Lecture Note #8 (Fall, 2020)

# Corrosion

1. Corrosion fundamentals
2. Thermodynamics of corrosion
3. Corrosion rate
4. Localized corrosion
5. Corrosion protection

Fuller & Harb (textbook), ch.16, Johns, ch.1-3

# Corrosion fundamentals

- Corrosion: unwanted attack of metals by their environment

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

- Components of corrosion systems

(1) The metal (anode)
(2) A cathode reactant with an equilibrium potential higher than that of the metal
(3) Electrical contact between the anode and cathode
(4) An electrolyte that permits current flow in solution between the anode and cathode

e.g.

galvanic corrosion (like Daniel cell (battery)): an active metal is electrically connected to a more noble metal (one that is less likely to corrode) → oxidation in one side + reduction in the other side

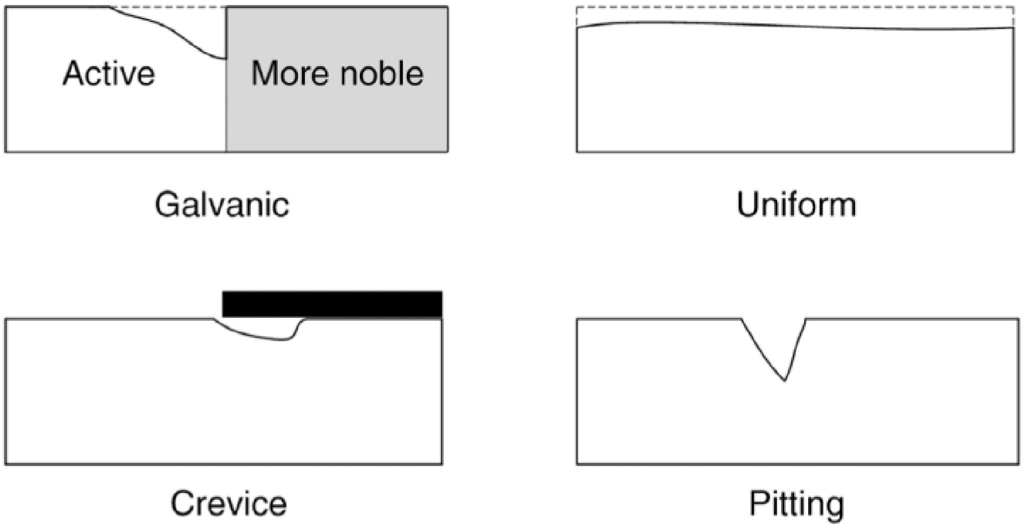

**Figure 16.1** Examples of different types of corrosion.

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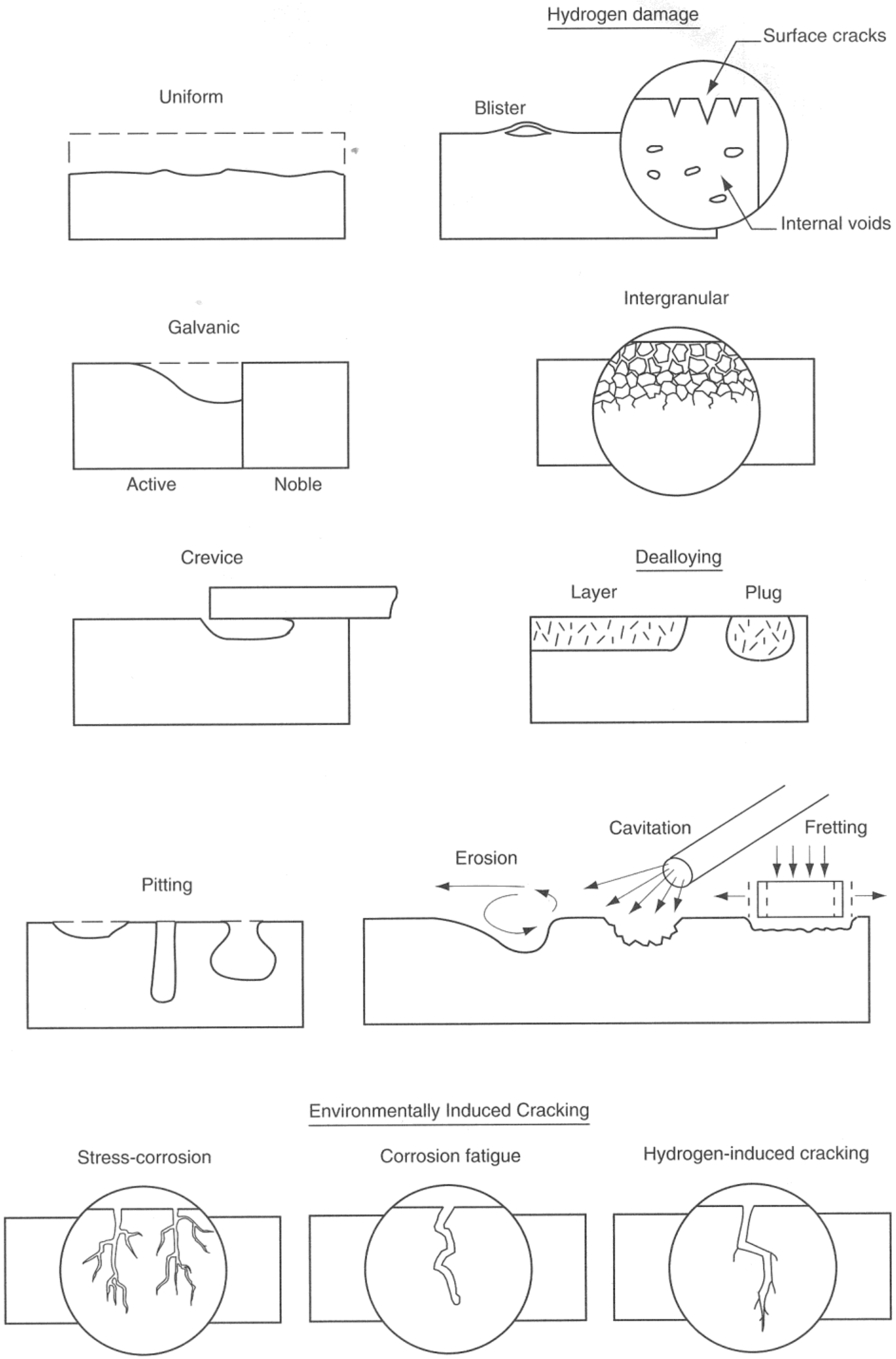
- Most common cathodic reactions in corrosion in aqueous systems

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$2H^+ + 2e^- \rightarrow H_2$$
$$H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

# 부식의 종류



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# Thermodynamics of corrosion systems

- Thermodynamically favorable corrosion reaction is a reaction that has a negative free energy (positive cell potential) with the metal as the anode

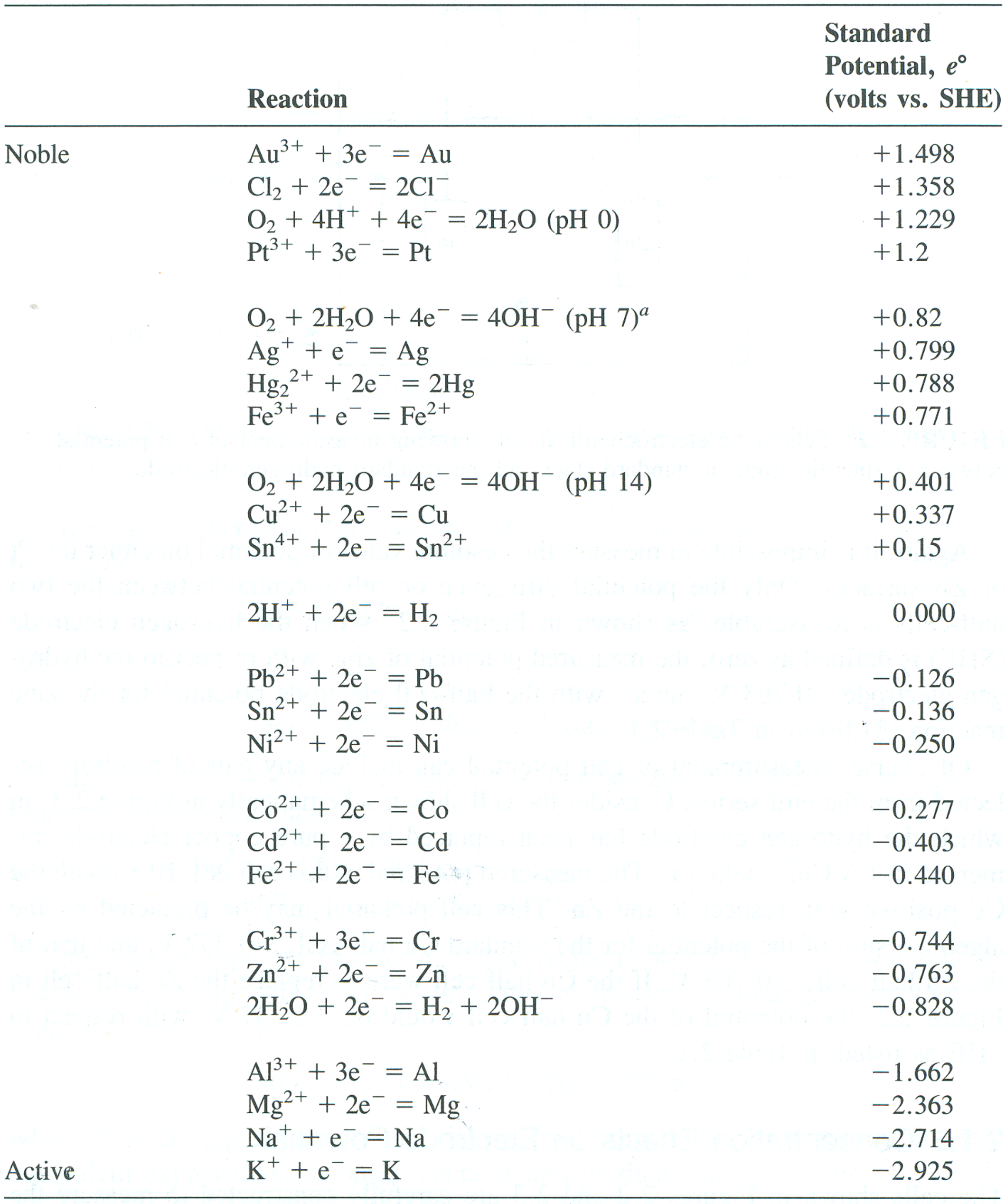
- Immunity: corrosion is not thermodynamically favorable

- Passive layer: Al is very reactive (standard potential = -1.66 V), but doesn’t corrode. Why? Oxide layer → passive layer, passivation

- potential, pH: critical variable in determining the stability of the surface layer → Porbaix diagram

# Standard electrode potential (표준전극전위)

$E^0$



| | Reaction | Standard Potential, $e^\circ$ (volts vs. SHE) |
|---|---|---|
| Noble | $Au^{3+} + 3e^- = Au$ | +1.498 |
| | $Cl_2 + 2e^- = 2Cl^-$ | +1.358 |
| | $O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0) | +1.229 |
| | $Pt^{3+} + 3e^- = Pt$ | +1.2 |
| | $O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)[a] | +0.82 |
| | $Ag^+ + e^- = Ag$ | +0.799 |
| | $Hg_2^{2+} + 2e^- = 2Hg$ | +0.788 |
| | $Fe^{3+} + e^- = Fe^{2+}$ | +0.771 |
| | $O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14) | +0.401 |
| | $Cu^{2+} + 2e^- = Cu$ | +0.337 |
| | $Sn^{4+} + 2e^- = Sn^{2+}$ | +0.15 |
| | $2H^+ + 2e^- = H_2$ | 0.000 |
| | $Pb^{2+} + 2e^- = Pb$ | −0.126 |
| | $Sn^{2+} + 2e^- = Sn$ | −0.136 |
| | $Ni^{2+} + 2e^- = Ni$ | −0.250 |
| | $Co^{2+} + 2e^- = Co$ | −0.277 |
| | $Cd^{2+} + 2e^- = Cd$ | −0.403 |
| | $Fe^{2+} + 2e^- = Fe$ | −0.440 |
| | $Cr^{3+} + 3e^- = Cr$ | −0.744 |
| | $Zn^{2+} + 2e^- = Zn$ | −0.763 |
| | $2H_2O + 2e^- = H_2 + 2OH^-$ | −0.828 |
| | $Al^{3+} + 3e^- = Al$ | −1.662 |
| | $Mg^{2+} + 2e^- = Mg$ | −2.363 |
| | $Na^+ + e^- = Na$ | −2.714 |
| Active | $K^+ + e^- = K$ | −2.925 |

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# Pourbaix diagrams

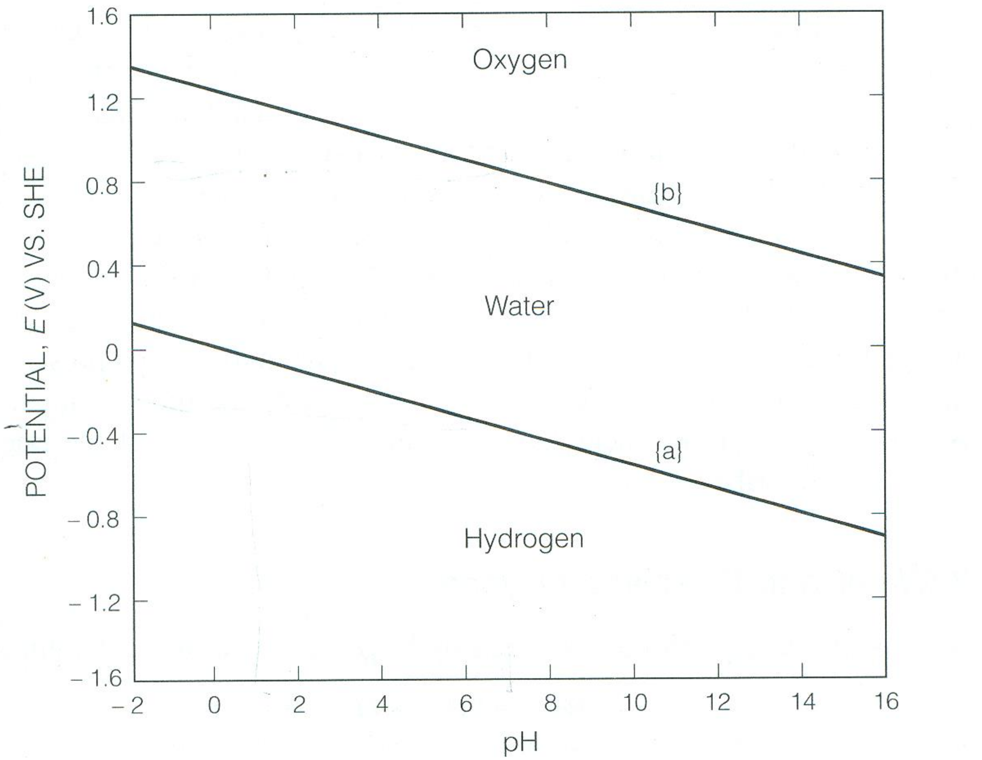
at 25°C, pH = $-\log_{10}a$

$2H^+ + 2e^- = H_2$

$E = E^0 - (RT/2F)\ln(1/a_{H+}^2)$
$= 0 + (RT/F)\ln(a_{H+})$
$= -(RT/F)(2.303pH)$
$= -0.0592pH$

$(1/2)O_2 + 2H^+ + 2e^- = H_2O$

$E = E^0 - (RT/2F)\ln(1/a_{H+}^2)$
$= 1.229 + (RT/F)\ln(a_{H+})$
$= 1.229 - (RT/F)(2.303pH)$
$= 1.229 - 0.0592pH$



# Pourbaix diagram for Zn at 25°C

$Zn^{2+} + 2e^{-} = Zn$

$E = E^{0} - (RT/2F)\ln(1/a_{Zn2+})$

$\quad = -0.763 + (RT/2F)\ \ln(a_{Zn2+})$

$[Zn^{2+}] = 10^{-6}$ M → -0.94 V (line c)

$Zn^{2+} + 2OH^{-} = Zn(OH)_2$

No electron transfer reaction (not a function of potential)

→ vertical line (line d)

→ pH calculation using $K_{sp}$

→ pH = 8,74

$Zn(OH)_2 + 2H^{+} + 2e^{-} = Zn + 2H_2O$

$E = -0.425 + (RT/F)(2.303pH)$

(line e)

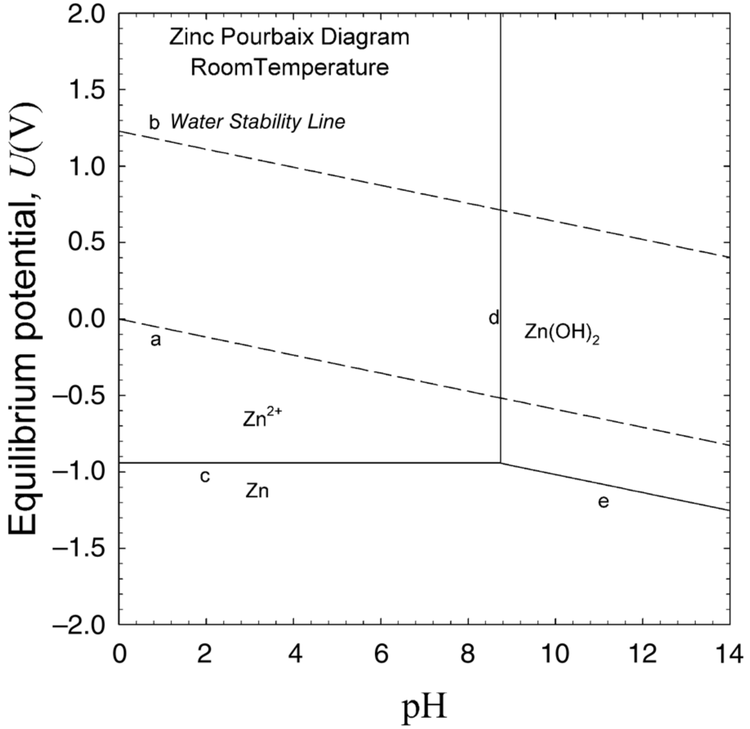


**Figure 2.2** Simplified Pourbaix diagram for Zn.

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# Ni

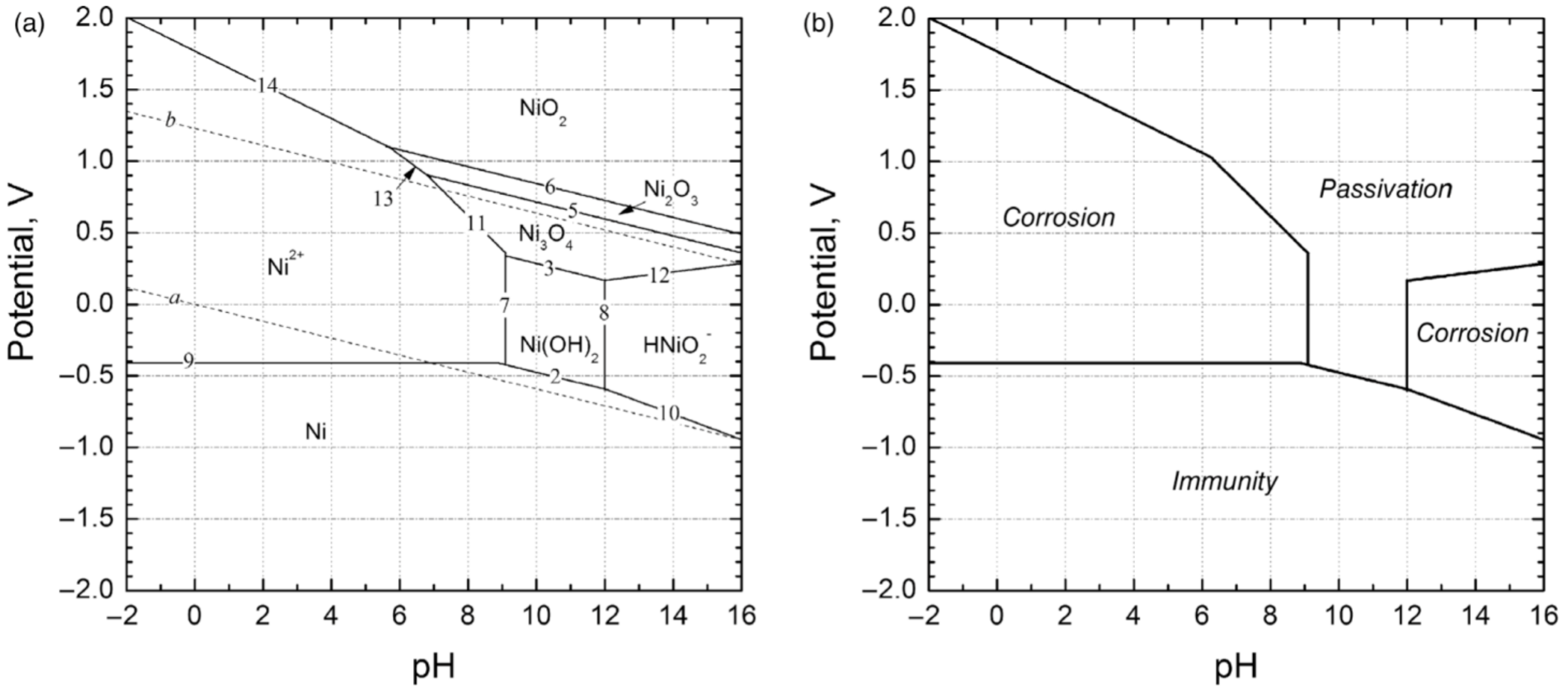

**Figure 16.2** Pourbaix diagram for nickel and resulting corrosion map showing regions of immunity, corrosion, and passivation. The numbers and letters correspond to the equations below and in those used in Pourbaix's book.

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- Dashed line a , b: hydrogen reaction and oxygen reaction
- Each solid line: equilibrium of an electrochemical or a chemical reaction

$$Ni + H_2O = Ni(OH)_2 + 2H^+ + 2e^- \tag{2}$$

$$3Ni(OH)_2 + H_2O = Ni_3O_4 + 2H^+ + 2e^- \tag{3}$$

$$2Ni_3O_4 + H_2O = 3Ni_2O_3 + 2H^+ + 2e^- \tag{5}$$

$$Ni_2O_3 + H_2O = 2NiO_2 + 2H^+ + 2e^- \tag{6}$$

$$Ni^{2+} + H_2O = Ni(OH)_2 + 2H^+ \tag{7}$$

$$Ni(OH)_2 + H_2O = HNiO_2^- + H^+ \tag{8}$$

$$Ni = Ni^{2+} + 2e^- \tag{9}$$

$$Ni + 2H_2O = HNiO_2^- + 3H^+ + 2e^- \tag{10}$$

$$3Ni^{2+} + 4H_2O = Ni_3O_4 + 8H^+ + 2e^- \tag{11}$$

$$3HNiO_2^- + H^+ = Ni_3O_4 + 2H_2O + 2e^- \tag{12}$$

$$2Ni^{2+} + 3H_2O = Ni_2O_3 + 6H^+ + 2e^- \tag{13}$$

$$Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e^- \tag{14}$$

- Vertical line in Porbaix diagram (e.g. pH = 8)

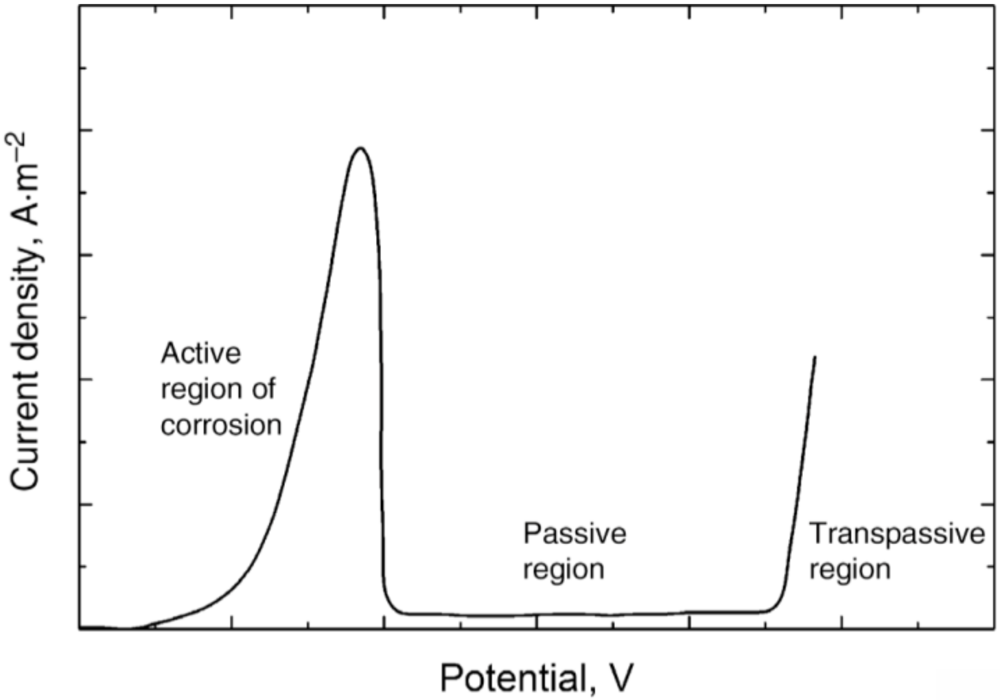

**Figure 16.3** Current–voltage curve illustrating passivation.

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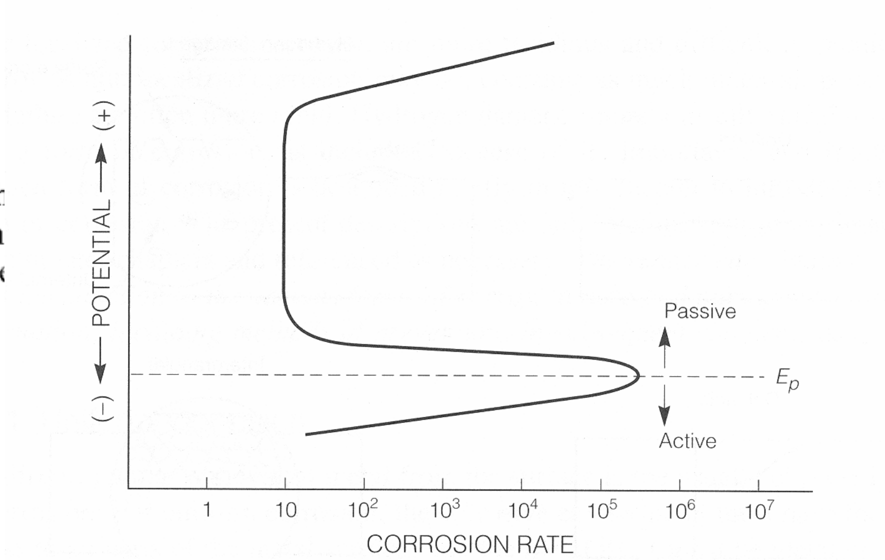

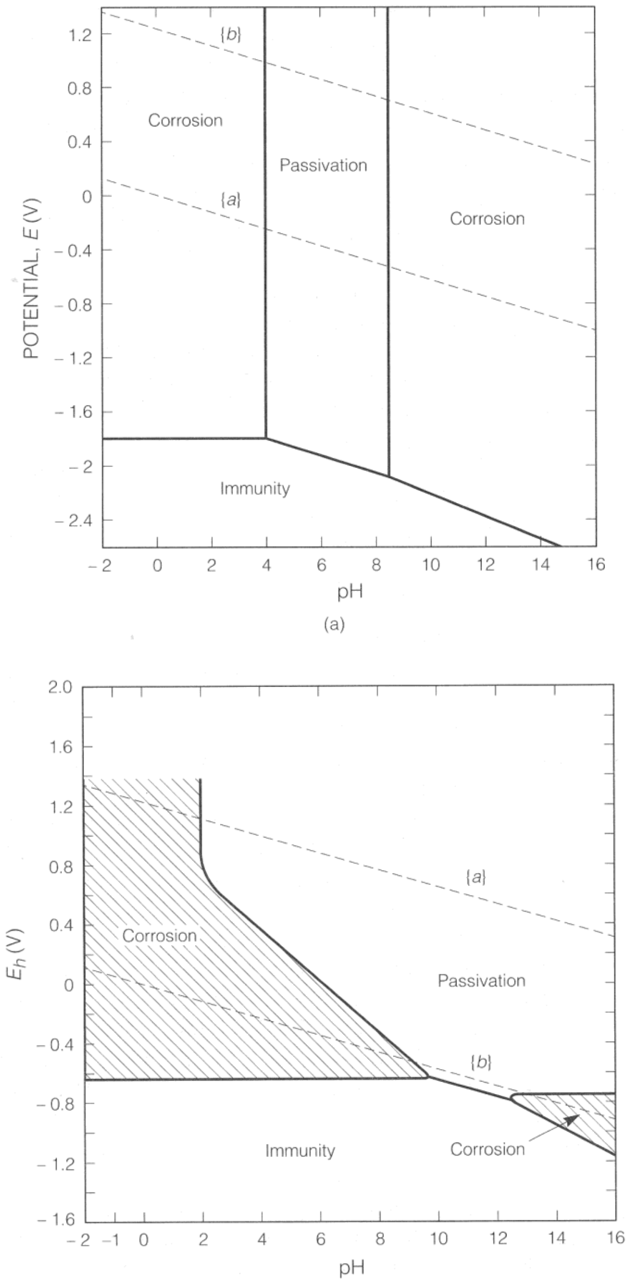

(a)

(b)

**FIGURE 2.5** Pourbaix diagrams for (a) aluminum and (b) iron. All dissolved species at activities of $10^{-6}$ g-equiv/L.

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# Corrosion rate for uniform corrosion

- For a uniformly corroding surface, the potential naturally moves to the corrosion potential, where the anodic and cathodic currents are equal

Evans diagrams

- Tafel plot can be used to illustrate and to help us analyze uniform corrosion
→ I-V curves for both the anodic and cathodic reactions on the same plot

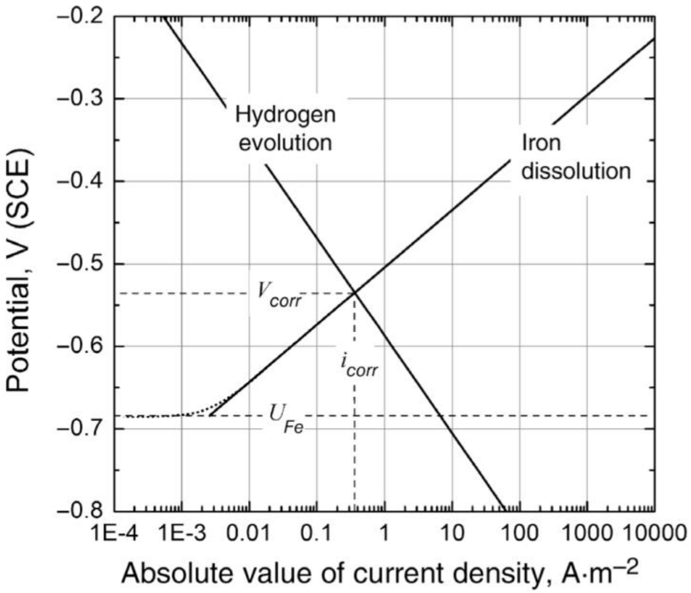

**Figure 16.4** Evans diagram showing iron dissolution and hydrogen evolution (pH = 0.9, 1 N HCl, deaerated). *Source:* Adapted from R. J. Chin and K. Nobe 1972, J. Electrochem. Soc., 119, 1457.

- The cathodic evolution of hydrogen and anodic dissolution of iron using Tafel expressions

- $V_{corr}$ (or $E_{corr}$): corrosion potential
→ zero net current (since the rates of the two reactions are balanced), $i_{corr}$ (corrosion current)
→ the rate at which the metal will dissolve

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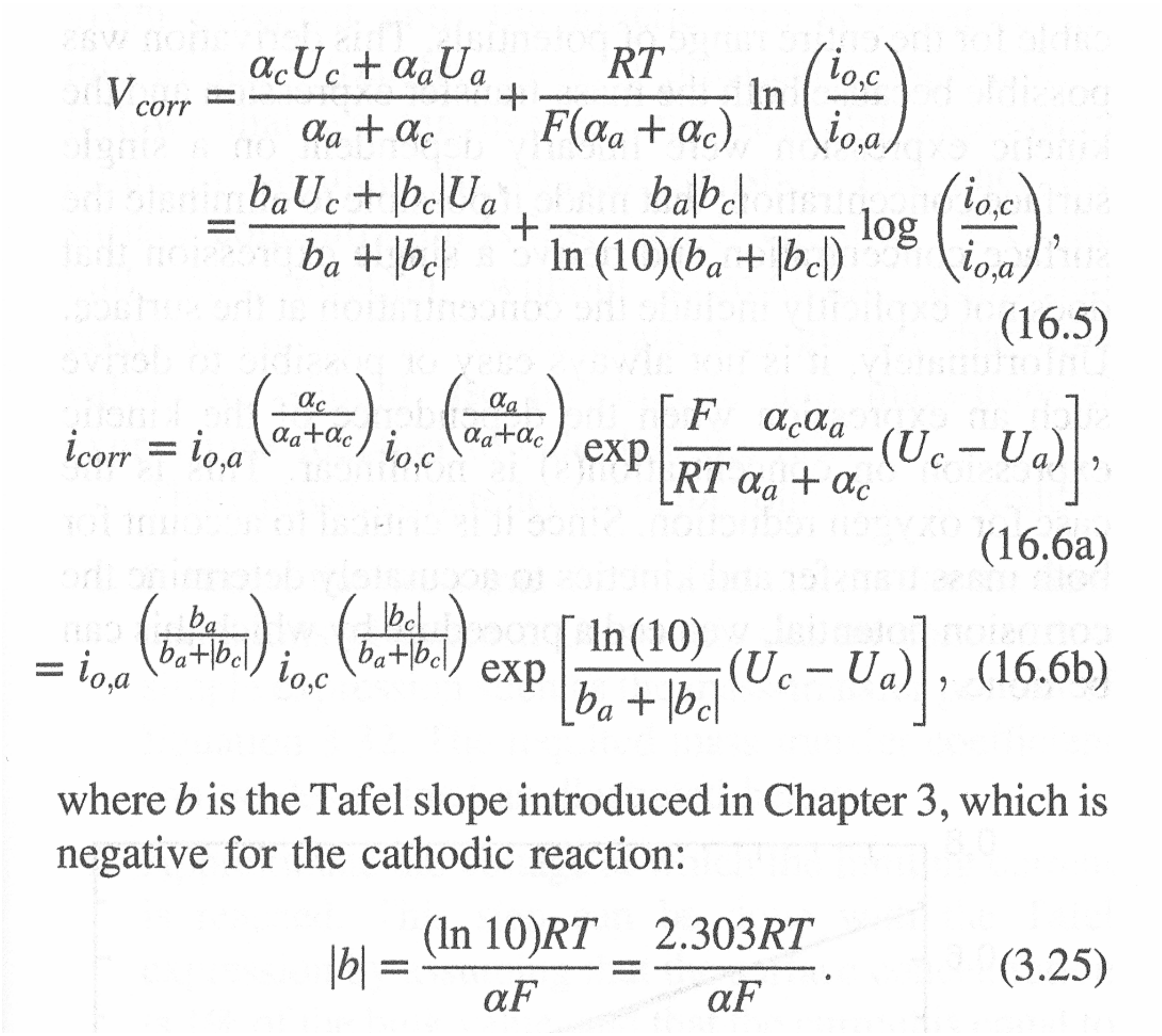
Using Butler-Volmer equation and Tafel kinetics



$$V_{corr} = \frac{\alpha_c U_c + \alpha_a U_a}{\alpha_a + \alpha_c} + \frac{RT}{F(\alpha_a + \alpha_c)} \ln\left(\frac{i_{o,c}}{i_{o,a}}\right)$$

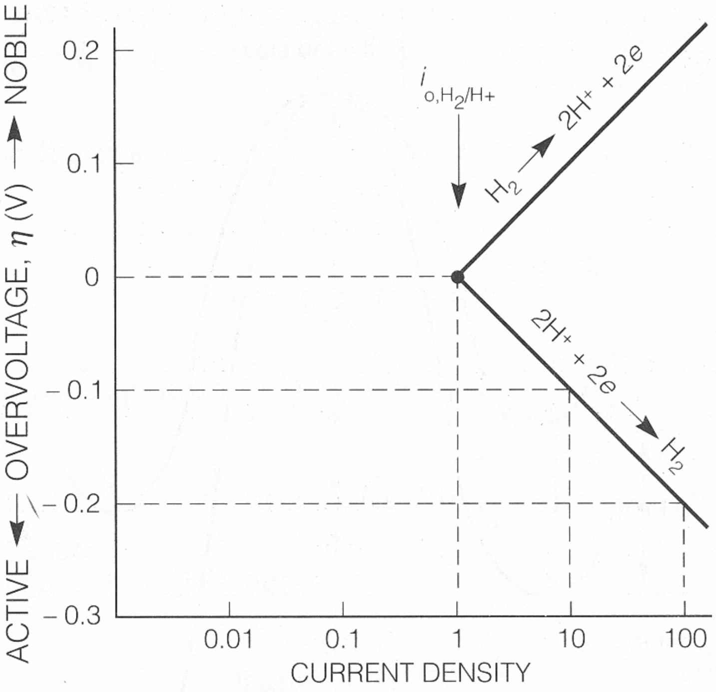
$$= \frac{b_a U_c + |b_c| U_a}{b_a + |b_c|} + \frac{b_a |b_c|}{\ln(10)(b_a + |b_c|)} \log\left(\frac{i_{o,c}}{i_{o,a}}\right), \tag{16.5}$$

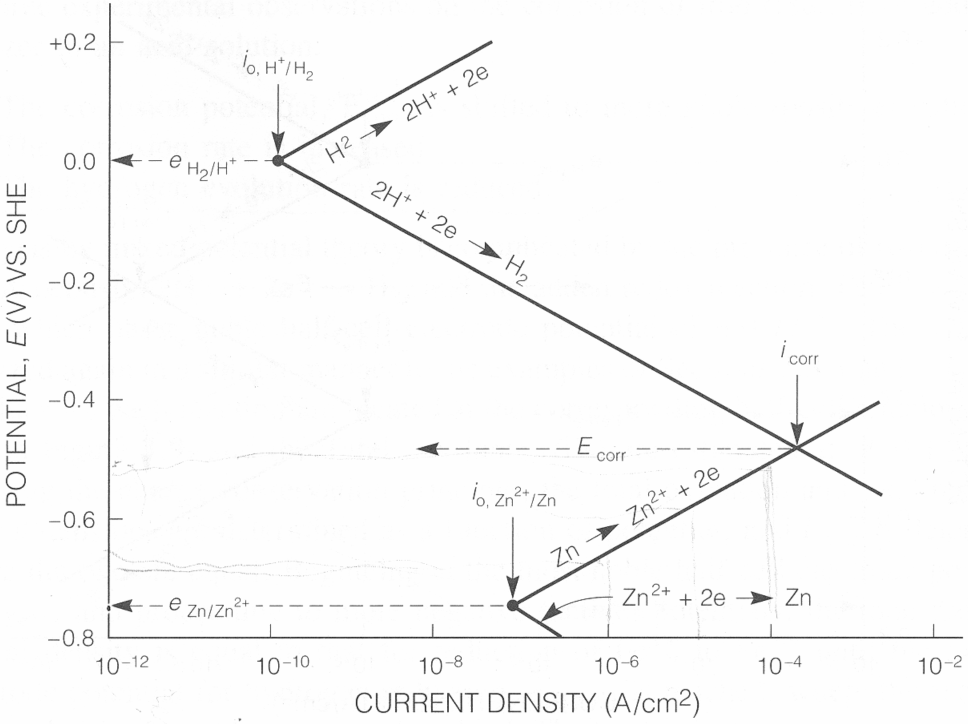
$$i_{corr} = i_{o,a}^{\left(\frac{\alpha_c}{\alpha_a+\alpha_c}\right)} i_{o,c}^{\left(\frac{\alpha_a}{\alpha_a+\alpha_c}\right)} \exp\left[\frac{F}{RT}\frac{\alpha_c \alpha_a}{\alpha_a + \alpha_c}(U_c - U_a)\right], \tag{16.6a}$$

$$= i_{o,a}^{\left(\frac{b_a}{b_a+|b_c|}\right)} i_{o,c}^{\left(\frac{|b_c|}{b_a+|b_c|}\right)} \exp\left[\frac{\ln(10)}{b_a + |b_c|}(U_c - U_a)\right], \tag{16.6b}$$

where *b* is the Tafel slope introduced in Chapter 3, which is negative for the cathodic reaction:

$$|b| = \frac{(\ln 10)RT}{\alpha F} = \frac{2.303RT}{\alpha F}. \tag{3.25}$$





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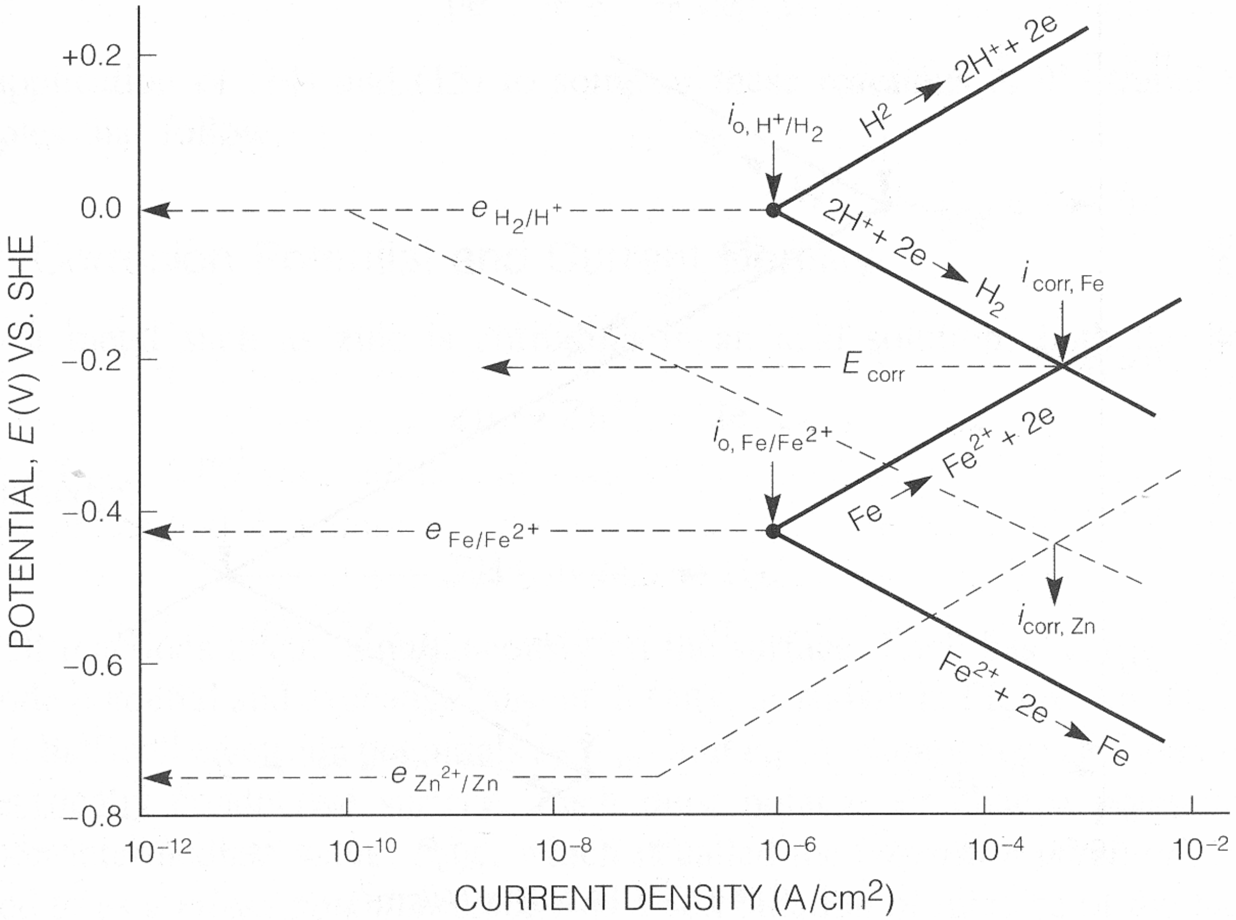

**FIGURE 3.8** Comparison of electrochemical parameters for iron and zinc in acid solution, demonstrating the importance of $i_o$ on determination of corrosion rates. Dashed lines represent lines from Figure 3.7 superimposed for comparison.

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# Experimental measurement of corrosion

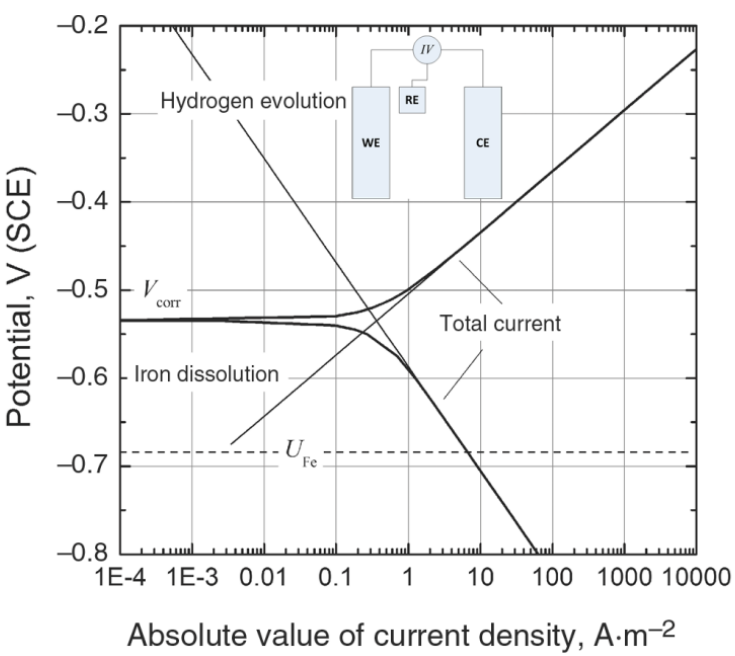

**Figure 16.5** Relationship between the total current and the anodic and cathodic currents for a corrosion sample at different potentials.

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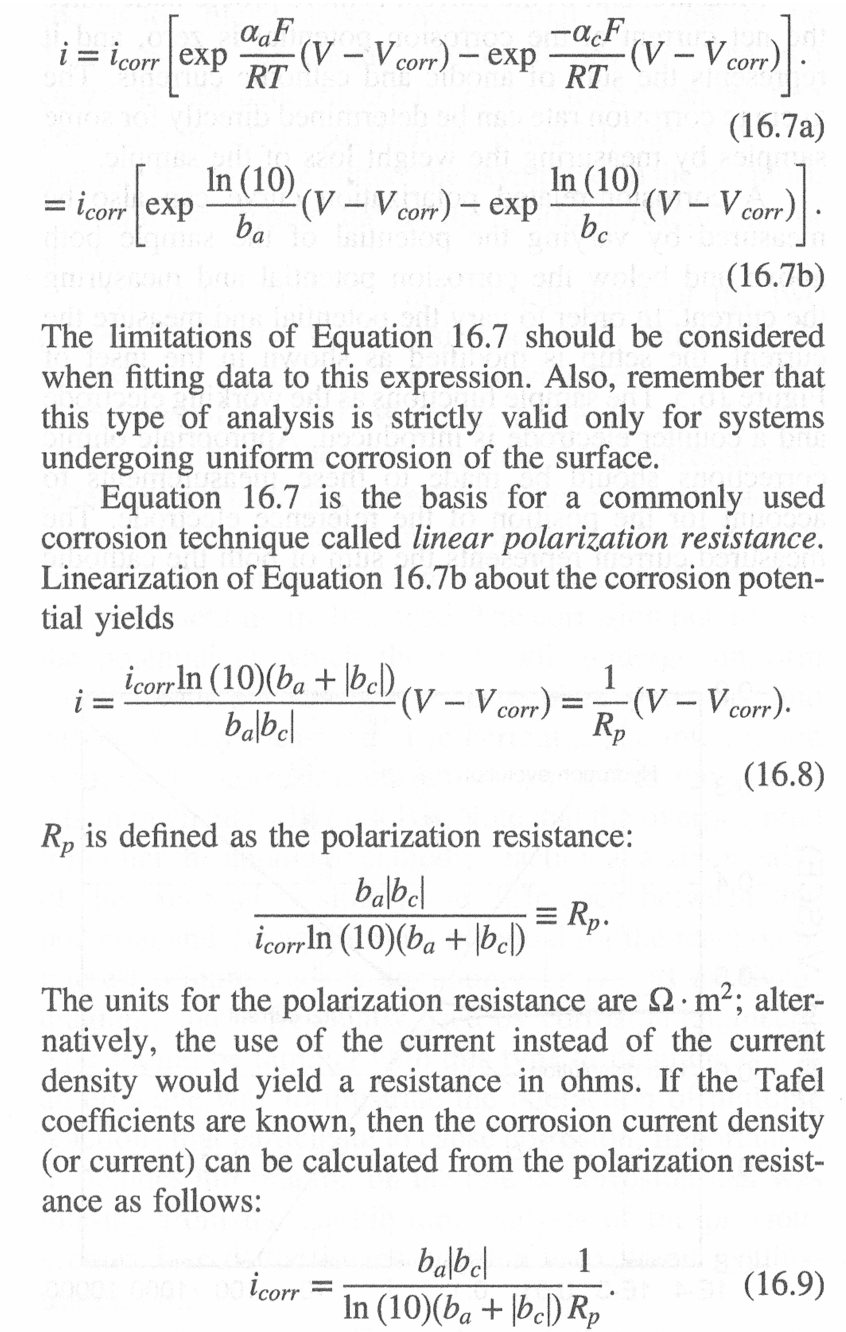

$$i = i_{corr}\left[\exp\frac{\alpha_a F}{RT}(V - V_{corr}) - \exp\frac{-\alpha_c F}{RT}(V - V_{corr})\right]. \tag{16.7a}$$

$$= i_{corr}\left[\exp\frac{\ln(10)}{b_a}(V - V_{corr}) - \exp\frac{\ln(10)}{b_c}(V - V_{corr})\right]. \tag{16.7b}$$

The limitations of Equation 16.7 should be considered when fitting data to this expression. Also, remember that this type of analysis is strictly valid only for systems undergoing uniform corrosion of the surface.

Equation 16.7 is the basis for a commonly used corrosion technique called *linear polarization resistance*. Linearization of Equation 16.7b about the corrosion potential yields

$$i = \frac{i_{corr}\ln(10)(b_a + |b_c|)}{b_a|b_c|}(V - V_{corr}) = \frac{1}{R_p}(V - V_{corr}). \tag{16.8}$$

$R_p$ is defined as the polarization resistance:

$$\frac{b_a|b_c|}{i_{corr}\ln(10)(b_a + |b_c|)} \equiv R_p.$$

The units for the polarization resistance are $\Omega \cdot m^2$; alternatively, the use of the current instead of the current density would yield a resistance in ohms. If the Tafel coefficients are known, then the corrosion current density (or current) can be calculated from the polarization resistance as follows:

$$i_{corr} = \frac{b_a|b_c|}{\ln(10)(b_a + |b_c|)}\frac{1}{R_p}. \tag{16.9}$$

# Mass transfer effects

- Mass transfer effect: e.g. oxygen reduction → limiting current

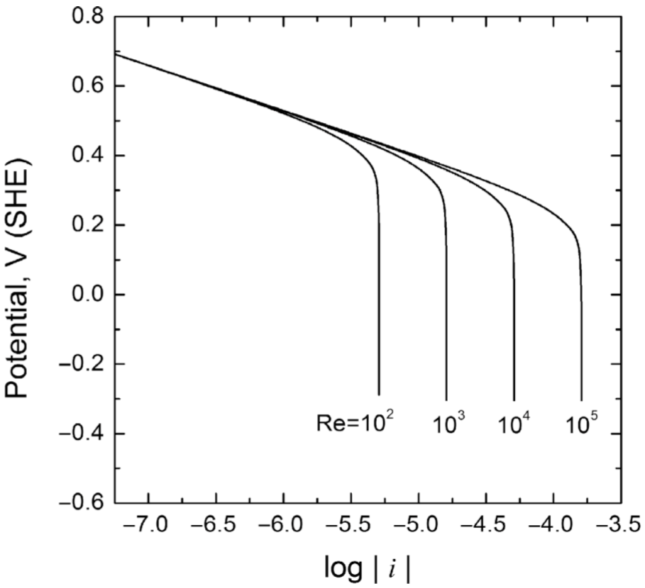

**Figure 16.6** Oxygen reduction current at different flow rates for fully developed laminar flow over a flat plate.

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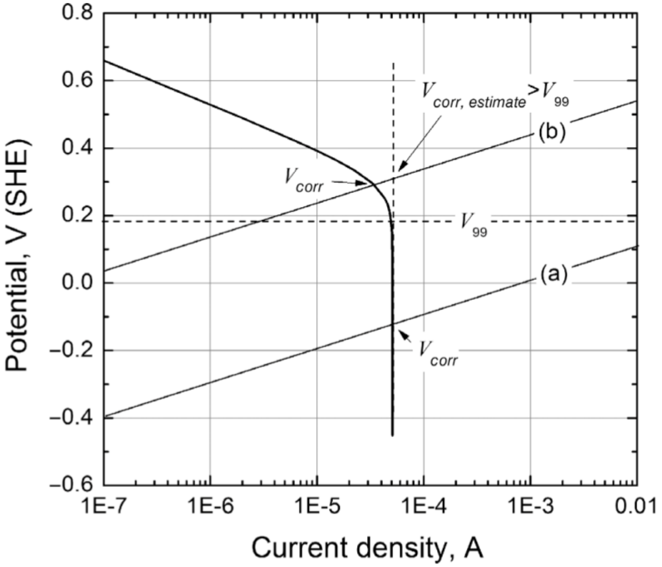

**Figure 16.7** Illustration of corrosion potential determination for a cathodic reaction that is mass-transfer limited.

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Two anodic curves
(a) One that intersects in the mass transfer limited region
(b) One that intersects in the region where rate effects also contribute

# Multiple reactions

- Multiple cathodic reactions (multiple anodic reactions later)

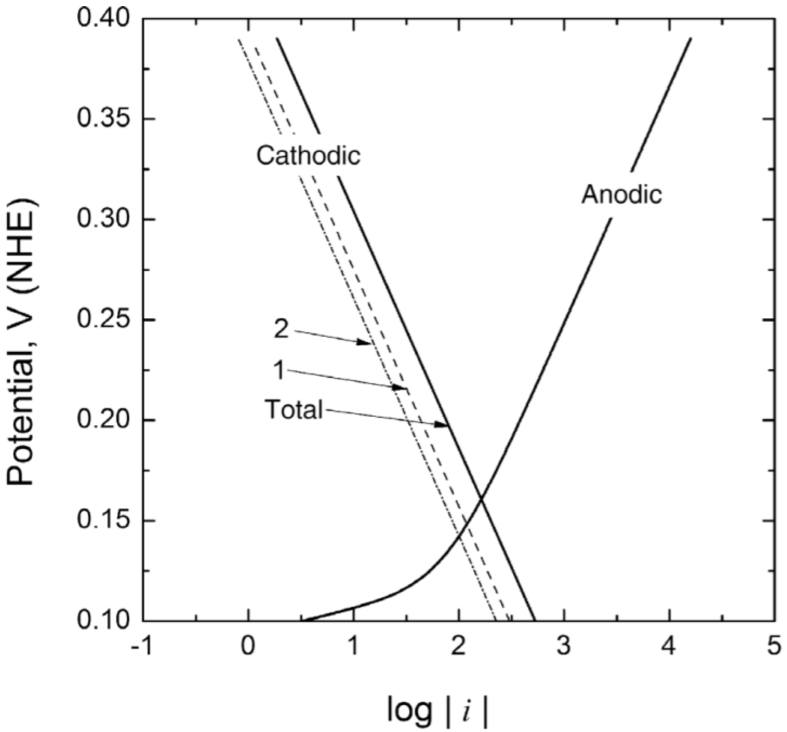

**Figure 16.8** Multiple cathodic reactions for the corrosion of copper metal by copper(II) ions in acid.

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# Localized corrosion

- Localized corrosion is very different from the uniform corrosion (Fig.16.1)

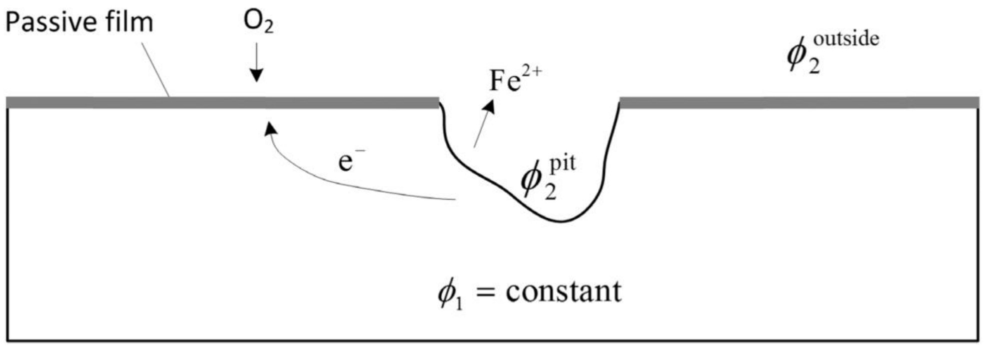

**Figure 16.9** Schematic diagram of corrosion pit. Current flows from the inside of the pit to the outside, driven by a potential difference in solution. The potential is greater in the pit than outside the pit.

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## Galvanic corrosion

- Galvanic corrosion is a form of localized corrosion that can occur when two different metals are in contact and exposed to a common electrolyte

- e.g. Zn + Fe

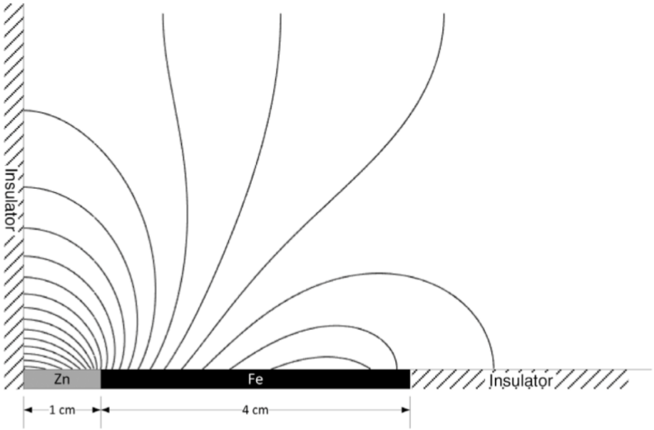

**Figure 16.10** Potential field for galvanic coupling of Zn and Fe. *Source:* Data adapted from Abootalebi 2010.

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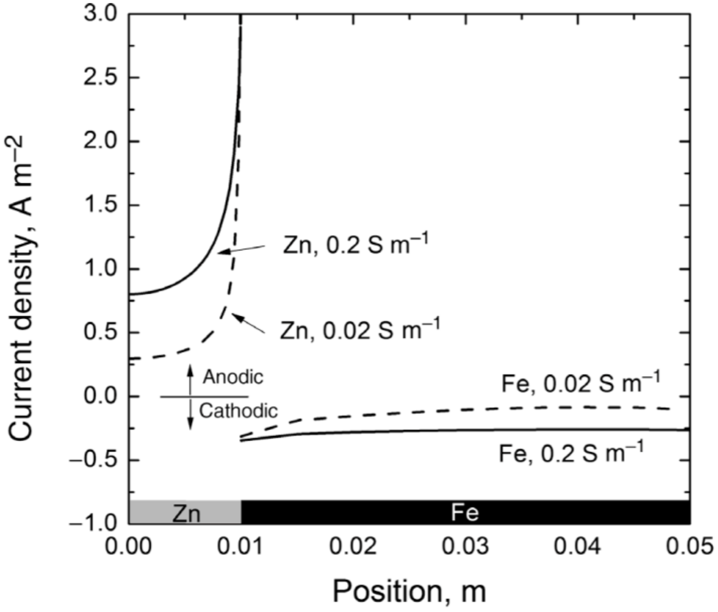

**Figure 16.12** Local current density for galvanically coupled Zn and Fe at solution conductivities of 0.2 and 0.02 $\mathrm{S{\cdot}m^{-1}}$.

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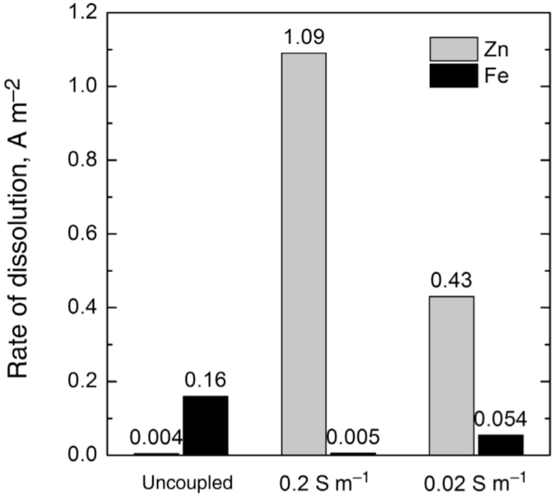

**Figure 16.11** Average dissolution rates: (1) without galvanic coupling, (2) coupled with a solution conductivity of 0.2 $\mathrm{S{\cdot}m^{-1}}$, and (3) coupled with a solution conductivity of 0.02 $\mathrm{S{\cdot}m^{-1}}$.

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# Corrosion protection

- Cathodic protection, anodic protection, electrophoretic coating (or e-coating)

Anodic protection: much less commonly than cathodic protection
-(i) Increasing potential in the anodic direction to passive region

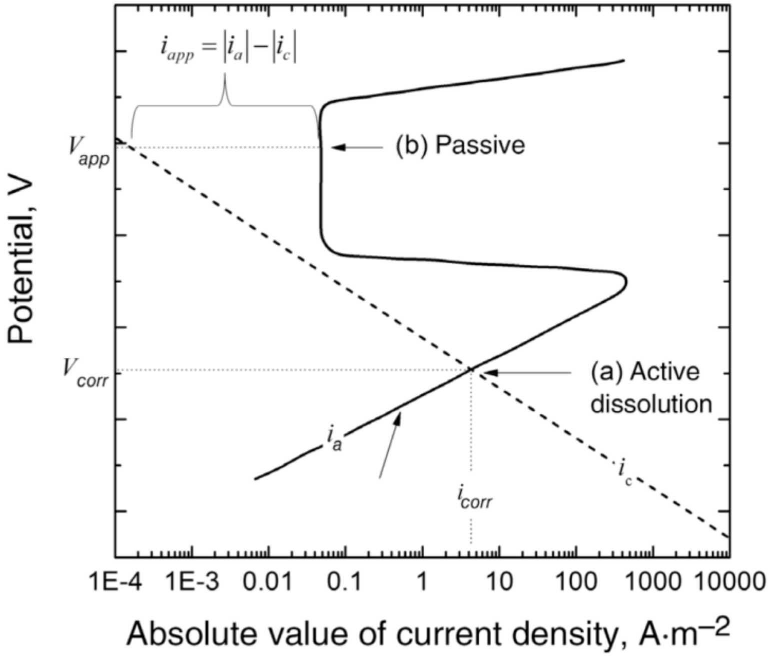

**Figure 16.13** Illustration of using anodic protection to reduce the rate of corrosion for metals that passivate.

- anodic corrosion current is reduced by two orders
- Cathodic current is reduced more

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# Anodic protection

-(ii) Changing the cathodic reaction so that the cathodic curve intersects the anodic curve in the passive region

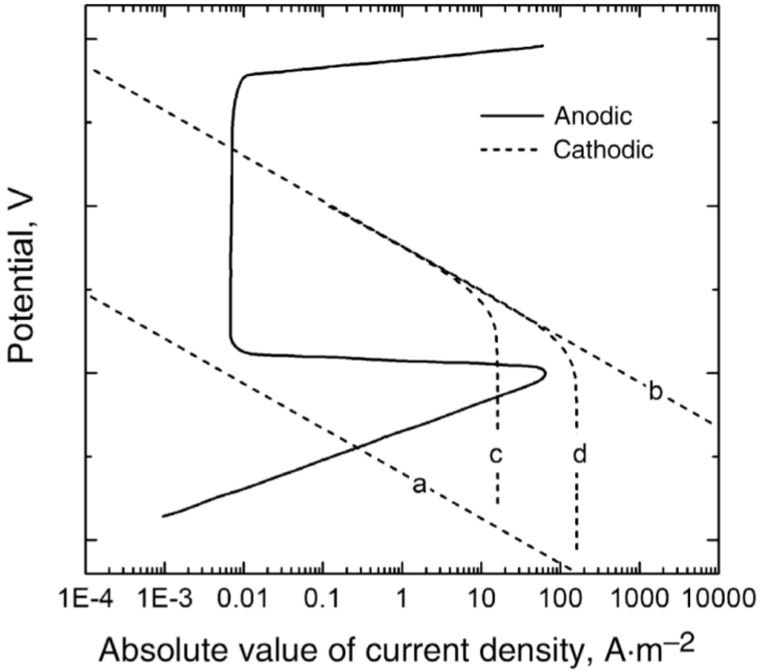

**Figure 16.14** Importance of mass transfer on passivating the metal.

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- Changing oxygen concentration

# Cathodic protection

- used to protect sea vessels, oil platforms, ocean structures, buried pipelines, storage tanks and so on
- lower the potential of the metal in the cathodic direction to decrease its dissolution rate → to reduce or eliminate corrosion → ideally to the immunity area (Poubaix diagram)

-Two ways for cathodic protection
(i) Use of a sacrificial anode
(ii) Use of an external power supply to apply a cathodic current to the metal to be protected

$V_1$: lower dissolution
$V_2$: eliminate dissolution

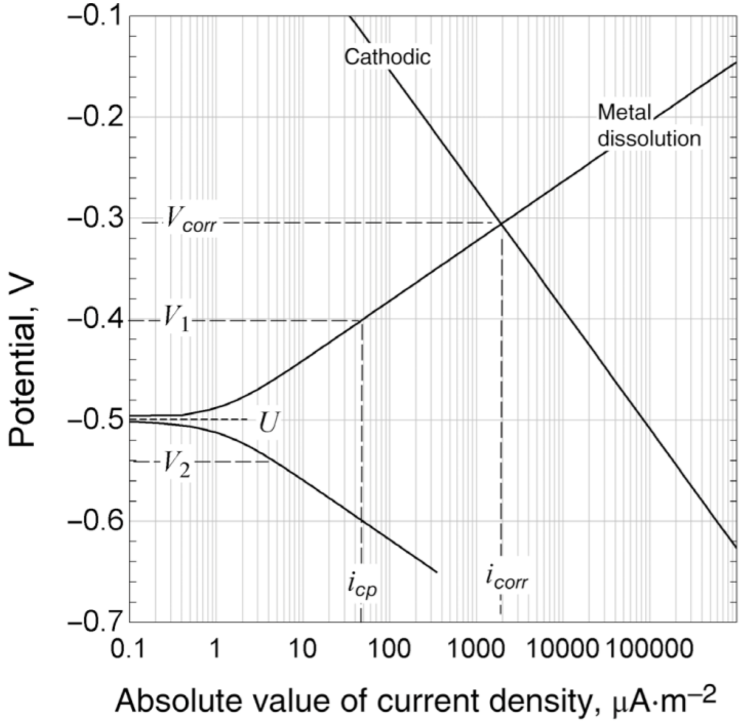

**Figure 16.15** Evans diagram showing corrosion potential and the reduction of corrosion current with a reduction in potential.

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## (i) Use of a sacrificial anode

- coupling the metal to be protected with a more active metal, that is, one with a lower equilibrium potential

→ sacrificial metal (by galvanic corrosion)

**Figure 16.16** Use of sacrificial anodes to protect against ship corrosion.

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## (i) Use of impressed current cathodic protection (ICCP)

- the external electrode is the anode (corroded) and the structure to be protected is the cathode

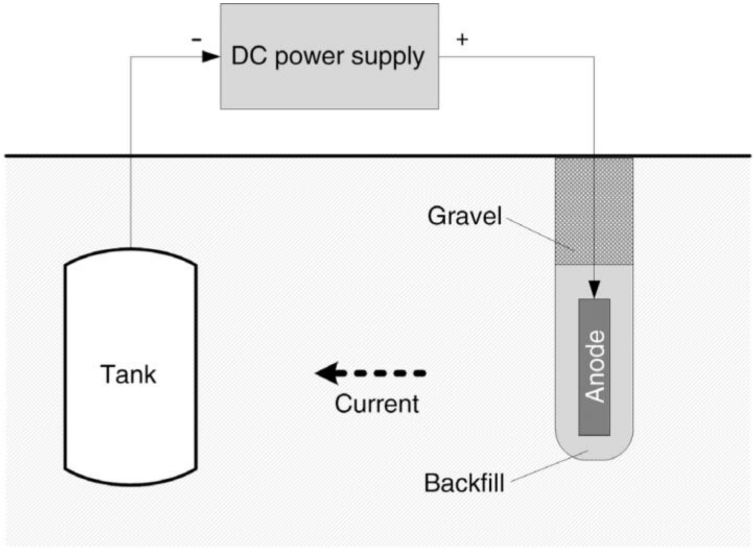

**Figure 16.17** Impressed-current cathodic protection used to reduce corrosion of an underground tank.

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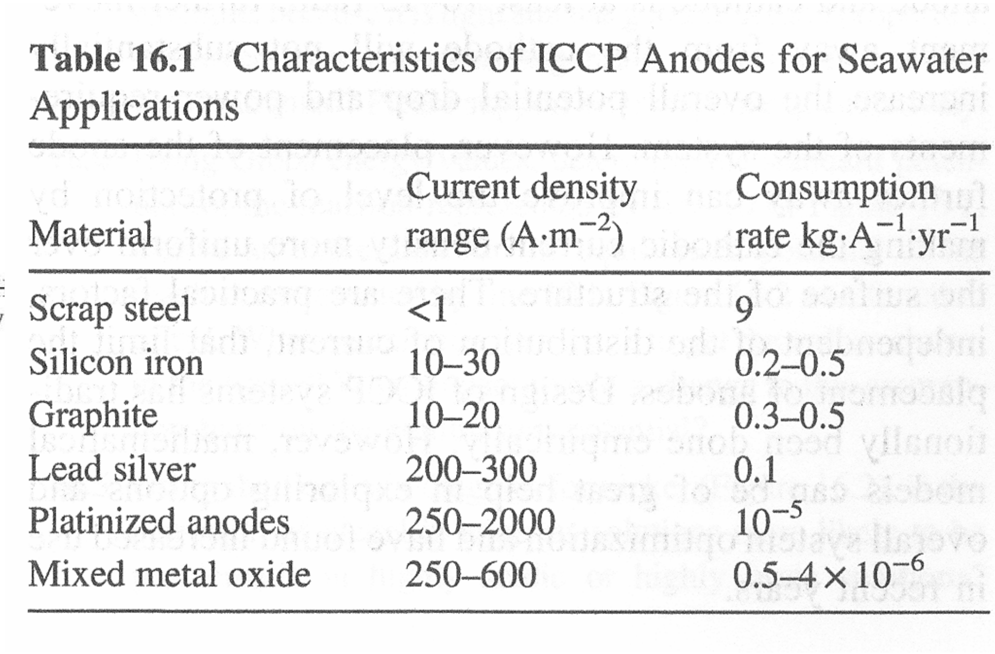


**Table 16.1** Characteristics of ICCP Anodes for Seawater Applications

| Material | Current density range ($A{\cdot}m^{-2}$) | Consumption rate $kg{\cdot}A^{-1}{\cdot}yr^{-1}$ |
|---|---|---|
| Scrap steel | <1 | 9 |
| Silicon iron | 10–30 | 0.2–0.5 |
| Graphite | 10–20 | 0.3–0.5 |
| Lead silver | 200–300 | 0.1 |
| Platinized anodes | 250–2000 | $10^{-5}$ |
| Mixed metal oxide | 250–600 | $0.5–4 \times 10^{-6}$ |

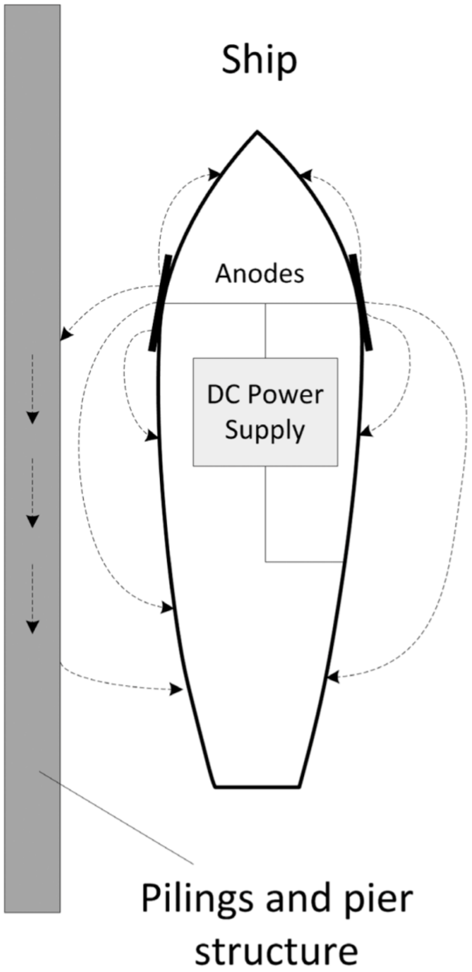


**Figure 16.18** Stray currents lead to increased corrosion of pier.

*Electrochemical Engineering*, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

**TABLE 1.1** Galvanic Series in Seawater

---

*Cathodic (noble)*

↑

platinum
gold
graphite
titanium
silver
zirconium
AISI Type 316, 317 stainless steels (passive)
AISI Type 304 stainless steel (passive)
AISI Type 430 stainless steel (passive)
nickel (passive)
copper-nickel (70-30)
bronzes
copper
brasses
nickel (active)
naval brass
tin
lead
AISI Type 316, 317 stainless steels (active)
AISI Type 304 stainless steel (active)
cast iron
steel or iron
aluminum alloy 2024
cadmium
aluminum alloy 1100
zinc
magnesium and magnesium alloys

↓

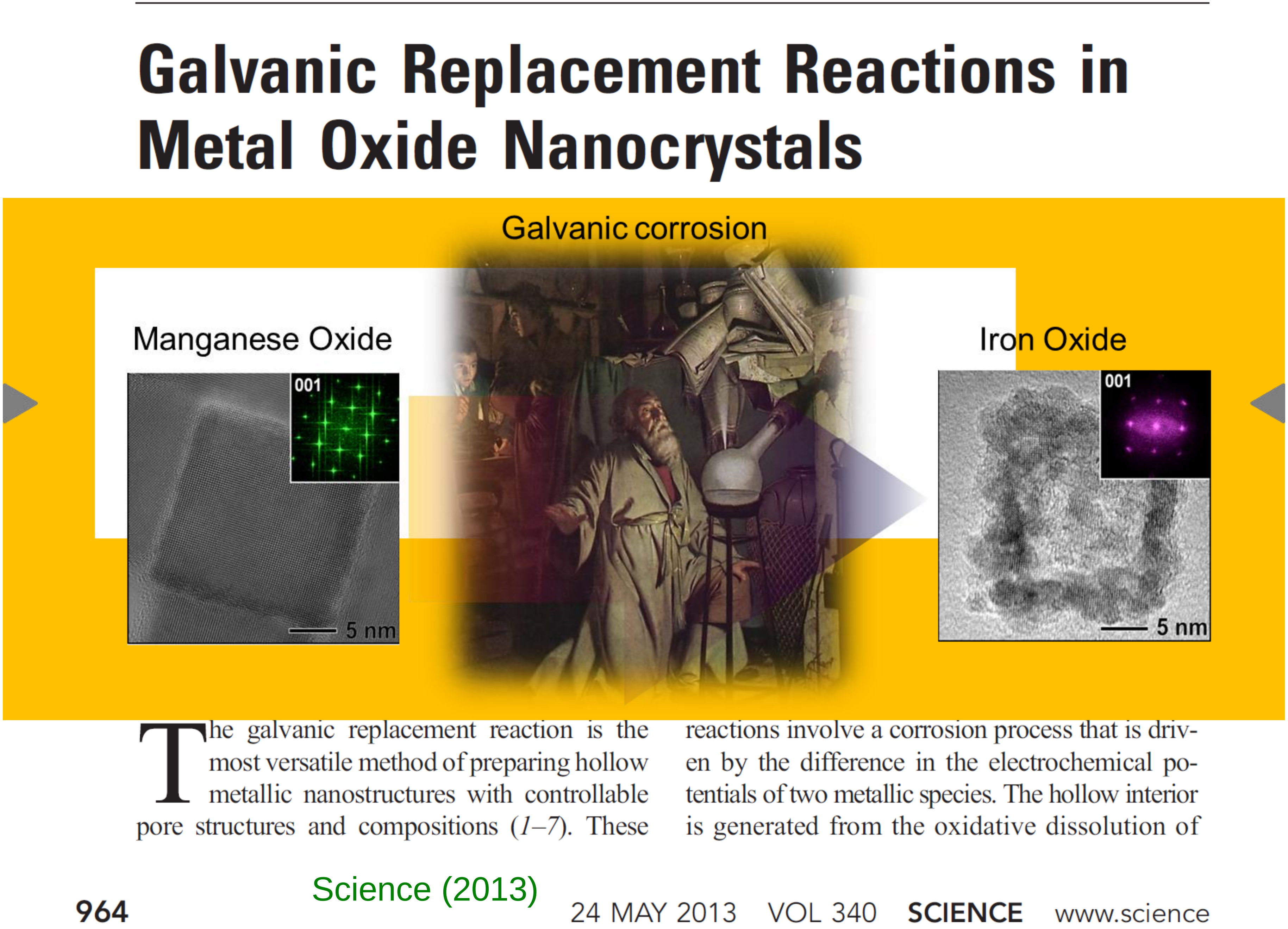
*Anodic (active)*

---

**FIGURE 6.1** Galvanic Series for seawater. Dark boxes indicate active behavior for active–passive alloys. *(From H. P. Hack,* Metals Handbook, *Vol. 13,* Corrosion, *9th ed., ASM, Metals Park, OH, p. 234, 1987. Reprinted by permission, ASM International.)*

D. A. Jones, Corrosion, Macmillan

# 도금/부식을 이용한 입자합성



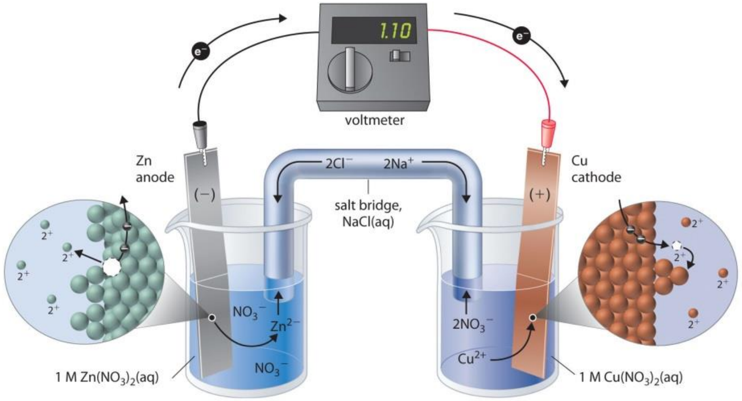
## Galvanic Replacement Reactions in Metal Oxide Nanocrystals

The galvanic replacement reaction is the most versatile method of preparing hollow metallic nanostructures with controllable pore structures and compositions (*1*–*7*). These reactions involve a corrosion process that is driven by the difference in the electrochemical potentials of two metallic species. The hollow interior is generated from the oxidative dissolution of

Science (2013)

# Galvanic Corrosion (갈바니 부식)

- Galvanic Cell

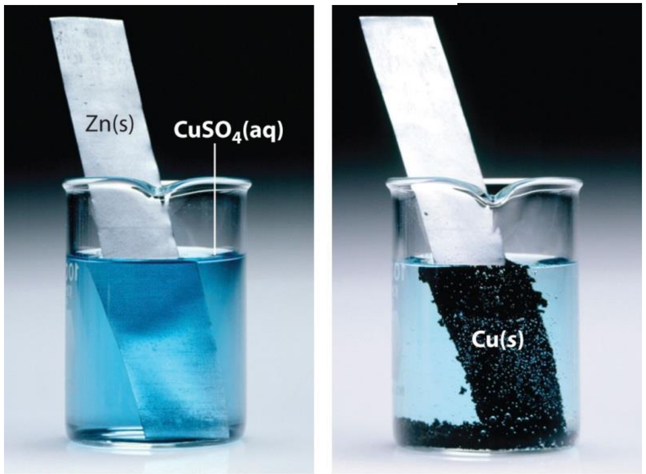


oxidation half-reaction:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

reduction half-reaction:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

- Galvanic Corrosion



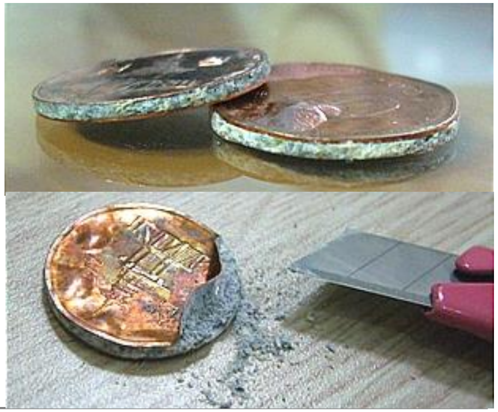
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

- Ionization Tendency of Metals

Active

Noble

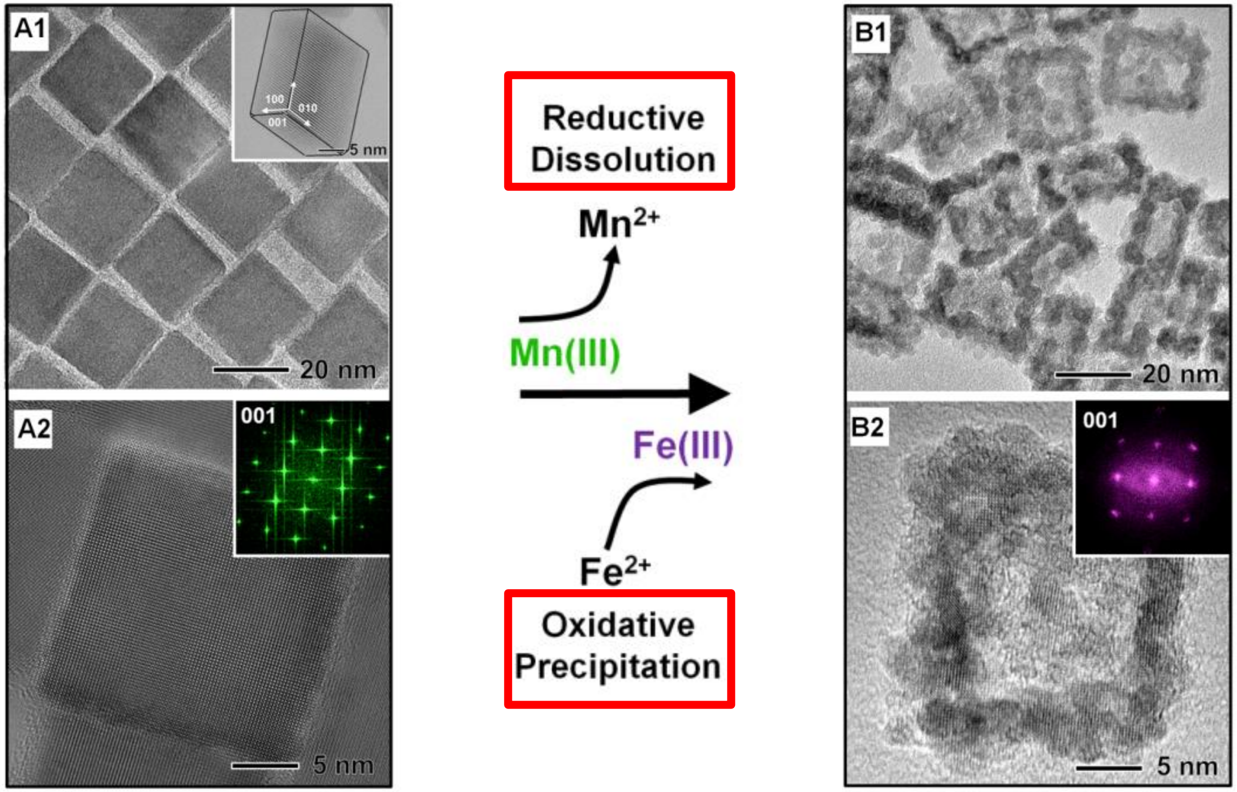
- Corroded Coin: copper+zinc



# 도금/부식을 이용한 입자합성

$Mn_3O_4$ Nanocrystals

γ-$Fe_2O_3$ Nanocages



| Standard reduction potential(V) | Multivalent ion pairs |
|---|---|
| 1.87 | $Co^{2+}/Co^{3+}$ |
| 1.67 | $Pb^{2+}/Pb^{4+}$ |
| 1.61 | $Ce^{3+}/Ce^{4+}$ |
| 1.51 | $Mn^{2+}/Mn^{3+}$ |
| 0.77 | $Fe^{2+}/Fe^{3+}$ |
| 0.16 | $Cu^{+}/Cu^{2+}$ |
| 0.15 | $Sn^{2+}/Sn^{4+}$ |
| 0.00 | $Ti^{3+}/Ti^{4+}$ |
| -0.40 | $Cr^{2+}/Cr^{3+}$ |

- $Mn_3O_4$ nanocrystals were reacted with Fe(II) perchlorate in a suspension.
- The lattice orientation of original $Mn_3O_4$ was preserved during the complete transformation.

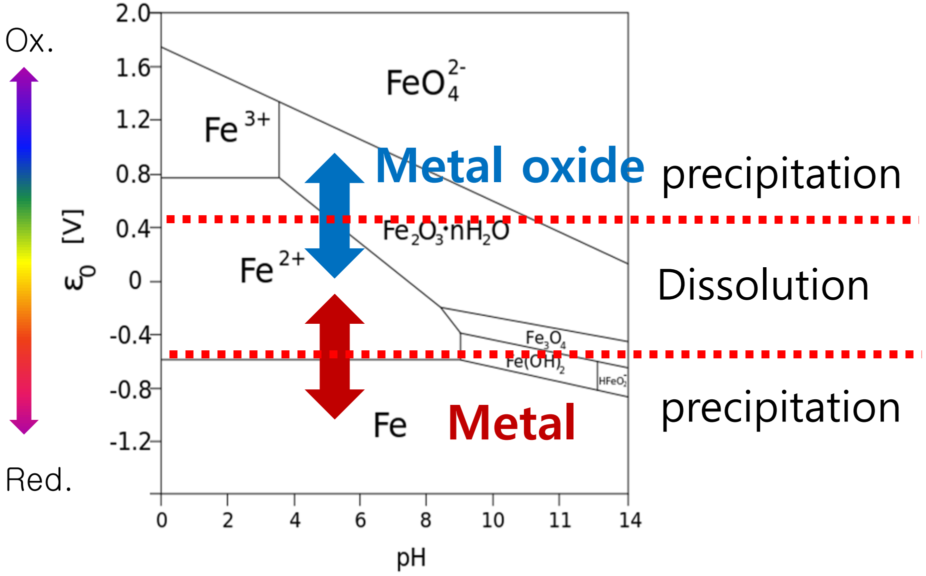
*Science* 2013, 340, 964.

# Galvanic Replacement Reactions in Metal Oxide Nanocrystals

## Metal Nanocrystal vs. Metal Oxide Nanocrystal

| | Metal nanocrystal | Metal oxide nanocrystal |
|---|---|---|
| **Representative equation** | $3Ag + HAuCl_4 \rightarrow 3AgCl + Au + HCl$ | $Mn_3O_4 + 2Fe^{2+} + 2H^+ \rightarrow \gamma\text{-}Fe_2O_3 + 3Mn^{2+} + H_2O$ |
| **Redox pair** | Metal vs Metal ion | Metal ion vs Metal ion |
| **Reaction mechanism** | Oxidative dissolution and reductive precipitation | Reductive dissolution and oxidative precipitation |

### Pour-baix diagram



Metal oxide precipitation

Dissolution

Metal precipitation

### standard reduction potentials of multivalent ions

| Standard reduction potential(V) | Multivalent ion pairs |
|---|---|
| 1.87 | $Co^{2+}/Co^{3+}$ |
| 1.67 | $Pb^{2+}/Pb^{4+}$ |
| 1.61 | $Ce^{3+}/Ce^{4+}$ |
| 1.51 | $Mn^{2+}/Mn^{3+}$ |
| 0.77 | $Fe^{2+}/Fe^{3+}$ |
| 0.16 | $Cu^{+}/Cu^{2+}$ |
| 0.15 | $Sn^{2+}/Sn^{4+}$ |
| 0.00 | $Ti^{3+}/Ti^{4+}$ |
| -0.40 | $Cr^{2+}/Cr^{3+}$ |

# (나노)입자 합성:환원법

*Gold sol*. Add 1 $cm^3$ of 1% $HAuCl_4.3H_2O$ to 100 $cm^3$ of distilled water. Bring to the boil and add 2.5 $cm^3$ of 1% sodium citrate. Keep the solution just boiling. A ruby red gold sol forms after a few minutes.

$$2HAuCl_4 + 3C_6H_8O_7 \text{ (citric acid)}$$
$$\longrightarrow 2Au + 3C_5H_6O_5 \text{ (3-ketoglutaric acid)} + 8HCl + 3CO_2$$

3. *Sulphur sol*. Mix equal volumes of aqueous solutions ($10^{-3}$ to $5 \times 10^{-3}$ mol $dm^{-3}$) of $Na_2S_2O_3$ and HCl.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 + S\downarrow$$

4. *Hydrous iron(III) oxide sol*. Add, with stirring, 2 $cm^3$ of 30% $FeCl_3(aq)$ to 500 $cm^3$ of boiling distilled water. A clear reddish-brown dispersion is formed.

$Fe_2O_3$

5. Hydrolysis + condensation of inorganic alkoxide precursors:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4\,C_2H_5OH$$
$$Si(OH)_4 \rightarrow 2\,H_2O + \underline{SiO_2}\downarrow$$

TEOS (tetraethyloxysilane) or TMOS(tetramethyloxysilane)

$$M(OR)_4 + x\,H_2O \rightarrow M(OR)_{4-x}(OH)_x + x\,ROH$$
$$2\,M(OR)_{4-x}(OH)_x \rightarrow (OR)_{4-x}(OH)_{x-1}MOM(OR)_{4-x}(OH)_{x-1} + H_2O$$

hydrolysis, condensation

M = metal