Corrosion - kinetics & measurements
Kinetics of corrosion

- Pourbaix diagrams – **no information about corrosion rates**

- Methods to determine corrosion rates:
  - Weight loss
  - Weight gain
  - Chemical analysis of solution
  - Gasometric techniques
  - Thickness measurement
  - Electrical resistance probes
  - Inert marker method
  - Electrochemical techniques
Kinetics of corrosion

- Corrosion = complex process
- Corrosion rate is defined by rate of the partial processes:
  - Transport processes e.g. convection, diffusion
  - Chemical reactions – metal/solution
- The overall corrosion rate is defined by the slowest process
Weight loss/gain method

- Weight loss – loose and non-adherent corrosion products (aqueous solutions)
- Weight gain – usually dry oxidation
- Corrosion rate = slope
Chemical analysis of solution

- Due to corrosion – cations accumulation in solution
- Corrosion rate = slope

![Graph showing the relationship between immersion time and moles Al^3+ dissolved per cm^2. The slope of the line is 4.8 x 10^-4 moles Al^3+/cm^2 hr.](image)
Gasometric techniques

- Most of the corrosion reactions – gas evolution
- Corrosion rate = slope
Electrochemical techniques

- Previous mentioned – information about rates but not about mechanisms
- Electrochemical techniques – **possibility of maintaining corrosion by controlling electrode potential**
- **DC techniques** – e.g. potentiodynamic test
- **AC techniques** – e.g. electrochemical impedance spectroscopy
Electrochemical polarization

• Change in the electrode potential due to the flow of the current - three types:
  – Activation – caused by slow electrode reaction
  – Concentration – caused by concentration changes in reactants or products near an electrode surface
  – Ohmic polarization – caused by IR drop in solution across films

• Degree of polarization = overvoltage:
  \[ \eta = E - E_0 \]
  – \( E \) – electrode potential for some conditions
  – \( E_0 \) – electrode potential for zero current flow = open circuit potential (OCP)
Anodic/cathodic polarization

• **Anodic polarization** – displacement of electrode potential in the positive direction = electrode acts more anodic

• **Cathodic polarization** – displacement of electrode potential in the negative direction = electrode acts more cathodic
Cathodic polarization

Cathodic polarization (activation)
Suppose the reaction is slow.

Electrons are supplied to the metal faster than they can react.

Thus, the concentration of $e^-$ is increased at the metal side of the interface.

$E$ becomes more $(-)$ due to activation polarization.

Cathodic polarization (concentration)
Suppose $H^+$ ions are slow to move into the electrical double layer.

Then, electrons flow into the surface faster than they can be consumed.

The concentration of $e^-$ is again increased at the metal side of the interface.

$E$ becomes more $(-)$ due to concentration polarization.
Anodic polarization

Anodic polarization (activation)

\[ 2e^- \rightarrow \text{Fe} \rightarrow \text{Fe}^{+2} \]

Suppose the reaction is slow.
Then, electrons exit from the surface faster than Fe atoms leave the matrix.
The concentration of \( e^- \) is decreased at the metal side of the interface.
E becomes more (+) due to \text{activation polarization}.

Anodic polarization (concentration)

\[ 4e^- \rightarrow \text{Fe} \rightarrow \text{Fe}^{+2} \]

Suppose the products are slow to diffuse away from the interface.
Again, the surface becomes more positively charged.
E becomes more (+) due to \text{concentration polarization}.
Ohmic polarization

Ohmic polarization is caused by the IR drop due to the inability to place the reference electrode directly at the metal surface under study.

\[ \text{IR}_{\text{soln}} \]

\[ \text{IR}_{\text{soln}} \] is negligible for high conductivity solutions.

\[ \text{IR}_{\text{soln}} \] is high for low conductivity solutions.

(organic media, some solis)
Electrode kinetics for activation polarization

- Electrode kinetics for activation polarization – treated using the **absolute reaction rate theory**
- Reactants to be converted to products – a transitory state is reached = **activated complex**
  \[ A + B \rightarrow [AB] \neq \rightarrow \text{products} \]
- Formation of activated complex = **overcoming a free energy barrier** \( \Delta G^\neq \)
- Rate constant is given by:
  \[
  \text{rate constant} = \frac{kT}{h} e^{-\Delta G^\neq /RT}
  \]
Electrode kinetics for non-corroding metal

- Consider substance Z in equilibrium with its ions $Z^{n+}$
- At equilibrium: rate of oxidation = rate of reduction
  \[ |i_Z^\rightarrow| = i_Z^- = i_0 \]
- $|i_Z^\rightarrow|$ - cathodic current density (reduction)
- $i_Z^- -$ anodic current density (oxidation, positive)
- $i_0$ - rate of reaction in either direction, at equilibrium
  \[ E_0 = \text{exchange current density} \]
- At OCP the net rate of reaction is zero
• It is possible to directly measure $E_0$ at OCP, but not $i_0$
  -> necessary to perturb system from equilibrium
• If electrode potential is changed from $E_0$ to some other value $E$ -> oxidation is raised or lowered to some value $i$ -> depending on the free energy barrier $\Delta G^{\neq}$ is raised or lowered
• If lowered:
  \[
  \Delta G^{\neq} = \Delta G_0^{\neq} - \alpha n F (E - E_0)
  \]
• $\Delta G_0^{\neq}$ - free energy barrier
• $\alpha$ – dimensionless constant (usually = 0.5)
• Therefore:
  \[
  rate\ constant = \frac{kT}{h} e^{-\Delta G_0^{\neq} / RT} e^{\alpha n F (E - E_0) / RT}
  \]
• Total current $i$ across surface $A$:

\[ I = \text{(rate constant)} C^{surf} nFA \]

• $C^{surf}$ - concentration of surface reactant (surface concentration of species Z)

• Therefore:

\[ \bar{i}_Z = \frac{I}{A} = \frac{kT}{\hbar} e^{-\Delta G_0^\pm /RT} e^{\alpha nF(E-E_0) /RT} C^{surf} nF \]

• when $E = E_0$ -> $\bar{i}_Z = i_0$

\[ i_0 = \frac{kT}{\hbar} e^{-\Delta G_0^\pm /RT} C^{surf} nF \]
• Therefore:

\[
\begin{align*}
\vec{i}_Z &= i_0 e^{\alpha nF(E-E_0)/RT} \\
|\vec{i}_Z| &= i_0 e^{(1-\alpha)nF(E-E_0)/RT}
\end{align*}
\]

• The net anodic reaction:

\[
\vec{i}_{\text{net}} = \vec{i}_Z - |\vec{i}_Z|
\]

\[
\vec{i}_{\text{net}} = i_0 \left[ e^{\alpha nF(E-E_0)/RT} - e^{(1-\alpha)nF(E-E_0)/RT} \right]
\]

• **Butler-Volmer equation**

• Important expression in electrode kinetics for both corroding and non-corroding metals

• **Electrochemical reaction depends on the electrode potential E**
Polarization curves

• Butler-Volmer eq. for $E_0 = -0.100$ V
• Tafel slopes of $dE/d\log|i| \pm 0.100$ V/decade
• Sufficiently high overvoltages – both cathodic and anodic polarization curves - linear regions
Tafel equation

- Linear region = negligible contribution of reverse reaction (Tafel regions)
- Can be extrapolated to obtain OCP current density $i_0$:
  \[ i = i_0 e^{\alpha n F (E - E_0) / RT} \]
- Sufficiently high overvoltage:
- Taking logarithms:
  \[ \log i = \log i_0 + \frac{\alpha n F}{2.303 RT} (E - E_0) \]
- Similar for cathodic side
Tafel equation

• Can be rewritten as Tafel equation:

\[ \eta_a = b_a \log \frac{i}{i_0} \]

• \( \eta_a \) - anodic overvoltage

• \( b_a \) - anodic Tafel slope:

\[ b_a = \frac{d E}{d \log i} = \frac{2.303 RT}{\alpha n F} \]

• Similar for cathodic side
Reversible and irreversible potentials

• **Reversible** – metal in solution of its own ions and rate of dissolution = rate of reverse deposition

• Rates are equal:
  – Dissolved ions $a = 1$ -> electrode potential = standard potential
  – Not $a = 1$ -> **not** Nernst equation

• **However in most cases:**
  – Solution does not initially contain ions of the metal
  – Solution contain foreign ions ($\text{Cl}^-, \text{SO}_4^{2-}$, ...)
  – Cations of different metals
  – Metal ions pass into solution continuously and irreversibly
Mixed potential theroy

• (1) Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions

• (2) at equilibrium, the total cathodic rate is equal to the total anodic rate (conservation of charge).
One reaction (anodic)

\[ i_0 = i_{0,a} = -i_{0,k} \]
Both anodic and cathodic
Both anodic and cathodic
Both anodic and cathodic
\[ i_{\text{net}} = i_0 \left[ e^{\alpha n F (E - E_0)/RT} - e^{(1-\alpha) n F (E - E_0)/RT} \right] \]

**Butler-Volmer equation**

\[ e^x = 1 + x + \frac{x^2}{2!} + \ldots \]
\[ e^{-x} = 1 - x + \frac{x^2}{2!} + \ldots \]

\[ i_{\text{net}} = i_{\text{corr}} \left\{ 1 + \frac{\alpha n F}{RT} \eta - \left[ 1 - \frac{(1-\alpha) n F}{RT} \eta \right] \right\} \]

\[ i_{\text{net}} = i_{\text{corr}} \left[ \frac{\alpha n F}{RT} + \frac{(1-\alpha) n F}{RT} \right] \eta \]

\[ i_{\text{net}} = 2.303 i_{\text{corr}} \left[ \frac{1}{b_a} + \frac{1}{-b_c} \right] \eta \]

**Tafel slope**

\[ b_a = \frac{d E}{d \log i} = \frac{2.303 RT}{\alpha n F} \]

\[ \left( \frac{d \eta}{d i_{\text{net}}} \right)_{\eta \to 0} = \frac{1}{2.303 \ i_{\text{corr}} \left( \frac{1}{b_a} + \frac{1}{|b_c|} \right)} \]

\[ \left( \frac{d \eta}{d i_{\text{net}}} \right)_{\eta \to 0} \equiv R_p \]
Activity, passivity, transpassivity

A

P

T

O₂

H₂

i_p

i_{kp}

E_{corr}

E_p

E_{pp}

E_{rp}

E_{dp}

E_t

E
Reaction control
Measurement

• Three electrode setup
  – 1 – sample
  – 2 – reference electrode
  – 3 – work electrode
  – 4 – salt bridge
  – 5 – glass frit
  – 6 – potentiostat
  – 7 – electrolyte
  – 8 – solution of ref. electrode own ions
Potentiodynamic test

- From cathodic to anodic
- Scan rate $\sim 1$ mV/s
- Tafel analysis

<table>
<thead>
<tr>
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<th>$E_{\text{cor}}$ [V]</th>
<th>$i_{\text{cor}}$ [mA/cm$^2$]</th>
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Electrochemical impedance spectroscopy

• Superposing small (10-20 mV) AC signal on the electrochemical system -> measuring the response
• Relaxation to new steady state -> relaxation time $\tau = \text{time constant}$
• Response to a characteristic frequency
• Electrochemical systems -> $\tau = RC$
• Impedance = resistance to AC current flow
• Measurement – frequency range 0.01-100 000 Hz
Metal/solution interface

- $C_{dl}$ - double layer capacitance
- $R_P$ - charge transfer resistance
- $R_S$ - solution resistance

\[
Z = R_S + \frac{R_P}{1 + j\omega R_P C_{dl}}
\]
Nyquist plot / Bode plot

\[ \omega_{\text{max}} = \frac{1}{R_p C_{\text{dl}}} \]