Principles of Corrosion in Marine Environments

References used:

Oxtoby, D.W., H.P. Gillis, and N.H. Nachtrieb (1999). Principles of modern chemistry, 4th edition. New York: Saunders College Publishing.

Chandler, K.A. (1985). Marine and offshore corrosion. London: Butterworths.

Wranglen, G. (1985). An introduction to corrosion and protection of metals. New York: Chapman and Hall.

Schweitzer, P.E., ed. (1996). Corrosion engineering handbook. New York: Marcel Dekker Inc.

Electrochemistry Facts

- Elements can be categorized by their tendency to attract electrons: electronegativity
- <u>Oxidation</u>: the loss of electrons, typically to oxygen anions (O^{-}, O^{2-}, etc.) but not always! E.g.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \qquad \text{“}\textit{Mg is oxidized}\text{”}$$

2+ 2-

- <u>Reduction</u>: the gain of electrons
- Reductions are associated with specific voltages; and the material ranking is similar to that of electronegativity, and the <u>galvanic series</u>.
- A galvanic cell converts chemical into electrical energy; spontaneous by definition (e.g., battery discharge)
- An electrolytic cell converts electrical into chemical energy; takes external power (e.g., battery charge)

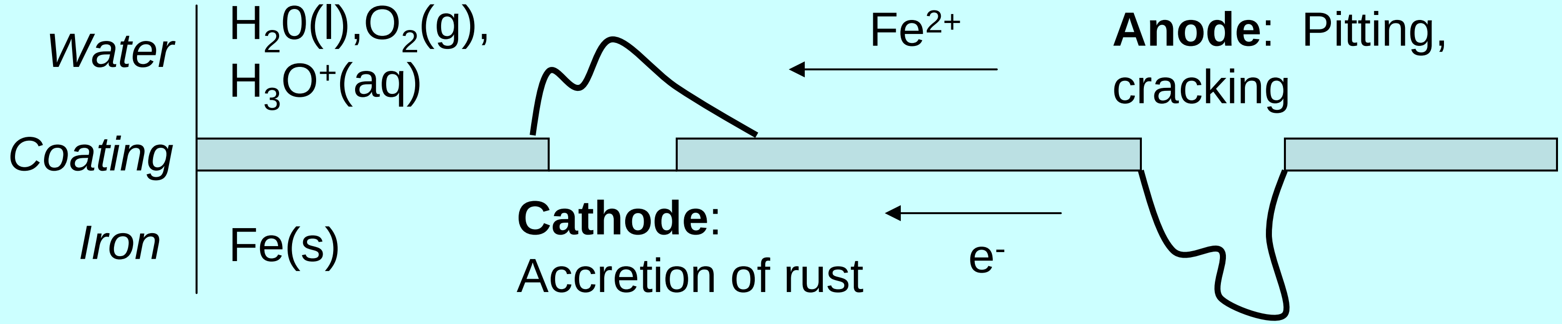
Some Reduction Potentials in the Marine Environment

More prone to lose electrons and to corrode

Oxygen	1.229V (O_2,H^+/H_2O)
Silver	0.800 (Ag^+/Ag)
Copper	0.340 (Cu^{2+}/Cu)
Hydrogen	0.000 (H^+/H_2 *REFERENCE*)
Iron	-0.036 (Fe^{3+}/Fe)
Iron	-0.409 (Fe^{2+}/Fe)
Zinc	-0.763 (Zn^{2+}/Zn)
Titanium	-0.860 (TiO_2,H^+/Ti)
Aluminum	-1.706 (Al^{3+}/Al)
Magnesium	-2.375 (Mg^{2+}/Mg)

Oxtoby et al.

Corrosion in Iron with Oxygenated Water: A Galvanic Cell



Anode: $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$ (Iron oxidized: -0.41V)
Cathode: $4H_3O^+ (aq) + O_2(g) + 4e^- \rightarrow 6H_2O(l)$ (Hydronium reduced: 1.23V)

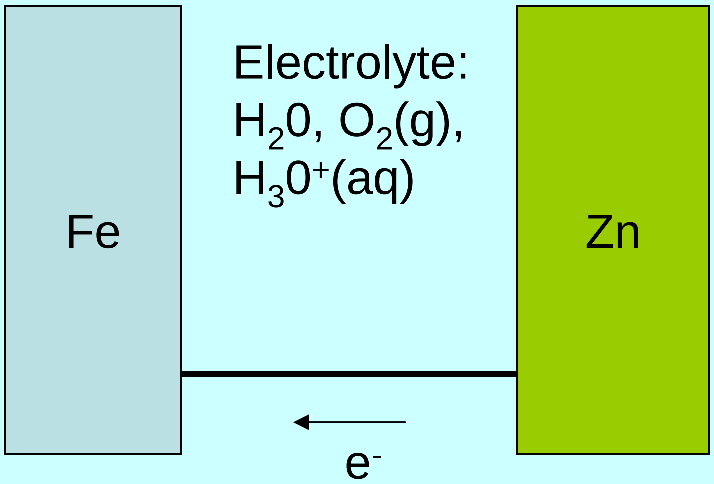
Also, iron cations are oxidized again, from Fe^{2+} to Fe^{3+} by oxygen in the water:

$4Fe^{2+}(aq) + O_2(g) + 12H_20(l) \rightarrow 2Fe_2O_3(s) + 8H_30^+(aq)$ and

making RUST! Hydronium created in this second reaction can supply the cathode primary half-cell reaction.

Adapted from Oxtoby et al.

1. Coatings (paint, rubber, grease, etc.)
2. Sacrificial Anodes:



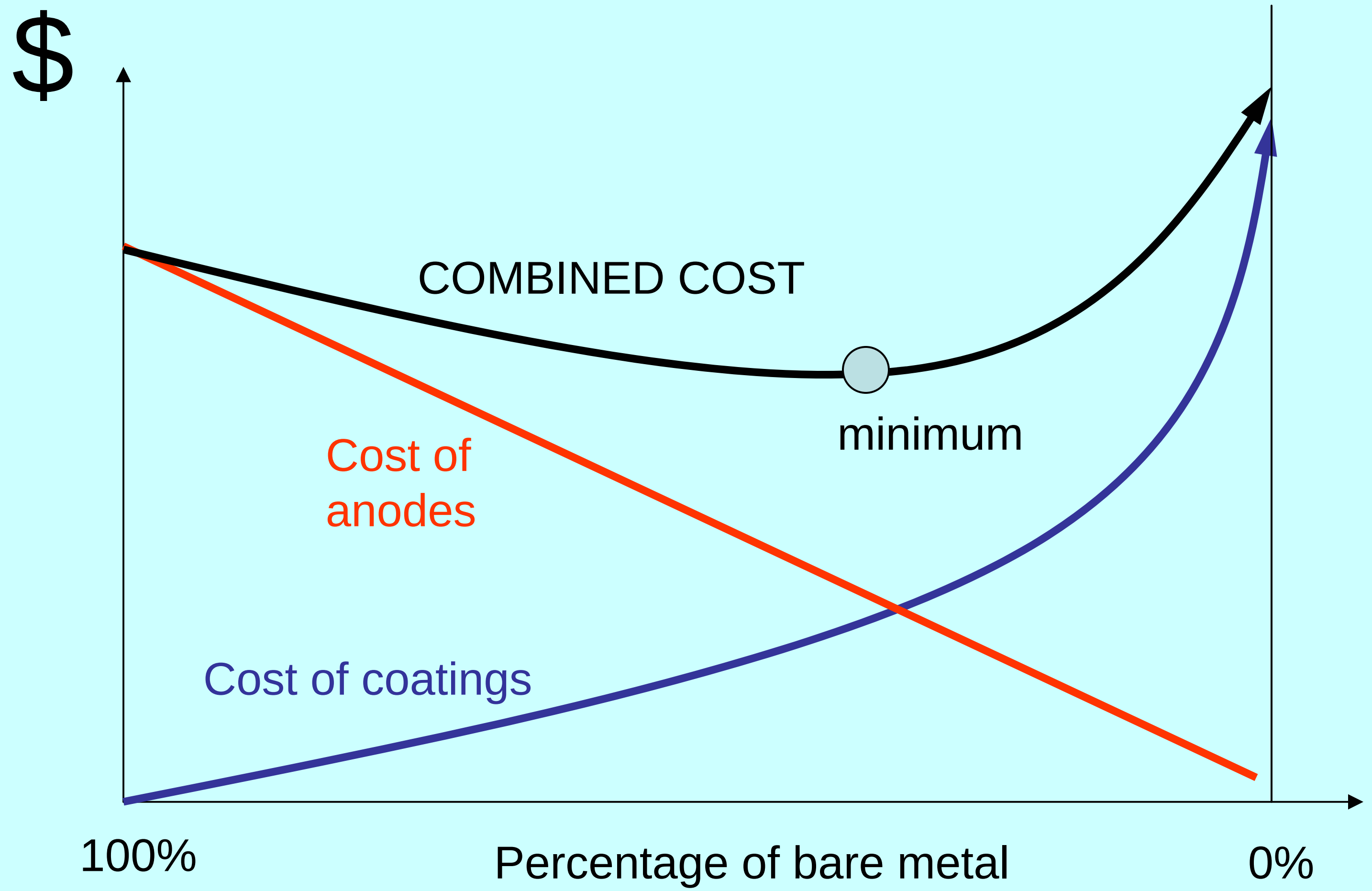
Anode:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
-0.763V

Cathode:
$4H_30^+(aq) + 4e^- + O_2(g) \rightarrow 6H_20(l)$
1.230V
(electrons move through the iron)

The iron oxidation is suppressed because the reduction potential is only -0.41V: Zinc loses and is oxidized!

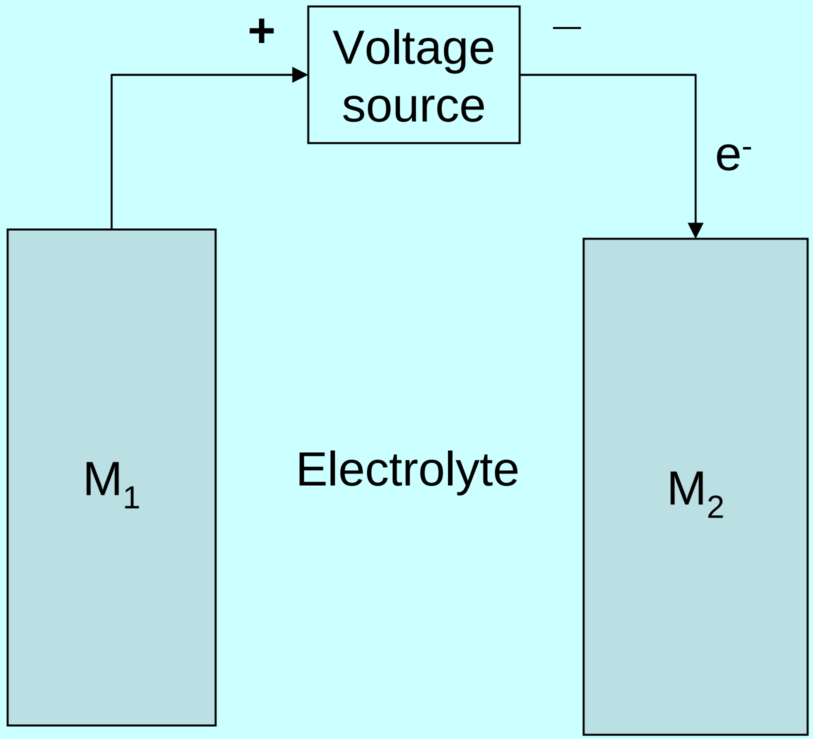
Other common anode materials:
Magnesium, Aluminum

Dual Use of Coatings and Sacrificial Anodes



Wranglen, p. 179

3. Impressed Current



Anode:
$M_1(s) \rightarrow M_1^{x+} + xe^-$

Cathode

Use of various materials for anode: high-silicon iron, lead alloys, platinised titanium

Voltage levels can be much higher than in a passive system

Recommended current densities are on the order of **100mA/m²** at the cathode (hull)

Typical current densities are on the order of **500A/m²** at the anode

4. Passivation

- The material develops a *protective barrier*, that is sufficient to protect against corrosion. Examples:
  - Tin coating on steel cans
  - Galvanized steel: a coating of zinc
  - Aluminum oxide in atmospheric conditions
  - Chromium in stainless steel forms a layer
- The barrier blocks oxygen from getting in and metal cations from getting out.

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