CCMX 2023 Summer School – Characterization of Materials

Corrosion

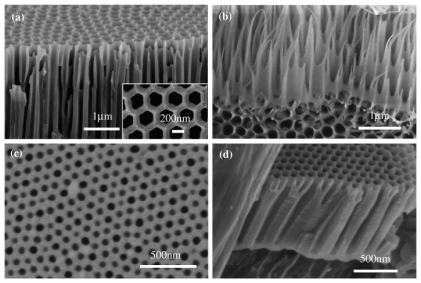
Anna Igual Munoz
Tribology and Interfacial Chemsitry Lab

1. Main concepts
2. Corrosion reactions
3. The electrode potential
4. Forms of corrosion
5. Determination of corrosion rate

Definition of corrosion

- Corrosion is the disintegration of a material into its constituent atoms due to chemical reactions with its surroundings. (Wikipedia)

- Corrosion is an irreversible interfacial reaction of a material with its environment, resulting in the loss of the material or in the dissolving of one of the constituents of the environment into the material. (ISO Standard)



Economic importance of corrosion

- Direct losses: replacement of corroded materials and of equipment ruined by corrosion

  5 tones of steel lost by corrosion every second

- Indirect losses: cost of repair and loss of production

- Cost of corrosion protection : Use of more expensive corrosion-resistant materials, application of surface coatings, cathodic protection systems

- Cost of corrosion prevention : maintenance, inspections, corrosion prevention by design

Corrosion as a system property

Corrosion depends on the combination of:

- - Material
  composition, structure, surface
- - Environment
  oxidizing agents, aggressive ions, ions, adsorbing species, complexing species
- - Physical parameters
  temperature, flow conditions, stresses, contact with other metals

1. Main concepts

2. Corrosion reactions

Corrosion systems

Cathodic and anodic reactions

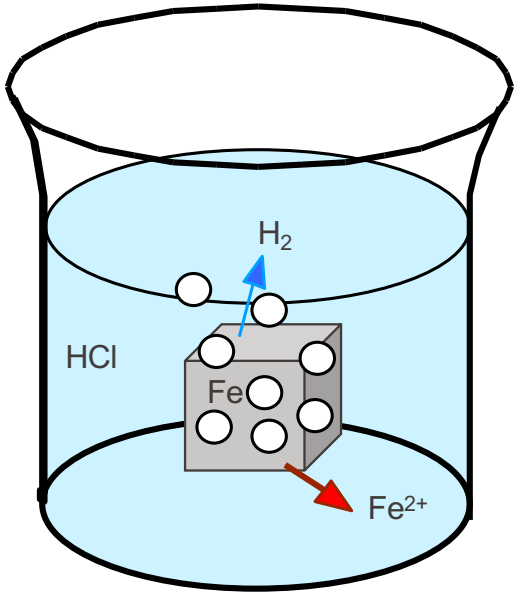
Corrosion products

3. The electrode potential

4. Forms of corrosion

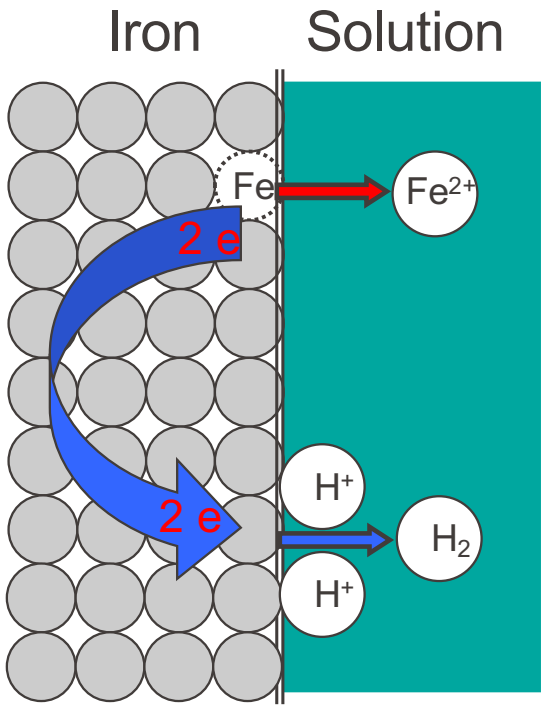
5. Determination of corrosion rate

Corrosion of iron in hydrochloric acid



$$Fe\,(s) + 2\,H^{+}\,(aq) \Rightarrow Fe^{2+}\,(aq) + H_2\,(g)$$

Electrochemical reactions



Oxidation half-reaction

$Fe \rightarrow Fe^{2+} + 2\ e^-$

Reduction half-reaction

$2H^+ + 2e^- \rightarrow H_2$

Typical oxidizing agents encountered in corrosion

- Acidic solutions (pH < 7):

  Oxidizing agent: proton H^+

  $2H^+ + 2e^- \Rightarrow H_2$

- Solutions in contact with air:

  Oxidizing agent: oxygen molecules O_2 dissolved in the solution

  $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

Example: corrosion of pillars

- Steel (Fe) pillars

  Oxidation: $Fe \Rightarrow Fe^{2+} + 2e^-$

- Natural water:

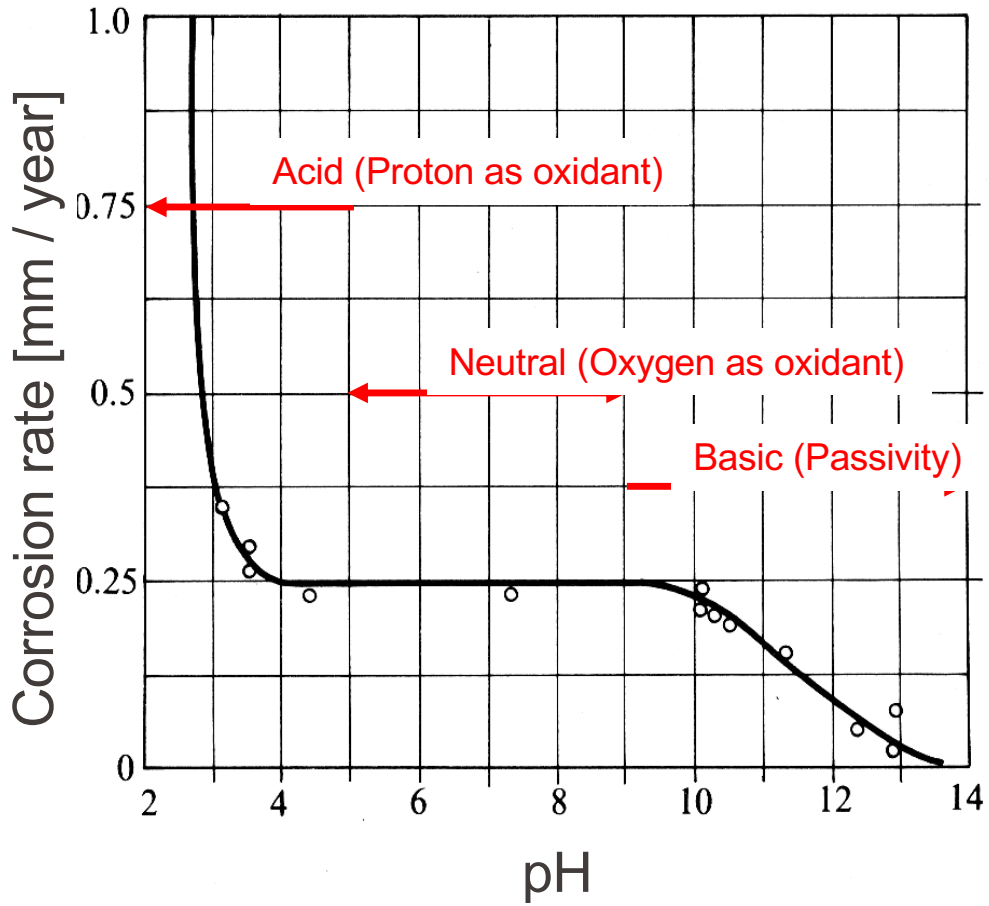
  H^+ concentration $\approx 10^{-6}$ M

  O_2 concentration $\approx 10^{-4}$ M

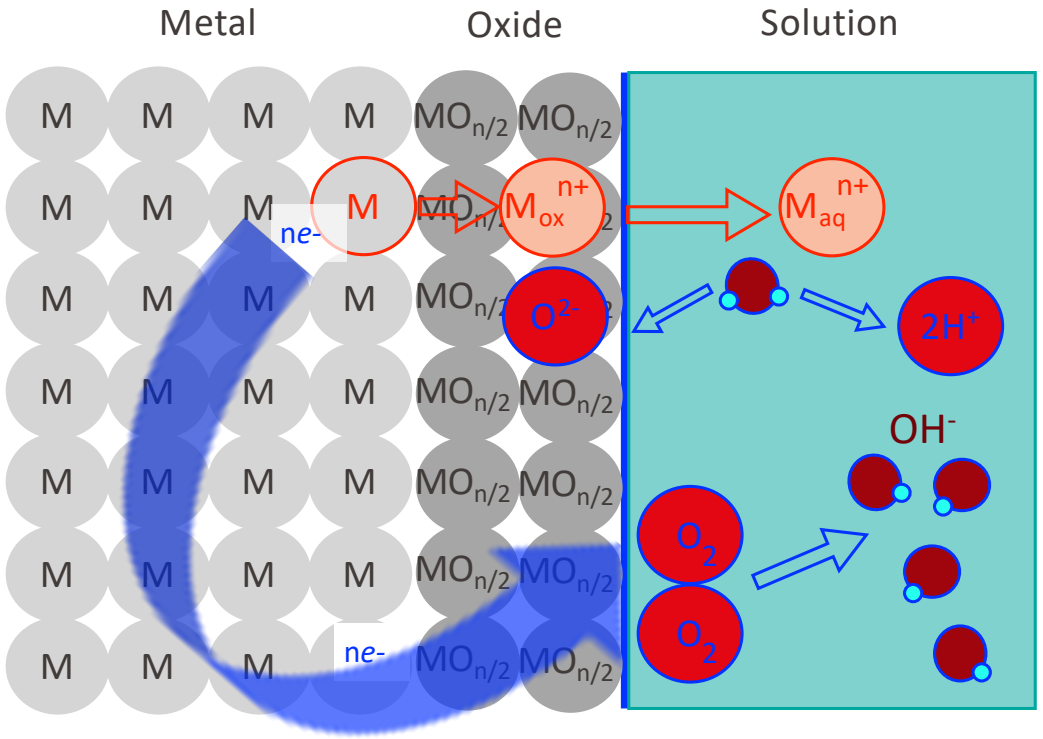
  Reduction: $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

- Global reaction: $2\,Fe + O_2 + 2H_2O \Rightarrow 2\,Fe^{2+} + 4OH^-$

Corrosion rate of iron changes with solution acidity



Electrochemical reactions in an actively and passively corroding metal



2-step oxidation reaction:

$M + nH_2O \Rightarrow MO_{n/2} + nH^+ + ne^-$ Oxide formation

$MO_{n/2} + nH^+ \Rightarrow M^{n+} + nH_2O$ Oxide dissolution

$M \Rightarrow M^{+n} + ne^-$

Reduction reaction:

$O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

Corrosion products

- Dissolved ions

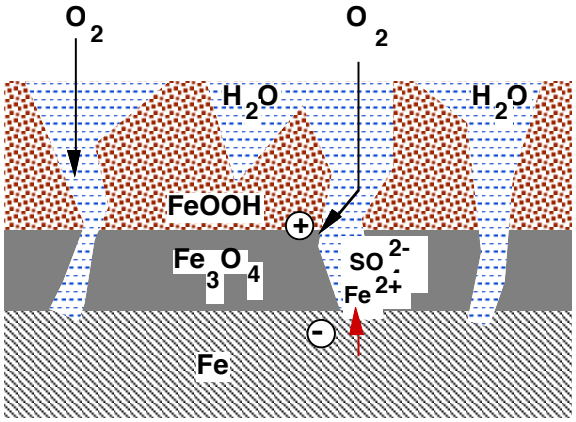
  Example: acid corrosion of iron: $Fe \Rightarrow Fe^{2+} + 2e^-$

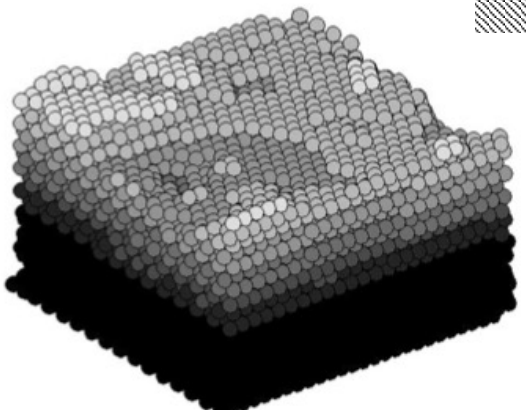
- Non compact films

  Examples: rust, copper patina

- Compact thin films

  Example: passive film on aluminium





oxide

metal

Consequences of the electrochemical nature of corrosion: Faraday's law and corrosion rate

- $M \Rightarrow M^{n+} + n\ e^-$

  $v_{cor} = i_{oxidation,\ metal} / n F$

v_{cor} = corrosion rate in (mol/cm^{2}s) F = Faraday constant (96500 C/mol)

- Conversion to engineering units:

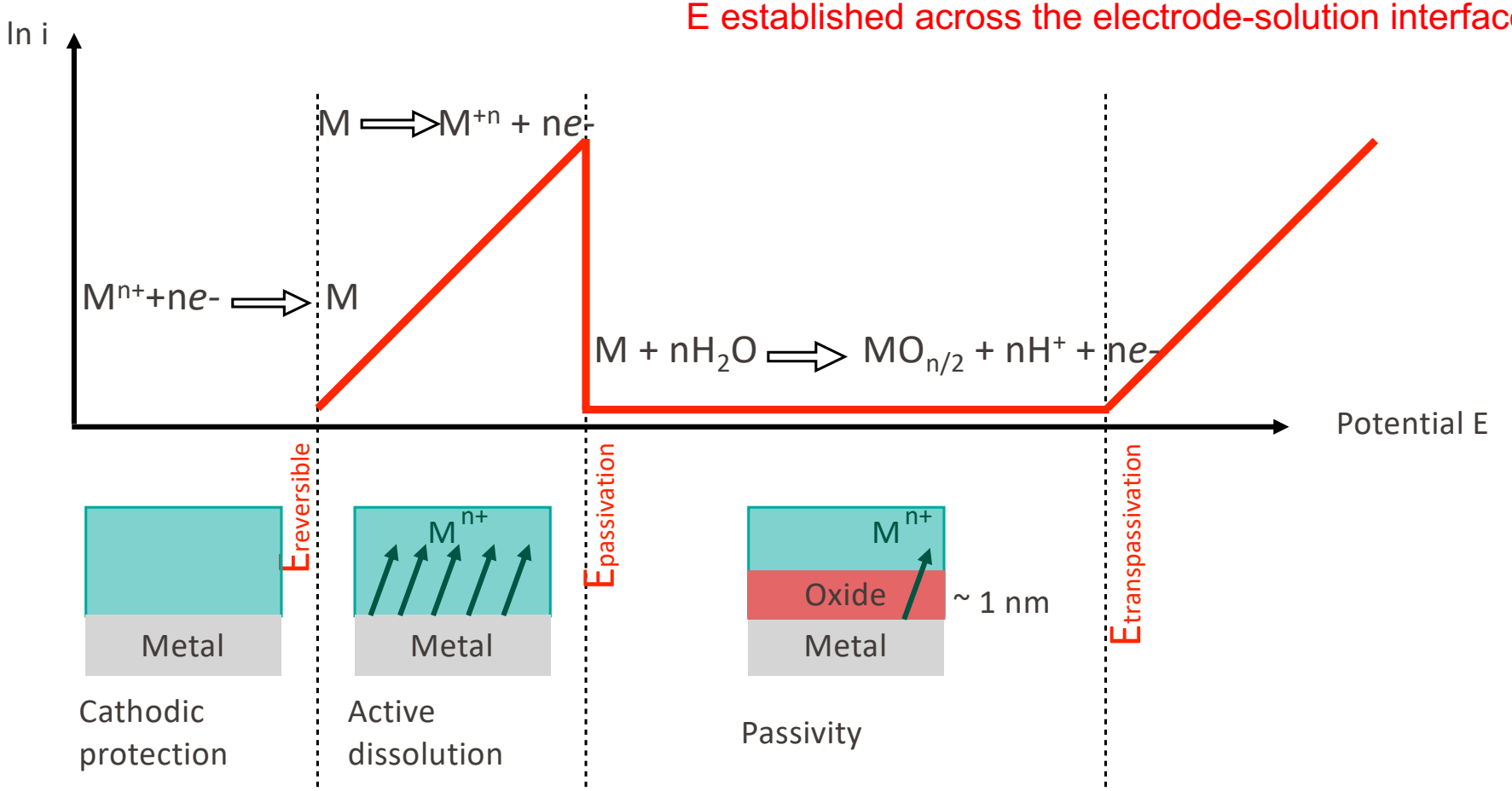
  $v_{cor,m}$ = corrosion rate in (g cm^{-2}s^{-1}) = M v_{cor}

  $v_{cor,l}$ = corrosion rate in (cm s^{-1}) = M ρ^{-1} v_{cor}

M = molar mass of metal (g/mol) ρ = density of metal (g/cm^3)

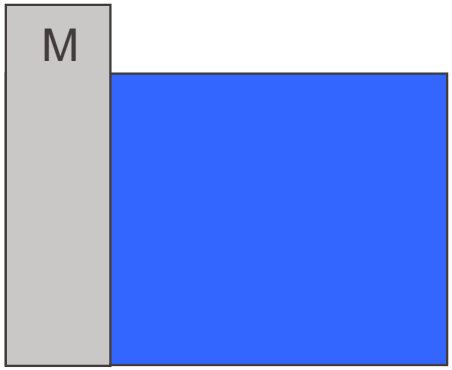
Consequences of the electrochemical nature of corrosion: corrosion versus electrode potential

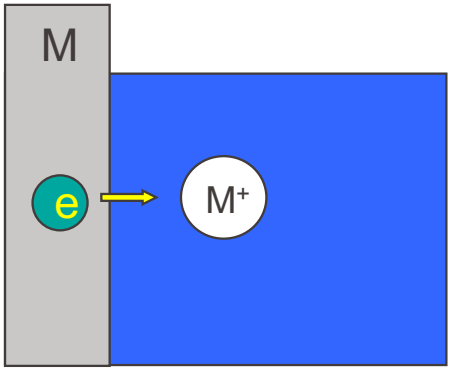
Corrosion reactions are driven by the electrode potential E established across the electrode-solution interface

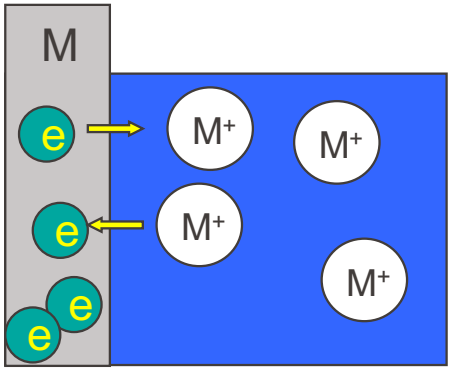


1. Main concepts
2. Corrosion reactions
3. **The electrode potential**
4. Forms of corrosion
5. Determination of corrosion rate

Electrode potential

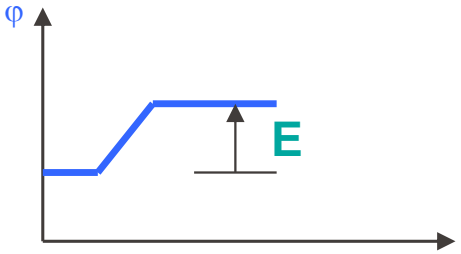


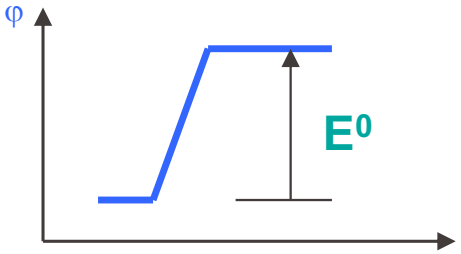




M -> M⁺ + e

M = M⁺ + e





Non equilibrium

Equilibrium: reversible potential E_{rev}

Standard equilibrium potentials E^0 of electrode reactions

Electrode reaction	E^0 (V)
$Mg^{2+} + 2e^- \leftrightarrow Mg$	-3.045
$Al^{3+} + 3e^- \leftrightarrow Al$	-1.670
$Ti^{2+} + 2e^- \leftrightarrow Ti$	-1.630
$Cr^{3+} + 3e^- \leftrightarrow Cr$	-0.900
$Zn^{2+} + 2e^- \leftrightarrow Zn$	-0.760
$Fe^{2+} + 2e^- \leftrightarrow Fe$	-0.440
$Ni^{2+} + 2e^- \leftrightarrow Ni$	-0.257
$2H^+ + 2e^- \leftrightarrow H_2$	0.000
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.340
$Ag^+ + e^- \leftrightarrow Ag$	0.799

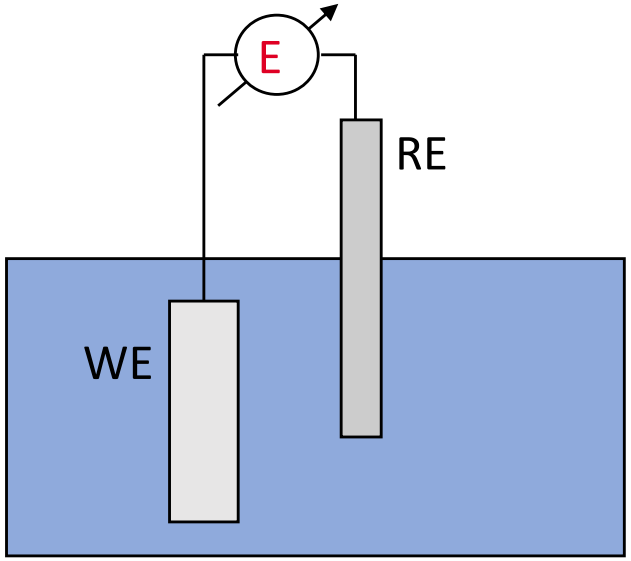
$$E^0 = - \Delta G^0 / n F$$

Conditions:

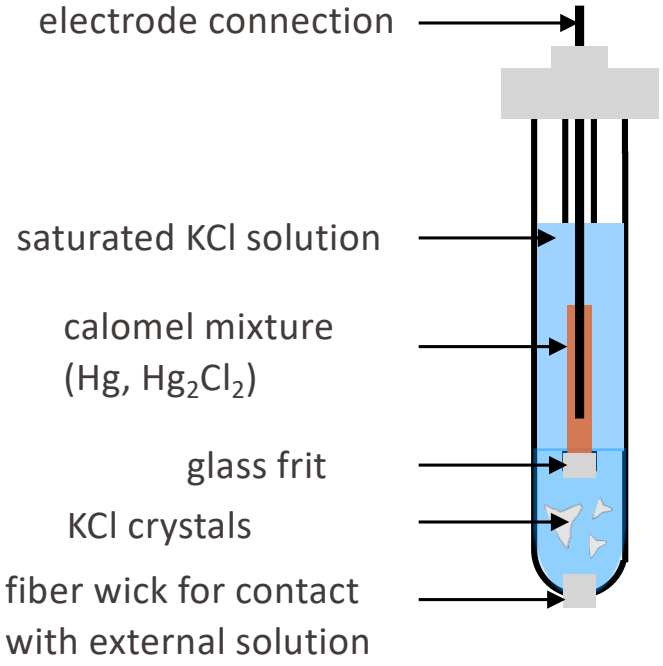
25°C
1 M activity of soluble species
1 atm activity of gaseous species

Open circuit potential (OCP)

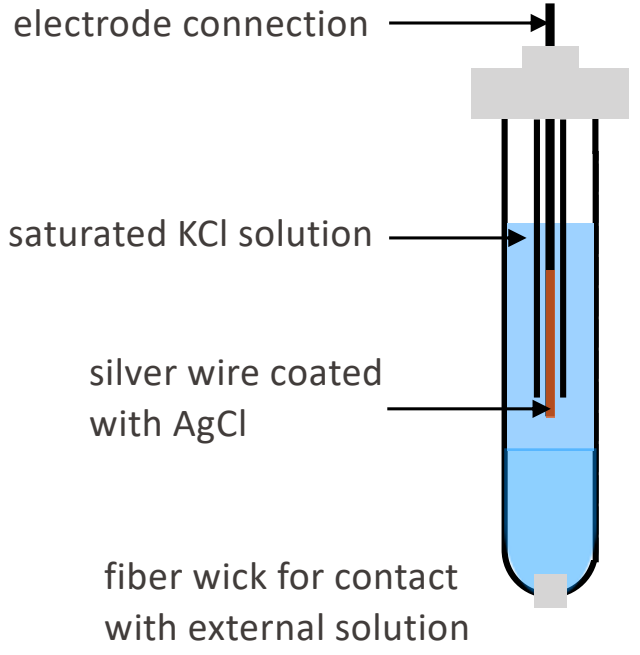
High impedance voltmeter



Calomel electrode (SCE)

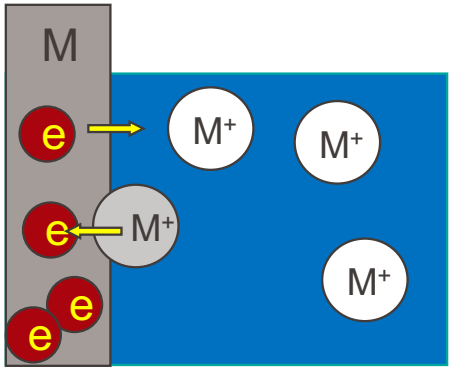


Ag/AgCl (SSE)

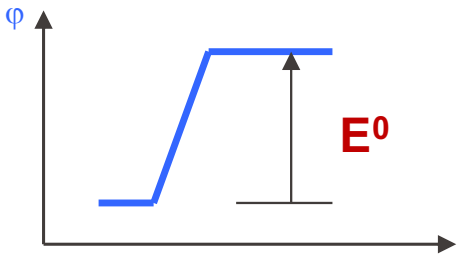


OCP vs Equilibrium potential

One reaction occurring on the electrode: simple electrode

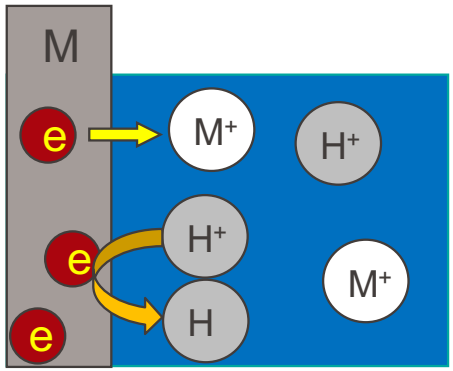


$M \leftrightarrows M^+ + e$



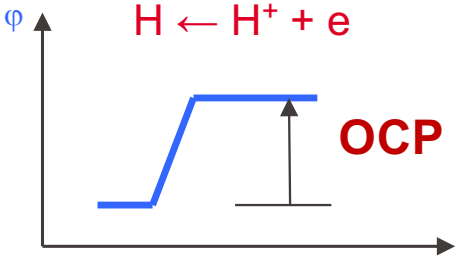
Equilibrium potential E^0

Two or more reactions occurring on the electrode: mixed electrode



$M \rightarrow M^+ + e$

$H \leftarrow H^+ + e$



Open Circuit Potential OCP

Equilibrium and OCP potentials

Standard (reversible) potential

Magnesium -3.045 V

Aluminium -1.67 V

Titanium -1.63 V

Chromium -0.90 V

Zinc -0.760 V

Iron -0.440 V

Nickel -0.257 V

Copper 0.340 V

Silver 0.799 V

Corrosion potential in flowing aerated seawater (average)

Magnesium -1.35 V

Zinc -0.75 V

Aluminum -0.65 V

Iron -0.40 V

Copper -0.1 V

Nickel 0.1 V

Silver 0.1 V

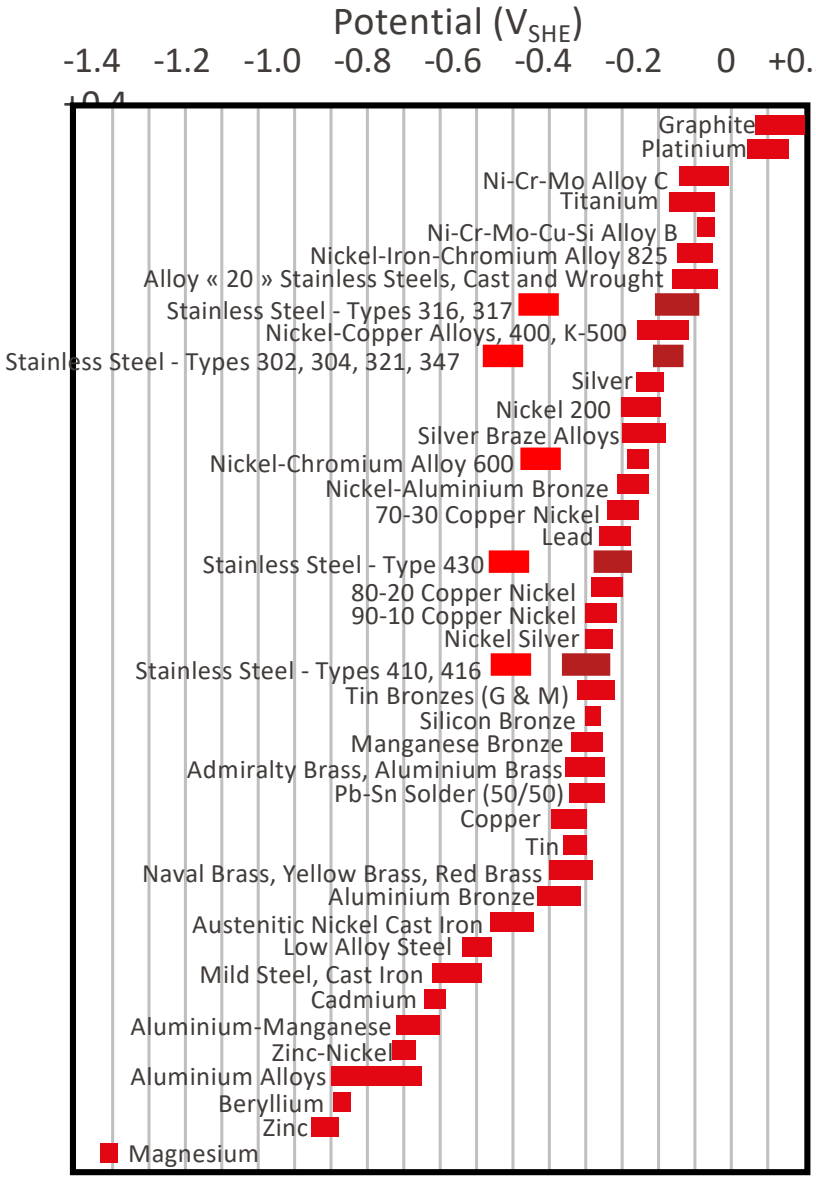
Titanium 0.25 V

Chromium 0.35 V

OCP of titanium and its alloys

Influence of	Material	Environment	OCP (V_{SHE})
Acidity	Ti CP	H_2SO_4 0.05 M H_2SO_4 0.5 M	-0.35 -0.69
Chemistry	Ti6Al4V	PBS* PBS +albumin PBS + collagen	-0.18 -0.32 -0.41
Oxidising agents	Ti6Al4V	Calf serum Calf serum + 0.1% H_2O_2	+0.19 +0.3
Alloying elements	Ti Ti 0.05% Pd	NaCl 4.3M	-0.51 -0.03

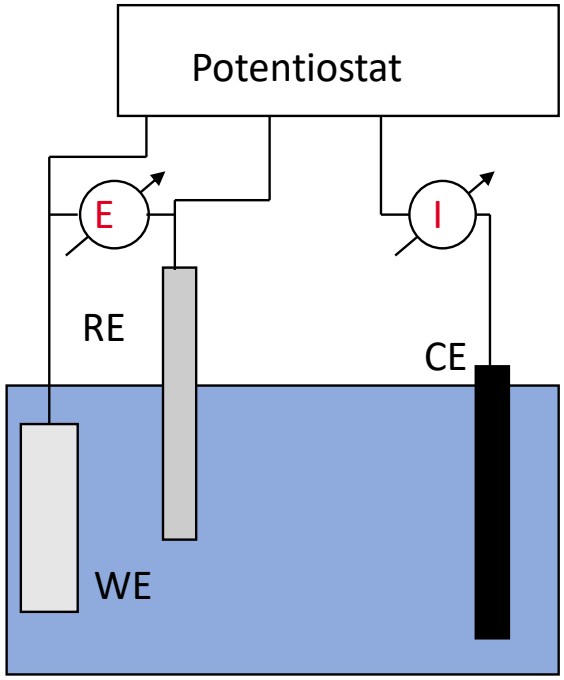
Galvanic series in seawater

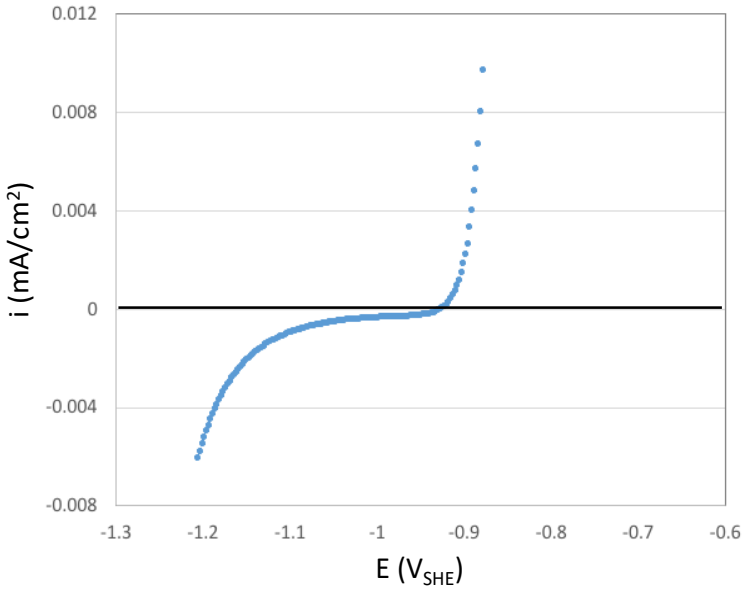


Active state

Passive state

Corrosion potential (Ecorr)

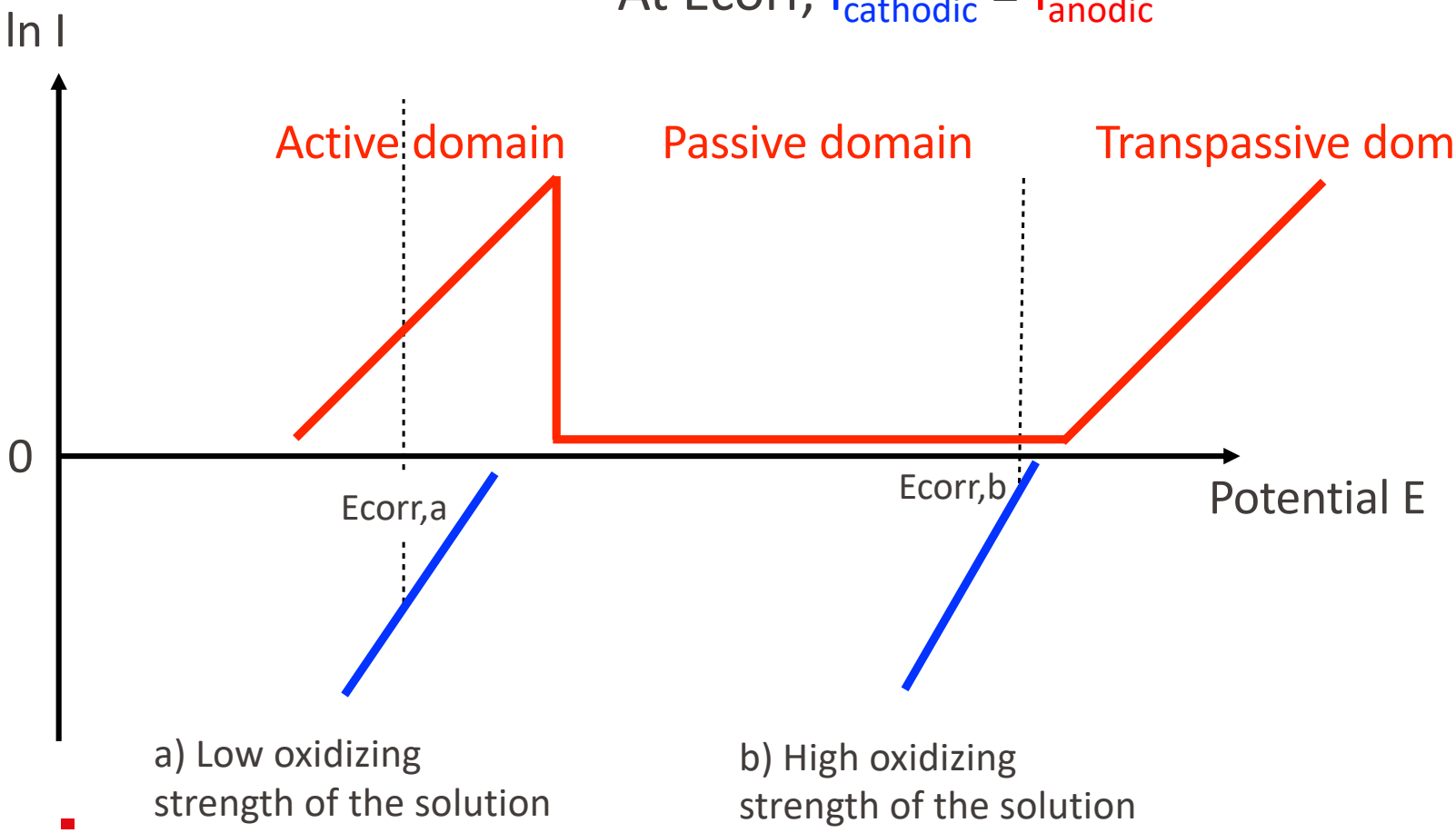




Polarization curve E-i of Sn in citrate buffer, pH 4.5

Corrosion potential

At Ecorr, $I_{cathodic} = I_{anodic}$



a) Low oxidizing strength of the solution

b) High oxidizing strength of the solution

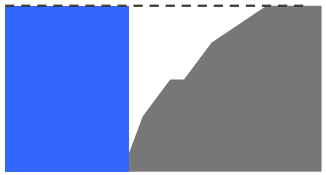
— Evans diagram of the anodic reaction, i.e. the metal oxidation

— Evans diagaram of the cathodic reaction, for exemple the reduction of oxygen

1. Main concepts
2. Corrosion reactions
3. The electrode potential
4. **Forms of corrosion**
5. Determination of corrosion rate

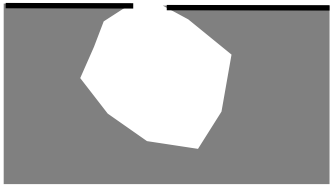
Eight types of corrosion: Fontana and Green

uniform corrosion

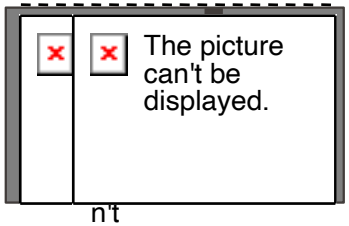


galvanic corrosion

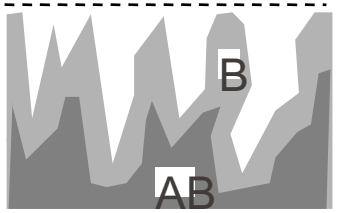
crevice corrosion



pitting corrosion

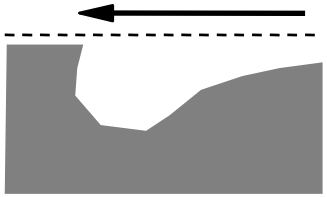


intergranular corrosion



selective leaching

flow



erosion corrosion

stress corrosion cracking

Eight types of corrosion: uniform corrosion

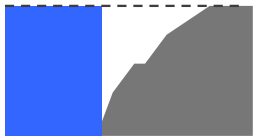
uniform corrosion

Material thinning due to chemical reaction between the metal and the environment.

Wet corrosion
(immersion in the corrosive fluid)

Atmospheric corrosion
(water condensation film)

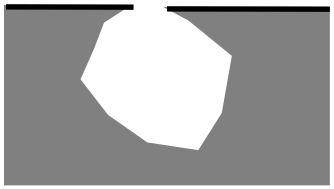
Eight types of corrosion: localized corrosion



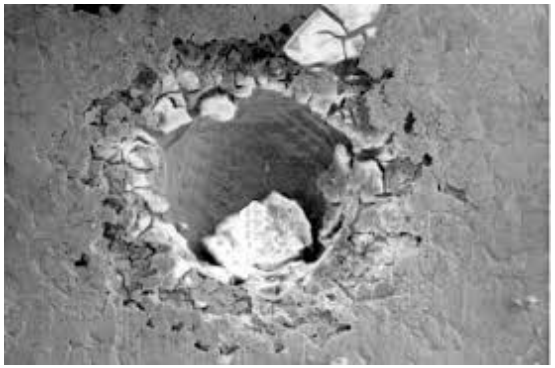
galvanic corrosion

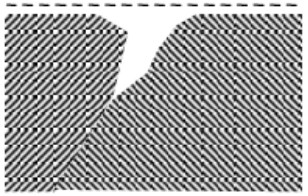
crevice corrosion

Eight types of corrosion: localized corrosion



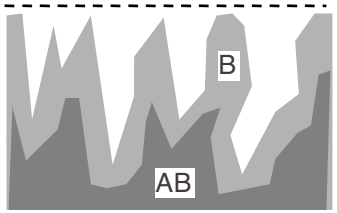
pitting corrosion





Intergranular corrosion

Eight types of corrosion: selective

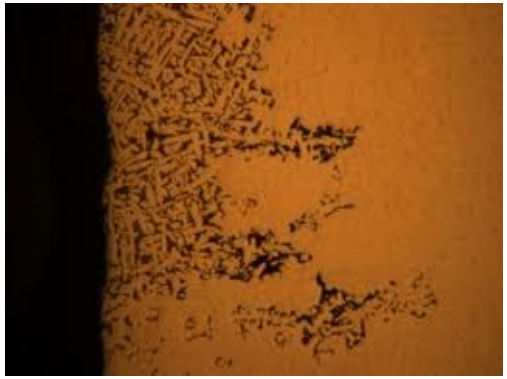


selective leaching

In an alloy, selective dissolution of the less noble (lowest corrosion potential) component. It generates porosity (loss of mechanical strength) and changes in colour.

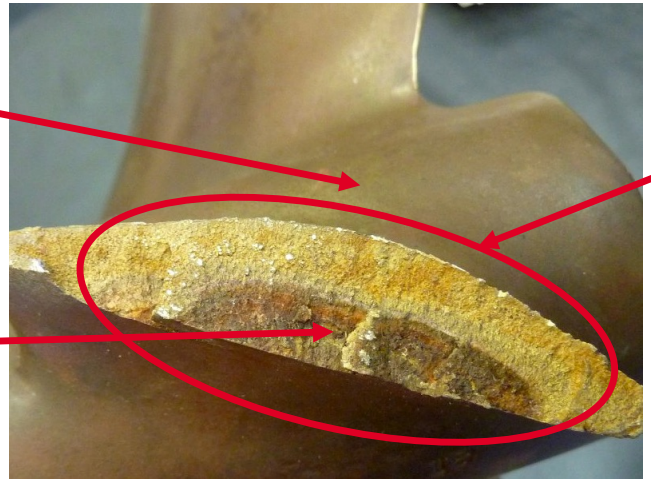
Examples:

- *Dezinfication of brass (Cu-Zn) alloy*
- *Loss of copper in carat gold alloys and thus of aesthetic properties*



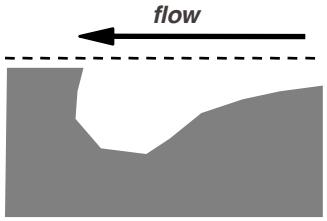
Brass propeller

Zone weakened by selective dissolution of Zn (red colour of copper)



Fracture of the blade

Eight types of corrosion: corrosion under mechanical stresses



erosion corrosion

stress corrosion cracking

1. Main concepts
2. Corrosion reactions
3. The electrode potential
4. Forms of corrosion
5. **Determination of corrosion rate**

Simple immersion tests

Samples of defined weight are kept immersed for a certain time.
Corrosion is measured by weight loss or by dimensional changes.

+ *Simple*
+ *Close to reality*
- *Changes of electrolyte (evaporation, accumulation of corrosion products) not controlled.*
- *Requires removal of the corrosion products*
- *No real time measurement*

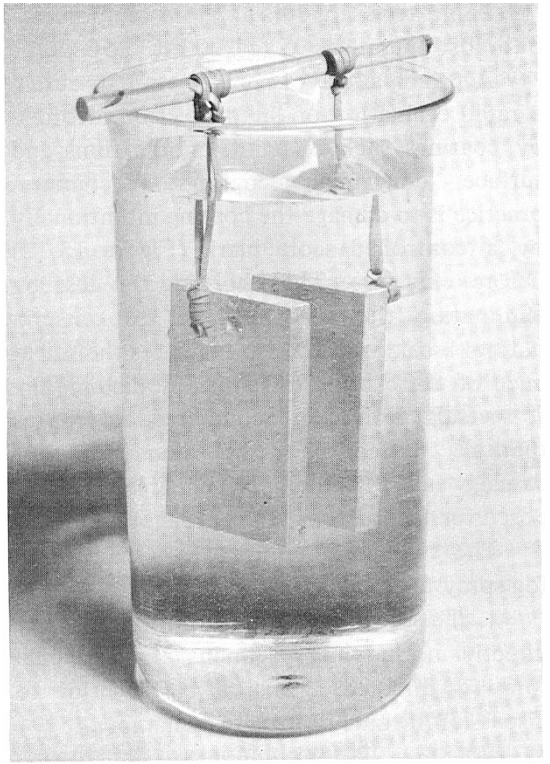
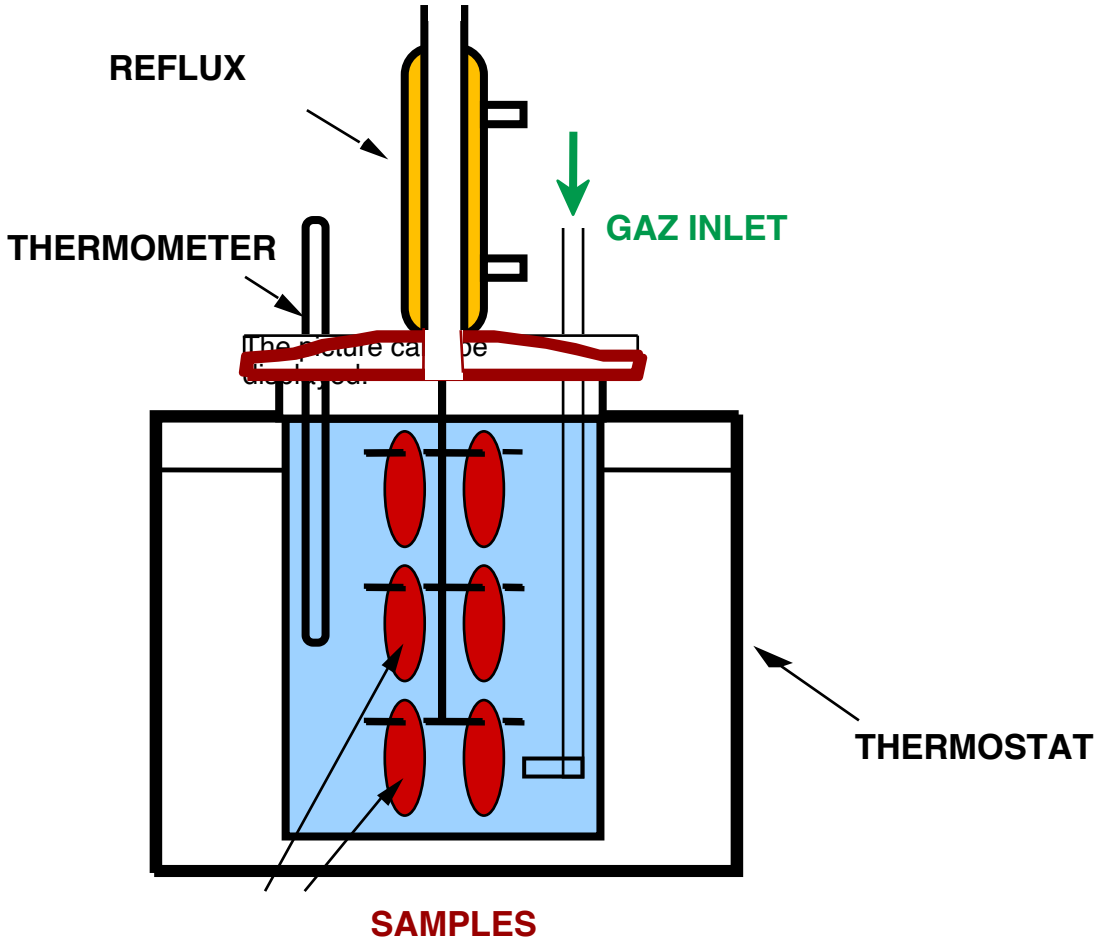


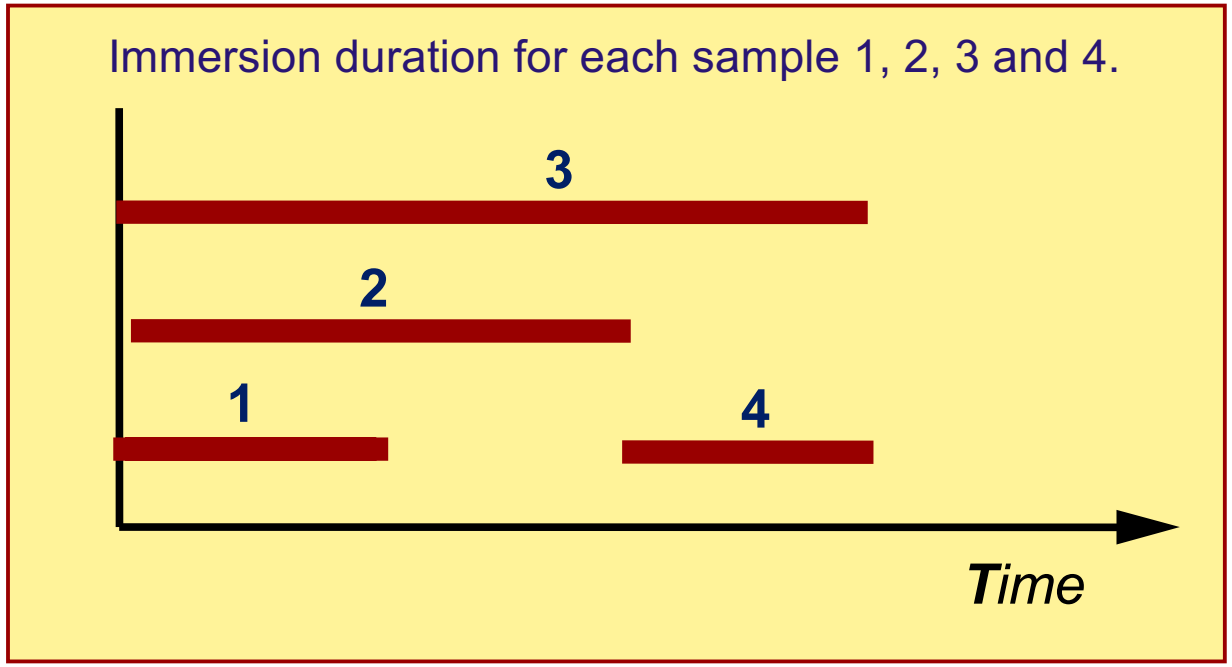
FIGURE 15-10 — Beaker test exposing two specimens. Note specimens are electrically insulated from each other and that supporting rod is suspended from a nonconductor.

NACE Basic Corrosion course,
A. deS. Brasunas Ed, NACE Houston 1970

Controlled immersion tests



4 sample immersion test sequence



Samples 1,2 and 3 for assessing corrosion rate evolution during time.
Comparison Sample 1 vs 4 for assessing effect of solution ageing.

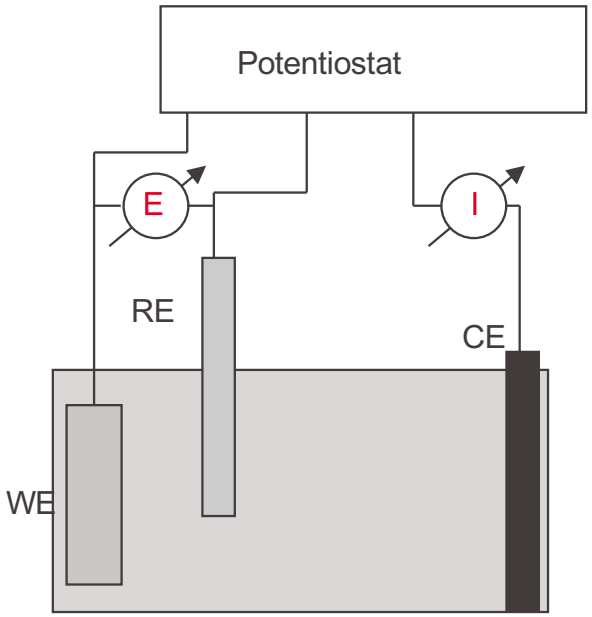
Real scale atmospheric corrosion tests

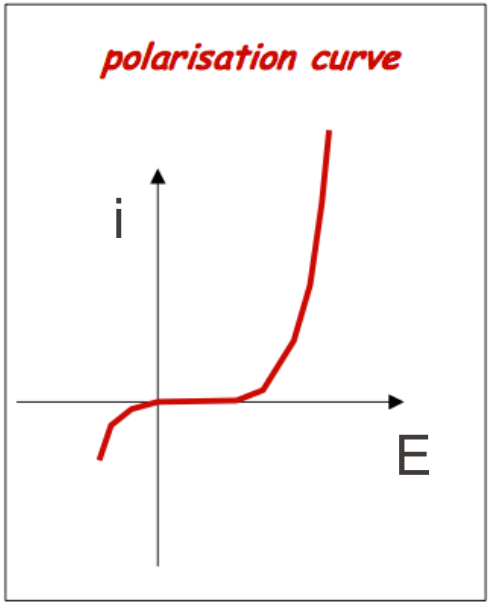
http://www.swerea.se/en/areas-of-expertise/corrosion-surfacing-technology/corrosion/atmospheric-corrosion (2016)

Potentiostatic method for measurement of polarisation curves

POTENTIOSTAT: electronic device that maintains a selected potential E between RE and WE by passing an appropriate current I between WE and CE.

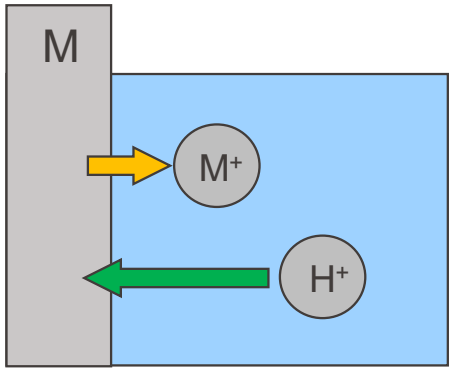
RE: reference electrode, CE: counter electrode, WE: working electrode





Polarisation (E-Ecor) of a mixed electrode (corrosion of iron in acid)

$E < E_{cor}$



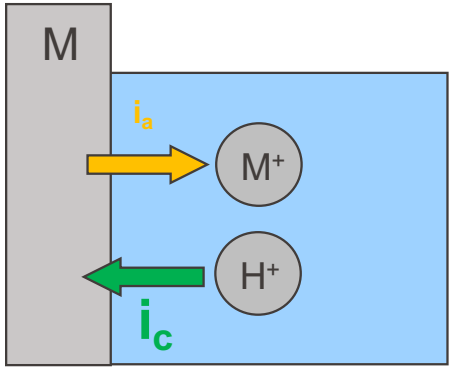
$M \rightarrow M^+ + e$

$H^+ + e \longrightarrow H$

Cathodic polarisation

$i_a < - i_c$

$E = E_{cor}$



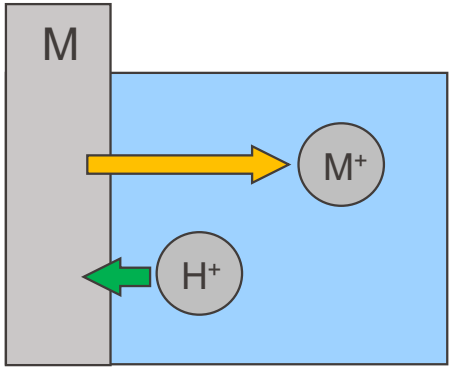
$M \longrightarrow M^+ + e$

$H^+ + e \longrightarrow H$

No polarisation

$i_a = - i_c$

$E > E_{cor}$



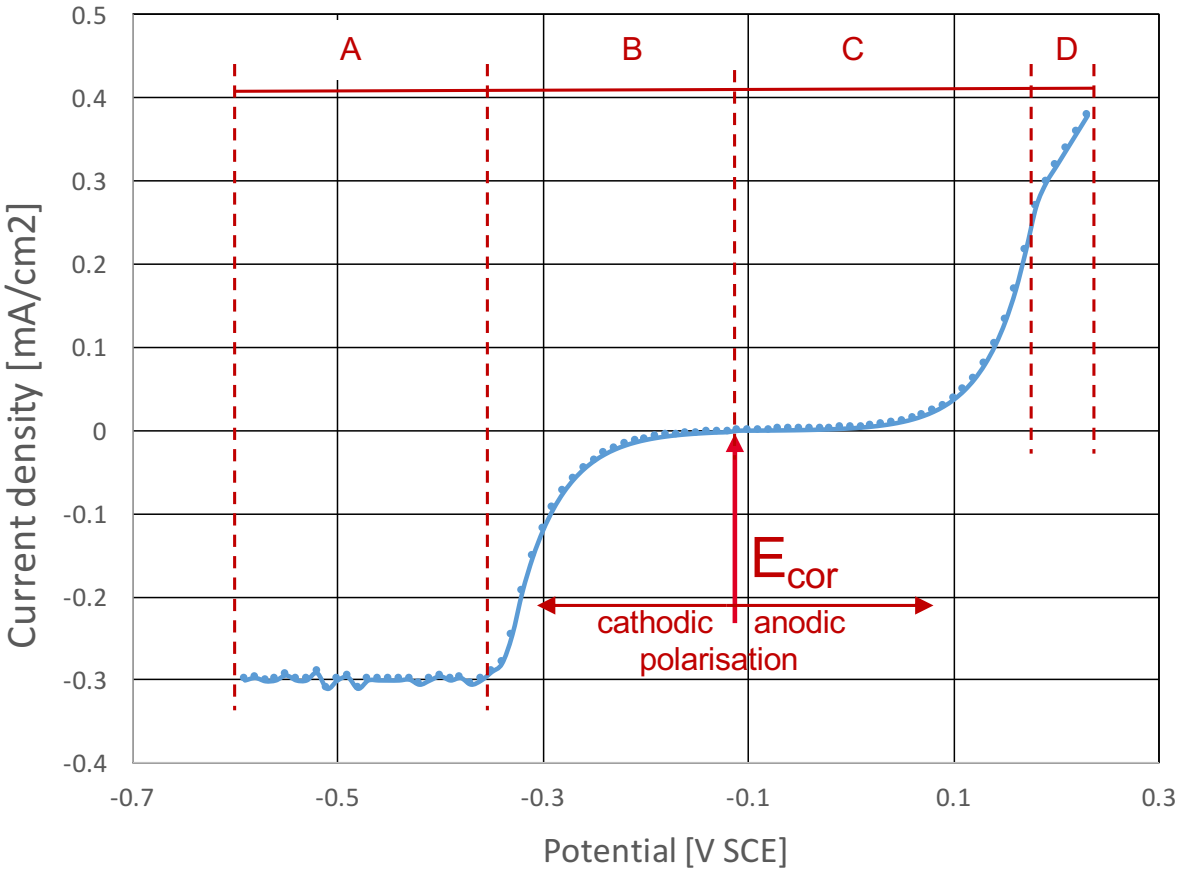
$M \longrightarrow M^+ + e$

$H^+ + e \rightarrow H$

Anodic polarisation

$i_a > - i_c$

Polarisation curve of copper in NaCl solution



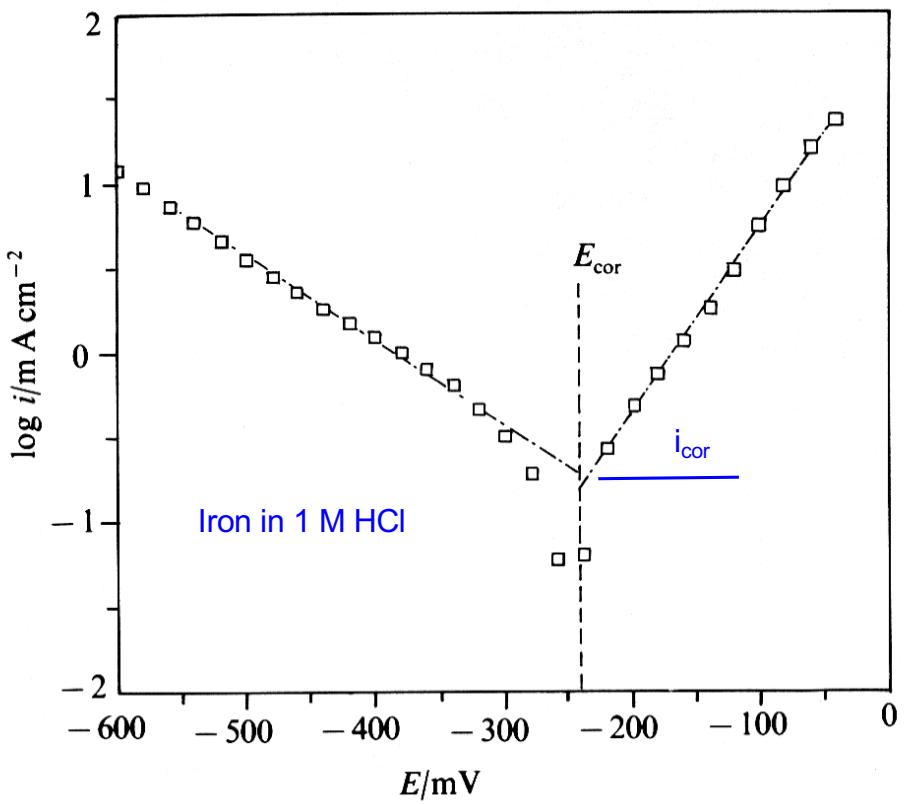
A: Constant current independent on potential.

B: Exponential increase in cathodic current.

C: Exponential increase in anodic current.

D: Linear increase in current.

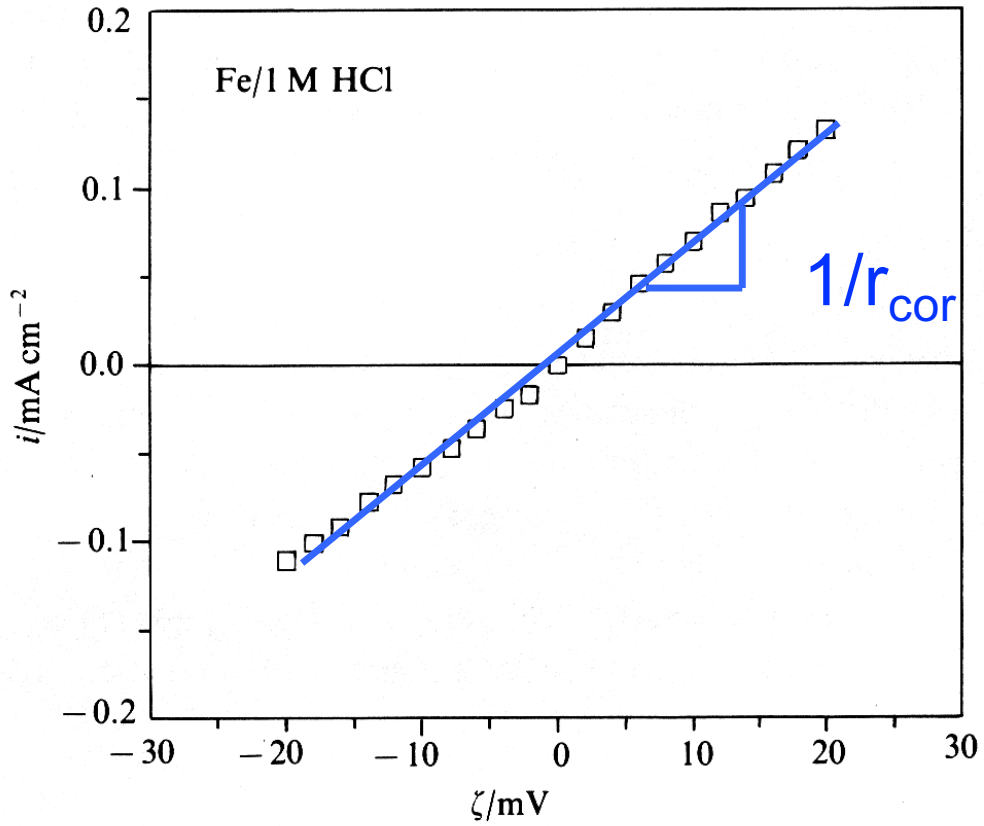
Determination of corrosion rates from polarisation curves



I_{cor} is determined by the extrapolation of the cathodic and anodic linear section of the polarisation curve.

Linear domains are usually observed for polarisations larger than 100 mV.

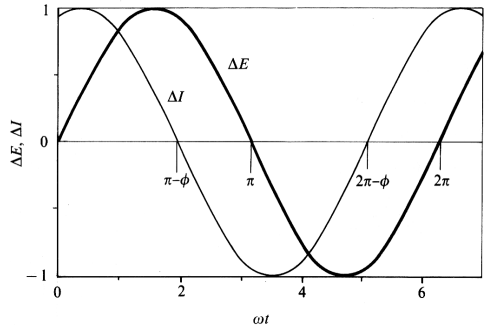
Polarisation curve of iron measured close to the corrosion potential



$$i_{cor} = \frac{\beta_a \beta_c}{r_{cor}(\beta_a + \beta_c)}$$

Other electrochemical techniques

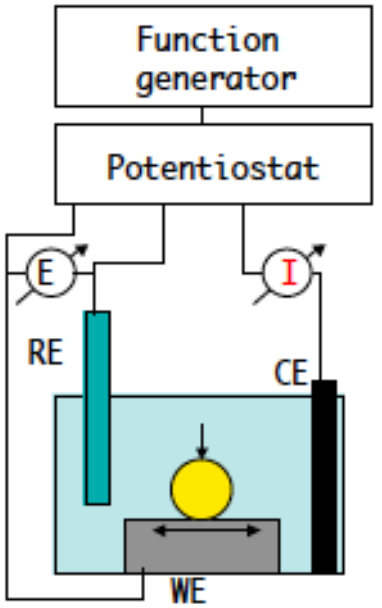
- Electrochemical Impedance Spectroscopy
  - Principle: measurement the response in current I to a sinusoidal potential E signal as a function of frequency



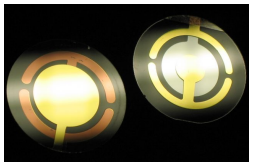
$E(t) = E_0 \sin(\omega t)$

$I(t) = I_0 \sin(\omega t - \phi)$

$$Z = \frac{E(t)}{I(t)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$



- Electrochemical Quartz Crystal Microbalance (EQCM)
- Principle: measurement of the change in frequency of a quartz crystal resonator



$$\Delta f_m = \frac{-2f_0}{\sqrt{\rho_q \mu_q}} \Delta m = -C_f \Delta m$$

Take-home messages

- Corrosion is a system property that depends on the combination of material, environment and physical parameters
- Corrosion is of electrochemical nature and it is determined by the type and kinetics of oxidation (i.e. $Fe \rightarrow Fe^{+2} + 2e^-$) and reduction (i.e. $2H^+ + 2e^- \rightarrow H_2$) reactions
- The corrosion reactions are driven by the electrode potential established at the electrode/solution interface and the reaction rate is given by the current

References

Corrosion and surface chemistry of metals (1st Edition)
Authors: Dieter Landolt
ISBN: 978-2-940222-11-7