

Corrosion and Degradation

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Chemical interactions with the environment can cause deterioration of material properties.

Metallic Corrosion: Electrochemistry

Reaction mechanism

Electrochemical reactions always occur in redox pairs:

Oxidation occurs at the anode (LEO): $M \rightarrow M^{n+} + ne^{-}$

Reduction occurs at the cathode (GER): Generally, $A + ne^{-} \rightarrow B$

Material is “eaten away” at the anode. One can think of anodic oxidation as the “starting step” of an electrochemical process, providing electrons which will be used up at the cathode surface. The metal ions formed at the anode can either be reduced by electrons and remain in the solution, or form an insoluble compound with another species that is present in the solution (ex. Fe^{2+} combines with oxygen and water to get rust).

Some metals are more active (prone to being “eaten” / acting as an anode) than others. The EMF and galvanic series tabulate the relative activity of metals with respect to a certain environment.

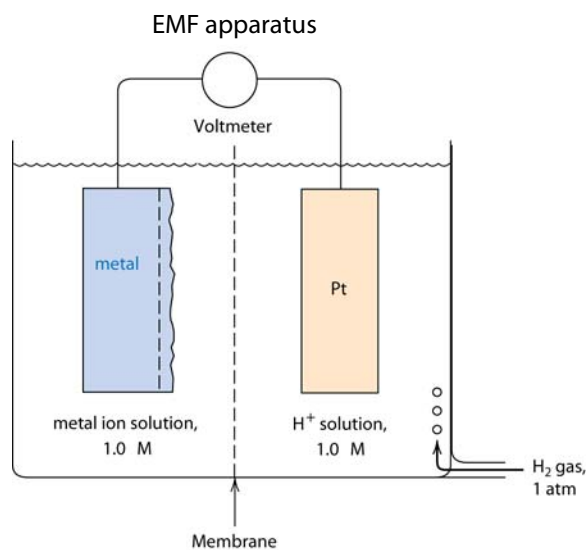


Table 17.2 The Galvanic Series (metal in salt water)

	Platinum
	Gold
	Graphite
	Titanium
	Silver
Increasingly inert (cathodic)	Stainless steel (passive)
	Nickel (passive)
	Bronzes (Cu–Sn alloys)
	Copper
	Brasses (Cu–Zn alloys)
	Nickel (active)
Increasingly active (anodic)	Tin
	Stainless steel (active)
	Iron and steel
	Aluminum
	Zinc
	Magnesium

Protection

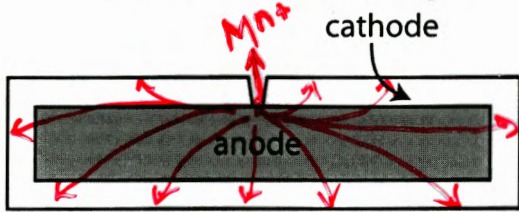
A passivated material has a thin coating (usually its oxide) around it that protects it from oxidation/corrosion. For the passivation layer to be effective, it must be adherent and non-porous.

Corrosion and Degradation

In the event of a break in the passivation coating, we must consider the reactions that might occur:

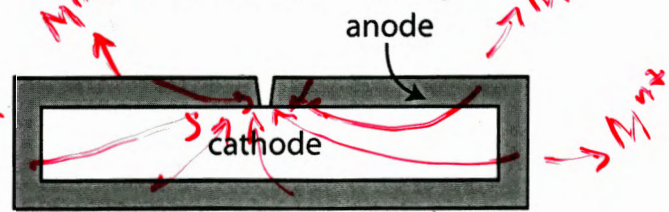
Case 1: bulk material is more active

(ex.: Fe-C with Sn coating)



Case 2: coating is more active (galvanized coating)

(ex.: Fe-C with Zn coating)



Firstly, note that electrochemical reactions can only take place at surfaces in contact with the electrolytic solution. Immediately, we see that in Case 1, the bulk metal will be in danger of corrosion, as its function is that of the anode. In contrast, in Case 2, the coating acts as an expendable sacrificial layer, and the bulk material will not be corroded at all (in both Cases, other species in the solution/environment will combine with available electrons at the cathode surface).

The **rate** of anodic corrosion \propto current density at the anode \propto $\frac{\text{cathode surface area}}{\text{anode surface area}}$:

Small anode-to-cathode surface areas have high current densities and a high corrosion rate (Case 1).

Large anode-to-cathode surface areas have lower current densities and a lower corrosion rate (Case 2).

Conclusion: Case 2 is safer because a) the bulk material won't corrode, and b) the anodic corrosion rate is slow!

Side note: Fe-C can be coated with Sn functioning as a galvanized coating (Case 2, above) to be used in liquid food environments such as soda cans. This is because Sn becomes more anodic/active than steel in that particular aqueous environment.

Types of Corrosion

Refer to notes for slightly more detail.

Uniform – self-explanatory!

Fretting – oxide protection removed mechanically

Crevice – depletion of oxygen at cracks causes nearby metal surfaces to become anodic/corrode

*Pitting – localized imperfections in oxide layer cause localized corrosion

e.g. stress corrosion cracking (p. 698-699, notes)

Intergranular/interface – unsatisfis bonds and disorder at interfaces increases activity; microscopic corrosion

Galvanic – attach a more active metal within solution; the more active metal will corrode instead (sacrificial)

Polymer Degradation

Refer to Dr. Wynarsky's handout and lecture notes.