CHAPTER 3

Corrosion Electrochemistry

3.1 Electrochemical Reactions

An electrochemical reaction is defined as a chemical reaction involving the transfer of electrons. It is also a chemical reaction which involves oxidation and reduction. Since metallic corrosion is almost always an electrochemical process, it is important to understand the basic nature of electrochemical reactions. The discoveries that gradually evolved in modern corrosion science have, in fact, played an important role in the development of a multitude of technologies we are enjoying today. Appendix A provides a list of some of these discoveries.

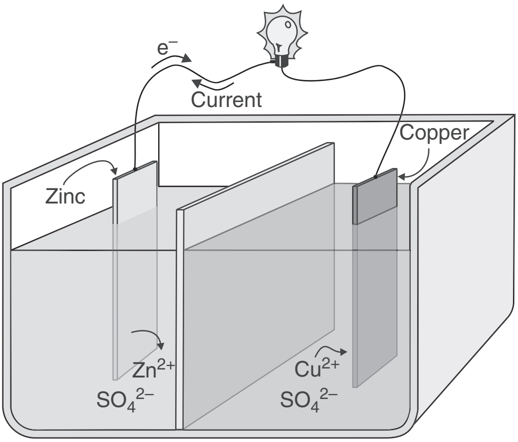
An important achievement early in the history of electrochemistry was the production of power sources, following the production of the first batteries by Alessandro Volta. Figure 3.1 illustrates the principle of a Daniell cell in which copper and zinc metals are immersed in solutions of their respective sulfates. The Daniell cell was the first truly practical and reliable electric battery that supported many nineteenth-century electrical innovations such as the telegraph. In the process of the reaction, electrons can be transferred from the corroding zinc to the copper through an electrically conducting path as a useful electric current. Zinc more readily loses electrons than copper, so placing zinc and copper metal in solutions of their salts can cause electrons to flow through an external wire which leads from the zinc to the copper.

$$\text{Zinc anode: Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \tag{3.1}$$

$$\text{Copper cathode: Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)} \tag{3.2}$$

The difference in the susceptibility of two metals to corrode can often cause a situation that is called galvanic corrosion named after Luigi Galvani, the discoverer of the effect. The purpose of the separator shown in Fig. 3.1 is to keep each metal in contact with its

FIGURE 3.1 Schematic of a Daniell cell.



own soluble sulfates, a technical point that is critical in order to keep the voltage of a Daniell cell relatively constant [1]. The same goal can be achieved by using a salt bridge between two different beakers as shown in Fig. 3.2. The salt bridge, in that case, provides the electrolytic path that is necessary to complete an electrochemical cell circuit. This situation is common in natural corrosion cells where the environment serves as the electrolyte that completes the corrosion cell. The conductivity of an aqueous environment such as soils, concrete, or natural waters has often been related to its corrosivity.

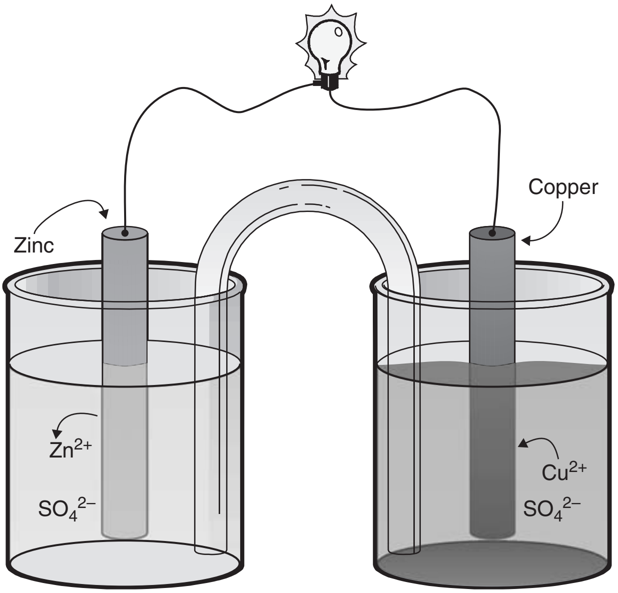


FIGURE 3.2 Schematic of a Daniell cell with a salt bridge.

The short-hand description in Eq. (3.3) is valid for both cells shown in Figs. 3.1 and 3.2. Such a description is often used to simplify textual reference to such cells.

$$(-)\mathrm{Zn}/\mathrm{Zn}^{2+}, \mathrm{SO}_{4\ (\mathrm{Conc}_1)}^{2-}//\mathrm{Cu}^{2+}, \mathrm{SO}_{4\ (\mathrm{Conc}_2)}^{2-}/\mathrm{Cu}(+) \tag{3.3}$$

Conc_1 and Conc_2 in Eq. (3.3) indicate respectively the concentration of zinc sulfate and copper sulfate that may differ in the two half-cells while the two slanted bars (//) describe the presence of a separator. The same short-hand description also identifies the zinc electrode as the anode that is negative in the case of a spontaneous reaction and the copper cathode as positive.

The fact that corrosion consists of at least one oxidation and one reduction reaction is not always as obvious as it is in chemical power cells and batteries. The two reactions are often combined on a single piece of metal as it is illustrated schematically in Fig. 3.3.

In Fig. 3.3, a piece of zinc immersed in hydrochloric acid solution is undergoing corrosion. At some point on the surface, zinc is transformed to zinc ions, according to Eq. (3.4). This reaction produces electrons and these pass through the solid conducting metal to other

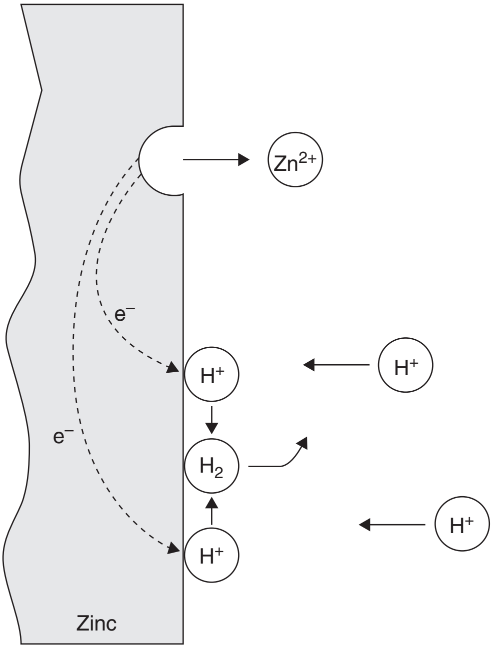


Figure 3.3 Electrochemical reactions occurring during the corrosion of zinc in air-free hydrochloric acid.

sites on the metal surface where hydrogen ions are reduced to hydrogen gas according to Eq. (3.5) (Fig. 2.7 in Chap. 2).

$$\text{Anodic reaction: Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \tag{3.4}$$

$$\text{Cathodic reaction: } 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{(g)} \tag{3.5}$$

Equations (3.4) and (3.5) illustrate the nature of an electrochemical reaction typically illustrated for zinc in Fig. 3.3. During such a reaction, electrons are transferred, or, viewing it another way, an oxidation process occurs together with a reduction process. The overall corrosion processes are summarized in Eq. (3.6):

$$\text{Overall corrosion reaction: Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{(g)} \tag{3.6}$$

Briefly then, for corrosion to occur there must be a formation of ions and release of electrons at an anodic surface where oxidation or deterioration of the metal occurs. There must be a simultaneous reaction at the cathodic surface to consume the electrons generated at the anode. These electrons can serve to neutralize positive ions such as the hydrogen ions (H^+), or create negative ions. The anodic and cathodic reactions must go on at the same time and at equivalent rates. However, what is usually recognized as the corrosion process occurs only at the areas that serve as anodes.

3.2 Anodic Processes

Let us consider in greater detail what takes place at the anode when corrosion occurs. For instance, reconsider Eq. (3.6). This reaction involves the reduction of hydrogen ions to hydrogen gas, according to Eq. (3.5). This hydrogen evolution reaction occurs with a wide variety of metals and acids, including hydrochloric, sulfuric, perchloric, hydrofluoric, formic, and other strong acids. The individual anodic reactions for iron, nickel, and aluminum are listed as follows:

$$\text{Iron anodic reaction: Fe(s)} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \tag{3.7}$$

$$\text{Nickel anodic reaction: Ni(s)} \rightarrow \text{Ni}^{2+} + 2\text{e}^- \tag{3.8}$$

$$\text{Aluminum anodic reaction: Al(s)} \rightarrow \text{Al}^{3+} + 3\text{e}^- \tag{3.9}$$

Examining the Eqs. (3.7) to (3.9) shows that the anodic reaction occurring during corrosion can be written in the general form:

$$\text{General anodic reaction: M(s)} \rightarrow \text{M}^{n+} + n\text{e}^- \tag{3.10}$$

That is, the corrosion of metal M results in the oxidation of metal M to an ion with a valence charge of $n+$ and the release of n electrons. The value of n, of course, depends primarily on the nature of the metal.

Some metals such as silver are univalent, while other metals such as iron, titanium, and uranium are multivalent and possess positive charges as high as 6 (see Fig. 2.8). Equation (3.10) is general and applies to all corrosion reactions.

3.3 Faraday's Law

If the current generated by one of the anodic reactions expressed earlier was known, it would be possible to convert this current to an equivalent mass loss or corrosion penetration rate with a very useful relation discovered by Michael Faraday, a nineteenth century pioneer in electrochemistry. Faraday's empirical laws of electrolysis relate the current of an electrochemical reaction to the number of moles of the element being reacted and the number of moles of electrons involved. Supposing that the charge required for such reaction was one electron per molecule, as is the case for the plating or the corrosion attack of silver described respectively in Eqs. (3.11) and (3.12):

$$\mathrm{Ag^+ + e^- \rightarrow Ag(s)} \tag{3.11}$$

$$\mathrm{Ag(s) \rightarrow Ag^+ + e^-} \tag{3.12}$$

According to Faraday's law, the reaction with 1 mol of silver would require 1 mol of electrons, or 1 Avogadro's number of electrons (6.022×10^{23}). The charge carried by 1 mol of electrons is known as 1 faraday (F). The faraday is related to other electrical units through the electronic charge; the electronic charge is 1.6×10^{-19} coulomb (C). Multiplying the electronic charge by the Avogadro number means that 1 F equals 96,485 C/(mol of electrons). Combining Faraday's principles with specific electrochemical reactions of known stoichiometry leads to Eq. (3.13) that relates the charge Q to chemical descriptors N and n:

$$Q = F \cdot \Delta N \cdot n \tag{3.13}$$

where N is the number of moles and ΔN the change in that amount
n is the number of electrons per molecule of the species being reacted

The charge Q can be defined in terms of electric current as in Eq. (3.14),

$$Q = \int_0^t I \cdot dt \tag{3.14}$$

where I is the total current in amperes (A)
t is the duration of the electrochemical process in seconds (s)

	mA cm^{-2}	**mm y^{-1}**	**mpy**	**g m^{-2} day^{-1}**
mA cm^{-2}	1	3.28 M/nd	129 M/nd	8.95 M/n
mm y^{-1}	0.306 nd/M	1	39.4	2.74 d
mpy	0.00777 nd/M	0.0254	1	0.0694 d
g m^{-2} day^{-1}	0.112 n/M	0.365 $/d$	14.4 $/d$	1

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where mpy = milli-inch per year
n = number of electrons freed by the corrosion reaction
M = atomic mass
d = density

*Note: the table should be read from left to right, i.e.,
1 mA cm^{-2} = (3.28 M/nd) mm y^{-1} = (129 M/nd) mpy = (8.95 M/n) g m^{-2} day^{-1}

Table 3.1 Conversion between Current, Mass Loss, and Penetration Rates for all Metals*

	mA cm^{-2}	**mm y^{-1}**	**mpy**	**g m^{-2} day^{-1}**
mA cm^{-2}	1	11.6	456	249
mm y^{-1}	0.0863	1	39.4	21.6
mpy	0.00219	0.0254	1	0.547
g m^{-2} day^{-1}	0.00401	0.0463	1.83	1

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*Note: the table should be read from left to right, i.e.,
1 mA cm^{-2} = 11.6 mm y^{-1} = 456 mpy = 249 g m^{-2} day^{-1}

Table 3.2 Conversion between Current, Mass Loss and Penetration Rates for Steel*

The corrosion current itself can be either estimated by using specialized electrochemical methods or by using weight-loss data and a conversion chart (Table 3.1) based on Faraday's principle. Table 3.1 provides the conversion factors between commonly used corrosion rate units for all metals and Table 3.2 describes these conversion factors adapted to iron or steel (Fe) for which $n = 2$, $M = 55.85$ g/mol and $d = 7.88$ g cm^{-3}.

3.4 Cathodic Processes

When hydrogen ions are reduced to their atomic form they often combine, as shown earlier, to produce hydrogen gas through reaction with electrons at a cathodic surface. This reduction of hydrogen ions at a cathodic surface will disturb the balance between the acidic hydrogen (H^+) ions and the alkaline hydroxyl (OH^-) ions and make the solution less acidic or more alkaline or basic at the corroding interface.

In neutral waters the anodic corrosion of some metals like aluminum, zinc, or magnesium develops enough energy to split water directly as illustrated in Fig. 3.4 and Eq. (3.15).

$$\text{Water splitting cathodic reaction: } 2H_2O(l) + 2e^- \rightarrow H_2 + 2OH^- \quad (3.15)$$

The change in the concentration of hydrogen ions or increase in hydroxyl ions can be shown by the use of pH indicators, which change color and thus can serve to demonstrate and locate the existence of surfaces on which the cathodic reactions in corrosion are taking place. There are several other cathodic reactions encountered during the corrosion of metals. These are listed below:

Oxygen reduction:

$$\text{(acid solutions) } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (3.16)$$

$$\text{(neutral or basic solutions) } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (3.17)$$

$$\text{Hydrogen evolution: } 2H^+ + 2e^- \rightarrow H_2(g) \quad (3.5)$$

$$\text{Metal ion reduction: } Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3.18)$$

$$\text{Metal deposition: } Cu^{2+} + 2e^- \rightarrow Cu(s) \quad (3.19)$$

Hydrogen ion reduction, or hydrogen evolution, has already been discussed. This is the cathodic reaction that occurs during

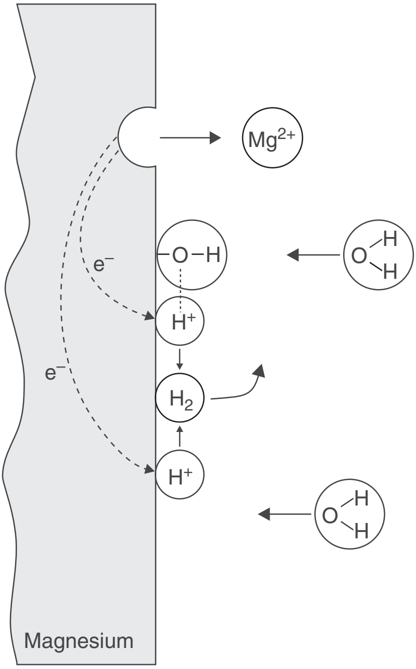

Figure 3.4 Electrochemical reactions occurring during the corrosion of magnesium in neutral water.

corrosion in acids. Oxygen reduction [Eqs. (3.16) and (3.17)] is a very common cathodic reaction, since oxygen is present in the atmosphere and in solutions exposed to the atmosphere. Although less common, metal ion reduction and metal deposition, can cause severe corrosion problems in special situations. One particular case worth mentioning here is the plating of copper ions, produced upstream in a water circuit, on the internal aluminum surface of a radiator, for example.

The plated nodules, which may form even at very low concentrations of copper ions, tend to be dispersed and are thus a good catalyst for the subsequent reduction of dissolved oxygen. It is therefore highly recommended to avoid using copper tubing in a water circuit where aluminum is also present. Such deposition corrosion can be avoided by preventing the pick-up of cathodic ions that will enter the equipment, or by scavenging them by passing the contaminated product through a tower packed with more anodic metal turnings (such as aluminum) on which the ions can deposit (Fig. 3.5).

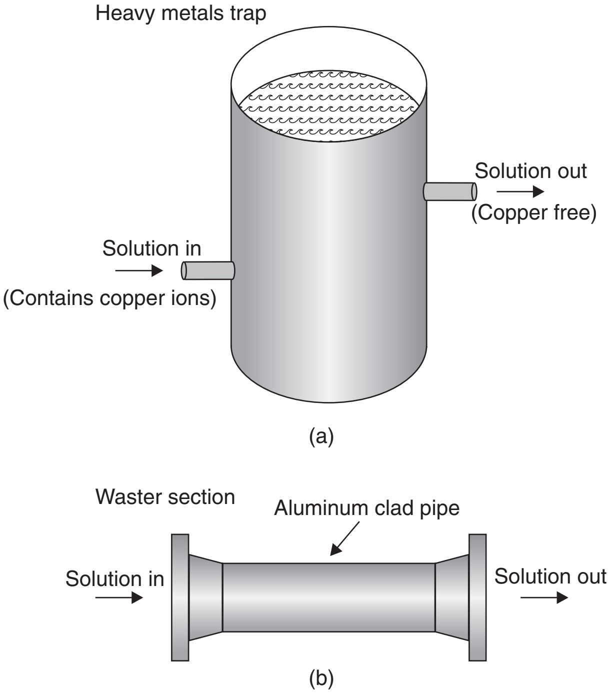

FIGURE 3.5 Method for removing troublesome ions from solution. (*a*) Heavy metal trap: Solutions containing copper ions enter barrel filled with aluminum shavings; (*b*) Waster section: Aluminum-clad pipe inserted in a system removes heavy metal ions. The section is replaced once corroded.

Note that all of the above reactions are similar in one respect—they consume electrons. All corrosion reactions are simply combinations of one or more of the above cathodic reactions, together with an anodic reaction similar to Eq. (3.10). Thus, almost every case of aqueous corrosion can be reduced to these equations, either singly or in combination.

Consider the corrosion of zinc by water or moist air. By multiplying the zinc oxidation reaction (3.4) by 2 and summing this with the oxygen reduction reaction, one obtains Eq. (3.21).

$$2\mathrm{Zn(s)} \rightarrow 2\mathrm{Zn}^{2+} + 4e^- \text{ (oxidation)} \tag{3.20}$$

$$\underline{+\,O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (reduction)}} \tag{3.17}$$

$$2Zn + 2H_2O + O_2 \rightarrow 2Zn^{2+} + 4OH^- \rightarrow 2Zn(OH)_2(p) \tag{3.21}$$

The products of this reaction are Zn^{2+} and OH^-, which immediately react to form insoluble $Zn(OH)_2$. Likewise, the corrosion of zinc by a solution containing copper ions is merely the summation of the oxidation reaction for zinc and the metal deposition reaction involving cupric ions in Eq. (3.19).

$$\mathrm{Zn(s)} \rightarrow Zn^{2+} + 2e^- \text{ (oxidation)} \tag{3.4}$$

$$\underline{+\,Cu^{2+} + 2e^- \rightarrow \mathrm{Cu(s)} \text{ (reduction)}} \tag{3.19}$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + \mathrm{Cu(p)} \tag{3.22}$$

During corrosion, more than one oxidation and one reduction reaction may occur. For example, during the corrosion of an alloy, its component metal atoms go into solution as their respective ions. Thus, during the corrosion of a chromium-iron alloy, both chromium and iron are oxidized. Also, more than one cathodic reaction can occur on the surface of a metal.

Consider the corrosion of zinc in a hydrochloric acid solution containing dissolved oxygen. Two cathodic reactions are possible: the evolution of hydrogen and the reduction of oxygen (Fig. 3.6). Since there are two cathodic reactions or processes which consume electrons, the overall corrosion rate of zinc is increased. Thus, acid solutions which either contain dissolved oxygen or are exposed to air are generally more corrosive than air-free acids. Therefore, removing oxygen from acid solutions will often make these solutions less corrosive.

If a piece of mild steel is placed in a solution of hydrochloric acid, a vigorous formation of hydrogen bubbles is observed. Under such conditions, the metal corrodes very quickly. The dissolution of the metal occurs only at anodic surfaces. The hydrogen bubbles form only at the cathodic surfaces, even though it may appear they

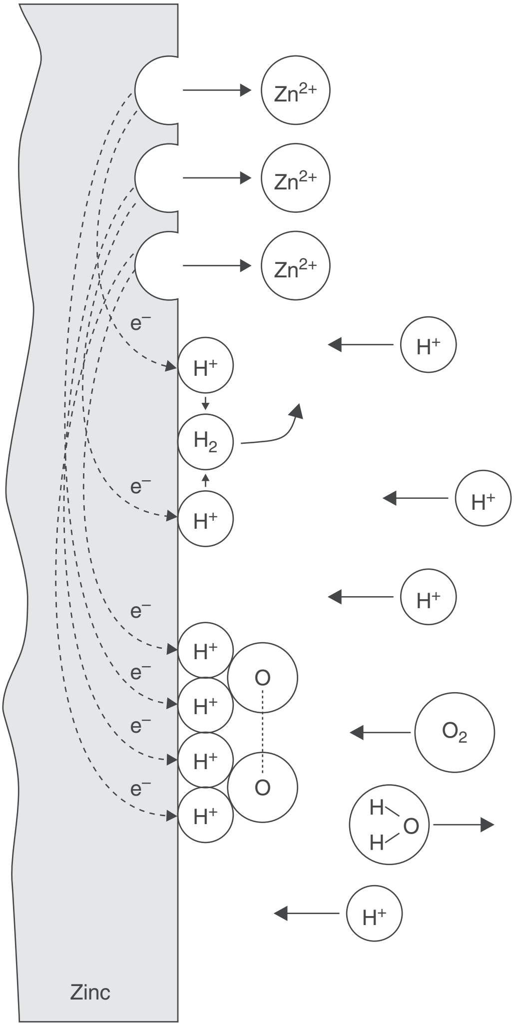

Figure 3.6 Electrochemical reactions occurring during the corrosion of zinc in aerated hydrochloric acid.

come from the entire surface of the metal rather than at well-defined cathodic areas (Fig. 3.7). The anodic and cathodic areas may shift from time to time so as to give the appearance of uniform corrosion.

If this action could be seen through a suitable microscope, many tiny anodic and cathodic areas would be observed shifting around on the surface of the metal. These areas, however, are often so small as to be invisible and so numerous as to be almost inseparable.

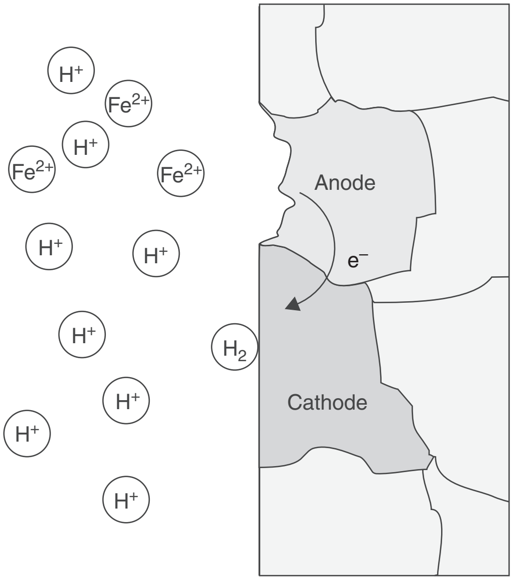

Figure 3.7 Formation of ions at an anodic area and release of hydrogen at a cathodic area in a local cell on an iron surface.

3.5 Surface Area Effect

When a piece of metal is freely corroding, the electrons generated at anodic areas flow through the metal to react at cathodic areas similarly exposed to the environment where they restore the electrical balance of the system. The fact that there is no net accumulation of charges on a corroding surface is quite important for understanding most corrosion processes and ways to mitigate them. However, the absolute equality between the anodic and cathodic currents expressed in Eq. (3.23) does not mean that the current densities for these currents are equal.

$$I_{\text{anodic}} = I_{\text{cathodic}} \tag{3.23}$$

When Eq. (3.23) is expressed in terms of current densities in Eq. (3.24) by considering the relative anodic (S_a) and cathodic (S_c) surface areas and their associated current densities i_a and i_c expressed in units of mA cm^{-2}, for example, it becomes clear that a difference in the surface areas occupied by each reaction will have to be compensated by inequalities in the current densities as expressed in Eq. (3.25).

$$I_{\text{anodic}} = i_a \times S_a = I_{\text{cathodic}} = i_c \times S_c \tag{3.24}$$

$$i_a = i_c \frac{S_c}{S_a} \tag{3.25}$$

The implications of the surface area ratio S_c/S_a in Eq. (3.25) are particularly important in association with various forms of local cell corrosion such as pitting and stress corrosion cracking for which a large surface area ratio is a serious aggravating factor. It is easy to understand that the effect of a certain amount of anodic current concentrated on a small area of metal surface will be much greater than when the effect of the same amount of current is dissipated over

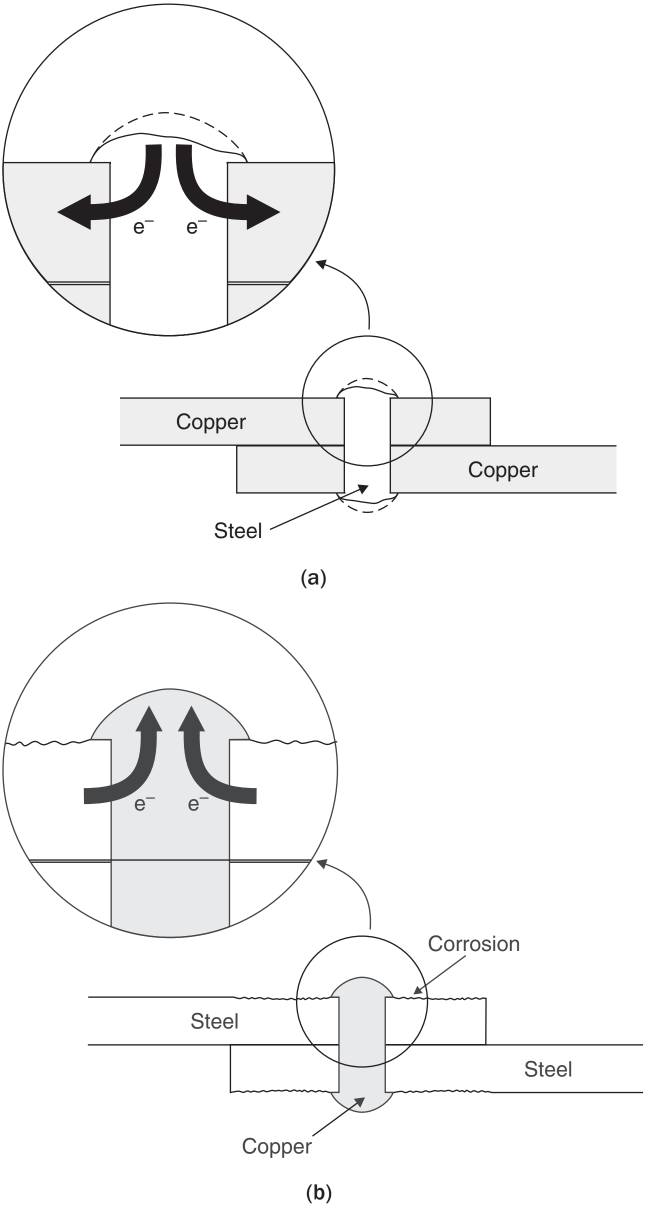

FIGURE 3.8 Galvanic coupling caused by riveting with dissimilar metals: (*a*) steel rivets on copper plates, (*b*) copper rivets on steel plates.

a much larger area. This factor is expressed in Eq. (3.25) which states that the ratio of cathodic to anodic surfaces is an important amplifying factor of the anodic current when S_c/S_a is >> 1 and a stifling factor when it is << 1.

This area effect in terms of current density is illustrated by combinations of steel and copper as either plates or the fasteners used to join them and immersed in a corrosive solution. If steel rivets are used to join copper plates, the current density on the relatively large cathodic copper plates will be low, cathodic polarization of the copper will be slight, and the voltage of the galvanic couple will maintain a value close to the open circuit potential. At the same time, the current density on the small anodic steel rivets will be high and the consequent corrosion quite severe, giving rise to a particularly vicious form of corrosion called galvanic corrosion [Fig. 3.8*(a)*].

With the opposite arrangement of copper rivets joining steel plates, the current density on the copper cathodes will be high, with consequently considerable cathodic polarization of the copper reducing the open circuit potential below its initial value. The diminished anodic current will be spread over the relatively large steel plates and the undesirable galvanic effect will hardly be noticeable [Fig. 3.8*(b)*].

Open circuit potential measurements are grossly inadequate for predicting the magnitude of galvanic effects since they do not take into account area and polarization effects. They are reliable only for predicting the direction of such effects.

Reference

1. Roberge PR. *Corrosion Basics—An Introduction.* 2nd ed. Houston, Tex: NACE International, 2006.