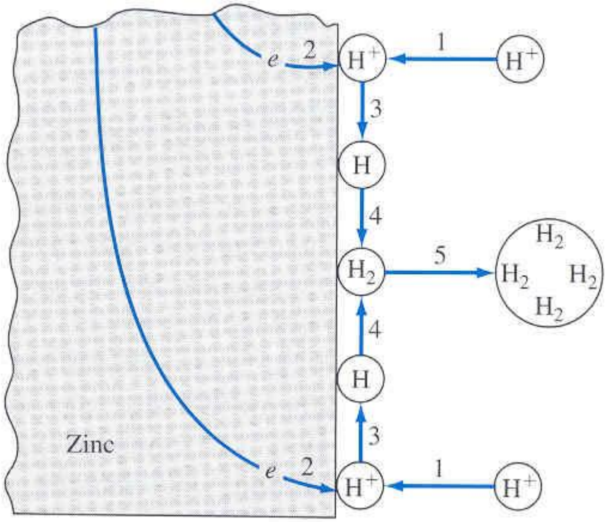
Components of Polarization

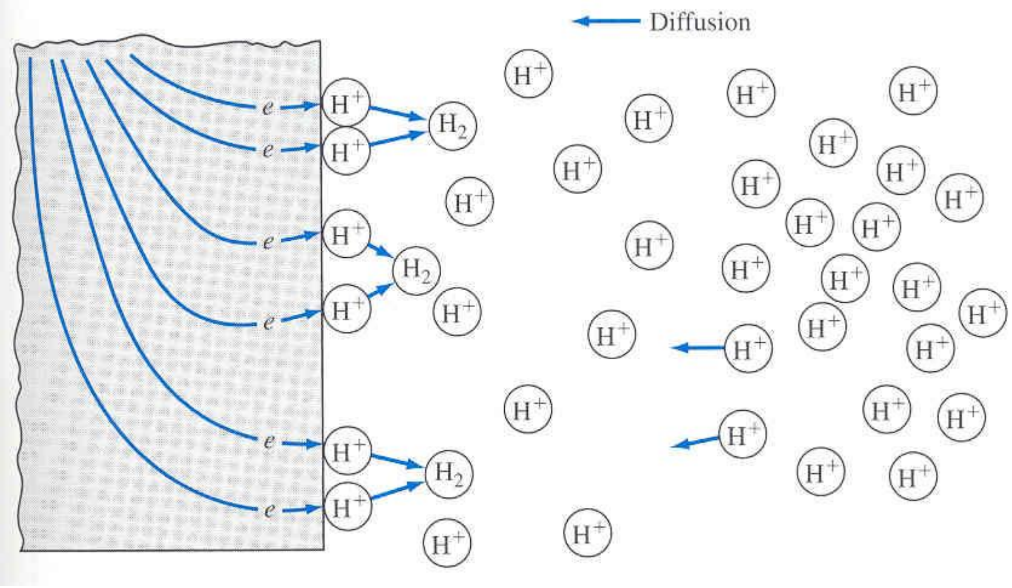
- **Activation polarization:**

In a multistep electrochemical reaction the rate is controlled by the slowest step.

- **Concentration polarization:**

Corrosion reaction may result in a build up or depletion of the ions or atoms that are required for a corrosion reaction.

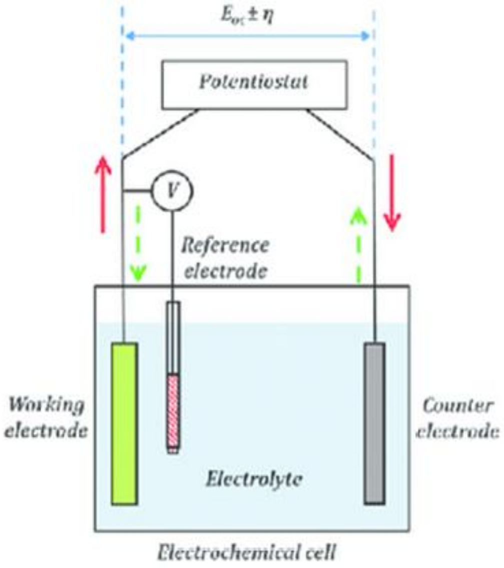


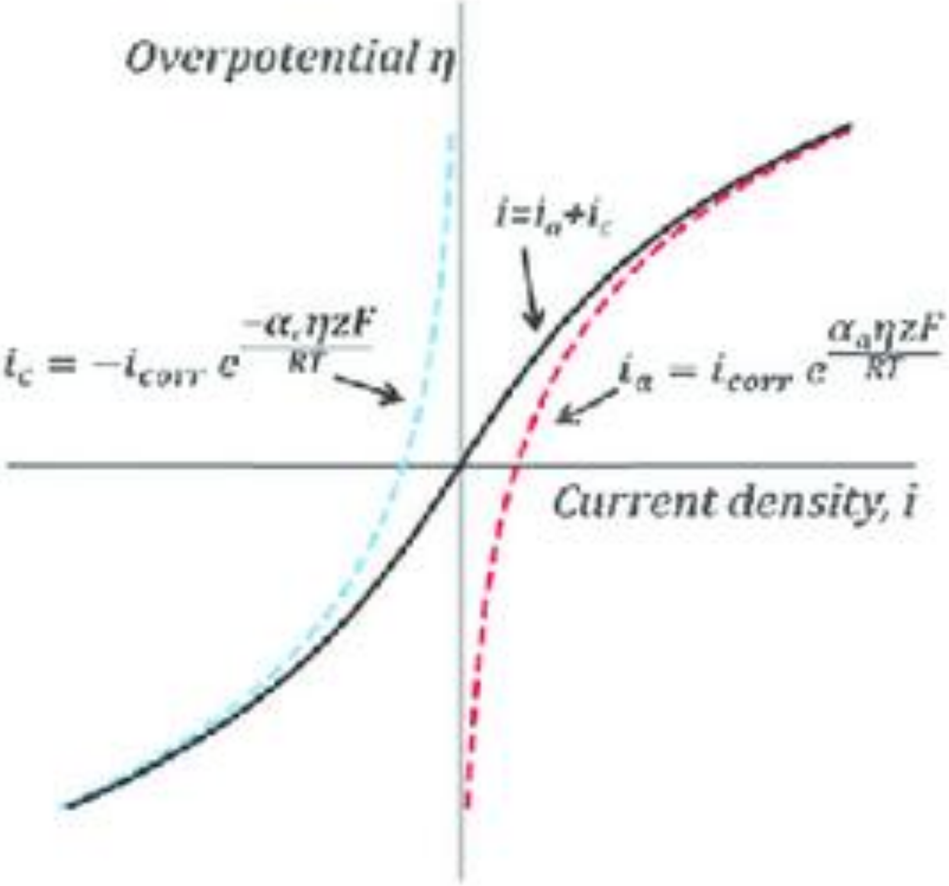


Polarization & Electrode Reactions Kinetics

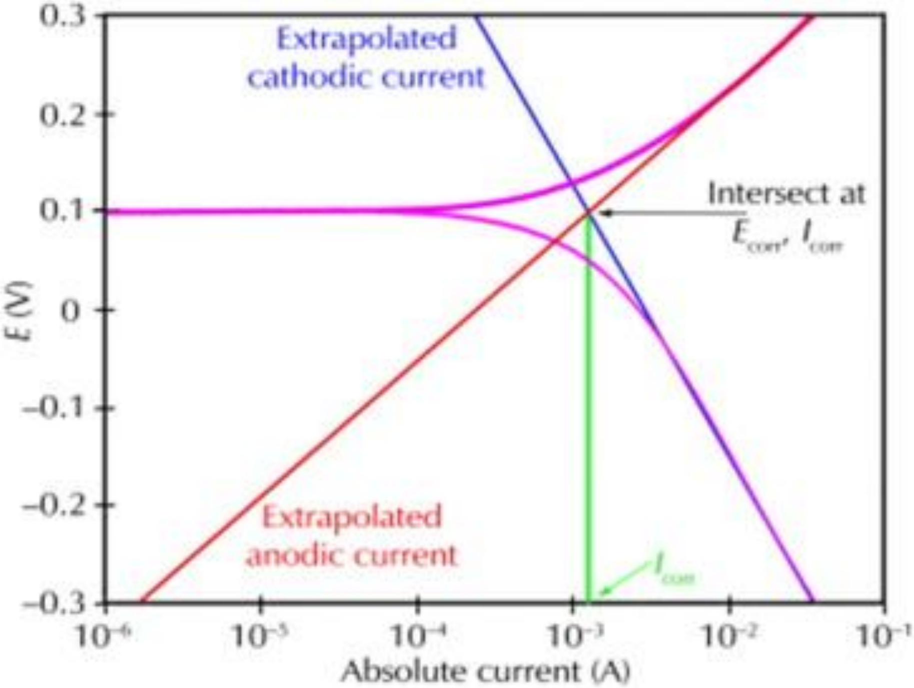
- Activation (Charge Transfer) overpotential is related to the current density by Bulter-Volmer equation (BVE), which is valid for all electrode reactions.
- BVE is one of the most fundamental relationships in electrochemistry.
- It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode:
- For corrosion studies, Tafel's equation, a simplified form of Bulter-Volmer equation is the commonly used. This will elaborated later in this chapter.

Polarization and Electrode Reactions Kinetics





Butler-Volmer equation



Tafel Extrapolation

Kinetics of Electrode Reactions

- The **Butler-Volmer is given below:**

$$i = i_0 \cdot \left[\exp\left(\frac{\alpha_A n F}{RT} \eta \right) - \exp\left(- \frac{\alpha_C n F}{RT} \eta \right) \right]$$

Where:

i = net reaction current density ($i = i_a - i_c$)

R = universal gas constant;

T = absolute temperature;

n = number of electron transferred in balanced reaction

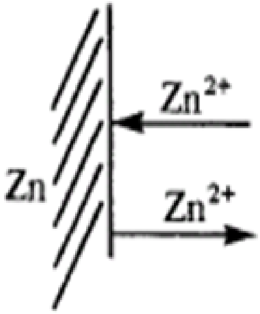
F = Faraday constant (96,485 Coul/mol)

η = overpotential (polarization) = $E - E_{eq}$

α_A & α_C = symmetry factors representing energy peak, usually taken as 0.5

i_o = exchange current density (a constant for the system).

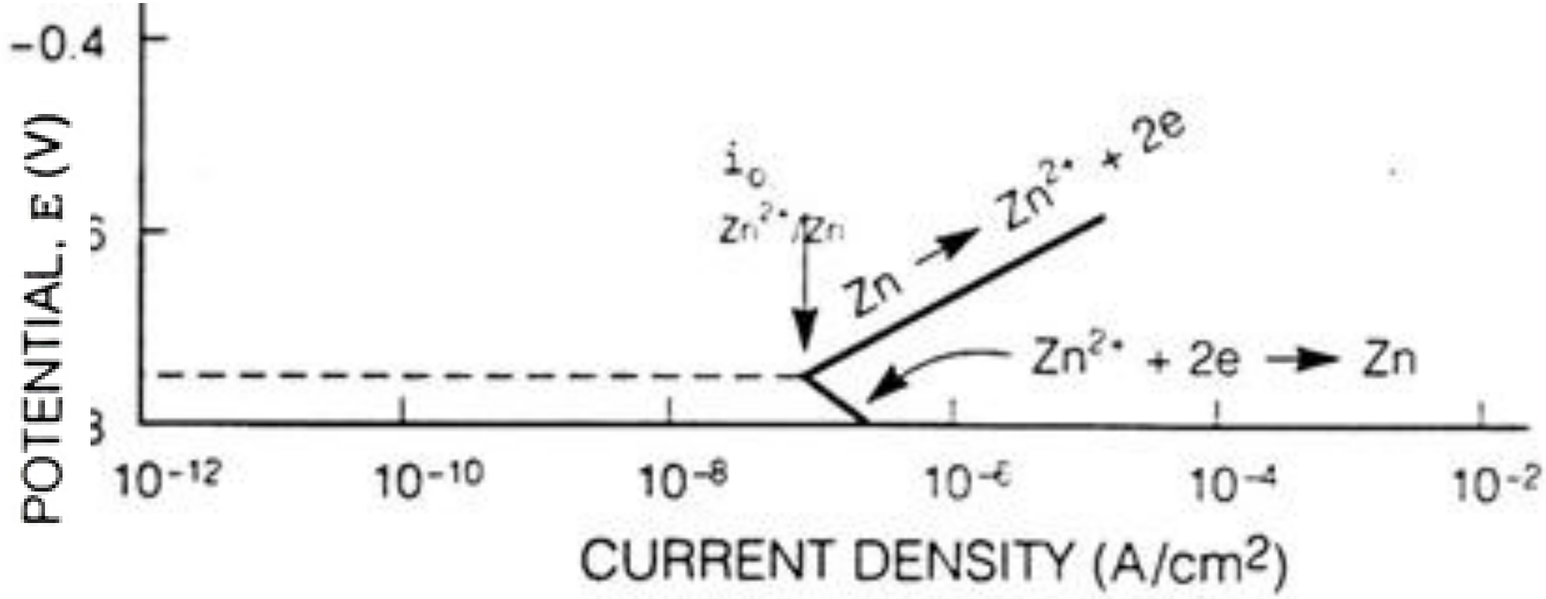
Exchange Current Density



$Zn \rightleftharpoons Zn^{2+} + 2e^-$

Exchange current is the current transferred between the forward and the reverse reactions at equilibrium
they are equal at equilibrium and the net current is zero

- For example, on the Zn electrode, Zn ions are released from the metal and discharged on the metal at the same rate:



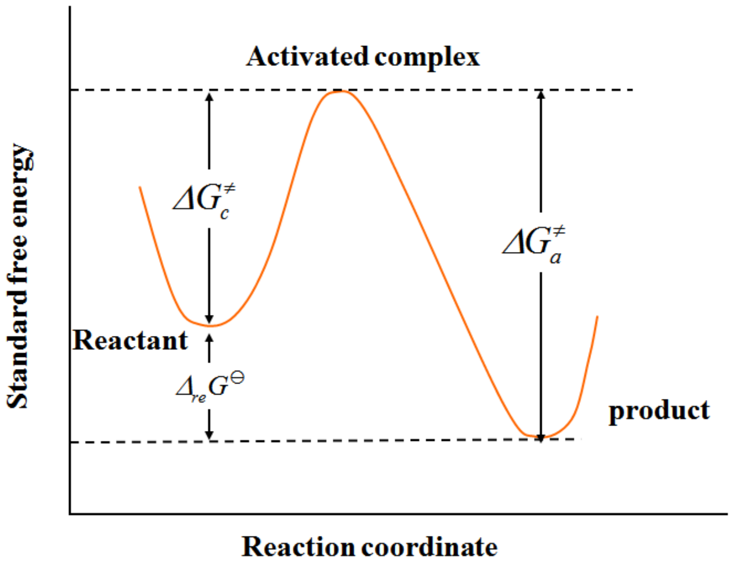
Exchange Current Density

- The reaction rate in each direction can also be expressed by the transport rate of electric charges, i.e. by current or current density, called, respectively, exchange current, I_o, and (more frequently used) exchange current density, i_o.
- The net reaction rate and net current density are zero.
- The exchange current is the current at equilibrium, i.e. the rate at which oxidized and reduced species transfer electrons with the electrode. In other words, the exchange current density is the rate of reaction at the reversible potential (when the overpotential is zero by definition).
- At the reversible potential, the reaction is in equilibrium, meaning that the forward and reverse reactions progress at the same rates.
- This rate is the exchange current density.

Bulter-Volmer Equation

Theoretically derived from chemical kinetics:

1. Expressing forward, backward and net reactions at electrode surface,
2. Incorporating activation energy in the form of activation Gibbs energy change, ΔG#, according to the conventional transition state theory (CTST),
3. Expressing reaction driving force in terms of overpotential (**$\eta = E - E_{eq}$**) and the reaction rate in terms of current density (i).
4. At equilibrium, **$\eta = 0$ and $i = i_o$** (exchange current density for a reversible surface reaction) and Bulter-Volmer Equation agrees with Nernst equation.



$$k_f = A \exp(-\Delta G_c^{\ddagger}/RT)$$

$$k_b = A \exp(-\Delta G_a^{\ddagger}/RT)$$

$$r_{net} = k_f C_{Ox} - k_b C_{Red}$$

$$\mathbf{r = i / nF}$$

$$\Delta G = -nFE$$

$$i_{net} = i_{cath} - i_{anod}$$

Bulter-Volmer & Tafel Equations

- While the **Butler-Volmer equation** is valid over the full potential range, simpler approximate solutions can be obtained over more restricted ranges of potential.
- As overpotentials, either positive or negative, become **larger than about 0.05 V,** the second or the first term of equation becomes negligible, respectively.
- Hence, simple exponential relationships between current (i.e., rate) and overpotential are obtained, or the overpotential can be considered as logarithmically dependent on the current density.
- This theoretical result is in agreement with the experimental findings of the German physical chemist Julius Tafel (1905).
- The plots of overpotential versus log current density are known as Tafel lines and the slope of a Tafel plot reveals the value of the transfer coefficient; for the given direction of the electrode reaction.

Bulter-Volmer & Tafel Equations

- At high **overpotential** the Butler-Volmer equation simplifies to:

$\eta_c = a - b\log(i_c)$ for a cathodic reaction

$\eta_a = a + b\log(i_a)$ for an anodic reaction

$$\eta_c = b_c \log \frac{i_c}{i_o}$$

$$\eta_a = b_a \log \frac{i_a}{i_o}$$

- The following is the experimentally obtained **Tafel equation**:

$$\eta = a + b \log i$$

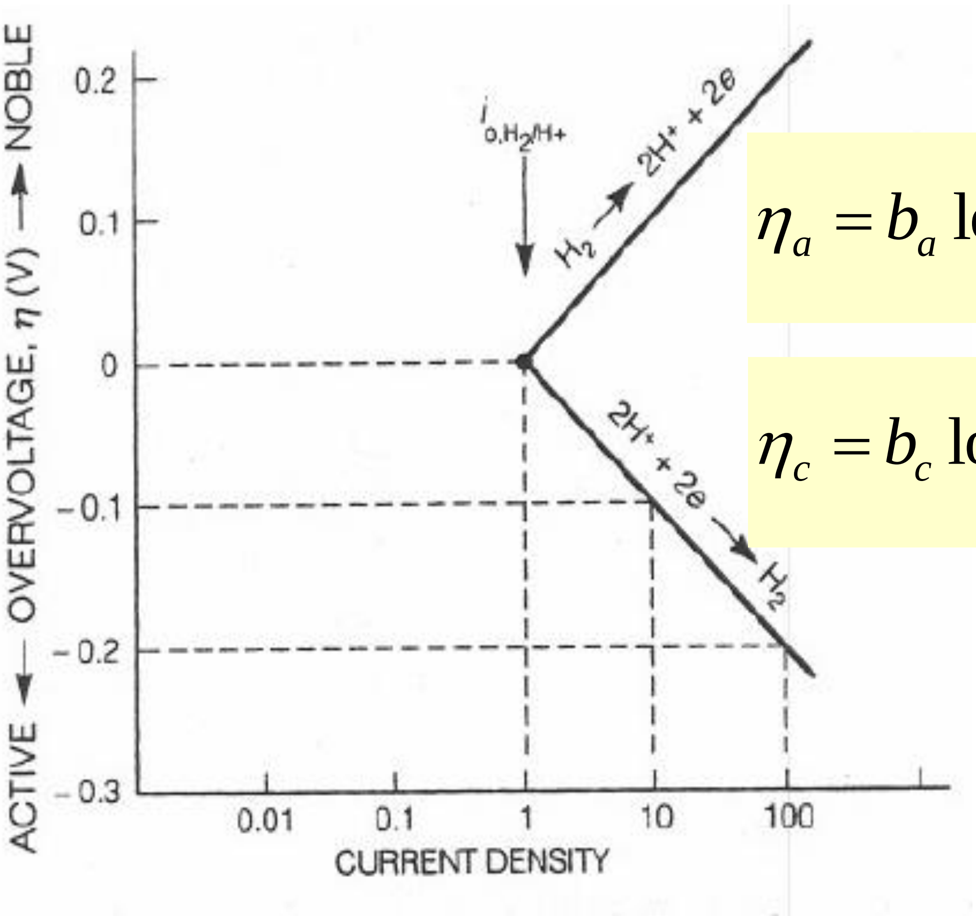
Where: $\boldsymbol{\eta}$ = the overpotential (volt) **=** $\eta_c + \eta_a$

$\boldsymbol{i}$ = the current density (amp/cm2)

a* & *b = Tafel constants (include R,T, n,F,α,…)

- The Tafel slope (b) is measured experimentally for a given electrochemical systems (e.g. corroding metal or alloy).

Tafel Equation and Plot



$$\eta_a = b_a \log \frac{i_a}{i_o}$$

$$\eta_c = b_c \log \frac{i_c}{i_o}$$

η_a=anodic over-potential
η_c=cathodic over-potential

b_a=anodic Tafel constant
b_c=cathodic Tafel constant

(units of b: V/decade where decade is interval between two quantities having the ratio of 10 to 1)

i_a=anodic current density
i_c= cathodic current density
i_o=exchange current density

(i_o depends on surface conditions and is a measured quantity) See Table 3.1 Next

When i_a=i_o or i_c=i_o, No polarization (i.e. equilibrium)

Tafel Equation and Plot

$$\eta = a + b \log i$$

- Applicability and Characteristics:

1. Where an electrochemical reaction occurs in two half reactions on separate electrodes, the Tafel equation is applied to each electrode separately.
2. The Tafel equation assumes that the reverse reaction rate is negligible compared to the forward reaction rate.
3. The Tafel slope, **b,** is an intensive parameter and does not depend on the electrode surface area.
4. **i_o** is and extensive parameter and is influenced by the electrode surface area and the kinetics or rate of the reaction.
5. The relationship between over-potential and current density (reaction rate) for the two half-cell reactions is known as Tafel plot (next).

Tafel Equation and Plot

$$\eta = a + b \log i$$

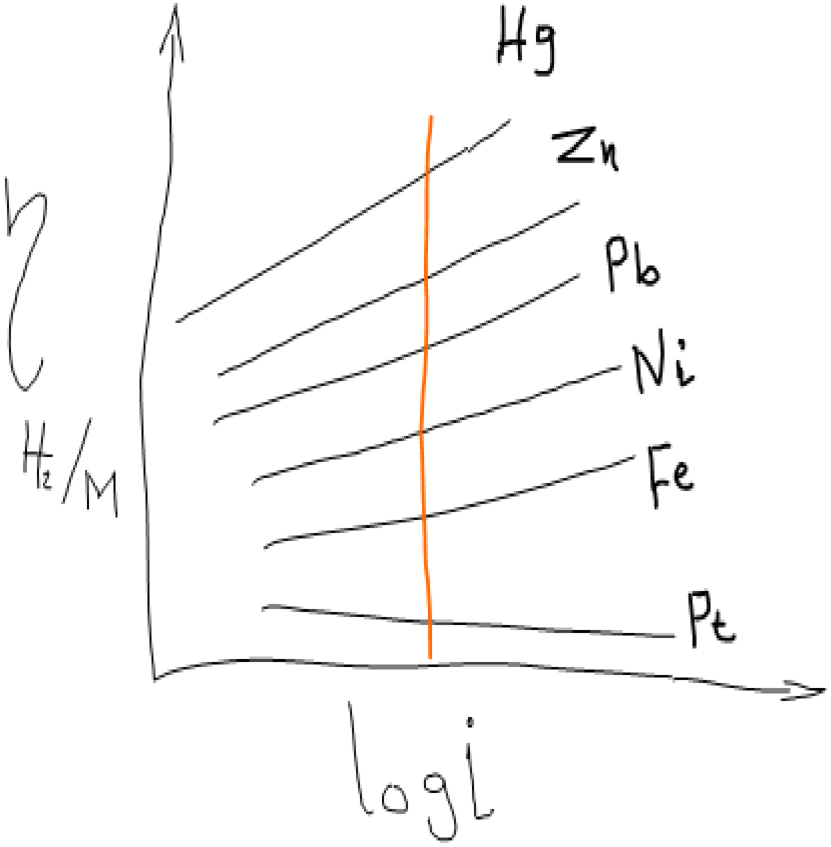
- For an electrochemical reaction under activation control, polarization curves exhibit linear behavior in the **E vs. log (i)** plots called Tafel behavior.
- Typical polarization behavior of metals in acid solution in the presence and absence of oxygen are illustrated below.
- Typical cathodic polarization curves with respect to Tafel behaviour are also given.
- Extrapolation of cathodic and anodic Tafel slopes back to the corrosion potential (Ecorr) are shown.
- Intersection point corresponds to corrosion current density ($\mathbf{i}_{corr}$) or corrosion rate, where: $\mathbf{i}_a = \mathbf{i}_c = \mathbf{i}_{corr}$

Exchange Current Densities (i_o) of H_2 Evolution in 1 M H_2SO_4

Electrode Material	**- $\log_{10} i_o$ (A/cm²)**
Palladium	3.0
Platinum	3.1
Rhodium	3.6
Nickel	5.2
Gold	5.4
Tungsten	5.9
Niobium	6.8
Titantium	8.2
Cadmium	10.8
Manganese	10.9
Lead	12
Mercury	12.3

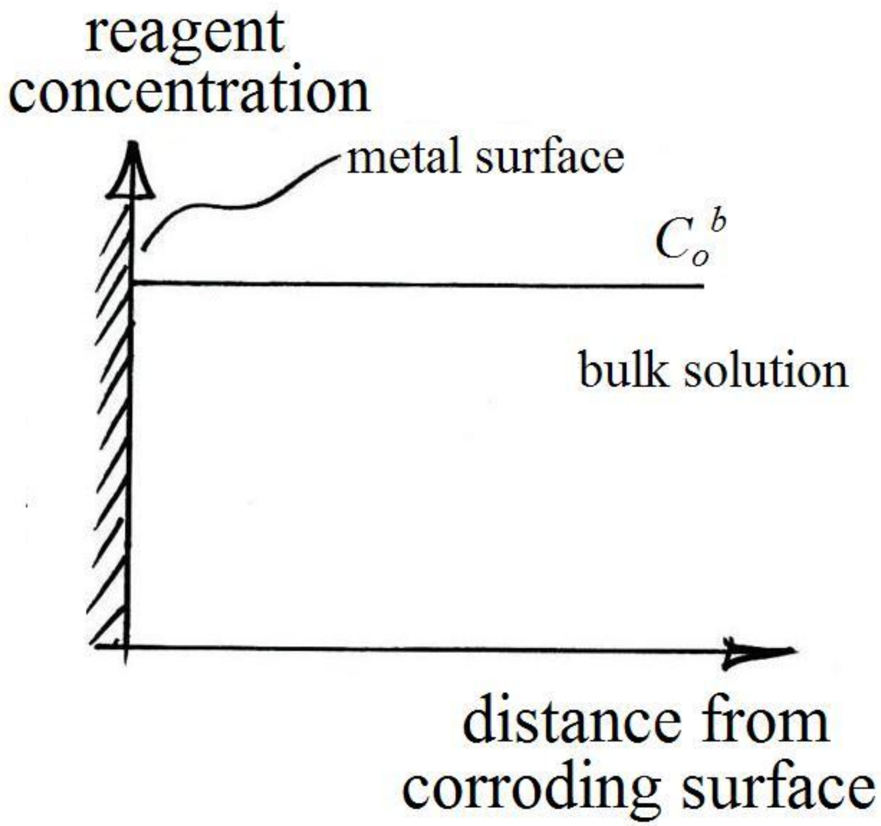
$$\eta = a + b \log i$$

Activation Over-potential of H2 gas over metals

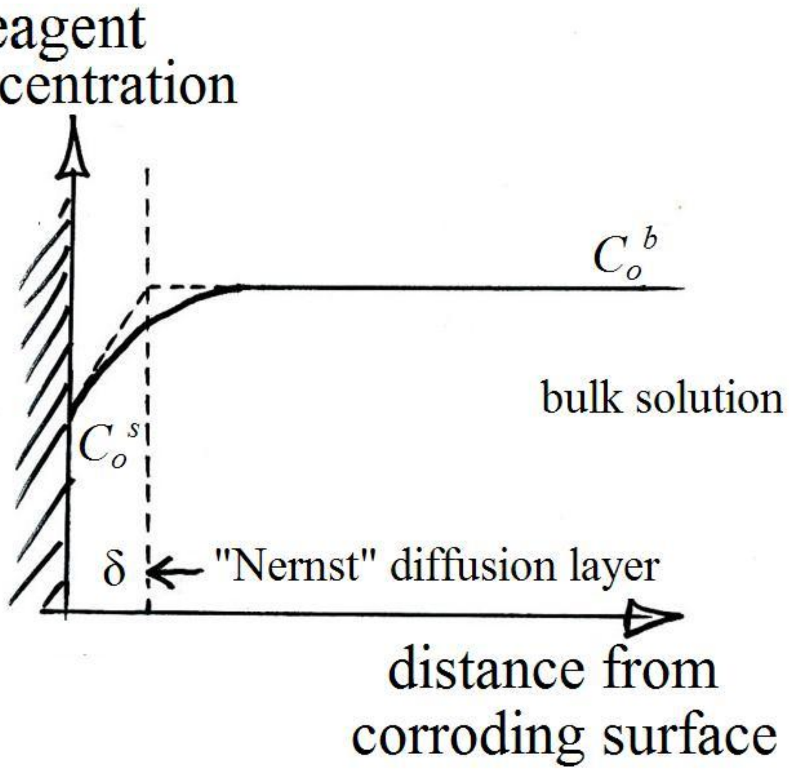


Concentration Polarization

Activation Controlled



Diffusion or Mass Transfer Controlled



Concentration Polarization

- At high current density, the consumption of electroactive species at the electrode surface results in a concentration gradient in solution.
- In such cases, the mass transport within the solution may become rate determining, thus we have concentration polarization
- Concentration polarization implies either there is a shortage of reactants at the electrode or that an accumulation of reaction product occurs (transport in both directions).

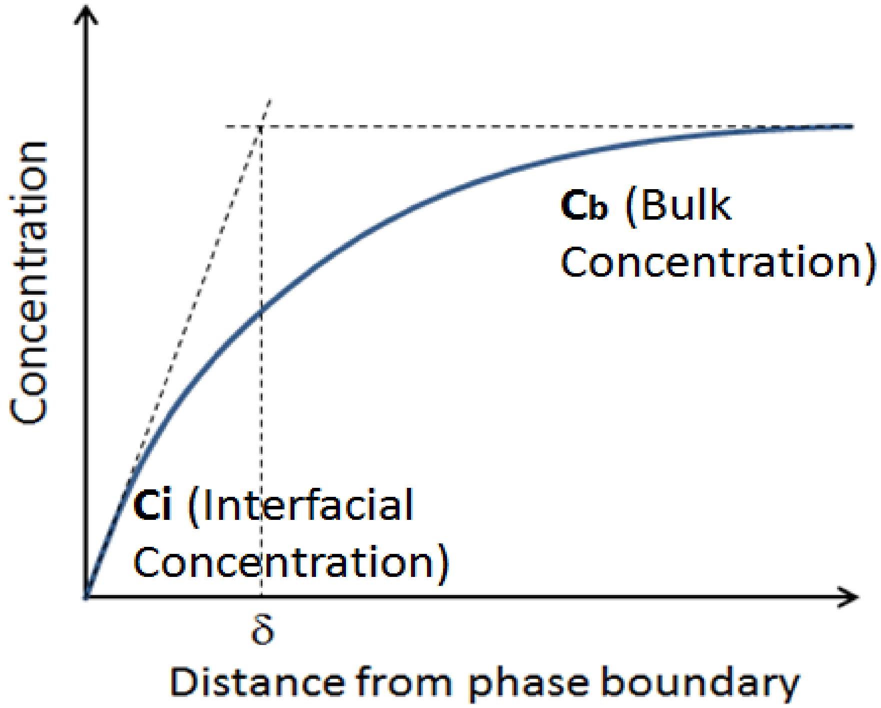


Figure Convective and Diffusive mass transfer of electroactive ion from bulk solution to electrode surface

Concentration Polarization

- The equilibrium potential needed to reduce an electroactive ion is given by the reversible value which is calculated from Nernst equation: $E_1 = E° - (RT/nF) \ln C_b$
- After reduction on cathode, the ion concentration drops from Cb in the bulk of solution to Ci at the electrode surface.
- Accordingly, the new potential which is needed to reduce the ion is given by: $E_2 = E° - (RT/nF) \ln Ci$
- The difference between e2 and el is known as the "concentration polarization or overpotential" and is given by:

$$\eta_c = E_2 - E_1 = (RT/nF) \ln (Cb/Ci)$$

This is illustrated in Figure (2.4) in which the current (I) is plotted against the voltage or potential “E”.

Concentration Polarization

Mass Transfer Control:

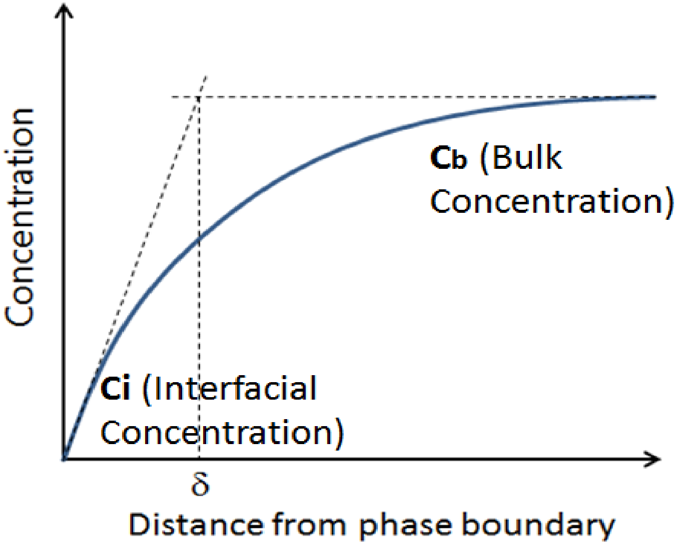
When the corrosion rate is limited by mass transfer it can be increased by:

1. By altering the bulk concentration
2. By stirring and reducing the thickness of the Nernst diffusion layer.

$$i_c = \frac{nFD(C_b - C_s)}{\delta}$$

$$(i_c)_{\text{Lim}} = \frac{nFD(C_b)}{\delta} = (i_{corr})_{\max}$$

(Derived from mass balance on electroactive ions transporting at steady state by diffusion and consumed according to Farady's law. See References for details.)



Where:

i_c = the cathodic current

n = the number of electrons

F = the Faraday constant

C_b = the bulk concentration

C_s = the surface concentration

δ = the Nernst diffusion layer