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Corrosion tests for metals and alloys

Michele Mascia and Annalisa Vacca



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What is CORROSION?

All materials are degraded in their operating environment (metals, plastics, ceramics, living tissues, etc.)

Degradation of metals is called corrosion.

The cost of corrosion is estimated in hundred billions of euros/year

DIRECT COSTS

Replacing the degraded parts
Overdesign
Use of costly resistant materials

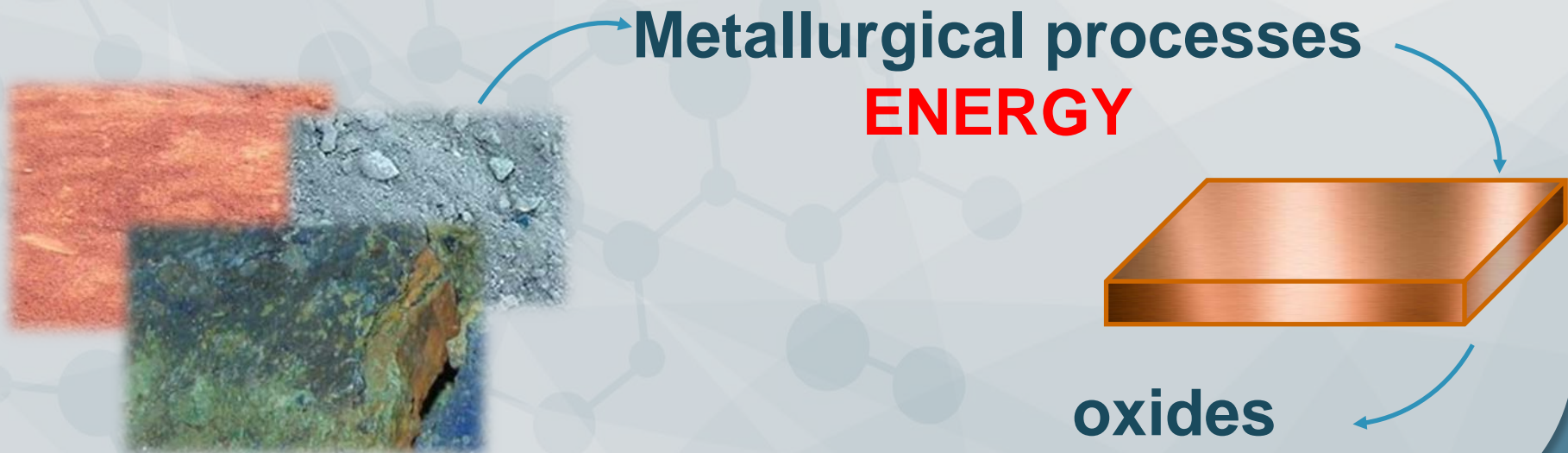
INDIRECT COSTS

Loss of productivity
Loss of materials
Catastrophic events

What is CORROSION?

Corrosion is a **spontaneous** degradation process

Most of the metals return to their more stable state as minerals (oxides and salts) from which they was “extract” by metallurgical processes



Corrosion is essentially the oxidation of a metal

- Dry corrosion → direct formation of metal oxide with oxygen in air. There is no water to aid the process
- Wet corrosion → occurs through electron transfer, involving two processes, oxidation and reduction.



Electrochemical process

Anode (where oxidation is taking place)

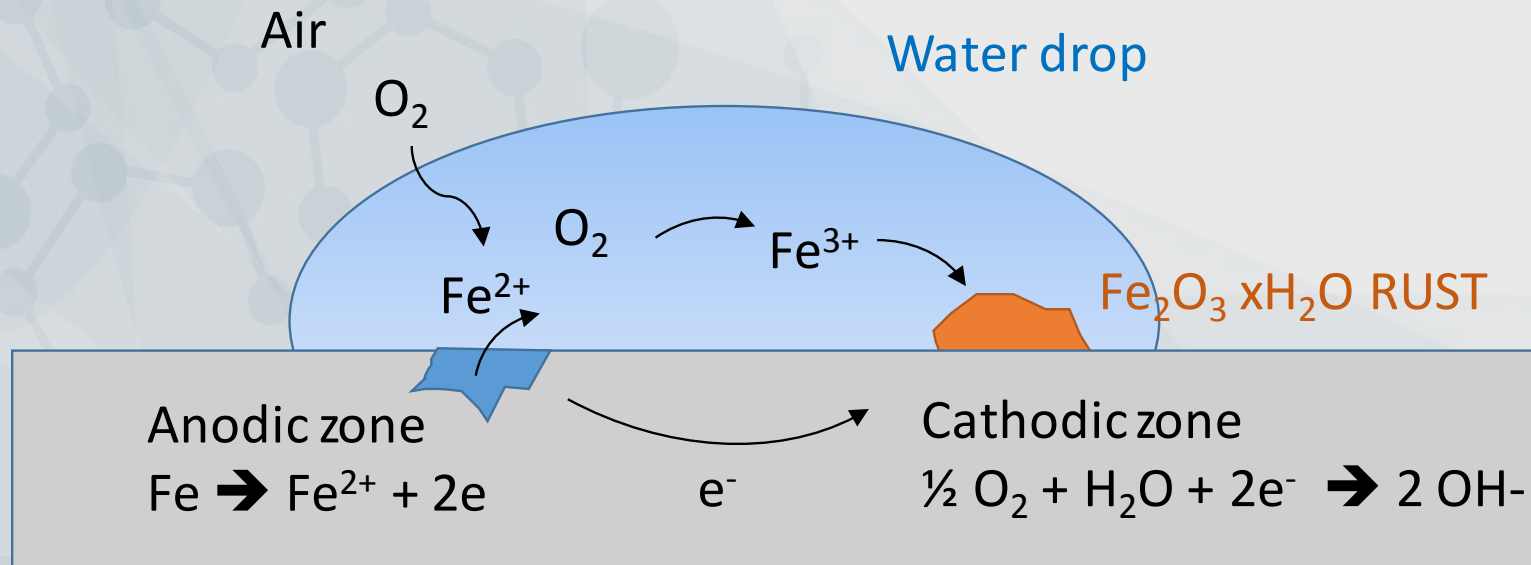
Cathode (where reduction is taking place)

Conductive electrolyte

Electrical contact between the Anode and Cathode

Corrosion and electrochemical process

Electrochemical reactions are heterogeneous reactions at the interface between solid electrode and electrolyte solution.



Red-ox reactions at metal/solution interphase:

- Half reaction at the anode - OXIDATION (loss of electrons)



- Possible half reactions at the cathode - REDUCTION (gain of electrons)

Acid conditions



Neutral or alkaline conditions



dissolved oxygen (acid)



dissolved oxygen (neutral or alkaline)



As all the chemical reactions, thermodynamics will describe what is the tendency for a chemical system to move towards a certain equilibrium state.

In electrochemistry thermodynamics is described by potential E (V), which is related to the free energy change G :

$$E = - \Delta G / nF$$

F is Faraday's constant (96490 C/mol)

n is the number of electrons exchanged

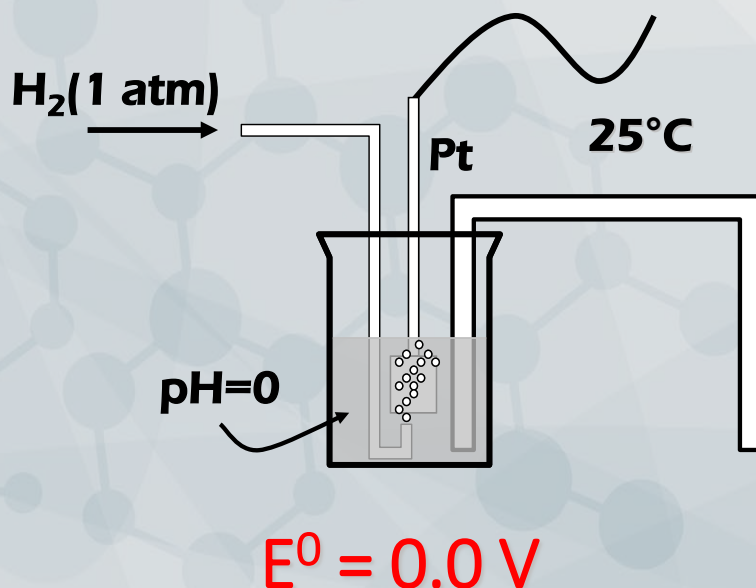
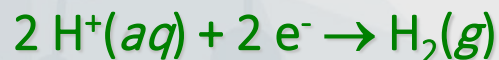
More spontaneous reactions ($\Delta G < 0$) will have more positive potential ($E > 0$).

POTENTIAL DIFFERENCE

THE ELECTRODE'S POTENTIAL IS ALWAYS MEASURED AS A DIFFERENCE WITH RESPECT TO ANOTHER ONE → REFERENCE ELECTRODE

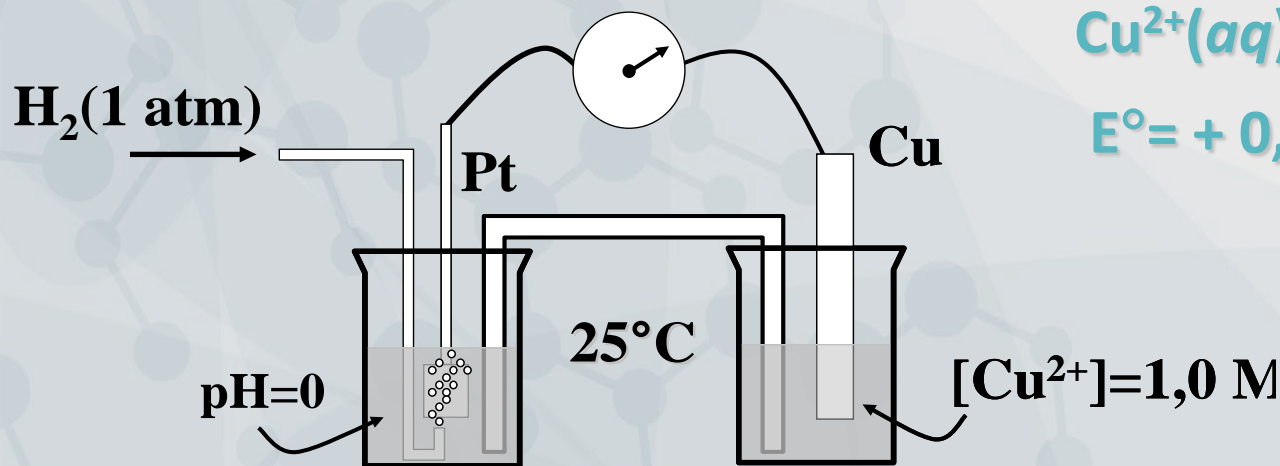
Standard reference electrode

The standard reference electrode is based on hydrogen where the concentration of H^+ ions is 1M, the partial pressure of H_2 is 1 atm and the temperature is 25°C .



Standard electrode potential E^0

Is the potential difference measured in a cell between the standard reference electrode and another semielements in standard conditions (concentration = 1M, partial pressure = 1 atm, $T=25^\circ\text{C}$)



$$E^0 = + 0,3419 \text{ V}$$

Standard electrode potentials E^0 are defined for the reduction process.

Quantification of the spontaneity of the reduction process

$$E^0 = - \Delta G^0 / nF$$

Half reduction	E° (V)
$\text{Au}^{3+}_{(\text{aq})} + 3e^- \rightleftharpoons \text{Au}_{(\text{s})}$	+1.42
$\text{O}_{2(\text{g})} + 4\text{H}^{+}_{(\text{aq})} + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$\text{Ag}^{+}_{(\text{aq})} + e^- \rightleftharpoons \text{Ag}_{(\text{s})}$	+0.80
$\text{Fe}^{3+}_{(\text{aq})} + e^- \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})}$	+0.77
$\text{Cu}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Cu}_{(\text{s})}$	+0.34
<u>$2\text{H}^{+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{H}_{2(\text{g})}$</u>	<u>0.00</u>
$\text{Sn}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Sn}_{(\text{s})}$	-0.14
$\text{Ni}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Ni}_{(\text{s})}$	-0.25
$\text{Co}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Co}_{(\text{s})}$	-0.28
$\text{Cd}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Cd}_{(\text{s})}$	-0.40
$\text{Fe}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Fe}_{(\text{s})}$	-0.44
$\text{Zn}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Zn}_{(\text{s})}$	-0.74
$\text{Mg}^{2+}_{(\text{aq})} + 2e^- \rightleftharpoons \text{Mg}_{(\text{s})}$	-2.37
$\text{Na}^{+}_{(\text{aq})} + e^- \rightleftharpoons \text{Na}_{(\text{s})}$	-2.71
$\text{Li}^{+}_{(\text{aq})} + e^- \rightleftharpoons \text{Li}_{(\text{s})}$	-3.05

$$E^\circ = -\Delta G^\circ/nF$$

More cathodic

The reduced form of the metal is more stable

$$E^\circ > 0$$

$$\Delta G^\circ < 0$$

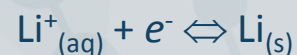
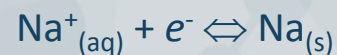
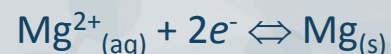
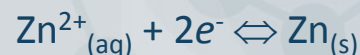
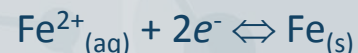
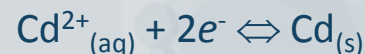
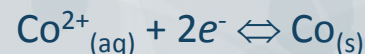
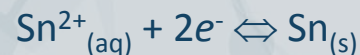
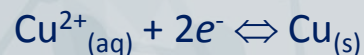
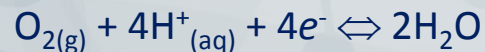
More anodic

The oxidized form is the more stable

$$E^\circ < 0$$

$$\Delta G^\circ > 0$$

Half reduction	E° (V)
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Reduction of oxygen

Oxidation of iron

Reduction of hydrogen

Oxidation of iron

Non-standard conditions: Nernst Equation

$$\Delta G = \Delta G^{\circ} + RT \ln(Q)$$



$$E = -\Delta G/nF$$

$$E = E^{\circ} - \frac{RT}{nF} \ln(Q)$$

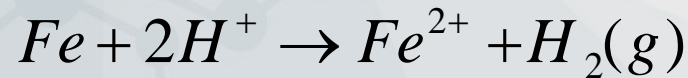
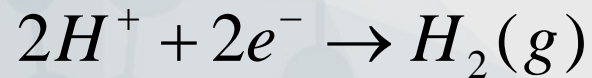


$$E_{H^{+}/H_2} = E_{H^{+}/H_2}^{\circ} - \frac{RT}{2F} \ln \frac{P_{H_2}}{[H^{+}]^2} = 0 - \frac{0.059}{2} \log \frac{1}{[H^{+}]^2}$$

$$E_{H^{+}/H_2} = -0.059 \text{ pH}$$

Non-standard conditions: Nernst Equation

For the oxidation of iron coupled with the reduction of hydrogen

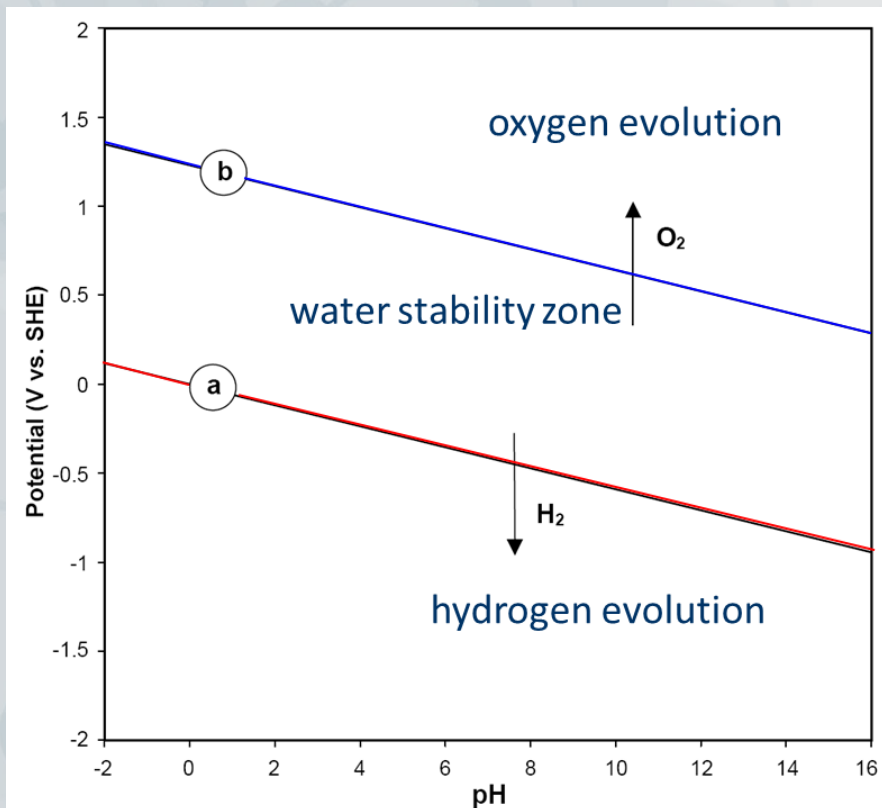


$$\Delta E = \Delta E^o - \frac{RT}{nF} \ln \left(\frac{a(Fe^{2+}) \cdot f(H_2)}{a(Fe) \cdot [a(H^{+})]^2} \right) = \Delta E^o - \frac{RT}{nF} \ln \left(\frac{[Fe^{2+}]}{[H^{+}]^2} \right)$$

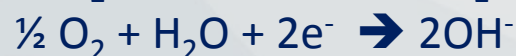
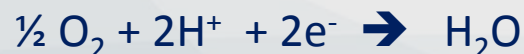
The red-ox spontaneity depends on the activity of the species

It is possible to represent the results of all the involved processes on a map-like “phase diagram” called Pourbaix Diagrams

Pourbaix diagrams consider the equilibrium potential between a metal and its various oxidised species as a function of pH.



Pourbaix diagram for water

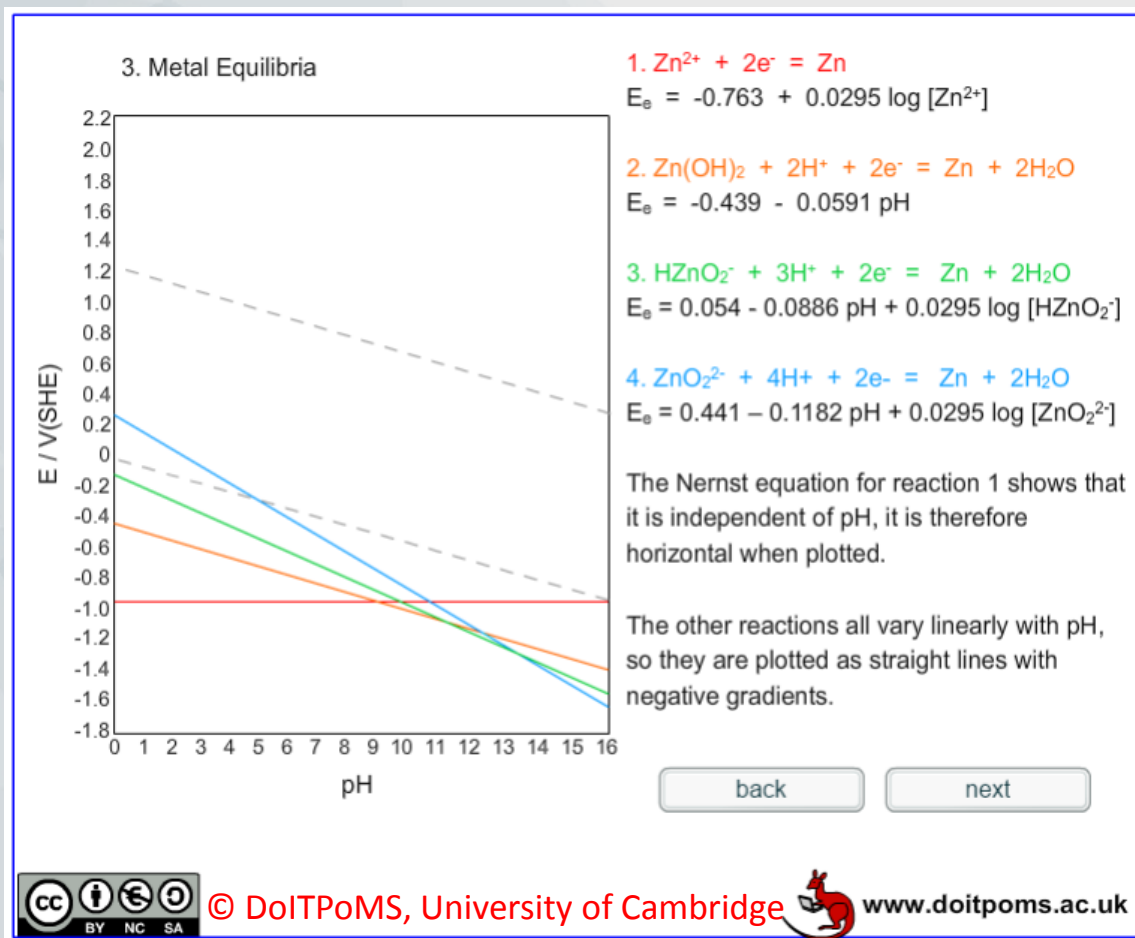


$$E_{\text{O}_2 / \text{H}_2\text{O}} = 1.23 - 0.059 \text{pH}$$

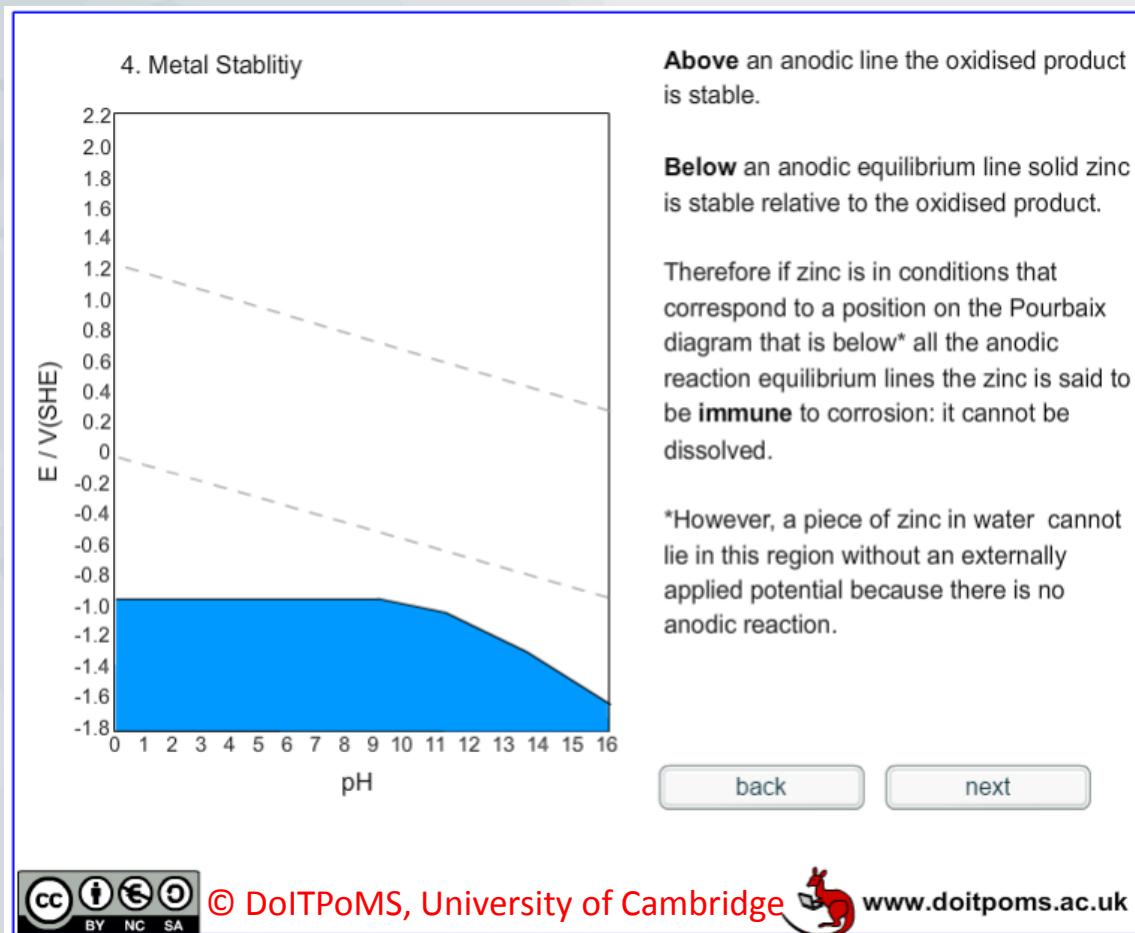
$$E_{\text{H}^+ / \text{H}_2} = -0.059 \text{pH}$$



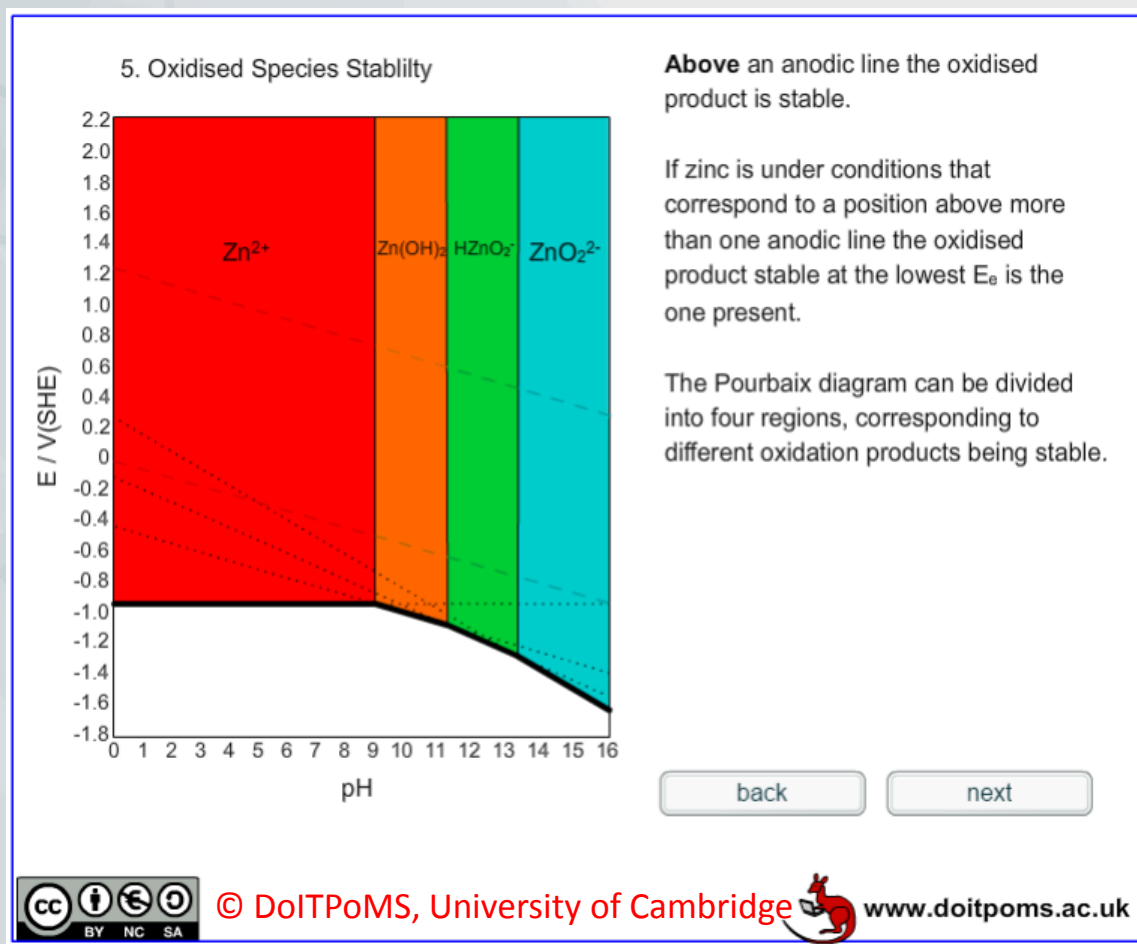
The Pourbaix diagram of metal considers all the possible oxidation reactions.
For Zn there are four oxidation products: Zn^{2+} , $\text{Zn}(\text{OH})_2$, HZnO_2^- and ZnO_2^{2-}



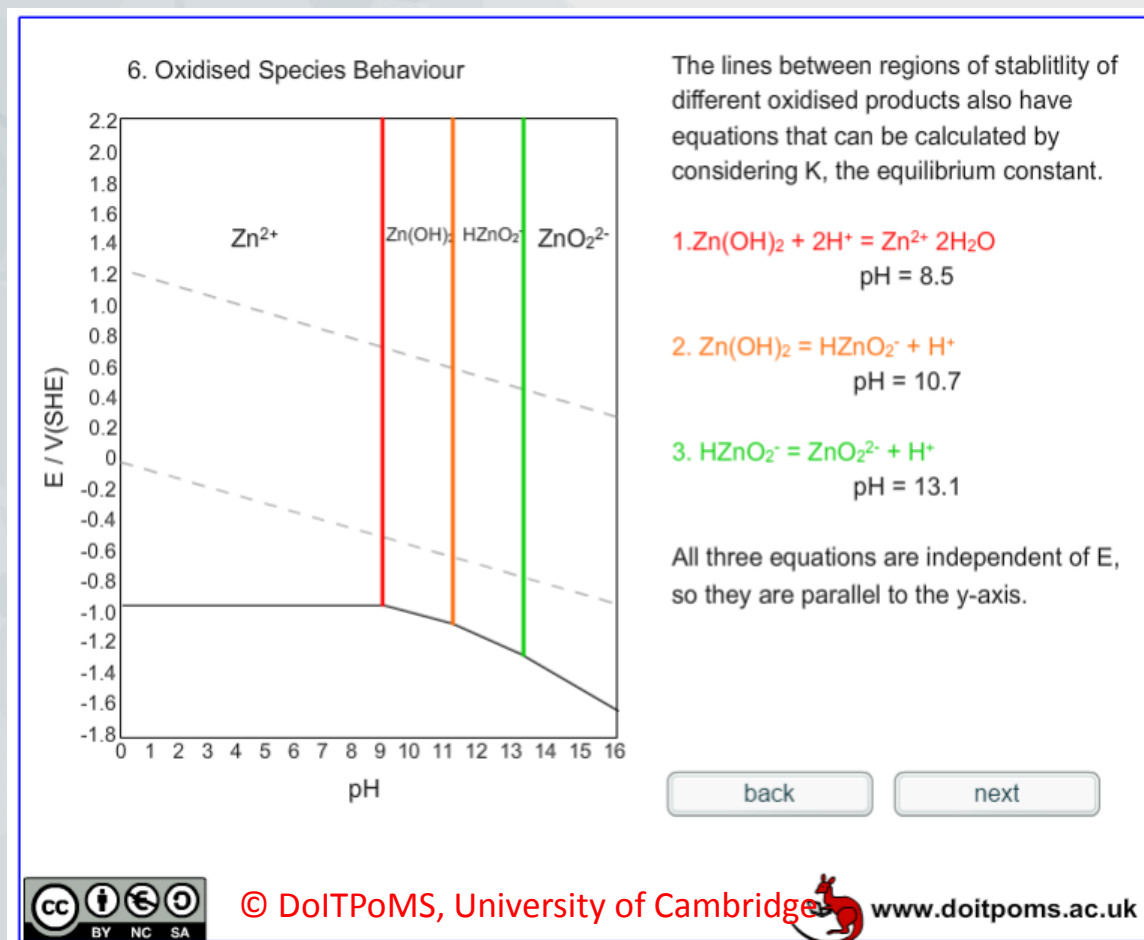
Immunity zone: area in the map where the zinc is stable in metallic form



Four regions of stability of the different oxidation products

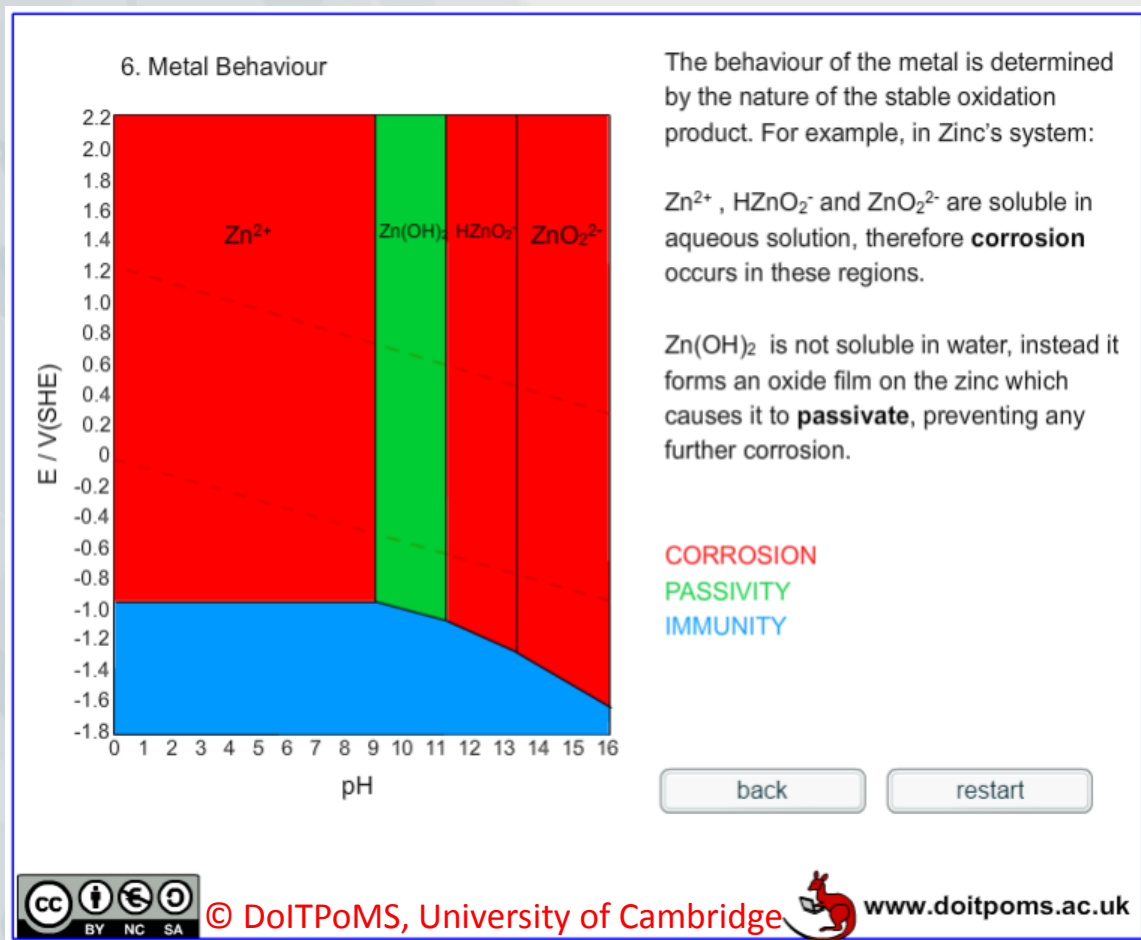


Boundary lines represent equilibrium between the different oxidation products

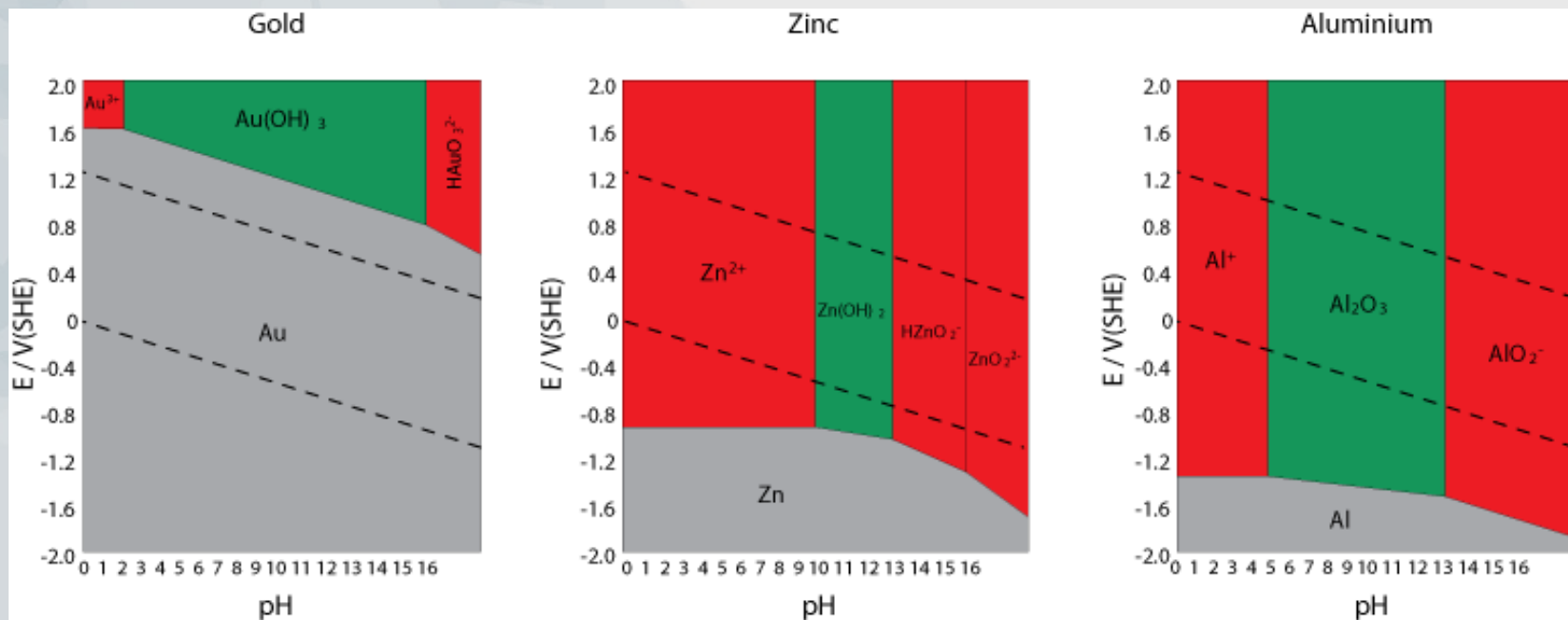


Passivity zone (green): formation of insoluble hydroxide Zn(OH)_2

Corrosion zone (red): formation of soluble products



Pourbaix diagrams



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https://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix_example.php

The Pourbaix diagram can be used to determine which species is *thermodynamically* stable at a given E and pH.

Note:

- it is withdrawn for concentration of ions conventionally equal to 10^{-6} M
- it considers equilibria related to pure water and pure metals.
- it gives no information about the *kinetics* of the corrosion process.

Set up

Working electrode => metal/alloy to be investigated

Electrolyte => medium of corrosion (saline water, acidic media)

Counter Electrode => supply the current required by the working electrode without limiting the measured response

Avoid: large overpotential, change of electrolyte composition (reverse reaction)

Set up

Reference electrode => provide a fixed potential which does not vary during the experiment

fast response time

independent of current density

Standard $\text{H}_2/\text{H}_3\text{O}^+$		0 V
Mercury-mercurous chloride	$\text{Hg}/\text{Hg}_2\text{Cl}_2$, 1 mol dm^{-3} KCl	+0.28 V
Silver-silver halide	Ag/AgCl , sat KCl	+0.197 V

The cell

- Inert material

- Degassing

- Easy of use

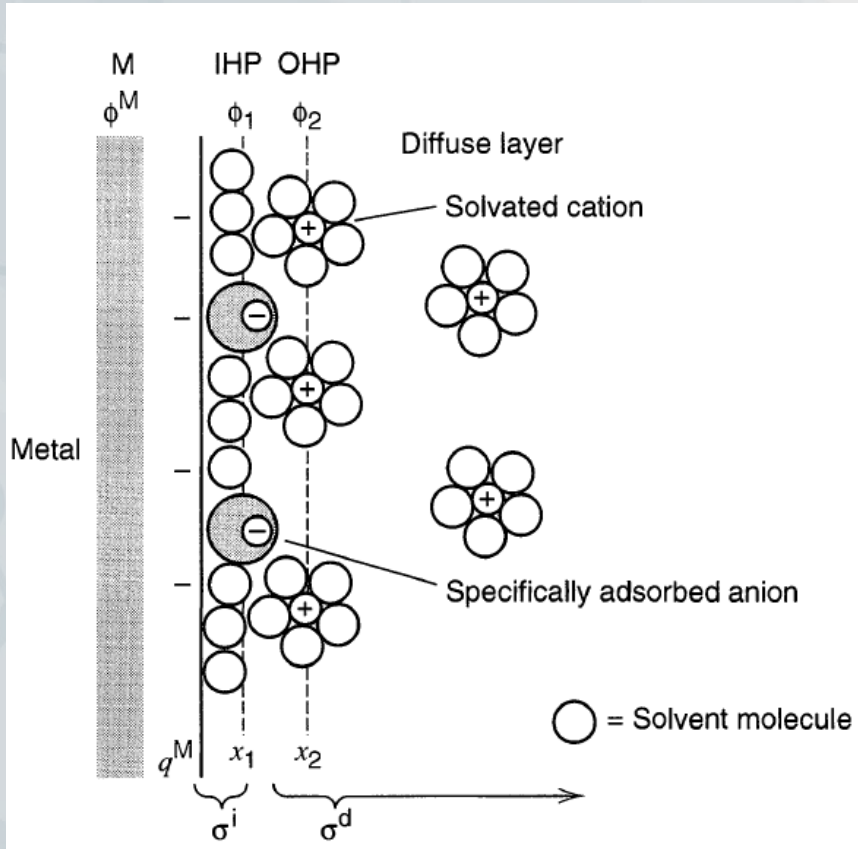
The instrumentation

- Fast response

- Different techniques allowed

- Signal processing

- User friendly software



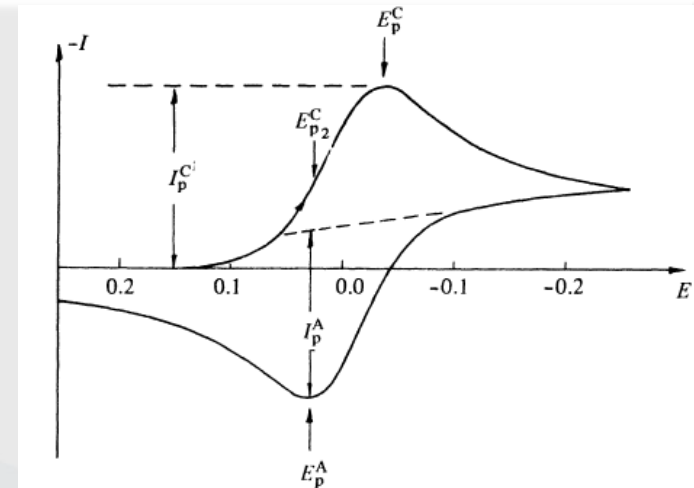
- Inner layer => compact, Helmholtz, or Stern layer => specifically adsorbed species
- Locus of the centers of the specifically adsorbed ions => inner Helmholtz plane (IHP)

Electrode processes:

- Oxidation of the metal (exchange of electrons)
- Surface oxide formation
- Diffusion of metal ions

Cyclic voltammetry => high scan rate

- At low potential value, the current is due to the migration of ions (polarization)
 - The current grows as the potential reaches the oxidation potential of the metal
 - The surface sites of the metal are oxidised
 - The current show a peak
- Reversing the scan => the behaviour depends on the reversibility of the system



Governing equations Cyclic voltammetry

Mathematical solution ($\text{Me}^{n+} + n\text{e} \Rightarrow \text{Me}$)

$$\frac{\partial \text{Me}}{\partial t} \frac{1}{V_s} = \frac{\partial C_{\text{Me}^{n+}}}{\partial t} + \nabla(-\nabla D_{\text{Me}^{n+}} C_{\text{Me}^{n+}}) = 0$$

For planar diffusion and constant D

$$\frac{\partial C_{\text{Me}^{n+}}}{\partial t} = -D_{\text{Me}^{n+}} \frac{\partial^2 C_{\text{Me}^{n+}}}{\partial x^2}$$

Initial and boundary conditions

$$t=0 \quad x>0 \quad C_{\text{Me}^{n+}} = 0$$

$$t>0 \quad x=0 \quad -D_{\text{Me}^{n+}} \frac{\partial C_{\text{Me}^{n+}}}{\partial x} = \frac{i}{nF}$$

$$t>0 \quad x=\infty \quad C_{\text{Me}^{n+}} = C_{\text{bulkMe}^{n+}} = 0$$

Governing equations Cyclic voltammetry

Mathematical solution for fully reversible systems at 25 °C (Randles-Sevcik equation)

$$I_p = -(2.69 \times 10^5) n^{1.5} C_{Me}^{n+} D^{0.5} SR^{0.5}$$

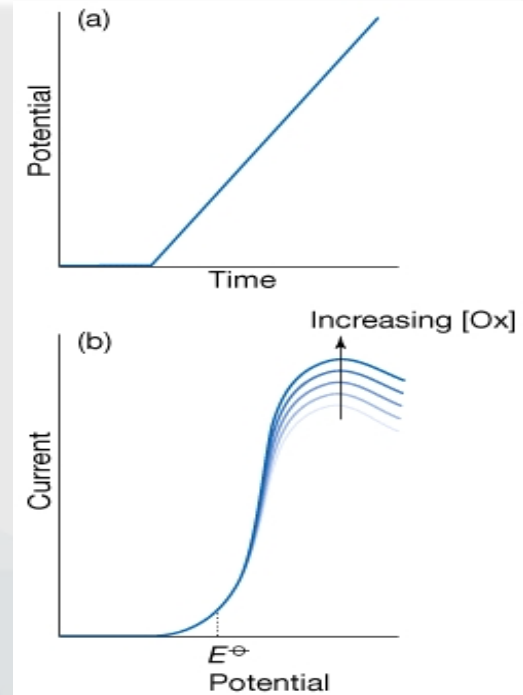
Test (25 °C)

	Fully Reversible	Fully irreversible	Quasi (ir)reversible
$ E_p^C - E_p^a $	59/n (mV)	No reverse peak	>59/n (mV) and f(SR)
I_p	$\propto SR^{0.5}$	$\propto SR^{0.5}$	increases with $SR^{0.5}$
I_p^C/I_p^C	1	No reverse peak	$\neq 1$
E_p^C	Indipendent of SR	$-30/(n*\alpha) \text{ mV} \times 10SR$	shift with SR

Experimental techniques

Linear-sweep voltammetry => low scan rate

- At low potential value, the current is due to the migration of ions (polarization)
- The current grows as the potential reaches the oxidation potential of the metal
- The current increases => corrosion
- The current reaches a plateau/peak => passivation



Governing equations Linear sweep voltammetry

The Current-Overpotential Equation

$$i = i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

No Mass-Transfer Effects => Butler – Volmer equation

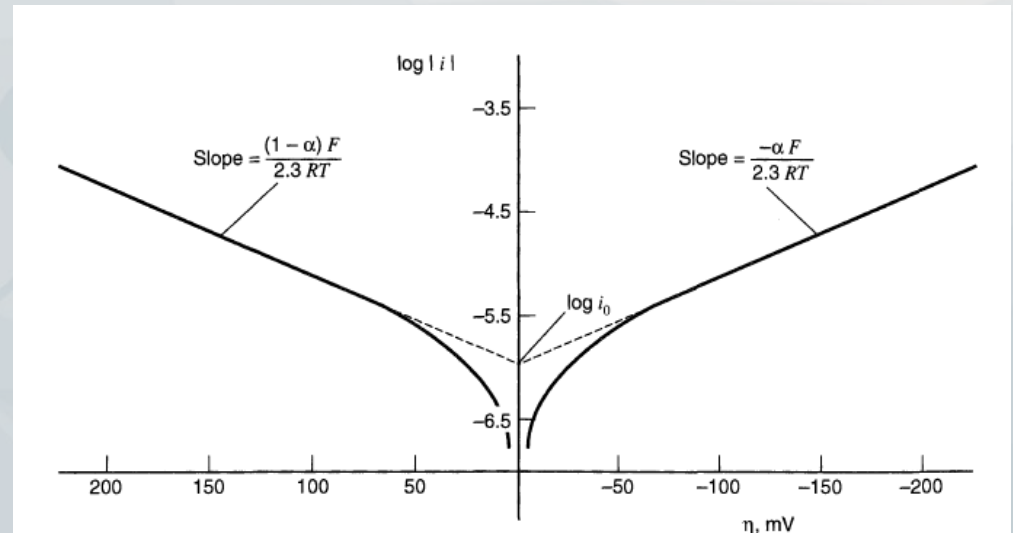
$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

Large overpotential => Tafel Behavior

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i$$

Small overpotential => Ohmic behavior

$$i = -i_0 f \eta$$



Governing equations: corrosion

$$i = i_{corr} \left[e^{\frac{2.3\eta}{a}} - e^{\frac{2.3\eta}{b}} \right]$$

$$\eta = E - E_{corr}$$

The overpotential η is the difference between applied potential and corrosion potential E_{corr}

The corrosion potential E_{corr} is the open circuit potential of the metal

Corrosion current and Tafel constants (a and b) can be calculated from the inverse of the LSV slope.

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