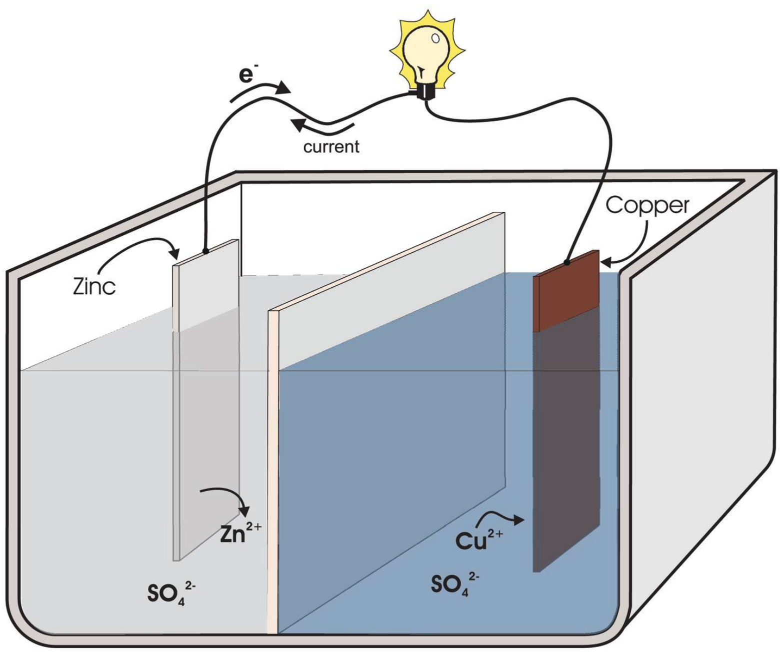
Corrosion Basics

Understanding the basic principles and causes of corrosion

Polarization

As is the case with other chemical reactions, the driving force of a corrosion reaction is related to the difference in energy between an initial equilibrium that is higher in energy than the final equilibrium. As corrosion action proceeds, this difference in energy tends to decrease as a result of the effects of the products of anodic and cathodic reactions in the vicinity of the corrosion sites. The cathodic reaction, and with it the overall corrosion reaction, would slow down if, for example, the hydrogen product of the cathodic reaction were not removed by evolution as gas or some reaction involving oxygen. This slowing down is said to be the result of cathodic polarization.

Figure 1



Schematic of a Daniell cell. The separator serves to keep each metal in contact with its own soluble sulfates, a technical point that is critical to keep the voltage of a Daniell cell relatively constant.

It is possible to measure this effect in terms of the potential of the metal on which the reaction is occurring. For example, if the potential of the surface of the more noble metal—the cathode—were to be measured before the flow of any galvanic current and again after current flow had occurred for some time, it would be found that the potential would have changed to a value closer to that of the less noble metal in the couple.

Similarly, measurements of the potential of the anodic member of the couple would show a drift in potential closer to that of the cathodic member of the couple. This could be partly because of an increase in the concentration of the ions of the anodic metal in the immediate vicinity of the corroding metal surface.

There are three different types of polarization or ways that electrochemical reactions are retarded. These are activation polarization, concentration polarization, and the ohmic potential that can occur when the anodic and cathodic reactions are physically separated, as is the case with the Daniell cell—the first truly practical and reliable electric battery (Figure 1).

In summary, polarization is the change from the open-circuit potential as a result of current across the electrode/electrolyte interface. Polarization effects control the balancing cathodic and anodic currents that are integrated components of corrosion processes.

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