CHAPTER 17: CORROSION AND DEGRADATION

ISSUES TO ADDRESS...

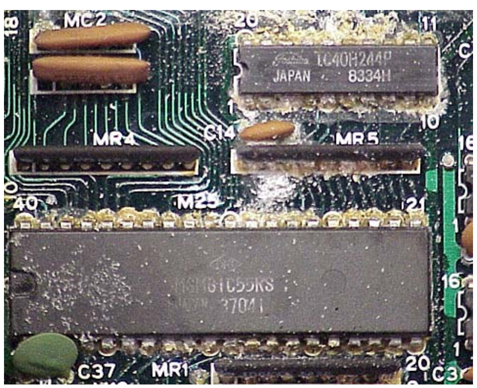
- Why does corrosion occur?
- What metals are most likely to corrode?
- How do temperature and environment affect corrosion rate?
- How do we suppress corrosion?

THE COST OF CORROSION

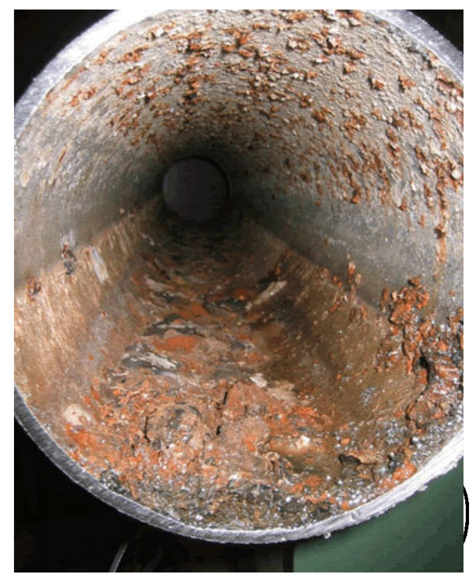
- Corrosion:
  -- the destructive electrochemical attack of a material.
  -- Al Capone's ship, Sapona, off the coast of Bimini.

Photos courtesy L.M. Maestas, Sandia National Labs. Used with permission.

- Cost:
  -- 4 to 5% of the Gross National Product (GNP)*
  -- this amounts to just over $400 billion/yr**



Leaking battery



Electrochemical Considerations

- Oxidation (anodic reaction)

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

metal atoms lose or give up electrons

- Reduction (Cathodic reaction)

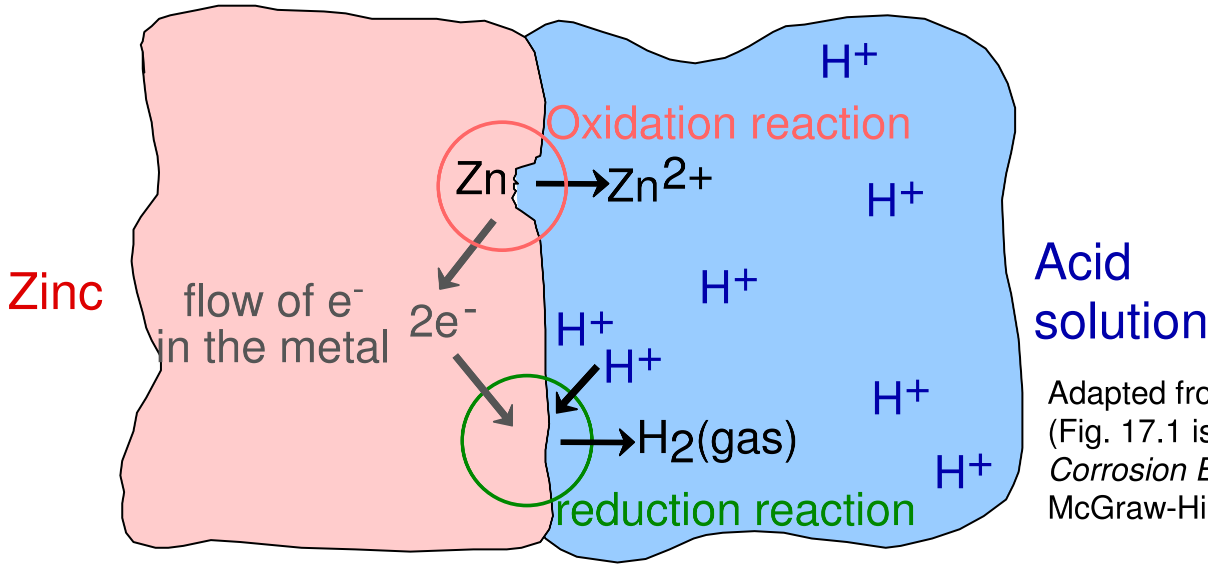
$$M^{n+} + ne^- \longrightarrow M$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)-}$$

metal ions gain electrons

CORROSION OF ZINC IN ACID

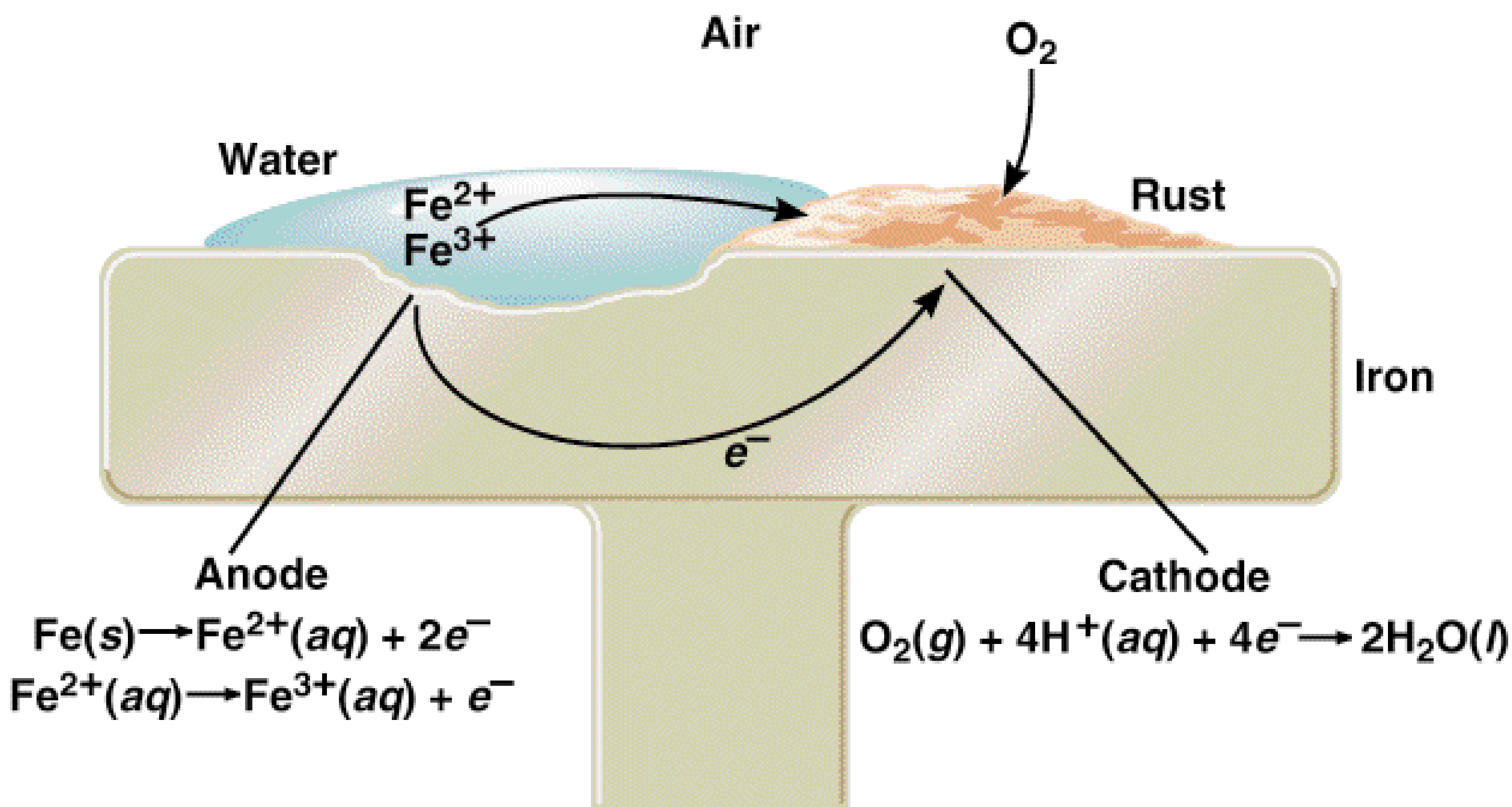
- Two reactions are necessary:
  - -- oxidation reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$
  - -- reduction reaction: $2H^{+} + 2e^{-} \rightarrow H_2(gas)$



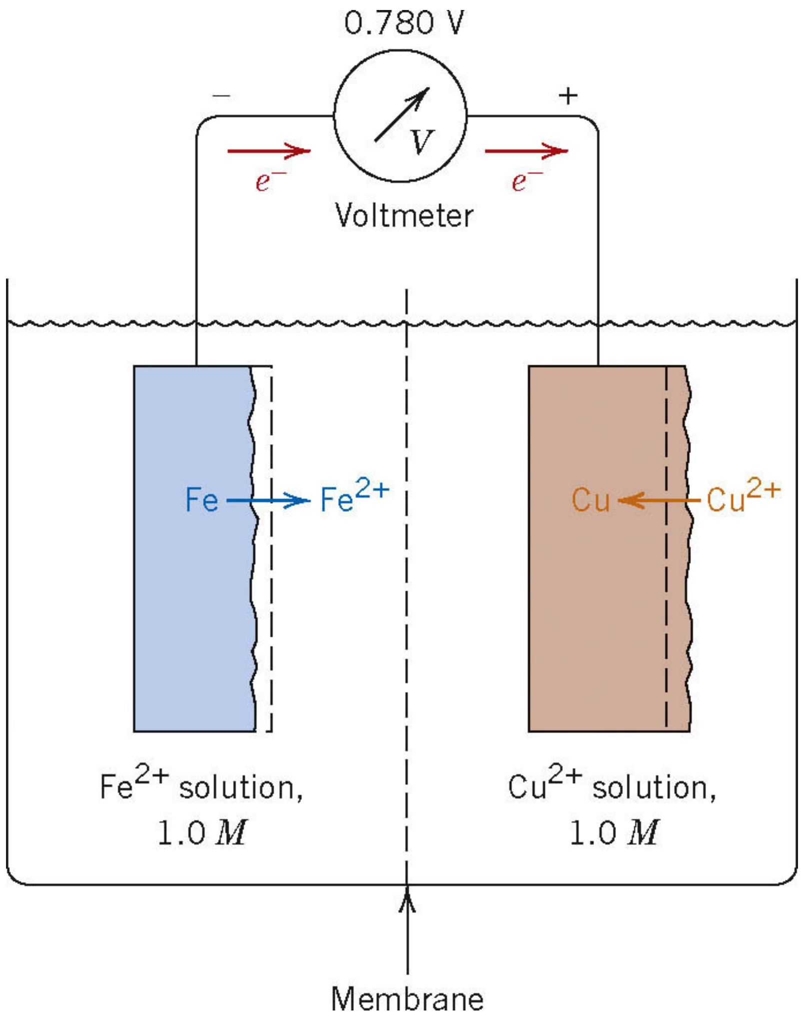
Adapted from Fig. 17.1, *Callister 7e*. (Fig. 17.1 is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- Other reduction reactions:
  - -- in an acid solution: $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$
  - -- in a neutral or base solution: $O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-}$

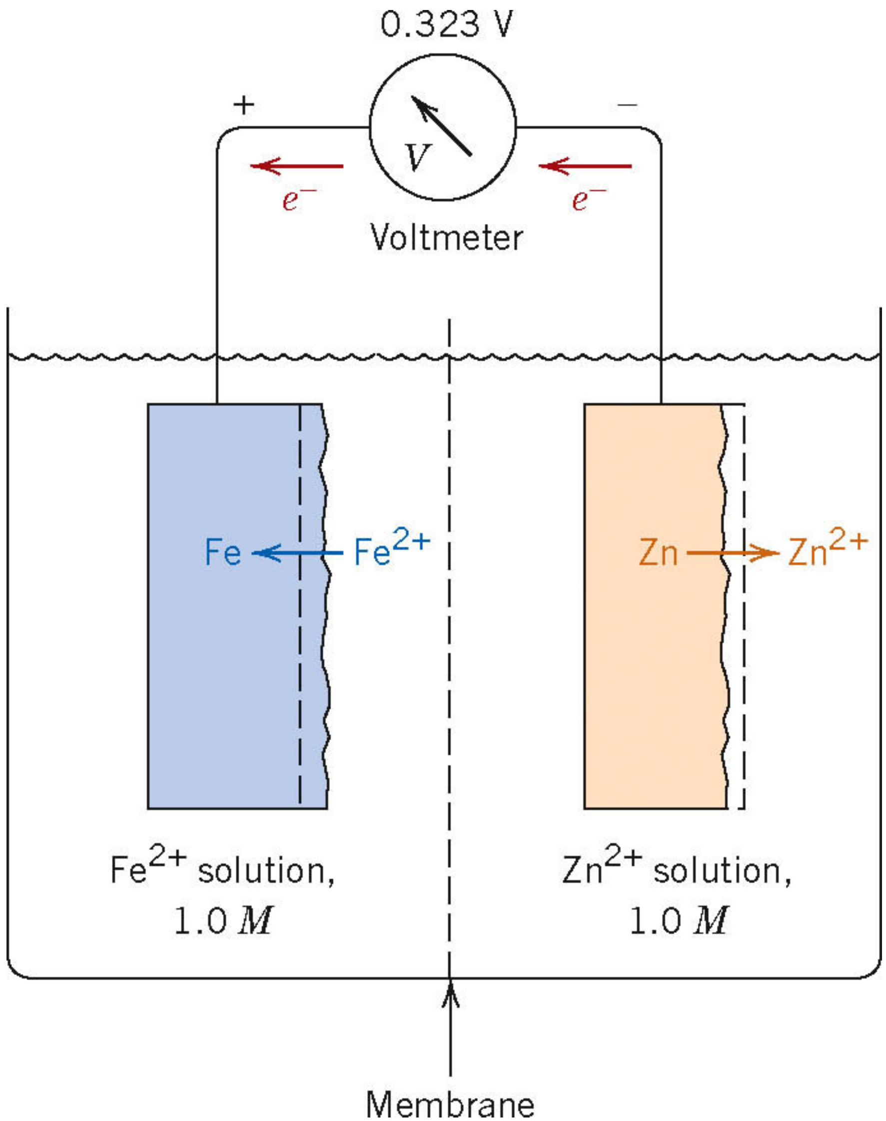
Rust Formation



Not all metallic materials oxidize to form ions with the same degree of ease.



Galvanic couple: two metals eclectically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode.



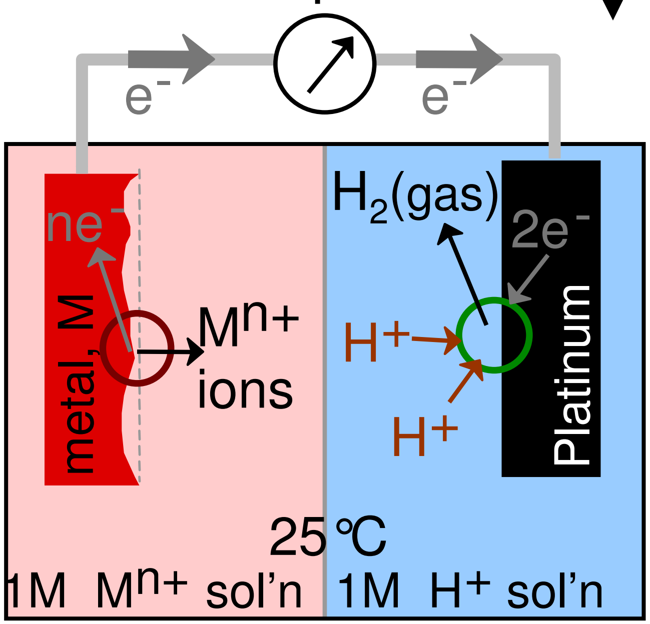
The magnitude of such a voltage is the driving force for the electrochemical oxidation-reduction reaction.

STANDARD HYDROGEN (EMF) TEST

electromotive force

- Two outcomes:

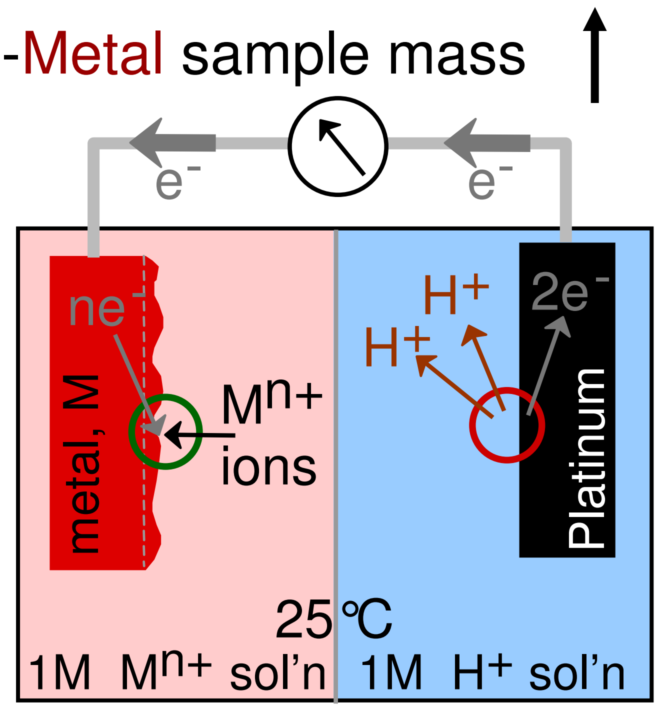
--Metal sample mass ↓



--Metal is the anode (-)

$V^o_{metal} < 0$ (relative to Pt)

--Metal sample mass ↑



--Metal is the cathode (+)

$V^o_{metal} > 0$ (relative to Pt)

Standard Electrode Potential

Adapted from Fig. 17.2, *Callister 7e.*

STANDARD EMF SERIES

- EMF series

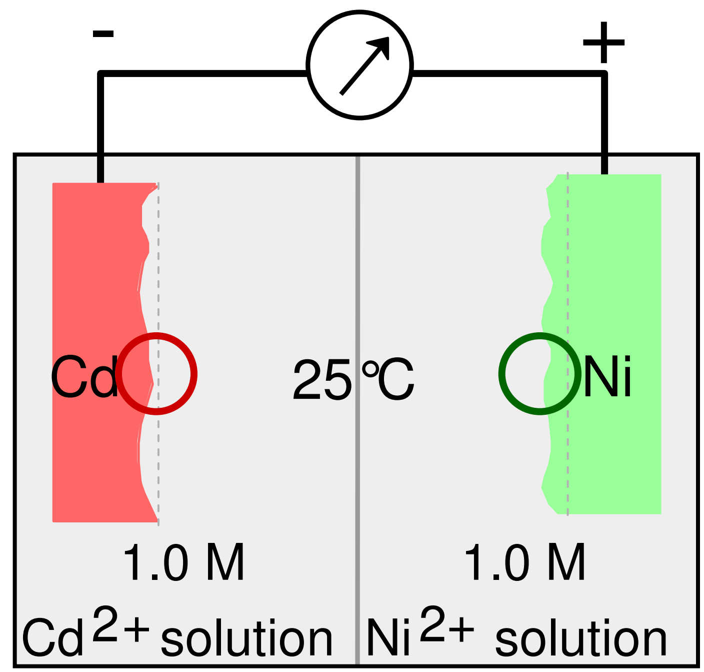
more cathodic ↑ / more anodic ↓

metal	V^o_{metal}
Au	+1.420 V
Cu	+0.340
Pb	- 0.126
Sn	- 0.136
Ni	- 0.250
Co	- 0.277
Cd	- 0.403
Fe	- 0.440
Cr	- 0.744
Zn	- 0.763
Al	- 1.662
Mg	- 2.363
Na	- 2.714
K	- 2.924

$\Delta V^o =$ 0.153V (Ni to Cd)

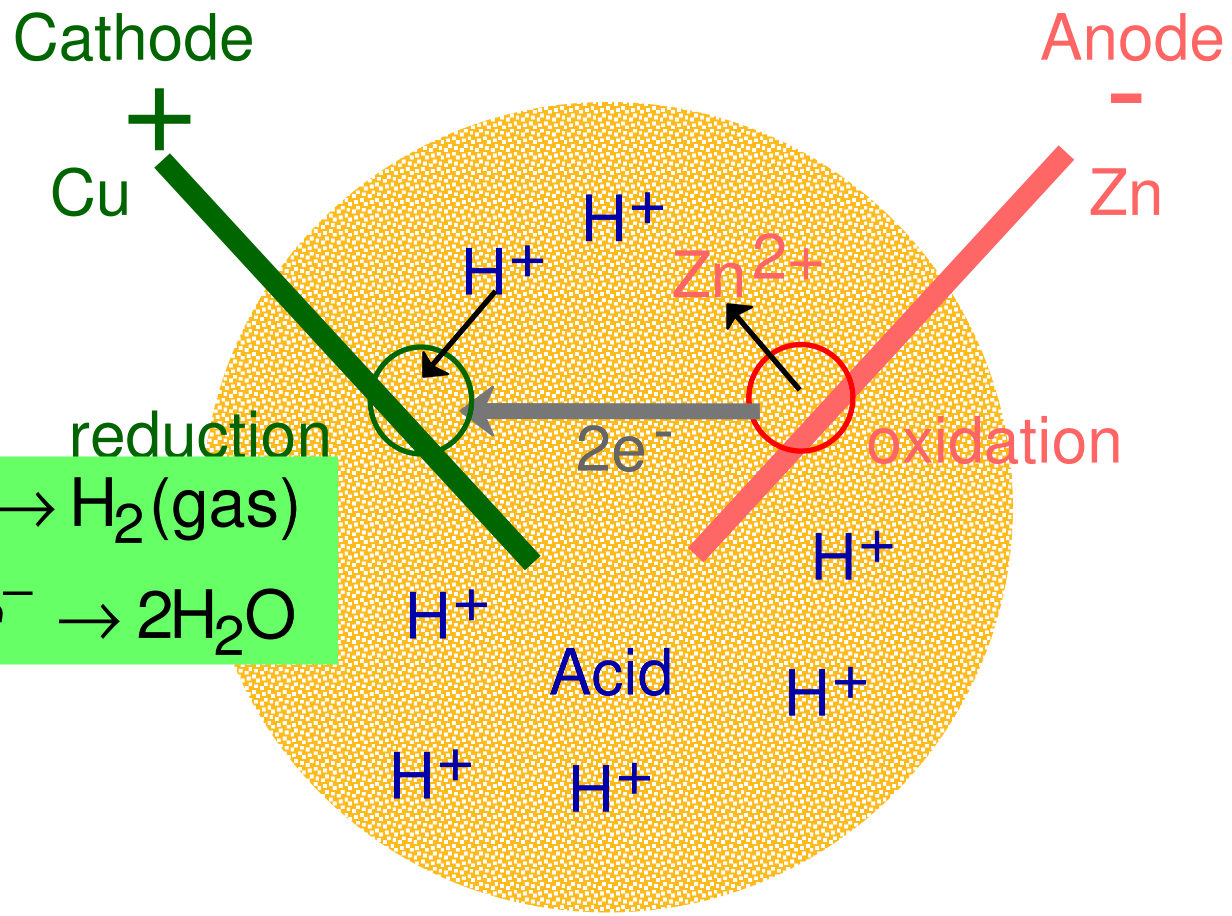
Data based on Table 17.1, *Callister 7e*.

- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell



Adapted from Fig. 17.2, *Callister 7e*.

CORROSION IN A GRAPEFRUIT



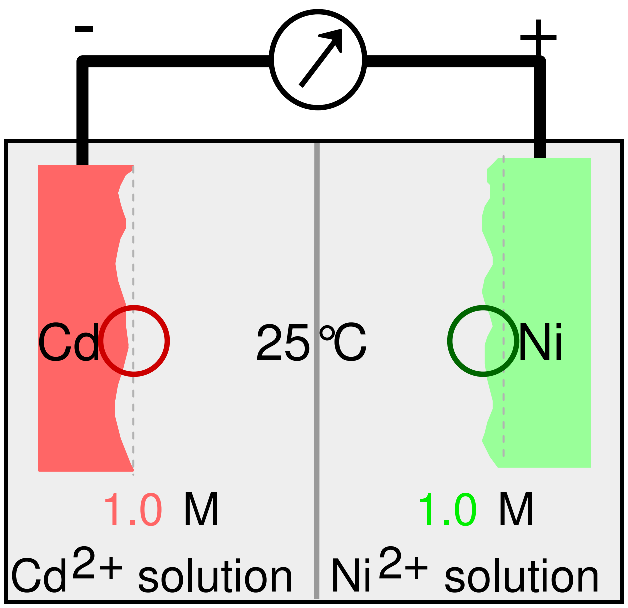
$$2H^{+} + 2e^{-} \rightarrow H_2(\text{gas})$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$$

EFFECT OF SOLUTION CONCENTRATION

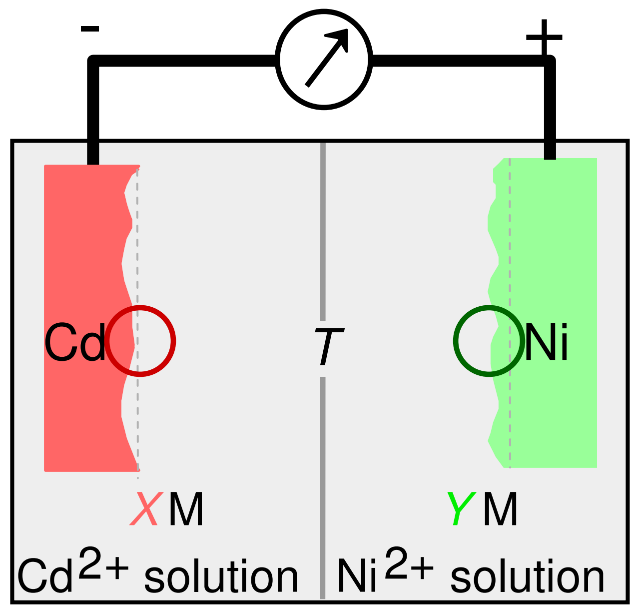
- Ex: Cd-Ni cell with standard 1 M solutions

$$V^{o}_{Ni} - V^{o}_{Cd} = 0.153$$



- Ex: Cd-Ni cell with non-standard solutions

$$V_{Ni} - V_{Cd} = V^{o}_{Ni} - V^{o}_{Cd} - \frac{RT}{nF} \ln \frac{X}{Y}$$



n = #e^- per unit oxid/red reaction (= 2 here)

F = Faraday's constant = 96,500 C/mol.

- Reduce V_{Ni} - V_{Cd} by
  - --increasing X
  - --decreasing Y

GALVANIC SERIES

- Ranks the reactivity of metals/alloys in seawater

more cathodic (inert)

Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

more anodic (active)

Based on Table 17.2, *Callister 7e*. (Source of Table 17.2 is M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

FORMS OF CORROSION

- Stress corrosion

Stress & corrosion work together at crack tips.

- Uniform Attack

Oxidation & reduction occur uniformly over surface.

- Erosion-corrosion

Break down of passivating layer by erosion (pipe elbows).

- Selective Leaching

Preferred corrosion of one element/constituent (e.g., Zn from brass (Cu-Zn)).

Forms of corrosion

- Pitting

Downward propagation of small pits & holes.

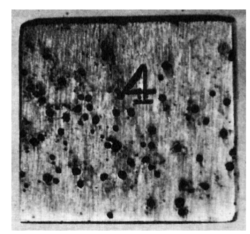


Fig. 17.17, *Callister 7e*. (Fig. 17.17 from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- Intergranular

Corrosion along grain boundaries, often where special phases exist.

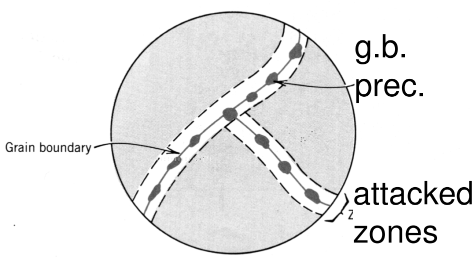


Fig. 17.18, *Callister 7e*.

- Galvanic

Dissimilar metals are physically joined. The more anodic one corrodes.(see Table 17.2) Zn & Mg very anodic.

- Crevice Between two pieces of the same metal.

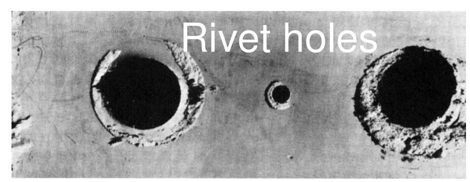


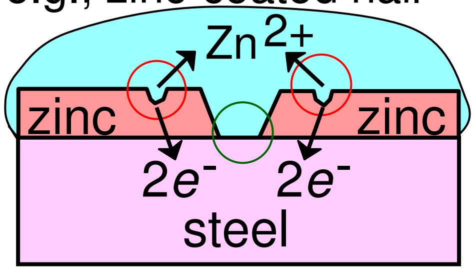
Fig. 17.15, *Callister 7e*. (Fig. 17.15 is courtesy LaQue Center for Corrosion Technology, Inc.)

CONTROLLING CORROSION

- Self-protecting metals!
  -- Metal ions combine with O to form a thin, adhering oxide layer that slows corrosion.

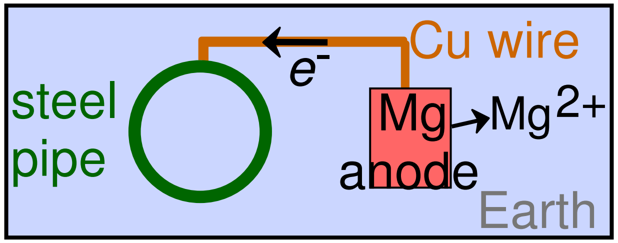
- Reduce *T* (slows kinetics of oxidation and reduction)
- Add inhibitors
  -- Slow oxidation/reduction reactions by removing reactants (e.g., remove O_2 gas by reacting it w/an inhibitor).
  -- Slow oxidation reaction by attaching species to the surface (e.g., paint it!).
- Cathodic (or sacrificial) protection
  -- Attach a more anodic material to the one to be protected.

e.g., zinc-coated nail



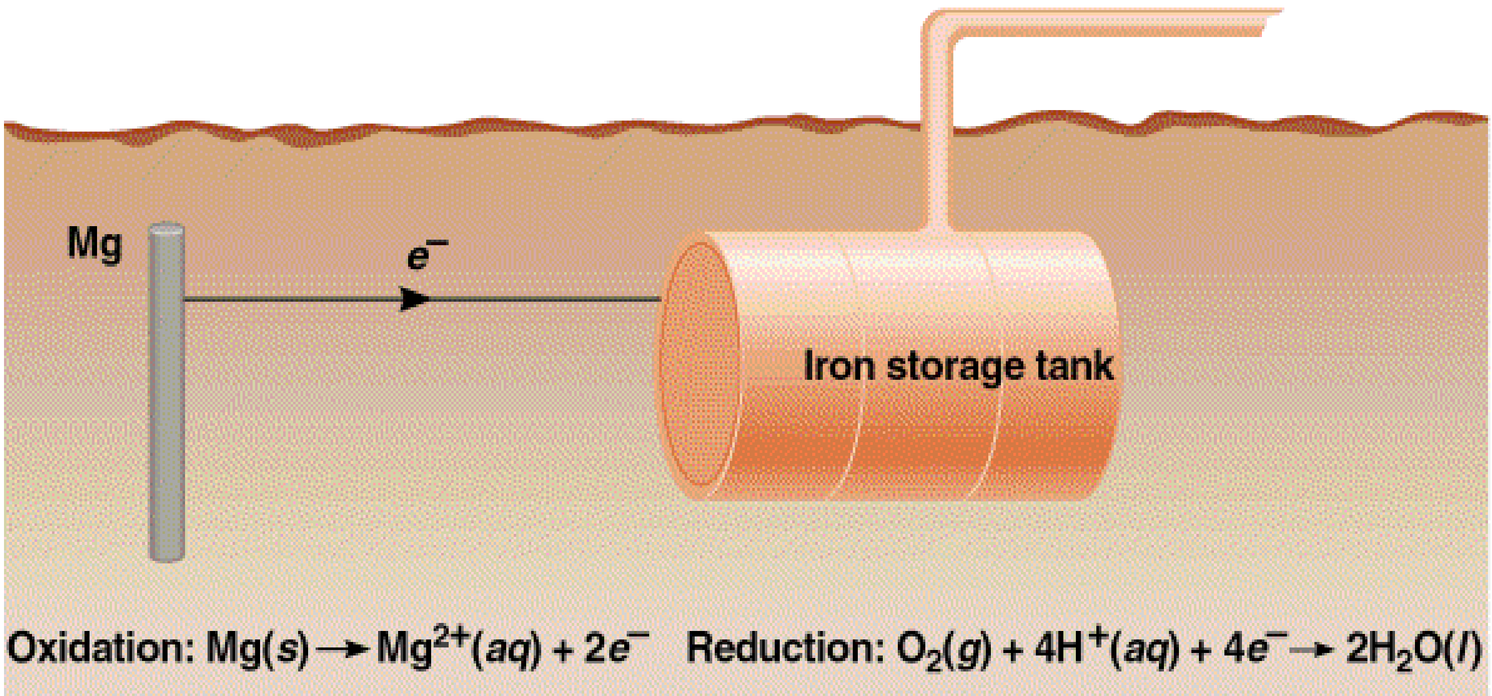
Adapted from Fig. 17.23, *Callister 7e.*

e.g., Mg Anode



Adapted from Fig. 17.22(a), *Callister 7e*. (Fig. 17.22(a) is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Co., 1986.)

Cathodic Protection of an Iron Storage Tank



SUMMARY

- Corrosion occurs due to:
  -- the natural tendency of metals to give up electrons.
  -- electrons are given up by an oxidation reaction.
  -- these electrons then used in a reduction reaction.
- Metals with a more negative Standard Electrode Potential are more likely to corrode relative to other metals.
- The Galvanic Series ranks the reactivity of metals in seawater.
- Increasing *T* speeds up oxidation/reduction reactions.
- Corrosion may be controlled by:
  -- using metals which form a protective oxide layer
  -- reducing *T*
  -- adding inhibitors
  -- painting
  -- using cathodic protection.