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CHEMISTRY II

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CORROSION: MECHANISMS AND CONTROL

1. INTRODUCTION

Corrosion results from the natural deterioration of metals and alloys through various chemical, biochemical, and electrochemical interactions with their surrounding environment. Corrosive conditions include moisture, oxygen, inorganic and organic acids, high pressure, elevated temperature, and chlorides. In chemical corrosion or direct dissolution, a material dissolves in a corrosive liquid medium until it is either completely consumed or the liquid becomes saturated. For instance, copper-based alloys develop a green patina on their surface due to the formation of copper carbonate and copper hydroxides. The Statue of Liberty's greenish appearance is a result of this chemical corrosion.

Controlled chemical corrosion processes are also utilized in specific applications, like producing flat silicon wafers through chemical mechanical polishing. Nature also employs chemical corrosion, such as the chemical corrosion of rocks by carbonic acid (H_2CO_3) and the mechanical erosion caused by wind and water, contributing to the formation of canyons and caverns.

1.1. Chemical and Electrochemical Corrosion

Electrochemical corrosion, the most prevalent form of metal deterioration, occurs when metal atoms lose electrons, turning them into ions. This process typically occurs in an aqueous medium, where ions are present in water, soil, or moist air, creating an electric circuit called an electrochemical cell. Examples include the corrosion of a steel pipe or automobile panel, leading to holes in the steel and rust as a byproduct.

Electrochemical cells can be intentionally created for beneficial purposes despite being responsible for corrosion. Deliberate electric circuit formation allows for processes like electroplating protective or decorative coatings onto materials. In some cases, electrochemical corrosion is even intentionally induced for applications such as etching polished metal surfaces to selectively observe features in the microstructure. This method facilitates examining characteristics like pearlite in steel or grain boundaries in copper.
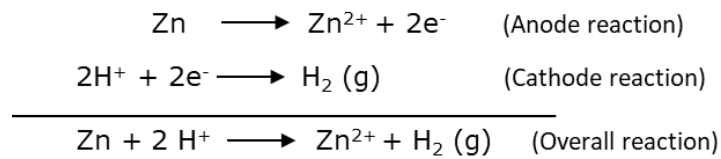
2. CORROSION: ELECTROCHEMICAL CONSIDERATIONS

The anode, composed of a metal, undergoes an oxidation process in which metal atoms lose electrons, generating metal ions. These metal ions then migrate into the electrolytic solution while the released electrons exit the anode through the electrical connection. Due to the departure of metal ions from the anode, the anode undergoes corrosion or oxidation. On the other hand, during electroplating, a cathodic reduction reaction, essentially the reverse of the anode reaction, transpires at the cathode. Metal ions, intentionally introduced into the electrolyte or formed through the anode reaction, combine with electrons at the cathode. This union prompts the deposition of metal, coating the surface of the cathode.

In typical electrochemical corrosion scenarios, metal plating does not occur; instead, the reduction reaction forms a gas, solid, or liquid byproduct at the cathode.
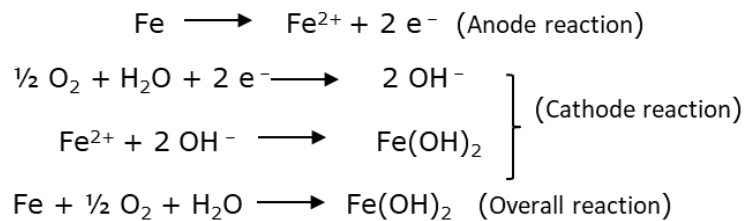
- *The Hydrogen Electrode*:

In oxygen-free liquids like hydrochloric acid (HCl) or stagnant water, hydrogen gas may evolve at the cathode. In an environment with zinc, the overall reaction becomes:

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Anode reaction)}$$
$$2H^+ + 2e^- \longrightarrow H_2\,(g) \quad \text{(Cathode reaction)}$$
$$\overline{Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2\,(g)} \quad \text{(Overall reaction)}$$

The zinc anode gradually dissolves, and hydrogen bubbles evolve at the cathode.

- *The Oxygen Electrode*:

In aerated water, oxygen is available at the cathode, leading to the formation of hydroxyl ions. The oxygen electrode enriches the electrolyte with OH^- ions, which react with positively charged metallic ions to produce a solid product. In the case of iron rusting:

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \quad \text{(Anode reaction)}$$
$$½\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$$
$$Fe^{2+} + 2\,OH^- \longrightarrow Fe(OH)_2 \quad \text{(Cathode reaction)}$$
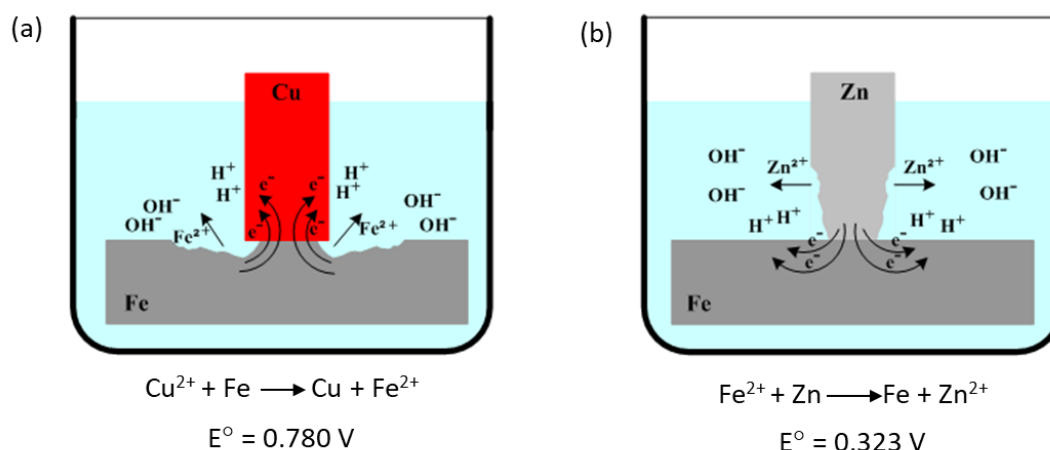$$Fe + ½\,O_2 + H_2O \longrightarrow Fe(OH)_2 \quad \text{(Overall reaction)}$$

- *The Water Electrode*:

In oxidizing acids, the cathode reaction yields water as a byproduct. If a continuous supply of both oxygen and hydrogen is available, the water electrode produces neither a buildup of solid rust nor a high concentration or dilution of ions at the cathode.

2.1. The Electrode Potential in Electrochemical Cells

When two metals are immersed in an electrolyte, they form a *galvanic couple* where the metal with a lower electrode potential undergoes oxidation (anodic reaction). In comparison, the metal with a higher electrode potential (more noble) undergoes reduction on its surface (cathodic reaction). Two instances of galvanic corrosion are depicted in the Figure 1, involving the use of a layer of another metal, such as zinc or copper, on an iron container.

(a) Cu | (b) Zn

$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$
$$E^\circ = 0.780 \text{ V}$$

$$Fe^{2+} + Zn \longrightarrow Fe + Zn^{2+}$$
$$E^\circ = 0.323 \text{ V}$$

Figure 1. Galvanic couples: (a) system Iron-Copper; (b) system Iron-Zinc.

A tin can is produced by applying a thin layer of tin over iron to prevent rust formation. However, once the tin layer is compromised, rapid rusting occurs. The standard electrode potentials are $E^0_{Fe} = -0.44$ V and $E^0_{Cu} = +0.33$ V, resulting in a difference of $E^0_{cell} = +0.78$ V. As the potential of iron is lower, it reacts anodically (dissolves) in this system. The cathodic reaction involves the electrons interacting with hydrogen ions on the copper surface. The cathode may be polarized by hydrogen atoms, forming a film covering the cathode surface, affecting corrosion kinetics by slowing down the reaction between electrons and hydrogen ions dissolved in the electrolyte. In electrolytes with a high concentration of hydrogen ions (acidic solutions), hydrogen atoms adsorbed on the cathode surface form hydrogen gas, promoting corrosion. Common aqueous solutions, which are aerated and contain dissolved oxygen, lead to hydrogen atoms formed on the cathode surface reacting with oxygen. The kinetic process in this case is determined by the diffusion of oxygen to the cathode surface.

In the case of the system iron-zinc, the standard electrode potentials are $E^0_{Fe} = -0.44$ V and $E^0_{Zn} = -0.763$ V, resulting in a difference of $E^0_{cell} = +0.323$ V. Since the potential of zinc is lower, it dissolves in the electrolyte through anodic reaction. The electrons released by the anode flow to the cathode (iron), where they participate in the cathodic reaction.

These examples highlight that different electrode pairs result in different voltages, representing the driving force for electrochemical oxidation–reduction reactions. The voltages for these half-cell reactions are measured against a reference point, the standard hydrogen electrode, which consists of an inert platinum electrode in a 1 M solution of H^+ ions saturated with hydrogen gas.

The corrosion tendencies of metals can be ranked using measured voltages, with noble metals like gold and platinum being chemically inert and metals lower in the ranking being more susceptible to oxidation. The emf series, generated with the standard hydrogen electrode, provides a basis for this ranking. The more negative the value for the oxidation of a metal, the more electropositive the metal and the higher its tendency to undergo oxidation reactions. However, the kinetics of the reaction and real-world conditions also play a role in determining the corrosion behavior of metals. The galvanic series, especially in practical environments like seawater, offers a more realistic ranking of the relative reactivities of metals and alloys.

3. CORROSION KINETICS

The half-cell potentials are thermodynamic parameters that pertain to systems in equilibrium. For instance, the discussions about the Galvanic pairs in the accompanying figures assumed no current flow through the external circuit. In actual corroding systems, a dynamic state exists with an electron flow from the anode to the cathode, resembling the short-circuiting of electrochemical cells. Consequently, the application of half-cell potential parameters becomes impractical. Moreover, these half-cell potentials signify the magnitude of a driving force, indicating the tendency for specific half-cell reactions to occur. However, it's crucial to recognize that while these potentials can determine the direction of spontaneous reactions, they offer no insights into corrosion rates. From an engineering standpoint, predicting corrosion rates necessitates the consideration of other parameters, as discussed below.

The corrosion rate, reflecting the speed of material removal due to chemical action, is a vital corrosion parameter. It can be expressed as the corrosion penetration rate (CPR), representing the thickness loss of material per unit of time. The formula for calculating CPR is:

$$CPR = \frac{KW}{\rho At} \quad (mm/year)$$

where W is the weight loss after exposure time t, and ρ and A denote the density and exposed specimen area, respectively. The constant K depends on the chosen system of units. CPR is conveniently expressed in millimeters per year (mm/yr). A corrosion penetration rate of less than 0.50 mm/yr is generally acceptable for practical purposes.

Given that electrochemical corrosion reactions involve an electric current, we can express the corrosion rate in terms of current density (i), specifically, the current per unit surface area of the corroding material. The corrosion rate r, measured in mol/m² s, is determined by the expression:

$$r = \frac{i}{nF} \quad (mol/m^2 s)$$

where n represents the number of electrons associated with the ionization of each metal atom, and F is Faraday's constant (96,500 C/mol).

4. FORMS OF CORROSION

Corrosion can be conveniently categorized based on its manifestation. Each form has distinct causes, and preventive measures for each are discussed briefly.

4.1. Uniform Attack

Uniform attack represents a form of electrochemical corrosion that occurs with consistent intensity across the entire exposed surface, typically leaving behind a scale or deposit. In a microscopic sense, oxidation and reduction reactions transpire randomly over the surface. Examples of this common corrosion form include the general rusting of steel and iron and the tarnishing of silverware (Figure 2).

Source: Bollard: PxHere, CC0 1.0, https://pxhere.com/en/photo/1374003.

*Figure 2*. Rusted bollard through uniform attack.

This prevalent form of corrosion is characterized by a chemical or electrochemical reaction that progresses uniformly over the entire exposed surface or a significant area. The metal undergoes gradual thinning and eventually experiences failure. For instance, when a piece of steel or zinc is immersed in dilute sulfuric acid, it typically dissolves uniformly over its entire surface. Similarly, a sheet iron roof exhibits a consistent degree of rusting across its entire exterior.

Uniform attack is the most widespread form of corrosion, leading to general wall loss or thinning over a large area. It poses a significant threat to metals on a tonnage basis. Prevention strategies include using appropriate materials, coatings, inhibitors, or cathodic protection.

4.2. Galvanic Corrosion

Galvanic corrosion ensues when two metals or alloys with disparate compositions are electrically coupled in the presence of an electrolyte. The less noble or more reactive metal in a specific environment undergoes corrosion, while the more inert metal, acting as the cathode, is shielded from corrosion. For instance, in a marine environment, steel screws corrode when in contact with brass, or if copper and steel tubing are joined in a domestic water heater, the steel corrodes near the junction. The reduction reactions at the cathode material surface depend on the nature of the solution.

The Figure 3 illustrating galvanic corrosion between stainless steel and mild steel showcases the protective nature of stainless steel due to the passive layer formed by chromium. The rate of galvanic attack depends on the anode-to-cathode surface area ratio exposed to the electrolyte, with the cathode–anode area ratio directly influencing the corrosion rate. Measures to mitigate galvanic corrosion include choosing dissimilar metals close in the galvanic series, optimizing the anode area, insulating dissimilar metals, and employing a third, anodic metal as a form of cathodic protection.
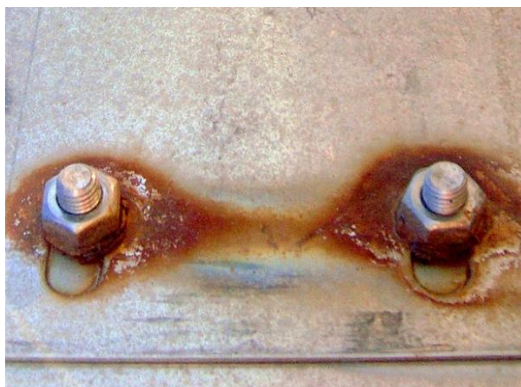
Figure 3. Galvanic corrosion occurred between a mild steel that was cast around a stainless steel core.

4.3. Crevice Corrosion

Electrochemical corrosion can also result from concentration differences of ions or dissolved gases within an electrolyte solution and between different regions of the same metal piece. In a concentration cell, corrosion transpires in the area with lower concentration, giving rise to crevice corrosion. This occurs in crevices, recesses, or beneath deposits where the solution becomes stagnant, leading to localized depletion of dissolved oxygen (Figure 4a). The width of the crevice must allow solution penetration yet promote stagnancy, typically several thousandths of an inch wide. Crevice corrosion's mechanism involves oxygen depletion within the crevice, leading to metal oxidation (Figure 4b). Electrons from this electrochemical reaction travel through the metal to adjacent external regions, where they are consumed by reduction.
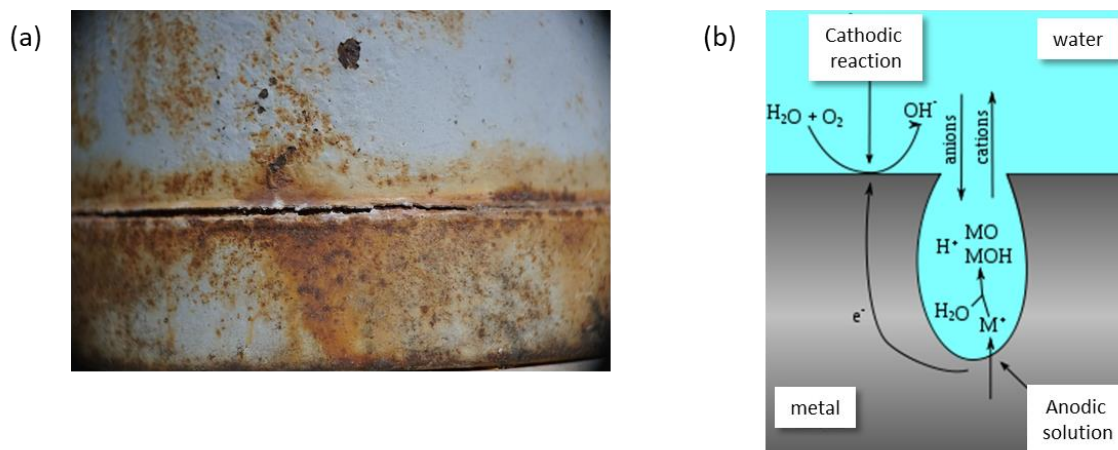
Figure 4. (a) Crevice corrosion; (b) mechanism of crevice corrosion.

High concentrations of H^+ and Cl^- ions within the crevice contribute to its corrosiveness. Alloys prone to passivation are susceptible to crevice corrosion due to the destruction of protective films by H^+ and Cl^- ions. Preventive measures include using welded joints, non-absorbing gaskets, regular deposit removal, and designing vessels to avoid stagnant areas and ensure complete drainage.

4.4. Pitting

Pitting corrosion presents as an extremely localized form of attack, resulting in the formation of small pits or holes. These pits typically penetrate a horizontal surface from the top downward in a nearly vertical direction. It is a subtle and insidious type of corrosion, often remaining undetected with minimal material loss until failure occurs. An illustrative example of pitting corrosion is depicted in the Figure5.

Figure 5. The pitting of aluminium plate.

The mechanism for pitting is likely akin to crevice corrosion, where oxidation occurs within the pit itself, accompanied by complementary reduction at the surface. Gravity is speculated to contribute to the downward growth of pits, with the solution at the pit tip becoming more concentrated and denser as pit growth advances. The initiation of a pit may arise from a localized surface defect, such as a scratch or slight composition variation. Polished surfaces have been observed to exhibit greater resistance to pitting corrosion. While stainless steels are somewhat susceptible to this corrosion form, alloying with approximately 2% molybdenum significantly enhances their resistance.

4.5. Stress Corrosion

Stress corrosion, often termed stress corrosion cracking, arises from the synergistic influence of applied tensile stress and a corrosive environment—both factors are imperative. Surprisingly, materials inert in a specific corrosive medium can become susceptible to stress corrosion when subjected to stress. Small cracks form and propagate perpendicularly to the stress, potentially leading to eventual failure (Figure 6). The failure behavior mimics that of a brittle material, even when the metal alloy is intrinsically ductile. Cracks may form at stress levels below the tensile strength, and most alloys are vulnerable to stress corrosion under specific environmental conditions.
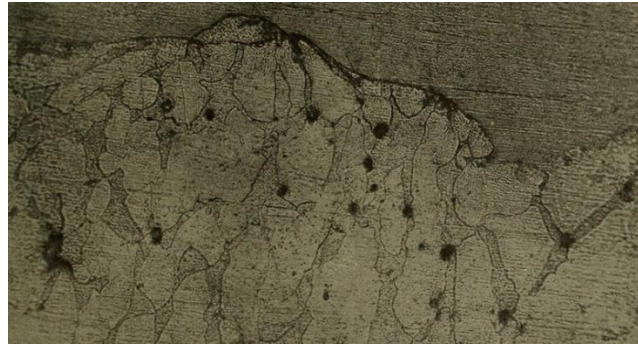
Source: Internet Archive Book Images, CC0 1.0, https://www.flickr.com/photos/internetarchivebookimages/14587063959.

Figure 6. Deterioration of Muntz (variety of brass) metal through stress corrosion.

For instance, stainless steels are prone to stress corrosion in chloride-containing solutions, while brasses are particularly vulnerable to stress corrosion in the presence of ammonia. Stress causing stress corrosion cracking need not be externally applied; it can be residual, resulting from rapid temperature changes, uneven contraction, or internal entrapped gaseous and solid corrosion products. Mitigation measures involve reducing stress magnitude by lowering external loads, increasing cross-sectional areas perpendicular to applied stress, or employing appropriate heat treatment to anneal out residual thermal stresses.

5. PASSIVITY

Certain metals and alloys, typically active under normal circumstances, exhibit an intriguing behavior under specific environmental conditions—they become exceptionally inert, a phenomenon known as *passivity*. Chromium, iron, nickel, titanium, and many of their alloys showcase this passive behavior. This passivity is attributed to developing a remarkably adherent and ultra-thin oxide film on the metal surface, acting as a robust protective barrier against further corrosion.

Stainless steels exemplify the benefits of passivation, boasting high resistance to corrosion across a broad spectrum of atmospheres. This resilience stems from their chromium content of at least 11%, which curtails rust formation when alloyed with iron, creating a protective surface film in oxidizing environments. However, it's worth noting that stainless steels are not impervious to corrosion in all environments and may not always live up to their "stainless" designation.

Similarly, aluminum displays impressive corrosion resistance in various environments due to its ability to passivate. In case of damage, the protective film typically regenerates swiftly. Nevertheless, alterations in environmental conditions, such as changes in the concentration of active corrosive species, can prompt passivated materials to revert to an active state. Consequently, any subsequent damage to the preexisting passive film may lead to a significant surge in corrosion rate, potentially by factors as high as 100,000 times.

6. CORROSION PREVENTION

Several approaches exist for preventing or minimizing corrosion, encompassing specific measures tailored to various corrosion types and more general techniques. The latter include material selection, environmental alteration, design modifications, coatings, and cathodic protection.

One of the most prevalent and straightforward strategies for corrosion prevention involves meticulous material selection once the corrosive environment has been characterized. Cost considerations often play a crucial role in this decision-making process, making it essential to balance optimal corrosion resistance and economic feasibility. Modifying the environment's characteristics, where feasible, can also substantially influence corrosion mitigation. Altering fluid temperature and velocity and adjusting the concentration of specific species in the solution can yield positive effects, such as inducing passivation in the metal.

Moreover, *inhibitors*, substances added in low concentrations to decrease corrosiveness, present another avenue for corrosion control. Their effectiveness arises from various mechanisms, such as eliminating chemically active species or forming a protective coating on the corroding surface. Commonly used in closed systems like automobile radiators and steam boilers, inhibitors can significantly impede corrosion.

Cathodic protection stands out as one of the most effective corrosion prevention methods, applicable to all forms of corrosion. This technique involves supplying electrons to the metal from an external source, transforming it into a cathode, and forcing the corrosion reaction in the reverse (reduction) direction. Galvanic coupling, employing sacrificial anodes like magnesium or zinc, and the use of impressed current from an external power source are common approaches in cathodic protection.

Finally, *Coatings* serve as an essential line of defense, isolating anode and cathode regions and preventing the diffusion of corrosive agents. From temporary coatings like grease to more robust options such as paint, ceramic coatings, or metallic coatings like tin and zinc-plating, various choices exist to safeguard against corrosion. Chemical conversion coatings, formed through reactions with the surface, also contribute to corrosion resistance. These coatings, including stable oxide layers on aluminum and stainless steel or corrosion-resistant linings like TeflonTM, play a vital role in preventing the formation of galvanic cells and enhancing the material's durability.