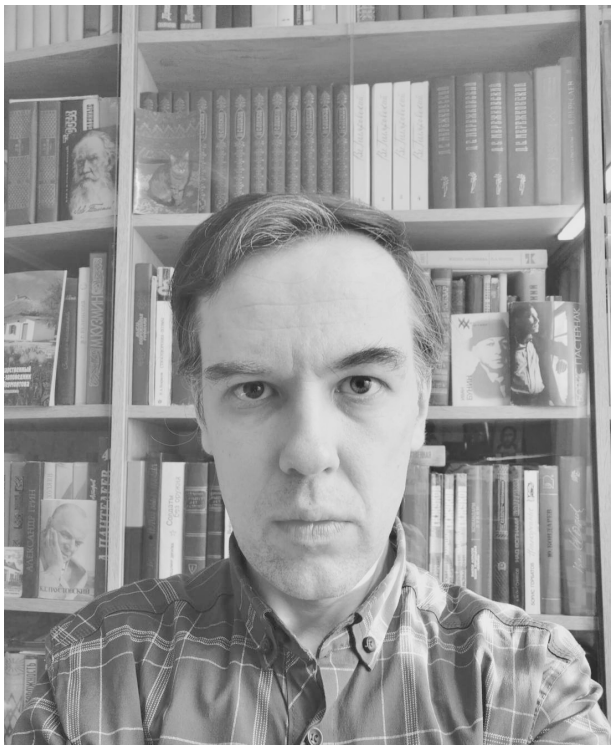
General & Inorganic Chemistry Department,
NTU "KhPI"

Corrosion of Metals



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Corrosion: basic definitions

- Corrosion is a spontaneous process of metal destruction due to its physicochemical interaction with the environment
- Classification by nature of destruction:
  - local corrosion
  - uniform corrosion
- The rate of corrosion is the most important indicator
- Classification by corrosion mechanism

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Chemical corrosion

- Corrosion occurs on the place of contact of the metal with the oxidizer
  - there is no electrical current
  - corrosion products are formed on the place of contact directly

Examples:
corrosion in gaseous environment;
non-electrolyte solutions
(oil)

- A thermodynamic prediction using ΔG, for example $3Fe_{(cr)} + 2O_{2(g)} = Fe_3O_{4(cr)}$, $\Delta G = -1014$ kJ

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  - recall: the reactions having $\Delta G < 0$ occur
  - corrosion products form a barrier on the metal surface
  - this prediction does not allow to estimate the corrosion rate

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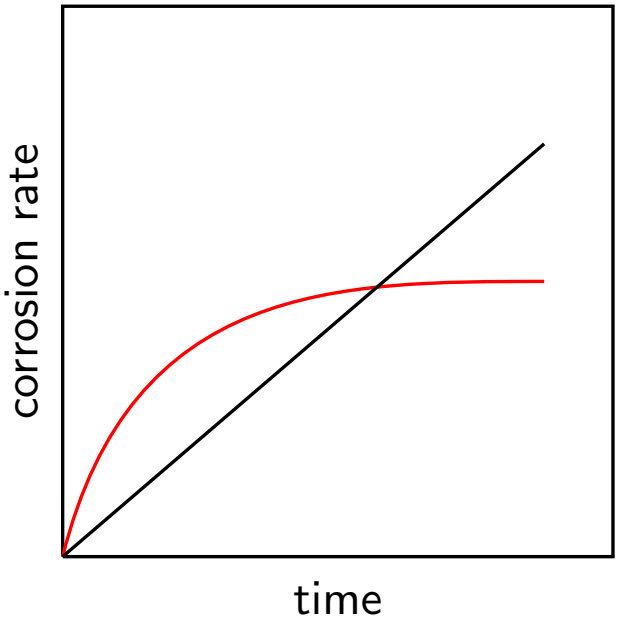

- The corrosion rate is determined by the nature of the layer of corrosion products
  a loose layer:
  $v_{corr} = kt \quad (Fe(OH)_3, Na_2O)$
  a continuous layer:
  $v_{corr} = k \ln t \quad (Cr_2O_3, Al_2O_3)$
- Thickness of the layer: thin (under 40 nm), medium (40-60 nm), thick (more than 60 nm)
- The best protection is a continuous layer of medium thickness
- Rising of T:

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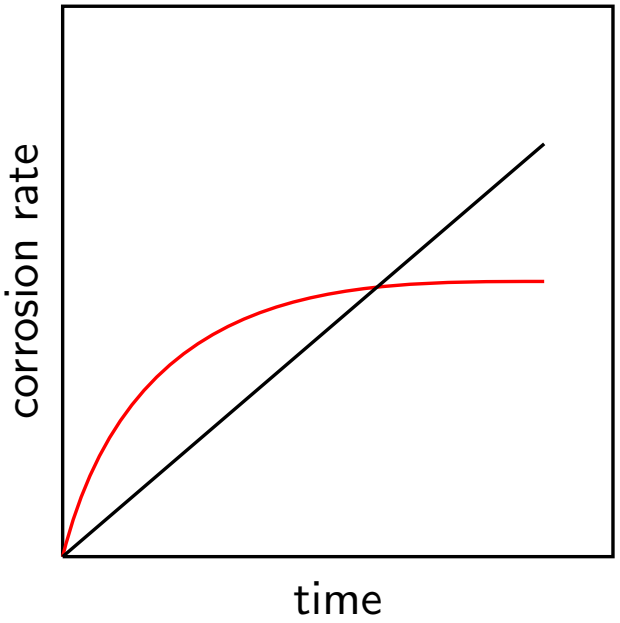

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  - The corrosion rate increases with the temperature in the case of a continuous layer
  - The mechanism of corrosion can change (copper in nitric acid for example) $Cu_2O \rightleftarrows H_2O$

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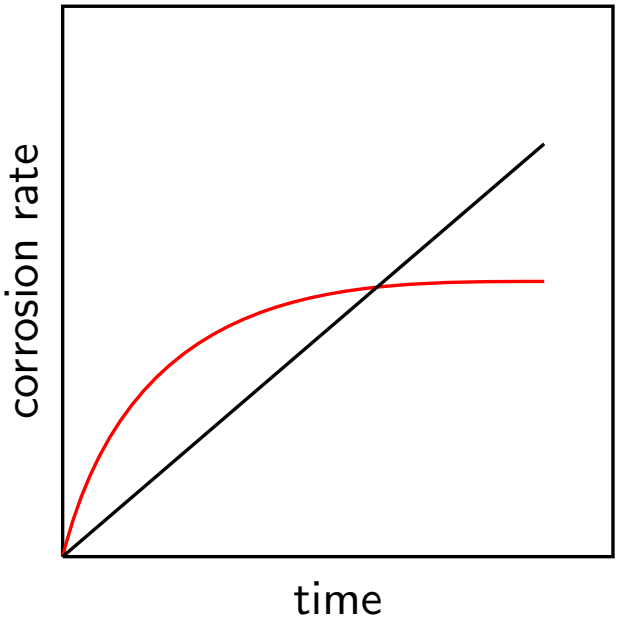

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- Rising of T:
  - The corrosion rate increases with the temperature by the parabolic law
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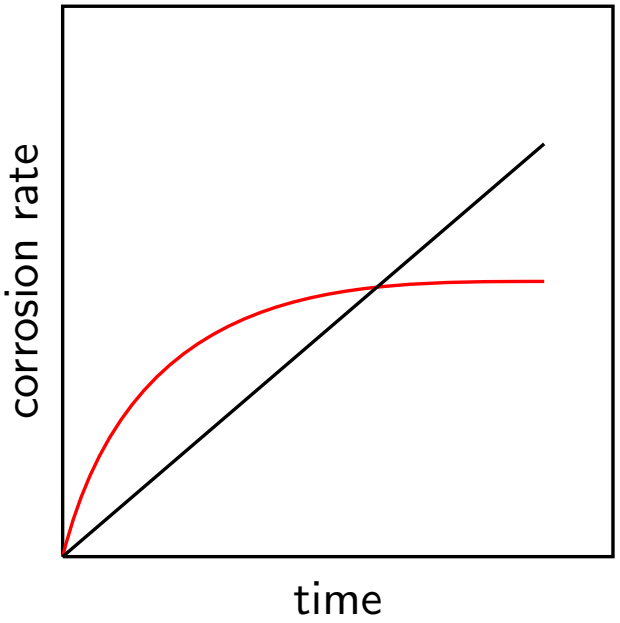

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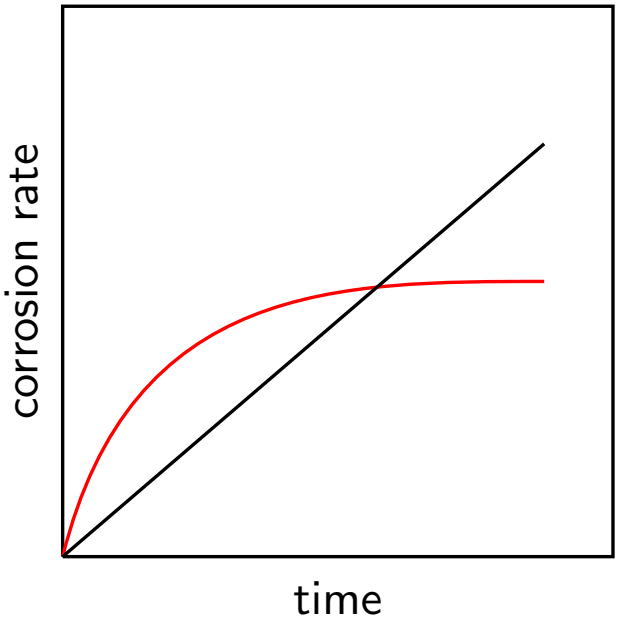
- 

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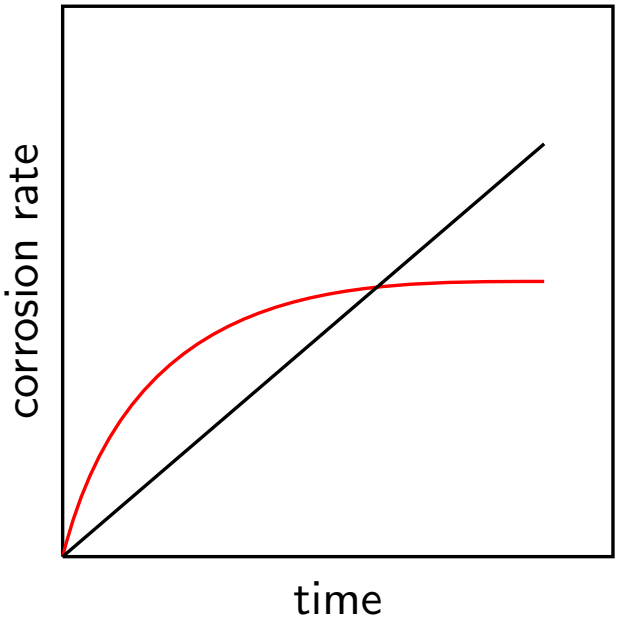
- 

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Electrochemical corrosion: a general description

- It occurs in conductive media (soil, solutions etc)
  - The oxidizer and the reductant are separated
  - just like in galvanic cell
- A corrosion galvanic cell (or corrosion cell, CC)
- The estimation of corrosion possibility

  if $\Delta E_{CC} > 0$ then corrosion can occur

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Metallic corrosion cells

- Both cathode and anode are metals
  1. two metals in different solutions ($Zn|Zn^{2+}||Cu^{2+}|Cu$)
  2. one metal in solutions of different electrolytes or in ones that have different concentrations
     ($Cu|Cu^{2+}, c_1 \,||\, Cu^{2+}, c_2|Cu,\ c_1 < c_2$)
  3. two metals immersed in one solution ($Fe|NaCl|Ni$)
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CC electrode reactions

- CC anode: oxidation of metal $\mathrm{M} - ne = \mathrm{M}^{n+}$
  - $E_{\text{anode}} = E^{\circ}(\mathrm{M}^{n+}/\mathrm{M})$ (if the concentration is unknown)
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- Electrode potentials (E_{cathode})
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  - $E(2H^+/H_2) = -0.059\,pH$
  - $E(O_2/H_2O) = 1.23 - 0.059\,pH$
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- CC anode: oxidation of metal $M - ne = M^{n+}$
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- Corrosion of metals at pH $\geqslant$ 7 can be accompanied by forming of insoluble hydroxide
- Corrosion of zinc in acidic media without oxygen
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Corrosion behaviour of contacting metals

- Basic rules for the case of corrosion of metal in contact with other metals
  - A metal having a more negative standard potential (anode) will destroy
  - Another metal stays unchanged and plays a role of cathode on which oxidizer (H^+ or O_2) is reducted
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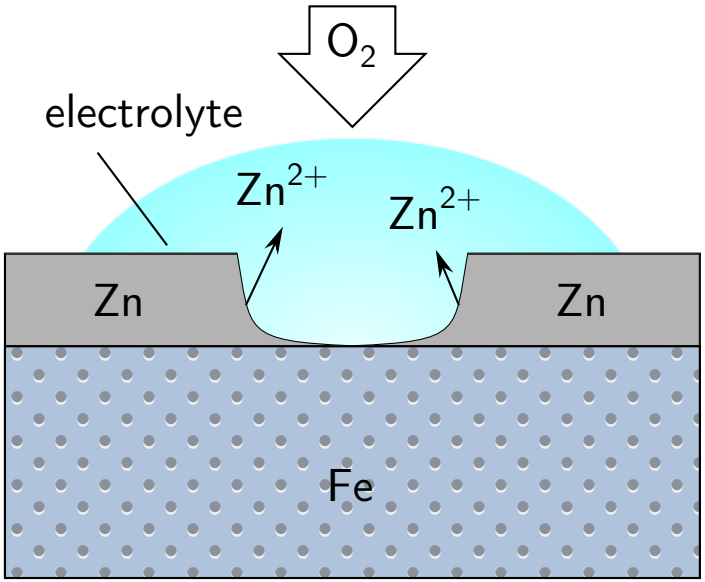

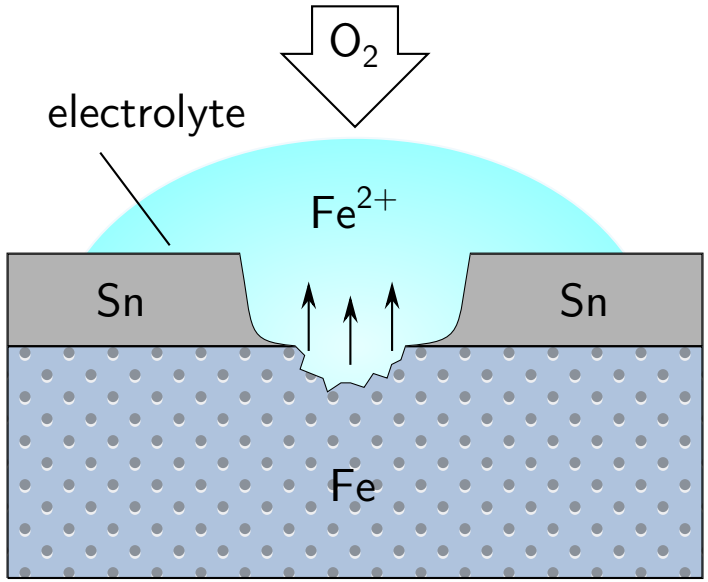

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- Corrosion pair Fe|Zn (anodic coating)

$$E^\circ(Fe^{2+}/Fe) = -0.44 \text{ V},$$
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$$\text{A: } Zn - 2e = Zn^{2+}$$
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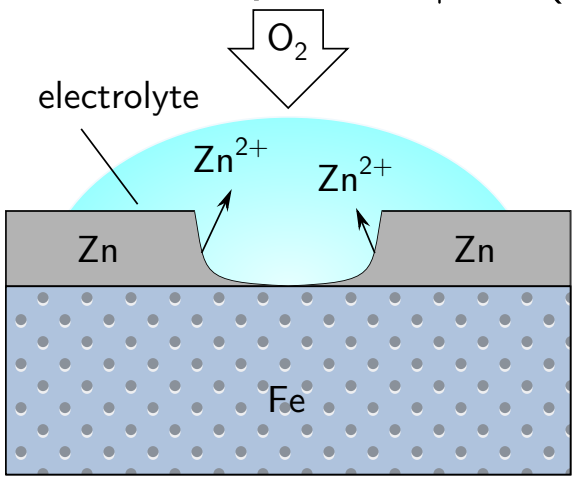

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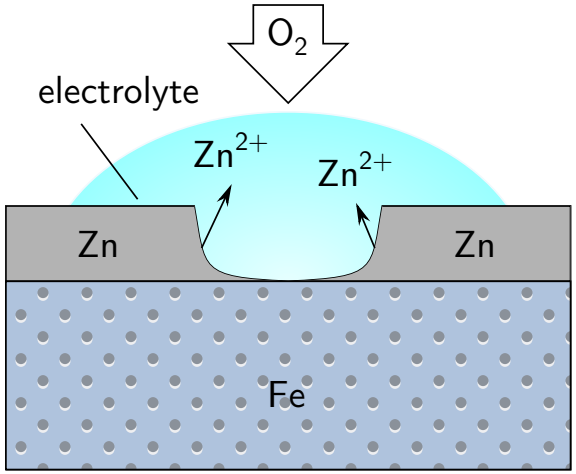

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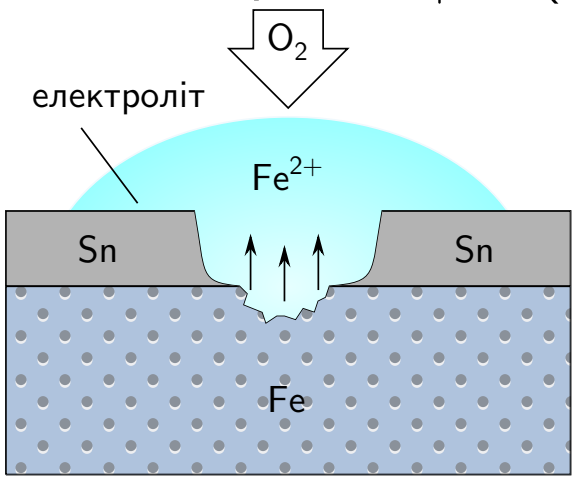

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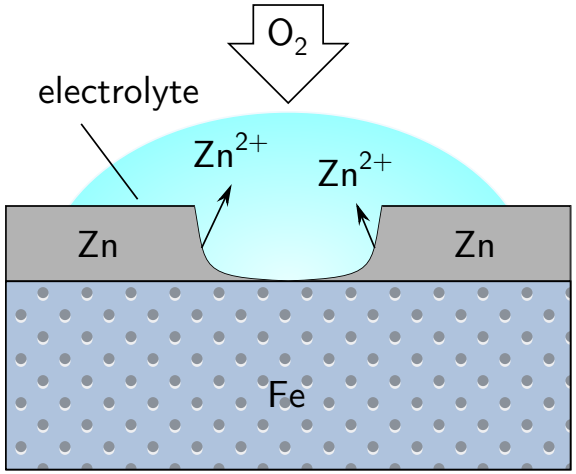

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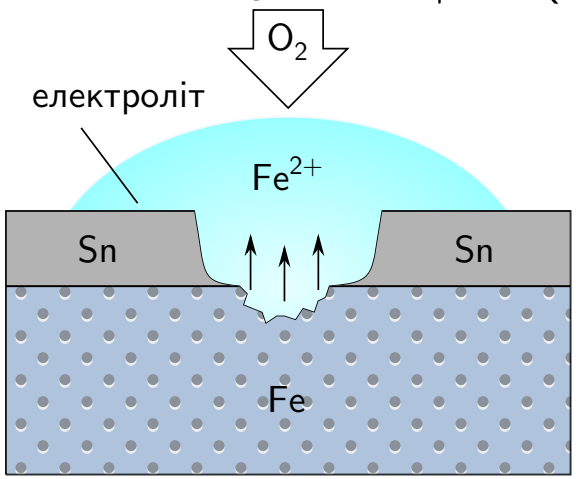

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Passivity of metal

- Passivation is a process of appearing of protective film on metal surface
- An example: $2Al + 2H_3PO_4 = 2AlPO_4\downarrow + 3H_2$
- Most often, the film is formed by oxide

  $2Al + 3H_2SO_{4(dil)} = Al_2(SO_4)_3 + 3H_2$

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  $SO_4^{2-}, OH^-, ClO_4^-, F^-, I^-, Br^-, Cl^-$
- An example:
- Oxidizing anions (MnO_4^-, CrO_4^{2-}) can both accelerate corrosion (with reduction at the cathode) and slow it down (metal passivation)

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Passivity of metal

- Passivation is a process of appearing of protective film on metal surface
- An example: $2Al + 2H_3PO_4 = 2AlPO_4\downarrow + 3H_2$
- Most often, the film is formed by oxide
  - $2Al + 3H_2SO_{4(dil)} = Al_2(SO_4)_3 + 3H_2$
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pH influence

- A common rule: the lower the pH, the more the cathode potential, so the more the corrosion rate
- Metals are separated on five groups: metals that
  - having full corrosion resistance (Pt, Ag, Ti, Au)
  - are stable in alkaline solutions, but unstable in acidic ones (Cd)
  - are stable in acidic solutions, but unstable in alkaline ones (Ta, Mo, W)
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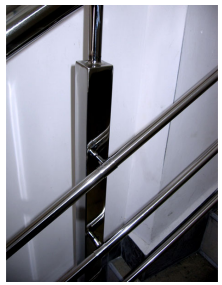
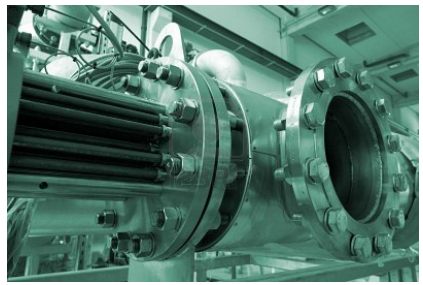


The materials for alloying

- Alloying not only protects from corrosion but improves the mechanical properties of the alloy
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Paintwork

- The varnish is a mixture of resin and volatile solvent. Solvent evaporates with time and the resin becomes hard because of polymerization.
- Paint is a mixture of pigment with a binder. As a pigment can be used
  - metal oxides (Fe_2O_3, TiO_2, ZnO, Cr_2O_3, Pb_3O_4)
  - other inorganic compounds ($BaSO_4$, $PbSO_4$, As_2S_3)
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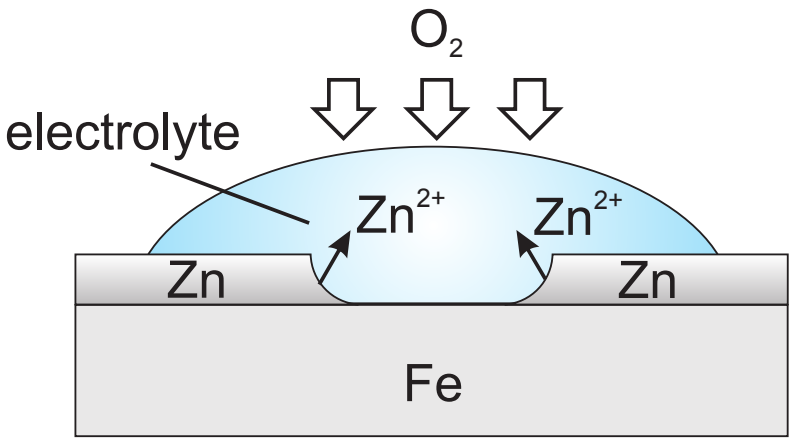
Metal coatings

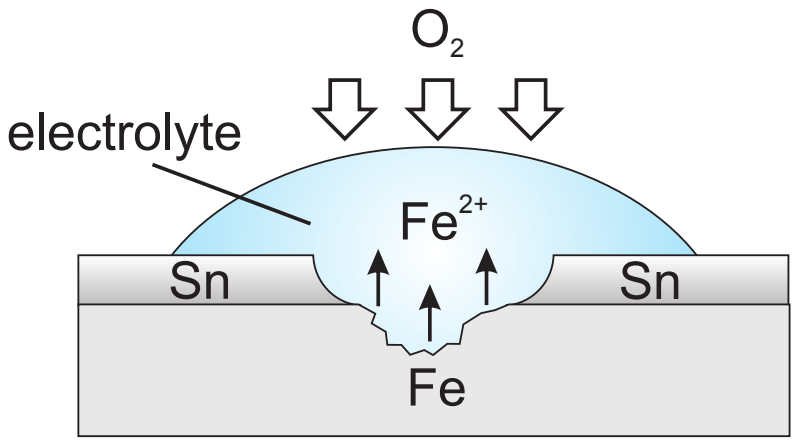
- Metal coatings are classified as anodic and cathodic

Anodic



$E^\circ(Fe^{2+}/Fe) = -0.44$ В,
$E^\circ(Zn^{2+}/Zn) = -0.76$ В
A: $Zn - 2e = Zn^{2+}$

Cathodic



$E^\circ(Fe^{2+}/Fe) = -0.44$ В,
$E^\circ(Sn^{2+}/Sn) = -0.14$ В
A: $Fe - 2e = Fe^{2+}$

$$C: O_2 + 2H_2O + 4e = 4OH^-$$

- Cathodic coating protects the basic metal until coating is damaged
- Anodic coating protects the basic metal even when it damaged

Metal coatings

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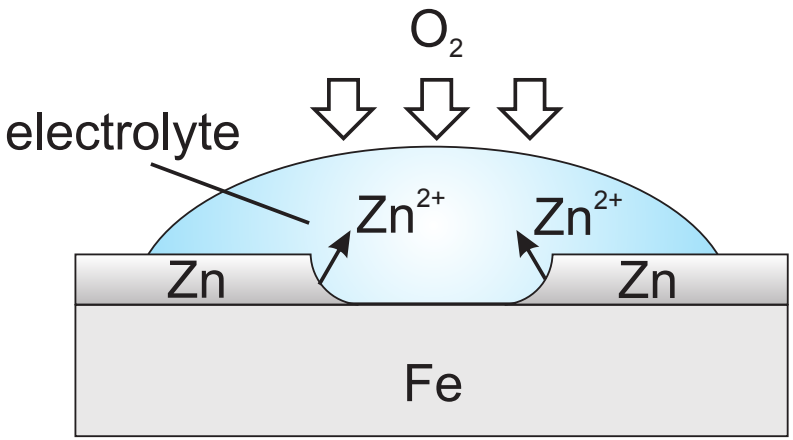
Anodic



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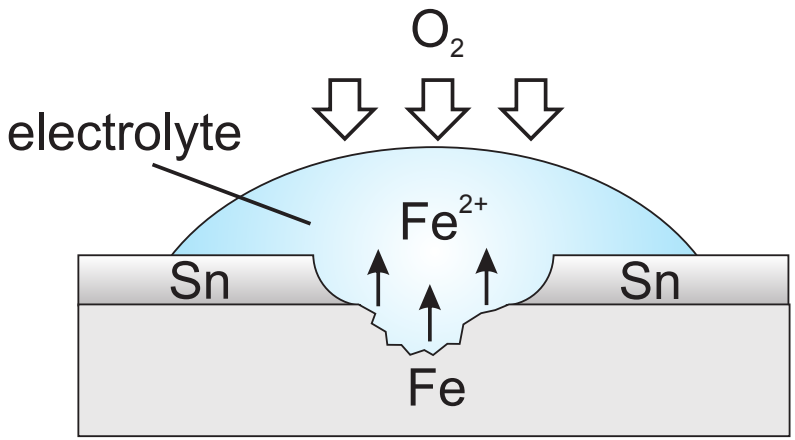
Cathodic



$E^\circ(Fe^{2+}/Fe) = -0.44$ В,
$E^\circ(Sn^{2+}/Sn) = -0.14$ В
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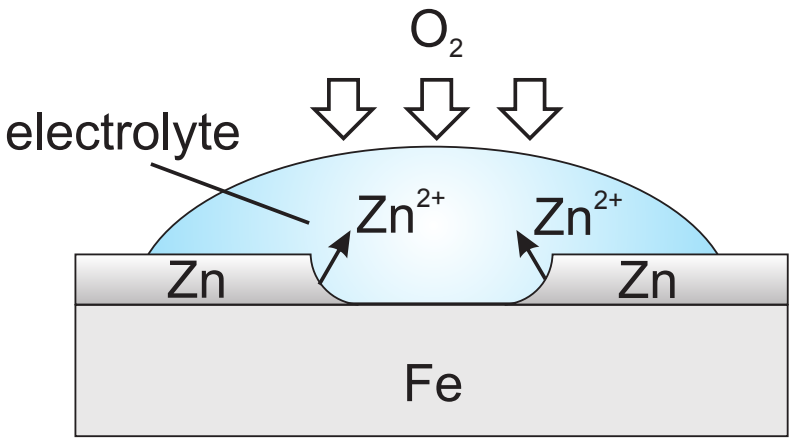
$$C: O_2 + 2H_2O + 4e = 4OH^-$$

- Cathodic coating protects the basic metal until coating is damaged
- Anodic coating protects the basic metal even when it damaged

Metal coatings

- Metal coatings are classified as anodic and cathodic

Anodic



$E^\circ(Fe^{2+}/Fe) = -0.44$ В,
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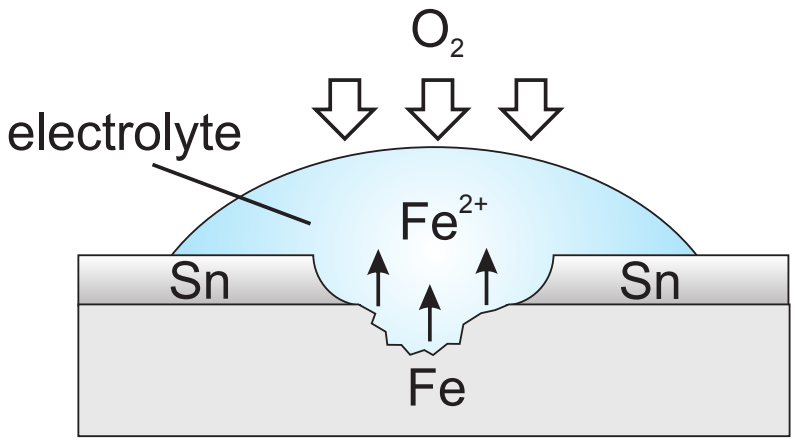

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Methods of applying metal coatings

- Sputter coating
  - well retained on the surface
  - can be applied on parts having any form
  - can be of any metal, theoretically
  - the disadvantage is its porosity
- Thermodiffusion: when molten metal of coating penetrates into the basic metal
- Plating: hot rolling or drawing of base metal together with a metal of coating

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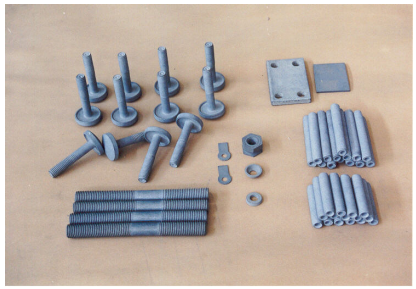
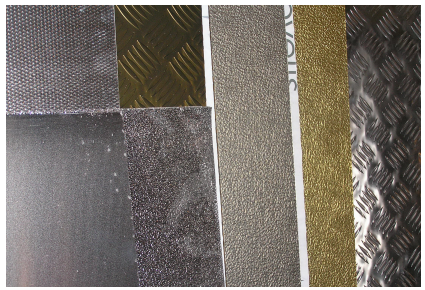
Coatings applied in different ways

Sputtering

Thermodiffusion



Plating



Coatings applied by oxidation of base metal

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  - BLUING is the oxidation of ferrous metals
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bluing

oxidation

phosphating

Electrochemical protection, the main principle

- can be used in conductive media (soil)
- A metal construction becomes polarized, i. e. its electrode potential changes due to
  - an external current source
  - a metal that has more negative potential

1 – construction, 2 – anode, 3 – direct current source
Cathode protection on the left picture, galvanic (sacrificial) protect
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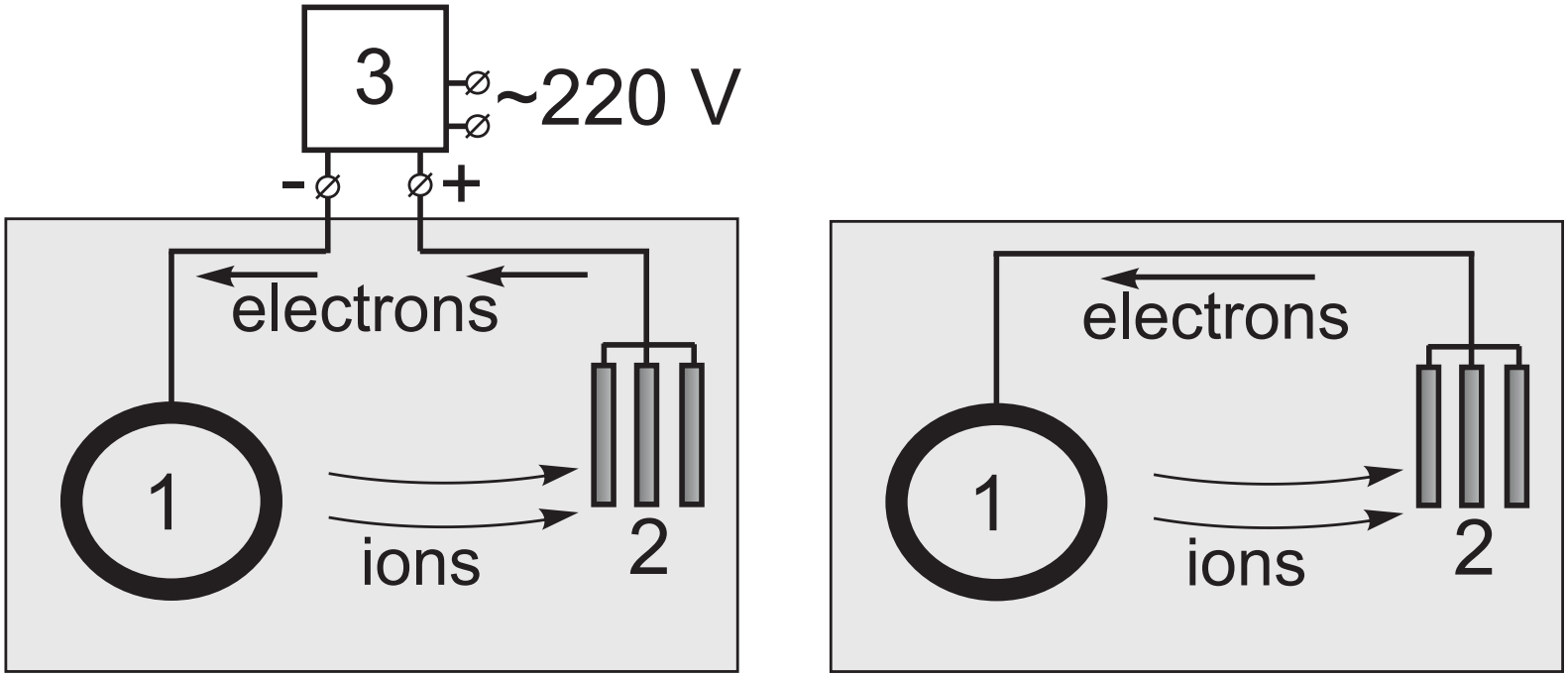
- 

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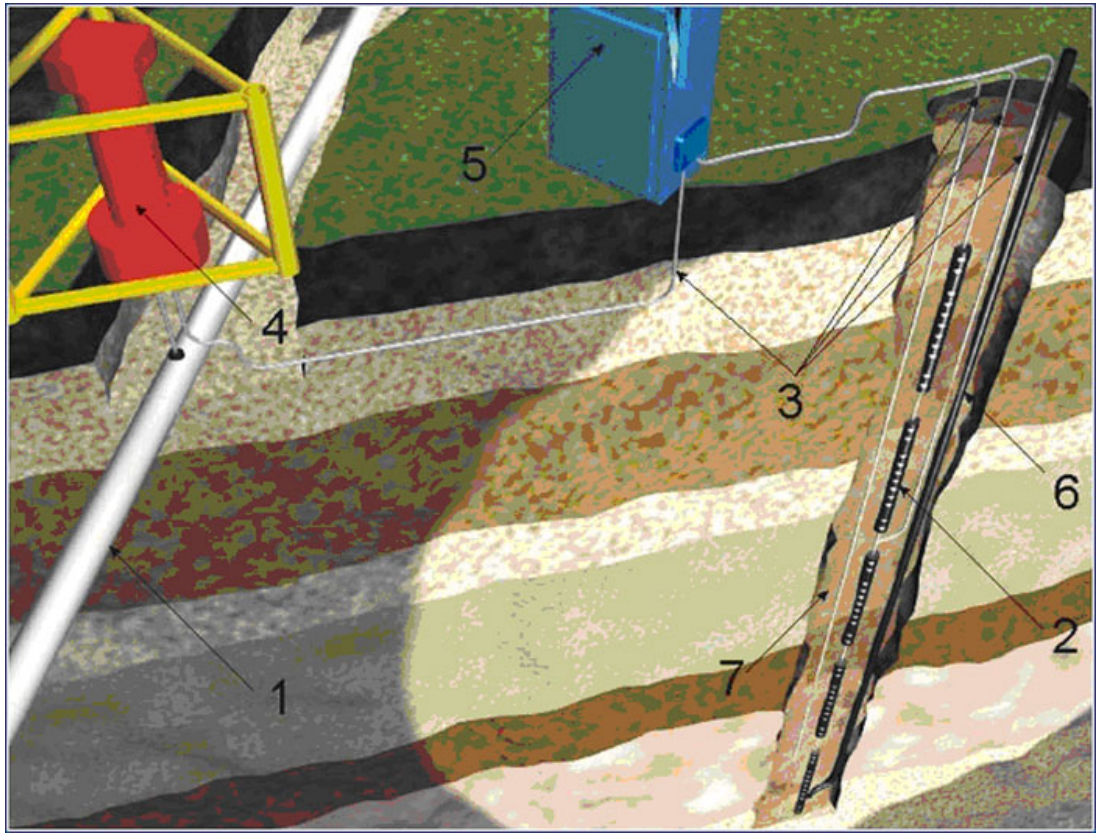
Impressed Current Cathodic Protection (ICCP)

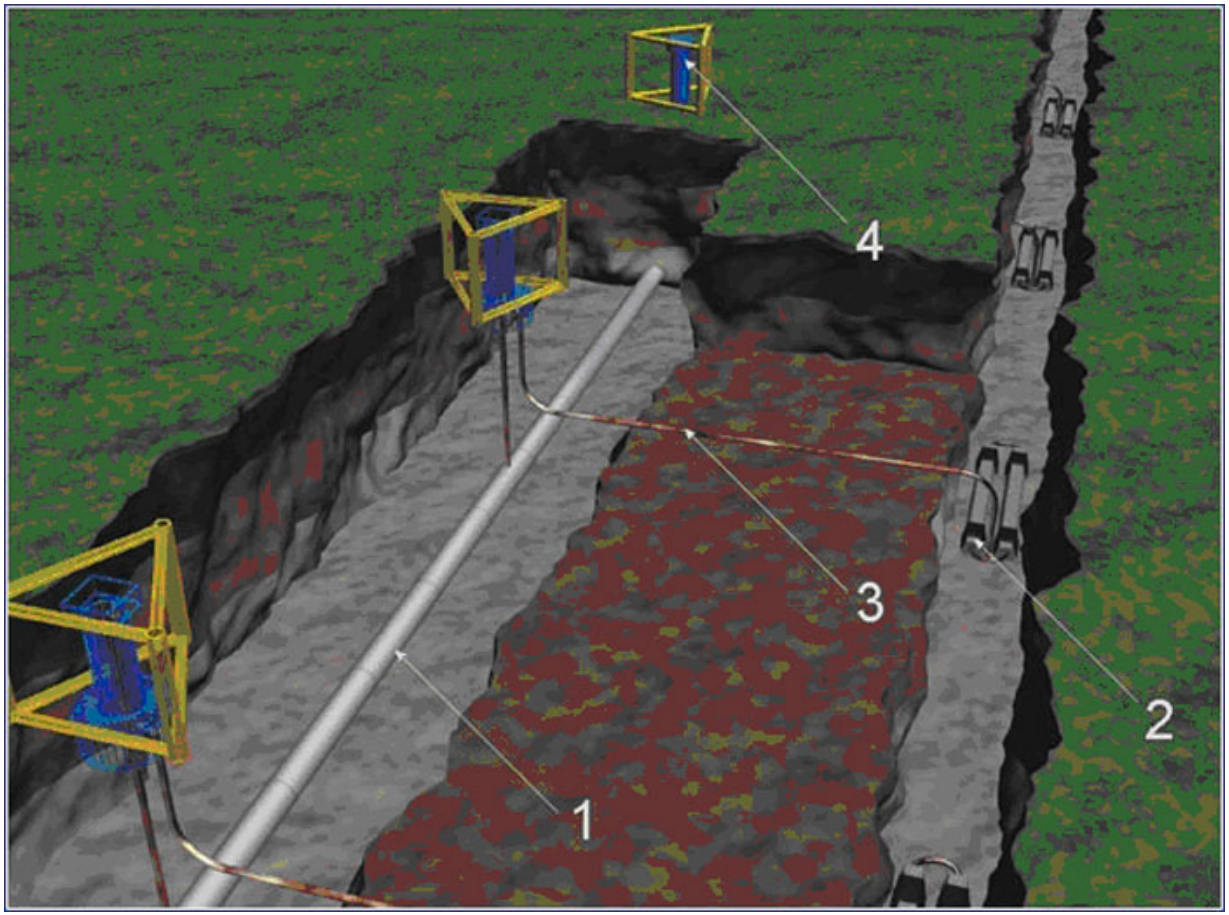
Scheme of ICCP



1 – pipeline, 2 – anodic earthing electrode, 3 – connection cable, 4 – checkpoint, 5 – cathodic protection station, 6 – gas tubule, 7 – clay roses

Passive cathodic protection

Passive cathodic protection scheme



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Changing in corrosion medium

- It can be carried out in two ways
  - agressive components eliminating
  - corrosion inhibitors adding
- First way usually applied to heat equipment
- Oxygen elimination ways
- pH controlling is important for processes accompanied by hydrogen depolarisation ($E(2H^+/H_2) = -0.059pH$)

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- They are effective for isolated systems (heating&cooling pipelines)
- By action mechanism, inhibitors can be anodic, cathodic and mixed
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