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Electrochemical Techniques for Corrosion and Tribocorrosion Monitoring: Fundamentals of Electrolytic Corrosion

Abdenacer Berradja

Abstract

This first chapter aims at giving a brief framework for understanding the principles of electrochemistry in corrosion and tribocorrosion, enabling potential users and readers to quickly apprehend the electrochemical nature of corrosion. The subsequent chapter will provide additional details on the methods derived from these principles in a clear manner and ready-to-use format. In particular, the implementation of electrochemical techniques for the study of tribocorrosion allows, *in situ* and in real time, to monitor and control the corrosion conditions during wear and to quantify the corrosion kinetics. An introductory to some of the basic terms and concepts of electrochemistry and corrosion is first presented. Then, an overview of the thermodynamic and kinetic parameters of relevance to corrosion electrochemistry is highlighted. A description on how the electrical nature of corrosion reactions allows the interface to be modeled as an electrical circuit, as well as how this electrical circuit can be used to obtain information on corrosion rates. These prerequisites are necessary to better understand the surface reactivity of metals and other electronic conductive materials immersed in ionic electrolyte media whether or not subjected to mechanical stimuli.

Keywords: corrosion, tribo-electrochemistry, tribocorrosion, standard potential, electrode kinetics

1. Introduction

The corrosion science is a complex subject that is not well defined, and still continues to progress as the subject evolves from the simple traditional definition of “destruction of metals through oxidation and its prevention” to “degradation of a material that involves one or more chemical and/or electrochemical reactions and its foresight”. This latter material definition encompasses a wide range of environments, and all classes of materials (ceramics, organics, composites), not just metals. The intentional conjunction with degradation due to non-chemical processes, such as tribology (i.e., science of friction, wear and lubrication), has open up a new global perspective topic of a rare universality that leads us to prospect many aspects of science and technology, namely tribocorrosion. To better understand the specificity of tribocorrosion, it is necessary to briefly recall what distinguishes corrosion from tribocorrosion.

Corrosion deals primarily with the electrochemical aspects related to physical-chemical oxidation and reduction processes taking place at the surface of materials and the effect of the reactivity of surfaces of materials with respect to their environment, time, pH, temperature, pressure, and electrolyte composition. It is almost without exception an irreversible heterogeneous reaction of a material with the environment, which usually (but not always) results in a degradation of the material or its properties (e.g., decadence of the functional properties of materials). Examples of corrosion phenomena include the transformation of steel into rust, oxidation of an electrical copper contact, cracking of brass in the presence of ammonia, pipeline degradation by H₂S, swelling of PVC in contact with a solvent, alkaline attack on refractory bricks, and mineral glasses. Occasionally, in certain cases, corrosion is valuable. For instance, the disposal of neglected metallic objects in the nature is not an uncommon corrosion phenomenon. It is still common to find beneficial corrosion reactions in the field practice. A typical example of corrosion protection processes is the anodizing of aluminum. Anodizing strengthens the passive oxide film on the surface of aluminum, and therefore its resistance to corrosion, but also serves as a decorative effect. Likewise, corrosion reactions are used to produce a smooth surface finish in chemical and electrochemical polishing processes.

Tribocorrosion occurs when surfaces of materials subjected to mechanical contacts and in relative motion and/or behaviors are affected by chemical, electrochemical and/or biological environmental factors. Accordingly, tribocorrosion damage (i.e., material loss) can be designated in a broad sense as a failure mechanism due to the mutual interaction of corrosion, friction, and wear processes and their synergy effects. It generates changes in surface and/or volume compositions (e.g., alteration of materials properties, surface and sub-surface transformations, cracking, tribo-chemical reactions, etc.), and often modifies the environment (e.g., surface contamination by tribo-reaction products or corrosion-produced compounds, pH changes, and so on), and ultimately can lead to system failure. Such a physical-chemical deterioration is well described in the literature by the following terms: corrosive wear, fretting-corrosion or corrosion-erosion [1–6]. Corrosion and wear often combine to cause aggressive damage and at last a shut-down in a number of industries, such as mining, mineral processing, chemical processing, metal components of machines, marine structures, pulp and paper production, ships, bridges, biomechanics (e.g., orthopedics), civil engineering structures and energy production, and so on. Although, corrosion can often occur in the absence of mechanical wear, the opposite is rarely true. Corrosion accompanies to some extent in all environments, except in vacuum and inert atmospheres. The combined effects of friction (wear) and corrosion can result in total material losses well above than that of the additive effects of each process taken apart, which is attributed to their synergy [1–3, 7]. These effects are still difficult to control. Knowledge of the tribological behavior of a material couple in the absence of any chemical attack and the knowledge of the electrochemical behavior in the absence of any mechanical impact are not sufficient to deduce the tribocorrosion behavior of that couple system of materials. In many articulation systems, it has been noticed that friction may alter the sensitivity, and modifies the composition of the surfaces of materials in moving contacts to corrosion. In turn, corrosion can affect the friction (and wear) process of moving contacting parts. This usually accelerates the tribochemical degradation of the material, which may affect the contact moving conditions, and thus the friction process and the coefficient of friction too [1–6]. The contact motion can be a continuous or discontinuous one; it can be a unidirectional or a reciprocating one. The complexity of a tribocorrosion system is illustrated in **Figure 1**.

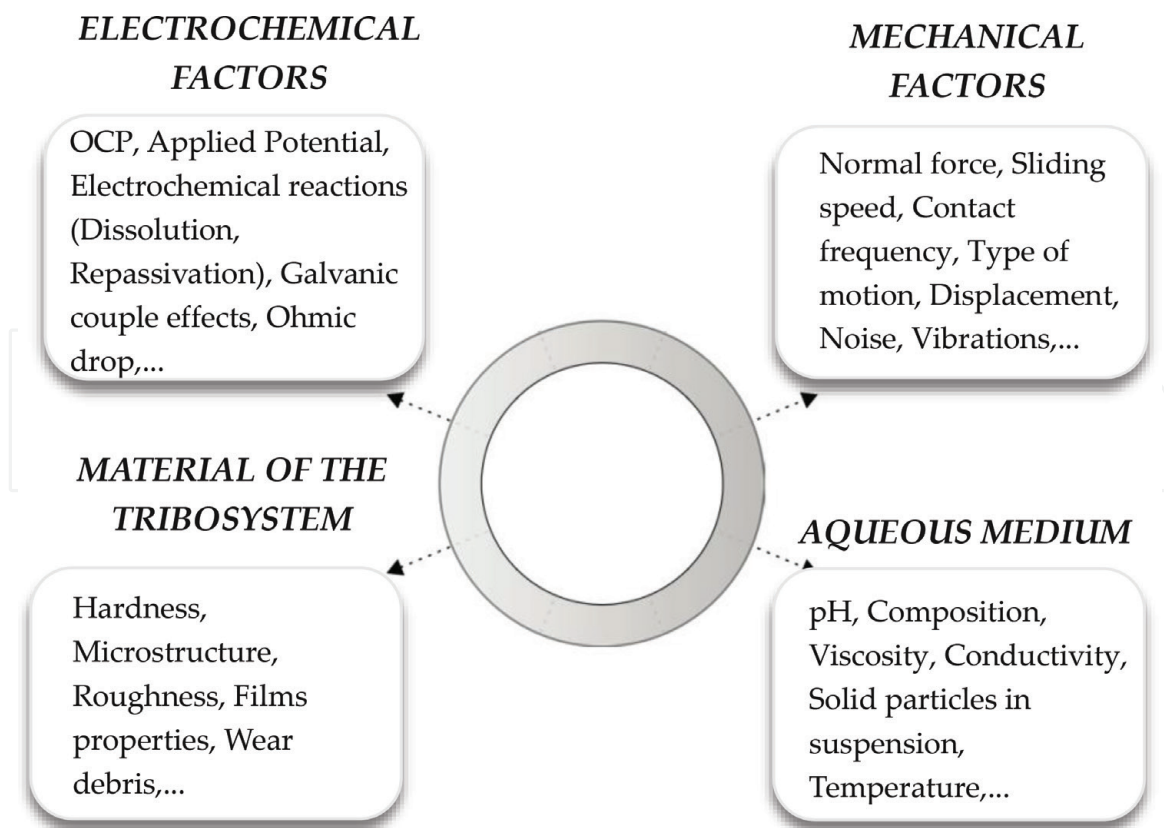


Figure 1.
Schematic of main factors which define the complexity of a tribocorrosion system.

Tribocorrosion of moving solids immersed in an aggressive environment is, just as friction, a system parameter. The tribo-electrochemical system consists of implementing *in-situ* electrochemical techniques to a tribological designed system under well-controlled conditions (i.e., tribometer type, and complete material system) [3]. A properly designed laboratory mechanical system allows for the best simulation as much as possible the entire material system used in the field, and the constraints that have associated with it (e.g., vibration mode, similarity of the wear mechanisms active in the laboratory test and in the field, such as abrasion, adhesion, fatigue, existence or not of a third body, erosion, corrosion, their combinations, and so on) [3]. Both mechanical and electrochemical methods allows for monitoring and recording *in-situ* and in real-time the following macroscopic quantities as normal or tangential force, relative or rotational displacement, sliding velocity, angular frequency, contact temperature, vibrations of the contacting parts and in relative motion, noise eventually emitted during the test, and the measurements of the electrochemical potential, the corrosion current and/or the impedance of the working materials. In most cases, both wear and corrosion rates can be determined *ex-situ* from a loss of material on one or both contacting materials by surface characterization methods and Faraday's law concepts respectively. Since the chapter does not cover comprehensive information regarding tribocorrosion nor it is the scope of the present work, a state-of-the art and critical reviews on tribocorrosion with specific discussions related to mechanisms, general procedures, and technological aspects may be found elsewhere [1–6], and it is left to the reader to locate further reading sources for that type of information.

The author assumes the reader is familiar with the background of corrosion phenomena and of conventional electrochemical methods in corrosion research. Many textbooks and review articles in the field are available but, for the sake of readability, a reminder of some aspects is given here.

2. Importance of corrosion and tribocorrosion

One of the primary reasons for the importance of corrosion or tribocorrosion lies on global economic losses. The destruction of nearly a quarter of the world's annual steel production is caused by corrosion. An estimate of about 150 million tons of losses per year, i.e. 300 tons per minute! [8]. Corrosion is definitely not limited to steel alloys but affects all sort of materials, namely metals, polymers, and ceramics. Corrosion and wear damage to materials, both directly and indirectly, cost industrialized countries hundreds of billions of dollars annually. For example, wear failures of metals costed the U.S. economy almost \$20 billion per year (in 1978) compared to about \$80 billion annually for corrosion during the same period [6]. The economic losses, due to friction and wear, related to these costs are estimated to be 6–10% of the Gross National Product (GNP). Wear represent 30% of the causes of dysfunction of the global mechanical engineering systems [2]. A recent study commissioned by the American Federal Highway Administration reveals that the annual direct cost of corrosion was \$ 276 billion in 1998, which represents 3.1% of the GNP [9]. Similarly, in the United Kingdom, Japan, Australia and Kuwait, the total annual cost of corrosion was estimated to range between 1 and 5% of each country's GNP [10].

Owing to many different types of expenses involved, in general, estimates of the total cost of corrosion and wear evolve over time and are sometimes difficult and uncertain. There is no doubt, however, that the cost is quite elevated. The direct losses concern replacement of corroded materials and equipment. The indirect losses are related to cost of repair and loss of production, cost of corrosion protection, and prevention. The direct losses are very often lower than indirect costs. For example, it is estimated that the price of repairing or replacing a corroded heat exchanger in a nuclear power plant is insignificant compared to the cost of lost production time. Another important aspect among major influential factors that contribute to corrosion or tribocorrosion relevance is related to reliability, or safety and preservation. Corrosion and wear can compromise the reliability and security of the operating equipment, leading to failure in-service, and at worst disasters, e.g., pressure vessels, metal reactors for toxic chemicals, turbine rotors, nuclear power plants, steering mechanisms for vehicles automobiles, and so on. Further, it requires the rebuilding or replacing the corroded structures and machinery or their components and an additional investment of the following supplies and facilities: metals, energy, water and human efforts to design these metal structures, without mentioning any other resources.

3. Relevance of corrosion and tribocorrosion monitoring

The importance of corrosion and/or tribocorrosion monitoring is that it allows people of interest to study the extent of damage due chemical and/or mechano-chemical attacks and to become aware of the rate at which such damage is progressing so that the necessary measures can be taken to avoid trouble. Generally, the application of continuous and adequate on-line corrosion or tribocorrosion monitoring includes the following advantages: enhanced security, ensuring operational reliability on-time, minimizing process contamination and maximizing product quality, providing a sentinel for equipment integrity, and preventing any further risk related to material or production. The most convenient way to successfully combat corrosion or tribocorrosion impact on materials and structures is (i) to understand the main causes of corrosion and/or wear, (ii) to use all available means to prevent it, (iii) and to implement a continuous improvement approach to corrosion and wear protection.

There are several factors that can come into play in the process of corrosion or tribocorrosion [1–3, 8]. Among the common influential criteria on corrosion, the following main parameters can generally be selected, namely the pH of the medium, the presence of chlorides (and other alkyl halides), the oxidizing power, the pressure, and the temperature. Fundamentally, corrosion depends on the dominating deterioration mechanism of surfaces exposed to chemical environment. The corrosion resistance properties can be characterized directly by the limits of use of the materials, which can be expressed, for example, in terms of maximum temperature in-service or maximum concentration of use. Under normal service conditions, the understanding and control of corrosion are based on the electrochemical interpretation of corrosion phenomena and the consideration of the relative ranking scales of materials in order to select, by successive approaches, the materials best suited to each application of interest [3].

Conversely, a more obvious mechanism of tribocorrosion is the periodic exposure of fresh bare surfaces when sliding friction between surfaces occurs in corrosive liquids or gases [3]. This results in reaction products mainly driven by chemical and electrochemical interactions. The surfaces of the materials are quickly covered by a scale of the reaction product, the oxide in the case of metals and metallic alloys, acting as a protective barrier layer. Often, the thinner the scale, the faster the reaction, and the weaker the protectiveness [3]. Though, tribocorrosion processes are complex, combining both wear and corrosion. Modern research has established a consensus on four main forms of wear, namely, chemical wear (i.e., corrosion and corrosive wear), adhesive wear, abrasive wear or surface fatigue wear [3, 11]. Each process obeys its own laws and, to confuse things, one of the modes of wear acts to affect the others, hence the complexity of corrosive wear [1–3]. As a general rule, there is a combination of competitive wear mechanisms in a dynamic mechanical-chemical contact.

3.1 Choice of technique (instrumentation)

There are many electrochemical and non-electrochemical techniques for the study of corrosion or tribocorrosion and many factors must be taken into account when choosing a technical method. The corrosion rate can be determined by extrapolation of Tafel from a potentiodynamic polarization curve [12, 13]. It can also be determined using the Stern-Geary equation from the polarization resistance derived from a linear polarization experiment or from electrochemical impedance spectroscopy [12, 13]. Furthermore, among the recently developed techniques, those using electrochemical noise analysis as a method of determining the rate of corrosion and estimating the tribocorrosion rate of some passive materials has been shown to be beneficial, although scientists are struggling through the interpretation of some conflicting results [2, 12–15]. Sensitivity to localized corrosion is often evaluated by determining a breakdown potential and a repassivation potential for passivating materials.

3.2 Corrosion forms

Obviously, the most typically known mode of corrosion is the rusting of iron, or iron oxide, and ordinary steel. Contemporary corrosion research has established several forms of corrosion, all which are important to understanding, as the best methods of preventing corrosion depend upon the form of corrosion, as shown in **Figure 2**.

- *Uniform corrosion*: the damage by general or uniform corrosion is fairly predictable; however, the damage caused by localized corrosion is rather unpredictable if no proper monitoring techniques are applied. When left uncontrolled, corrosion will not only cause costly equipment maintenance and replacement

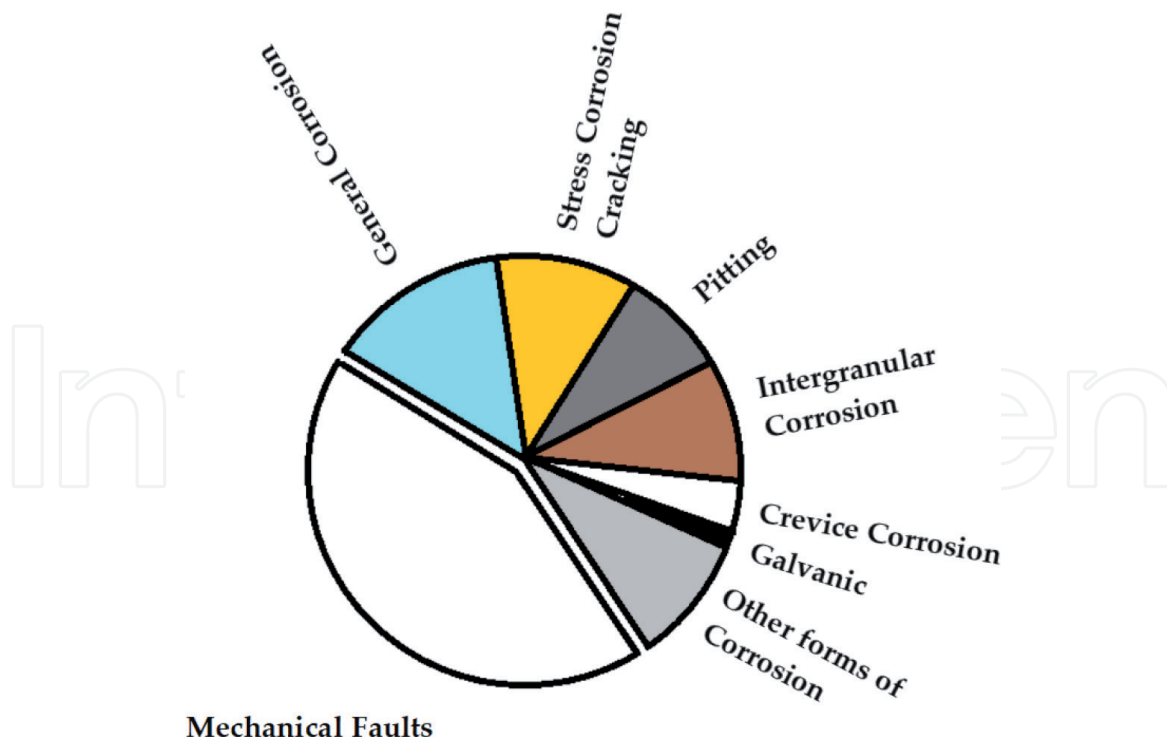


Figure 2.
Forms of corrosion.

but may be responsible for the loss of revenue from unexpected system shut-down and the possibility for hazardous leaks causing major safety issues and possible environmental contamination [16].

- *Pitting* is a form of localized corrosion that occurs when the thin passive protective film on most corrosion-resistant engineering alloys is compromised. The rate of attack at pits can be extremely high so pitting can lead to perforation of a structure or initiation of a crack [17].
- Localized corrosion often initiates at an occluded region where the environment has limited access. This form of corrosion, so-called *crevice corrosion*, is extremely important in fastened structures which often contain many crevices [17].
- Localized corrosion is sometimes observed at grain boundaries when the composition of the grain boundary or region near the grain boundary is different than that in the metal grain. This type of corrosion, so-called *intergranular corrosion* is a severe problem, in particular for stainless steels and aluminum alloys [17].
- Corrosive attack can be localized at one component of a structure made from different metals that are electrically connected as a result of *galvanic corrosion* [17].
- The corrosion of metal alloys often results in preferential reaction of one or more of the alloying elements, so-called *dealloying* [17].
- A common by-product of the corrosion process is hydrogen. Hydrogen can interact with metals in various ways to result in a degradation of properties, primarily mechanical properties (e.g., pipeline gas transportation by H₂S). A generic name for such degradation is *hydrogen damage* [17].

- The mechanical properties of metals can be severely degraded by the combined effects of the environment and an applied stress. *Stress corrosion cracking* is the premature failure of metal structures as a result of these effects [17].
- *Corrosion fatigue* occurs when the applied stress is fluctuating rather than being constant [17].

4. Aspects of corrosion prediction in aqueous media

Although, air in atmosphere is the most omnipresent environment, the aqueous solutions (e.g., atmospheric moisture, acid rain, natural waters, artificial solutions, and so on) are the most common environments associated with corrosion issues. Due to the conditions under which a material, e.g., a metal or a metallic structure is exposed to the environment, corrosion processes usually take place at the metal/environment interface through ionic conduction processes. Corrosion is due to electrochemical reactions involved in that interface and strongly affected by a number of factors, among others, such as the power oxidizing (electrode equilibrium potential), hydrogen ion activity (pH, acidity level of the solution), driving force for metal stability (Gibbs free energy change), rate-determining step reaction or reaction rate (corrosion current), and temperature (Arrhenius oxidation rate or the Pilling-Bedworth ratio).

The prediction of corrosion of a metal or an alloy in environments such as aqueous solutions requires information on the expected state of the metallic alloy (e.g., oxide or non-oxidized metal, etc.) and the rate at which the metallic alloy moves to that state. So first, thermodynamic principles can be applied to determine what processes can occur, and under which conditions the reactions are at an electrochemical equilibrium and, in case of deviation from that equilibrium, in which directions the reactions can proceed and what is the driving force involved. The kinetic laws then describe the reaction rates. These are strongly related to the activation energies of the electrode processes, to the mass transport and to the fundamental properties of the metal/environment interface, such as the resistance of surface films. A general method, namely the mixed potential theory, is implemented for interpreting or predicting the corrosion potential and reaction rates.

In what follows, a very brief reminder of corrosion principles is given.

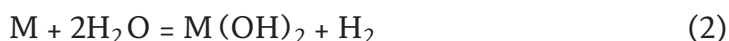
4.1 Electrochemical nature of metal/electrolyte exchange reaction

The corrosion process is electrochemical in nature. In a more general sense, a corrosion process involving a metal/aqueous solution or any other metal/ionically conducting medium exchange or interaction interface is defined as any process causing the metal, M, to lose one or more of its loosely bound electrons in the metallic state (i.e., oxidation reaction) to generate a solvated cation in the solution, and it is simultaneously balanced, in order to ensure an exact count of the electrons involved, by a reduction reaction by which one or more atoms of a molecule or an ion (anion) of species in solution gain one or more of these electrons (conservation criteria).

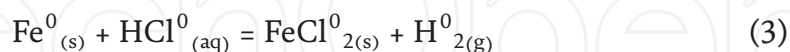
The aqueous corrosion sometimes requires that the oxidation product is either an oxide of the metal itself according to (1):



or is a metal hydroxide and the reduction product of hydrogen ions in solution is gaseous hydrogen as claimed in the equation (2):



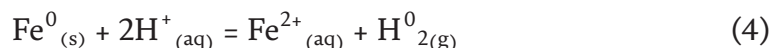
However, it is of course not necessary for an oxide or hydroxide to be formed as an oxidation product of the metal. For example, in the overall reaction of corrosion of iron in a dilute chloridric acid, the ferrous chloride compound is generated as an oxidation product according to the reaction (3),



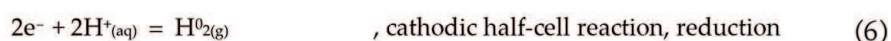
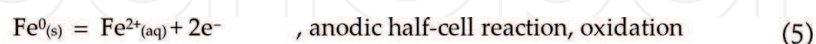
The superscript associated at each reactant or reaction product refers to the valence charge or the oxidation state. The subscript corresponds to the matter phase state for each element of the reaction or compound.

The foregoing overall reaction involves vigorous oxidation and reduction (*viz.* redox) processes. This requires that hydrogen gas is released, more likely by a desorption process, and the solid Fe is oxidized by the acid, forming an ionic bond with the chloride ions. The ferrous ions are removed from the metal lattice and get solvated as they diffuse into the solution. The ferrous chloride compound can be dissociated at normal concentrations.

It is worthy of note that the chloride ions are not actually involved in the redox reaction, this equation (4) can be written in the simplified form as follows:



It is worthy of note that this also applies to aqueous corrosion involving other acidic media (e.g., orthophosphoric acid, H_2SO_4 , HF), and water-based organic acids (e.g., methanoic or ethanoic acids). In each case, no more than hydrogen ion is active, whereas the other ions such as phosphate, sulfate or acetate take no part in the corrosion reaction. Hence, iron reacts with the hydrogen ions of the acid solution to form iron ions (oxidation process) and hydrogen gas (reduction of process). Thus, Eq. (4) can be conveniently divided into two reactions (partial half-cell reactions), namely the oxidation of iron and the reduction of hydrogen ions. This provides the basis for the thermodynamic consideration of the overall corrosion process as stated by equations (5), (6), and (7):



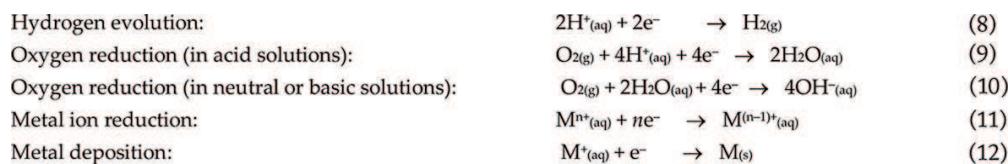
Oxidation or commonly referred to as the anodic reaction is indicated by an increase in the valence charge or electron production. A decrease in the valence charge or an electron consumption represents a reduction or commonly a cathodic reaction.

Equations (5) and (6) outline the two half-cell electrode reactions-both need to occur simultaneously and at the same speed on the metal surface otherwise it would charge spontaneously electrically, which is impossible. This explains one of the fundamental principles of corrosion, namely: the oxidation rate is equal to the reduction rate (in terms of electron production and consumption).

The sites for the oxidation reactions are called *anodes*, and the sites for the reduction reactions are called *cathodes*. Anodes and cathodes can be spatially separated at fixed locations associated with heterogeneities on the electrode surface. Otherwise, the locations of the anodic and cathodic reactions can randomly fluctuate across the electrode surface. The former case results in a localized form of corrosion, such as pitting, crevice corrosion, intergranular corrosion, or galvanic corrosion, and the latter case results in nominally uniform corrosion [17].

The above concept is illustrated in **Figure 3**. An iron atom undergoes a transformation into a ferrous ion and two electrons. These electrons, which remain in the metal, are immediately consumed during the reduction of hydrogen ions. **Figure 3** illustrates the separation of these two processes in space, merely for the sake of transparency. In fact, whether or not they separate or take place at the same surface location, this does not impact the principle of charge conservation. In some cases, the oxidation reaction takes place in a uniform manner on the surface. In other situations, the corrosion reaction occurs at specific locations of the surface (i.e., localized corrosion).

It should be noted that there are several different cathodic reactions encountered repeatedly during metallic corrosion. The most common are:



n is the number of electrons involved in the reaction. The evolution of hydrogen is a common cathodic reaction because acidic media are frequently encountered. Oxygen reduction is very common because any aqueous solution in contact with air is able to produce this reaction. In nearly neutral electrolytes, the reduction of oxygen is normally one of the most universal cathodic reactions. Concentrations of ≈ 6 ppm dissolved oxygen are usually present in dilute aqueous electrolytes at ambient temperature (25°C). The reduction of metal ions and the deposition of metals are less frequent reactions and are most often encountered in chemical processes.

4.2 Thermodynamic approach to corrosion

Thermodynamic data estimations are meaningful in corrosion field because they can be used to predict the tendency of a metal to corrode in a given environment. Details on thermodynamic principles can be found in a number of manuals [18, 19]. The Atlas of Electrochemical Equilibria in Aqueous Solutions by Marcel Pourbaix provides a complete summary of the application of thermodynamic corrosion for all elements in water [20]. Dr. Pourbaix originally developed “corrosion maps or corrosion road charts” in the form of potential-pH diagrams [20], which enables for displaying the stability of metals (the lowest free energy state) as a function of the activity of hydrogen ions (pH) and equilibrium potential (oxidizing power). So, the diagrams can, in principle, indicate under which conditions of pH and equilibrium potential, an expected corrosion does not occur (immunity region, e.g., pure Fe) or might cause the metal to transform to an ion (metal loss, state of corrosion, e.g., ions of Fe and its compounds) or even indicate whether an oxidized solid should be formed or not (possible passivity, e.g., oxides of Fe). A typical example showing all of these common aspects of metal corrosion is depicted in **Figure 4** for Fe-H₂O system [20].

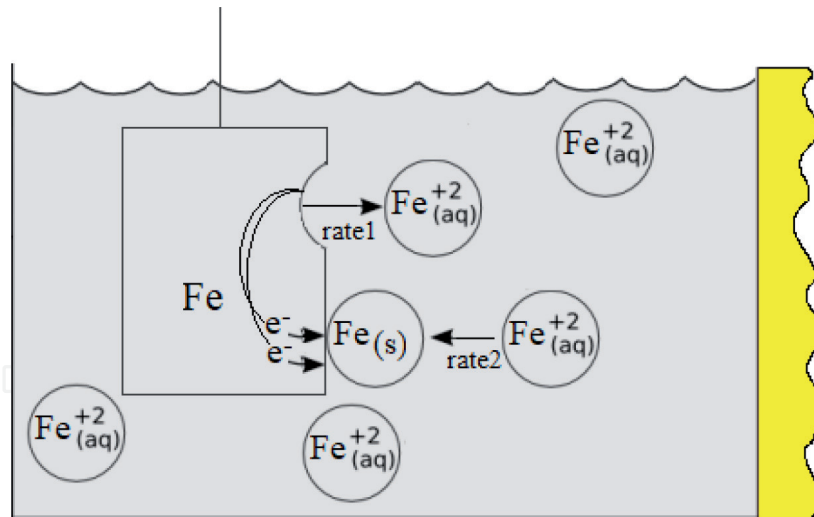


Figure 3.
Reversible iron electrode.

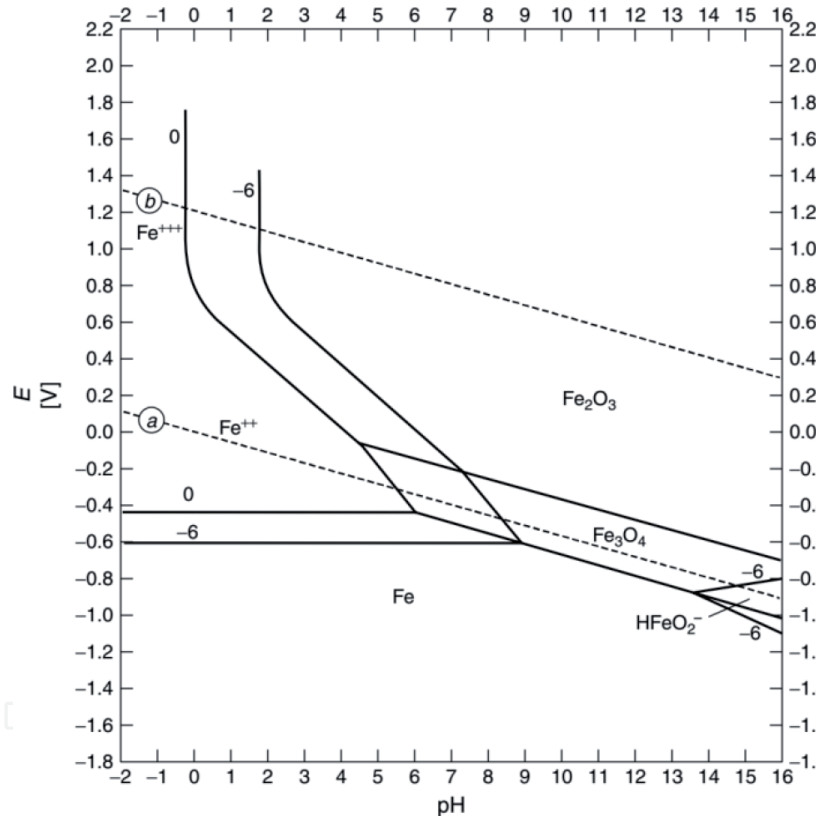


Figure 4.
Pourbaix potential-pH diagram for Fe/H₂O system at 25°C. Reprinted from [20] with permission from NACE international.

4.2.1 Change in Gibbs free energy

A myriad of chemical oxidation-reduction reactions can be performed in an electrochemical cell in which electrons released by the oxidation of species at an electrode (anode) flow through an external conductor (e.g., electrolyte) to a second electrode (cathode) where they are consumed by a reduction reaction [19]. An equivalent ion current flows in the electrolyte which separates the electrodes from the electrochemical cell. In such a device system, the change of chemical energy results from the change of free energy. This change in free

energy or commonly termed Gibbs free energy, ΔG , can be defined as a direct measurement of the maximum available electrical energy of a system or in other words it is an indicative measure of the driving force for the reaction to proceed. If the free energy change accompanying the transition of a system from one state to another is negative ($\Delta G < 0$), it indicates a loss of free energy as well as the direction of spontaneous reaction of the system. In particular, if no external force acts on the system, it will tend to transform into its lowest energy state and for a given reaction, it will tend to proceed spontaneously. If the free energy change is positive ($\Delta G > 0$), it indicates that the transition represents an increase in energy, which requires the addition of an extra energy to the system for the reaction to proceed.

The free energy change accompanying an electrochemical reaction can be calculated by the following equation:

$$\Delta G = -nFE \quad (13)$$

where ΔG is the standard free energy in the overall reaction, n the number of electrons involved in the reaction, F the Faraday constant, and E equals the cell potential or the difference between the two standard half-cell potentials. Noting that the term “standard” potential is the potential of a metal or any reactant in contact with its own ions at a concentration equal to the unit activity (i.e., approximately 1 g atom weight per 1 l solution) and at 25°C.

Although Eq. (13) forms the basis for thermodynamic calculations, it is rarely used in studying corrosion phenomena. This is because it is not possible to accurately predict the velocity of a reaction from the change in free energy. It is worth remembering that in most cases, the true magnitude of free energy change is trivial in corrosion applications. The most important factor is the sign of the free energy change for a given reaction, because it indicates whether the reaction is spontaneous or not. Hence, this parameter only reflects the direction of reaction by its sign. Reactions occur exceptionally in the direction that reduces the Gibbs free energy. The more negative the value of ΔG , the greater the tendency for the reaction to proceed. For example, for any overall corrosion reaction of Fe in dilute chloridric acid solution to be thermodynamically possible, it is necessary that the anodic dissolution potential of Fe (i.e., oxidation of Fe) be more active (less noble) than that of the cathodic reaction (i.e., hydrogen evolution). If the change in free energy is positive, the reaction does not occur spontaneously.

4.2.2 Cell potentials

The cell potential of the overall electrochemical or corrosion reaction, as specified above for the example of Fe in a dilute HCl solution, is directly associated with the change in free energy accompanying that reaction via Eq. (13) according to,

$$E = -\frac{\Delta G}{nF} \quad (14)$$

A simple rule can be derived from Eq. (14) to predict the spontaneous direction of any electrochemical reaction. This rule can be clearly stated as: “In any electrochemical reaction, the most negative or active half-cell tends to be oxidized, and the most positive or noble half-cell tends to be reduced”. Therefore, the potential is a measure of the reaction (corrosion) tendency. Positive potential corresponds to negative ΔG and hence to spontaneous reaction.

A potential can be assigned to each of the half-cell reactions (anodic oxidation and cathodic reduction). In that respect, the choice of an appropriate reference (half-cell reaction) will therefore allow the measurement of the potential between two electrodes (i.e., working and reference electrodes). An arbitrary half-cell reaction is used as a reference by setting its potential to zero and all other half-cell potentials are calculated with respect to this zero reference. It is common to use the normal or standard hydrogen electrode (SHE) as a universal reference when enumerating the potential of a half-cell [19]. The SHE corresponds to the half-cell reaction (15) given hereafter:



under standard conditions, *viz.* the activity of the protons is unity ($a_{\text{H}^+} = 1$), and the partial pressure of $\text{H}_{2(\text{g})}$ is 1 bar ($p(\text{H}_2) = 0.987 \text{ atm}$). The potential of the SHE is arbitrarily set at zero ($E^{\circ}_{\text{SHE}} = 0 \text{ V}$), and therefore ΔG° ($a_{\text{H}^+} = 1$) is arbitrarily set to 0 as a reference free energy change. The superscript “0” in the SHE potential refers to a standard or reversible potential.

Since it is not possible to manufacture an electrode from hydrogen, an inert electrode is used. Generally, a platinum electrode acts as an inert metal substrate for the electrochemical reaction. Consider an electrochemical cell containing iron and platinum electrodes immersed in a sulfuric acid, both in equilibrium with their reaction product ions and separated by a porous membrane to retard mixing, as illustrated in **Figure 5**. In the reversible divided cell, equilibrium is established between iron and its ions on the iron electrode and hydrogen gas and hydrogen ions on the platinum electrode respectively.

At different locations on the platinum electrode, the hydrogen ions are reduced to gaseous hydrogen and the gaseous hydrogen is oxidized to hydrogen ions, with electron transfer occurring between these spots. It is worthy of note that the platinum electrode does not participate in this reaction but merely serves as a solid interface at which this reaction can occur. Many metals function as reversible hydrogen electrodes (e.g., $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (Calomel), Ag/AgCl , Hg/HgO , $\text{Hg}/\text{Hg}_2\text{SO}_4$, $\text{Ag}/\text{Ag}_2\text{SO}_4$, Cu/CuSO_4 , etc.); platinum is generally preferred because of its inertia

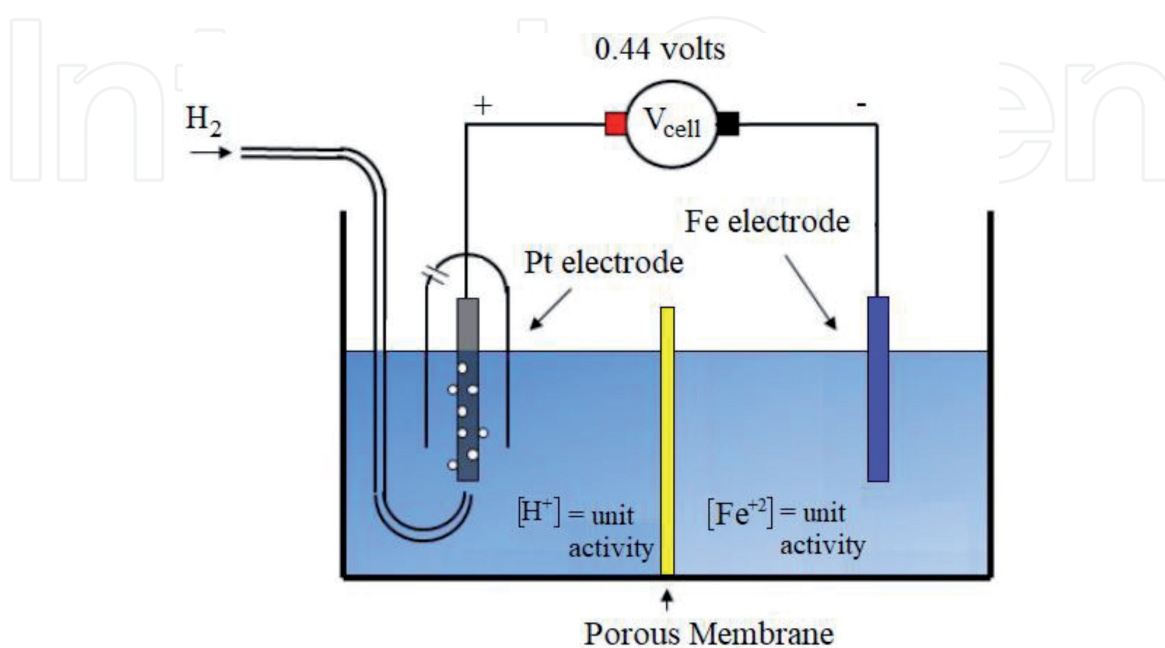


Figure 5.
Electrochemical cell containing reversible iron and hydrogen electrodes (Pt.).

and the ease with which electron transfer occurs on its surface (e.g., properties of catalytic surface exchange or easy current flow rate). As with the other half-cell electrodes, at certain infinitesimal areas on the metal iron surface, iron atoms are oxidized to ferrous ions, and at other spots ferrous ions are reduced to metallic iron. Equilibrium conditions dictate that the rates of the reactions in each half-cell compartment be equal; there is no net change in the system. Noting that the interactions taking place at the metal electrode/electrolyte are quite complex and closely related to electrochemical kinetics and physical phenomena (e.g., electrical double layer, diffusion, etc.).

Consider now the case, under standard conditions, where two dissimilar metals each immersed separately in their own ions in an aqueous medium and electrically connected. Under these conditions, the corrosion control is governed by the determination of the mechanisms involved in the redox reactions. Standard redox potentials can be used to understand the corrosion tendency of metals. A disposition of metals based on their standard potentials has been established and known as standard equilibrium oxidation-reduction potential or standard reversible potential or electromotive force series. The standard potential series of metals is given in **Table 1**. In this series, electrode potential values are invariant, given *vs.* SHE, and attributed to reduction reactions. The same series can be developed on the basis of the oxidation reactions, in which case the potential values will be the same but the “signs” will be reversed.

Redox potentials are very useful for predicting corrosion behavior of metals and upon certain conditions, the tendency of chemical degradation of passivating materials under sliding contacts [22]. Any electrochemical reaction can, therefore, be studied on the basis of the half-cell reaction concept and the foregoing potential standards involving the combination of metals in aqueous solutions with or without any mechanical contact. For example, consider two dissimilar metal pieces, namely silver and zinc, each immersed separately in a dilute acid solution (e.g., H_2SO_4) with their own ions (**Figure 6**) and electrically connected via a potentiostat (i.e., a high-resistance voltmeter). It is necessary that the two electrodes are in equilibrium in their own compartment. The positive terminal of the potentiostat must be connected to the silver electrode, and the negative terminal must be connected to the zinc electrode to have the potentiostat read on scale. According to data in **Table 1**, the standard redox

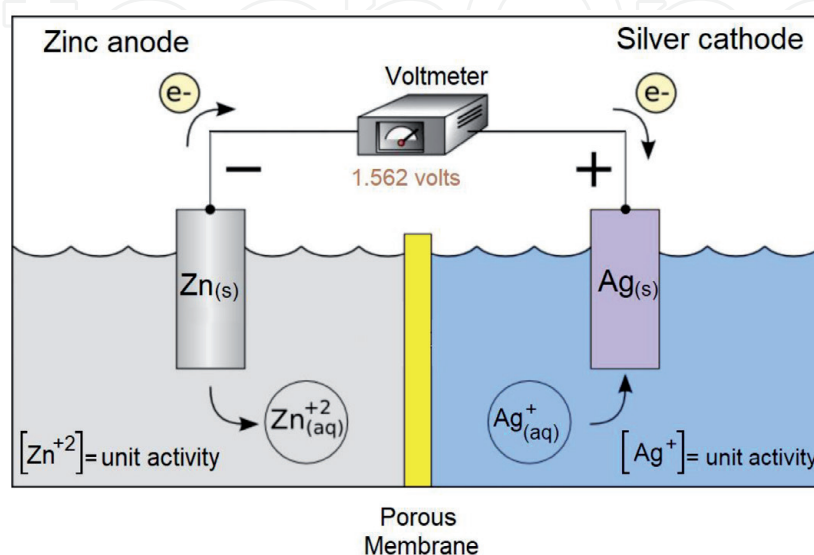


Figure 6. Electrochemical reversible cell containing silver and zinc in equilibrium with their ions and electrically interconnected via a high-resistance voltmeter.

Electrode red-ox reaction	E° (volts)
$\text{Au} = \text{Au}^{3+} + 3e$	+1.498
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	+1.229
$\text{Pt} = \text{Pt}^{2+} + 2e$	+1.2
$\text{Pd} = \text{Pd}^{2+} + 2e$	+0.987
$\text{Ag} = \text{Ag}^+ + e$	+0.799
$2\text{Hg} = \text{Hg}_2^{+} + 2e$	+0.788
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	+0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^-$	+0.401
$\text{Cu} = \text{Cu}^{2+} + 2e$	+0.337
$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	+0.15
$2\text{H}^+ + 2e = \text{H}_2$	0.000
$\text{Pb} = \text{Pb}^{2+} + 2e$	-0.126
$\text{Sn} = \text{Sn}^{2+} + 2e$	-0.136
$\text{Ni} = \text{Ni}^{2+} + 2e$	-0.250
$\text{Co} = \text{Co}^{2+} + 2e$	-0.277
$\text{Cd} = \text{Cd}^{2+} + 2e$	-0.403
$\text{Fe} = \text{Fe}^{2+} + 2e$	-0.440
$\text{Cr} = \text{Cr}^{3+} + 3e$	-0.744
$\text{Zn} = \text{Zn}^{2+} + 2e$	-0.763
$\text{Al} = \text{Al}^{3+} + 3e$	-1.662
$\text{Mg} = \text{Mg}^{2+} + 2e$	-2.363
$\text{Na} = \text{Na}^+ + e$	-2.714
$\text{K} = \text{K}^+ + e$	-2.925

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Table 1.

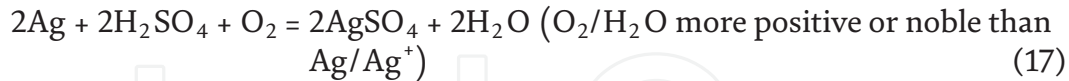
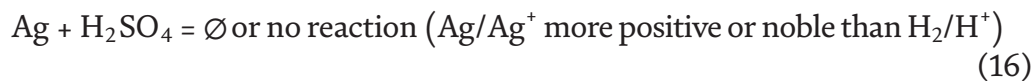
Electromotive force series (Emf or standard potentials redox in volts vs. SHE at 25°C).

potential of silver is +0.799 volts (*vs.* SHE) and that of zinc is -0.763 volts. In this manner, zinc oxidation and silver reduction reactions are spontaneous at +0.763 and +0.799 volts respectively. Their equivalent non-spontaneous reactions occur at -0.763 volts for zinc reduction and at -0.799 volts for the oxidation of silver.

The potentiostat shows a potential difference of approximately 1.562 volts when the silver and zinc electrodes are connected. In this reversible electrochemical cell, zinc is negative with respect to silver. Thus, zinc undergoes anodic oxidation (corrosion) while silver ions undergo cathodic reduction at the silver cathode. The use of redox potentials greatly simplifies the calculation of potential cells and simultaneously allows to determine the trend in metal corrosion.

It follows from the above principle that all metals having a more active (negative) reversible potential than hydrogen will tend to be corroded by acid solutions. Silver, with its higher positive and noble potential, is not corroded in acid media. Though, the presence of dissolved oxygen may alter this latter rule, leading to oxygen reduction (cathodic reaction) and silver oxidation (anodic reaction). **Table 1** indicates that in the presence of oxygen, silver tends to corrode spontaneously.

In that respect, the following conclusions may be drawn from the outcome of the standard redox potential series:



As the reversible potential of a metal becomes more noble, its tendency to corrode in the presence of oxidizing agents decreases.

It is important to note that all the above discussions refer to conditions for corrosion systems at unit activity. Since half-cell potentials change with concentration, Nernst calculations must be made before predicting spontaneous direction at concentrations other than unit activity. To determine the potential of a metal in which the reactants are not at a unit activity, the familiar Nernst equation has been formulated as follows,

$$E = E^\circ + \frac{2.303RT}{nF} \log \left[\frac{a_{\text{oxid}}}{a_{\text{red}}} \right] \quad (18)$$

where E represents the potential of the half-cell reaction, E° the standard potential of the redox reaction. R , T , n , and F are the gas constant, the absolute temperature in kelvin, the number of electrons, and the Faraday's constant respectively. a_{oxid} and a_{red} represent the activities (concentrations) of both oxidized and reduced species respectively.

As indicated in Eq. (18), the half-cell potential becomes more positive as the amount of oxidized species increases. For each tenfold increase in oxidized reactant, the half-cell potential increases by 59 mV for a single electron reaction ($n = 1$).

In practice, for corrosion to occur, it is not necessary for a metal to be in contact with its own ions. Local anode and cathode zones may exist on the same surface of the metal or alloy, thus acting as an electrical conductor of the electrochemical flow. When such a metal is immersed in an electrolyte, it can no longer equilibrate to experimental thermodynamic scales. Therefore, corrosion is a direct consequence of a new equilibrium potential change, which depends on a myriad of physical and chemical properties of these electrochemical systems (e.g., pH, temperature, oxidizing agents and their power, IR drop of solution, etc.). This potential is called corrosion potential or mixed potential, which is far different from the standard potential. In this respect, corrosion will depend on the rate-limited electrode kinetics (e.g., charge transfer rate, mass transport, diffusion, etc.).

4.3 Polarization (overvoltage)-exchange current density

The concept of polarization or overvoltage is very briefly addressed here because of its importance for understanding corrosion reactions and its behavior. It represents a prerequisite for electrochemical methods. The rate of an electrochemical reaction is limited by various physical and chemical factors. Therefore, an electrochemical reaction is said to be polarized or delayed by these environmental factors.

Consider an electrochemical half-reaction for an electrode M at equilibrium:



When a reaction is at equilibrium, it does not necessarily mean that the system is at rest and/or inactive. On the contrary, for a system in equilibrium, the reaction

rate in the forward direction is equal to that in the backward or reverse direction. This equal rate at equilibrium is defined as the exchange current density, i_0 .

It is worth of note that i_0 is dependent on surface concentrations of the reactants, c_R , and those of the products, c_P , according to: $i_0 \propto c_R^m c_P^n$ m and n are exponents.

As reported in the previous section (Section 4.1), the reaction of hydrogen evolution is very often when a metal corrodes in an acidic environment. Interestingly, the current exchange rate for this cathodic hydrogen evolution reaction strongly depends on the catalytic properties of the metal surface on which the reaction occurs. For example, it ranges from 10^{-12} A cm⁻² for lead (Pb) to 10^{-3} A cm⁻² for palladium (Pd) at 25°C in 1 M H₂SO₄ [23]. This variability can have broad implications for the rate of corrosion. In fact, the rate of the reaction can be limited by the rate of the cathodic reaction, which is highly dependent on the current exchange rate of the reaction.

Figure 7 shows the point for an equilibrium of a given reaction at the electrode. It suggests a finite exchange current density at a given potential (e.g., reversible potential E_{rev} or $E^{\circ}_{M/M^{n+}}$). Notwithstanding, in electrochemistry, potential and current are interdependent. It is possible to control one and measure the other. Since the former current density involves a “two-way” rate process (forward-backward), the net current density is null. However, at a different potential of E_{rev} (i.e., overvoltage), the half-cell reaction will preferentially proceed in one direction and a net current will be measured.

The overvoltage, $\eta = E - E_{rev}$, is defined as a potential variation with respect to the reversible potential in the equilibrium of a given electrode reaction. This change in potential is associated with a change in the net reaction rate, and it is therefore related to a change in the direction of the reaction taking place, so that the reaction will mainly proceed in one direction according to the reaction rate. The current is anodic (oxidizing or positive) for a potential change to a value greater than the reversible potential (i.e., anodic polarization) and it is cathodic (reducing or negative) for a potential change to a value below the reversible potential (i.e., cathodic polarization), *cfr* **Figure 7**.

Polarization can be conveniently divided into three different types, activation polarization, concentration polarization, and ohmic potential drop (iR).

- Activation polarization refers to an electrochemical process controlled by the reaction sequence at the metal/electrolyte interface (e.g., by possible steps of

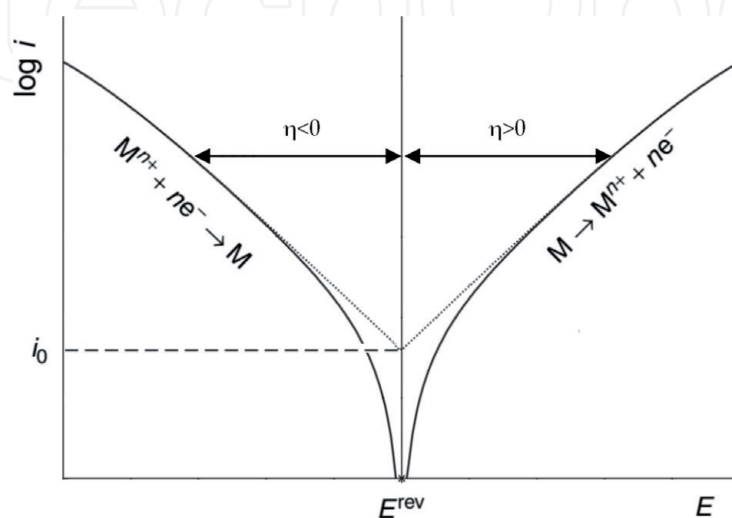


Figure 7.

Illustration of the relation between the current density and the potential for a simple electrochemical reaction under activation control.

adsorption, desorption, and charge transfer processes). It is caused by a slow electrode reaction. In particular, an activation overvoltage or charge transfer overvoltage alludes to an overvoltage resulting from a potential change when the concentrations of the reactants and products at the electrode surface are the same as in the bulk solution. This is because the charge transfer rate at the electrode/electrolyte interface is not infinitely fast. Note that the concentration at the surface of the electrode is equal to the bulk concentration when the mass transport rate is fast compared to the rate of charge transfer.

- Concentration polarization (Diffusion Overpotential) refers to electrochemical reactions controlled by the rate of diffusion in the electrolyte of ions on the surface of the metal.
- iR drop occurs in a portion of the electrolyte surrounding the electrode, or through a reaction product film on the surface of the metal, or in both cases [24]. An ohmic potential drop takes place between the working electrode and the capillary tip of the reference electrode. This contribution to polarization is equal to iR , where i is the current density, and R , equal to l/κ , represents the value in ohms of the resistance path of the solution of length l (cm) and specific conductivity κ ($\Omega^{-1} \text{ cm}^{-1}$). Therefore, the resistance of an electrolyte of length measuring l (cm) with a cross-section S (cm^2) is equivalent to $l/\kappa S$ (ohms). Hence, the iR drop in volts equals il/κ . The product, iR , decays in parallel with the shutting-off of the current, while the concentration polarization and the activation polarization generally decay at measurable speeds. For instance, for a cathodic protection of steel in seawater ($\kappa = 0.05 \Omega^{-1} \text{ cm}^{-1}$), it is necessary to apply a current density of 0.1 A/m^2 , which may result in a iR drop correction equal to $(10^{-5} \text{ V})/(0.05) = 0.2 \text{ mV}$ with respect to 1 cm separation of the probe from the cathode. This value is negligible with regards to the critical minimum current density required for convenient cathodic protection. However, in certain soft/fresh waters, where κ can reach the value of $10^{-5} \Omega^{-1} \text{ cm}^{-1}$, the corresponding iR drop is equal 1 V/cm.

Noting that the concentration polarization decreases with stirring, whereas the activation polarization and iR drop are not affected significantly.

5. Quantitative measurements of corrosion and tribocorrosion rates

5.1 Corrosion rate

The foregoing discussion on the thermodynamics of corrosion under equilibrium conditions yields information on the driving force of the corrosion process. Since corroding systems are not always at equilibrium, therefore thermodynamic calculations cannot be applied. Notwithstanding that the information on the corrosion tendency accessible from thermodynamic calculations is important and useful. However, most scientific and technical aspects in the field of corrosion focus on the knowledge and the reduction of corrosion rate. Thermodynamics does not address the rate of corrosion.

Metals and non-metals are compared on the basis of their corrosion resistance. For these comparisons to be meaningful, the attack rate of each material must be expressed quantitatively. Corrosion rates can be given in a number of different units using different measures of material loss. A convenient way to determine the rate of corrosion is by the immersion of a sample in a corrosive environment for a period

of time and measure the weight loss during that time [25]. The weight loss should be normalized to the exposed surface area of the sample in order to determine its rate of corrosion. Therefore, among the set of units adapted to the corrosion rate is the weight loss per unit area per unit of time; for example, $\text{mg cm}^{-2} \text{s}^{-1}$. It is also common to use the percentage of weight loss, milligrams per square centimeter per day and grams per square inch per hour. Though, these do not express the corrosion resistance in terms of penetration. From a technical point of view, the penetration rate, or the thinning of a structural part, can be used to predict the lifetime of a given component. An easy way is to divide this measurement by weight loss by the density of the corroding material to obtain a corrosion rate in units of thickness lost per unit of time. The term mils per year is the most desirable way to express corrosion rates (mpy) or mm yr^{-1} . This expression can be easily calculated from the weight loss of the metal sample during the corrosion test by the formula (20), given below:

$$r = \frac{CM}{\rho nF} i_{\text{corr}} \quad (20)$$

where r is the rate of material loss (mm yr^{-1}), M the molecular weight of the corroding metal (g mol^{-1}), ρ the density of metal (g cm^{-3}), i_{corr} the corrosion current density (A cm^{-2}), and C a constant to change the units of thickness and time.

5.2 Tribocorrosion rate

Wear is an unavoidable and a potentially serious problem in all areas of engineering [3]. Designers and engineers who have to make optimal decisions in situations where tribocorrosion considerations are significant, need to know “how long will a component last?”. To solve this question, numerous models have been developed so far to distinguish this material loss due to tribocorrosion [3]. These models usually correlate a wear volume or a wear rate with physical and geometrical quantities. Various expressions have since been attributed to this material loss, of which the material loss can be defined in terms of weight, volume, surface, depth, width or even charge density or current density, per unit hardness, per unit frictional dissipated energy (work due to the tangential force), per unit input energy (work due to the normal force), or even per unit sliding distance, or sliding time, sliding frequency, contact frequency, etc. [3]. It becomes readily understandable of the complexity of comparing results between the various wear data published so far. It is expected then that the terminology in this field is rather uncertain, and it will remain so for a certain time, hence the need for a specific standardization, despite some recent progress made in this area [3, 26].

One of the earlier attempts to predict the wear rate or wear volume loss of a material in sliding contact is the commonly Archard wear criterion [27] used during the second half of the 20th century. That criterion is usually expressed as follows [3],

$$W_v = k \frac{F_N}{H} = k A_r \quad (21)$$

where W_v and W_r represent the volumetric loss (assigned as total volume of wear debris produced), and the wear rate (usually expressed per unit sliding distance), respectively. k is the dimensionless Archard wear coefficient, A_r the real area of contact, F_N the applied normal load, and H the hardness of the worn material.

This equation was originally used for the case of adhesive wear [28, 29], then it was extended to more cases including that of tribocorrosion [3]. This is because the k parameter in Eq. (21) exclusively remained the only flexible parameter consistent

with the case to which the wear may originate [3]. For example, unidirectional sliding of mild steel against mild steel without any lubricant has a k of 10^{-2} , whereas, for stellite sliding against tool steel, k is 10^{-5} [3, 30]. Even more confusing is that, according to literature, the Archard wear coefficient can vary by two orders of magnitude for the same couple of materials just due to a slight change in load or speed [31]. These findings should be taken with precautions in view of the number of empirical error cases reported with respect to the wear reproducibility and validation of test methods [3]. Friction and wear properties are often considered as subjects of poor accuracy in comparison with materials intrinsic properties. Indeed, comparative round robin studies on the topic have shown that the reproducibility of wear derived from different inter-laboratories with the same material pairing was often very poor [32]. Using the wear track width, the scattering was roughly 50% whereas the scatter in the wear coefficient was over three orders of magnitude. No clear correlation was found between a single and constant parameter (type of tribometer, normal force, and sliding velocity) and the wear rates measured in inter-laboratories [3]. Interestingly, a good convergence was found between the wear volume loss and the energy dissipated in the tribo-contact zone [33–37]. This can readily be explained by the fact that the dissipation of frictional energy is one, among others, of the main causes of tribo-electrochemistry, playing an essential contributing role in wear mechanism, in this case entailing an acceleration (e.g., chemical wear rates) or modification of tribo-chemical reactions [3]. The yielded frictional heat between interacting surfaces leads to a stationary rise in temperature at surface contact asperities and flashes. Furthermore, such frictional energy can take the form of high quantum excitations with short lifetime of surface and bulk sites due to the mechano-chemical forces involved during the sliding process. Those excitations are also responsible for the occurrence of triboluminescence and triboelectricity [3].

Tribologists nowadays are seeking for an agreement due to the fact that there is an unavoidably need to address more fundamental research towards the establishment of an original formulation or a universal methodology to define a “wear criterion” in order to better understand the complexity of the wear process in a tribocorrosion test [3]. Although, this aim has not yet been achieved, a fair amount of progress has been made on this matter-oriented approach. This remains so far valid only as part of the case-by-case study. To conclude, research must focus on establishing a functional-mechanistic based approach that emphasizes the nature of the dependence of the mechano-chemical wear rate (output) on the energetic aspect of sliding friction, the electrochemical aspect of the exposure of bare metal surface, and the transformation of the subsurface material (input). This usually should incorporate materials properties, and behavior. If it does, this could be very useful to help solving the issues and struggling difficulties encountered in the specific field. This will lead to a better improvement of the reliability life of selected material and design technologies when adopted in specific mechanical articulations and under aggressive environments. Further, this could predict materials performance in an environment where tribocorrosion plays a significant role [3].

In tribocorrosion phenomena, where tribological contacts are exposed to corrosive environments, such as aqueous lubricants, the contact materials are subject to both mechanical, and chemical/electrochemical solicitations, which contribute to material removal from sliding surfaces [3]. The rate of material degradation/removal cannot be predicted simply by adding the wear rate in absence of corrosion to the corrosion rate in absence of wear. The reason is that corrosion and wear do not proceed independently and synergistic effects usually (but not always) result in accelerated material degradation (tribocorrosion) [3]. In that respect, theoretical models have been developed so far with respect to mechanical, chemical, and electrochemical factors and

their mutual interactions, and which can be tested under well-controlled experimental conditions. In general, modeling has followed either an empirical or a mechanistic approach [3]. The empirical approach is based on the independent measurement of material loss due to wear and corrosion. These parameters are summed up and compared to the material loss due to tribocorrosion. The difference between the two is termed synergy (ΔW_{syn}). A general equation for this approach is of the form [7, 38, 39],

$$W_{tot} = W_{mec} + W_{corr} + \Delta W_{syn} \quad (22)$$

where W_{mec} represents the material loss due to wear measured in the absence of corrosion, and W_{corr} is the material loss due to corrosion only without any influence of mechanical wear.

Although, the empirical approach is technically feasible which allows for the ranking and the performance of materials based on their resistance to tribocorrosion in engineering systems, it is still time-consuming, quite economically not justifiable in the long-term, and furthermore, it integrates a synergy term, which has no physical meaning [3].

The advantage of a mechanistic approach is that it leads for a better understanding of the physical processes involved in tribocorrosion by incorporating the notion of synergism into the mechanical and electrochemical terms [3]. Many factors can be responsible for the mutual dependence of mechanical and chemical material removal in a tribocorrosion system [3]. For example, local abrasion of the passive film can lead to wear accelerated corrosion due to rapid dissolution of the locally depassivated metal surface, followed by repassivation [40]. The abrasive action of hard oxide particles formed by corrosion can accelerate the mechanical metal removal by wear [41]. The plastic deformation of the surface layer of a rubbing metal can lead to a transfer of material to the opposite body resulting in a reduction of the corrosive wear rate [42].

Therefore, it is important to distinguish material loss due to chemical or electrochemical oxidation (i.e., wear accelerated corrosion) from material removed due to mechanical wear (i.e., mechanical material removal from the sliding contact) [3]. The former arises from the fact that an asperity sliding on a material surface produces a fresh wear track zone of clean bare material (i.e., metal), which is usually more susceptible to corrosion than the same surface subjected to free corrosion under no mechanical plastic contact or sliding conditions [3]. The effect of repeated sliding may cause the removal of metal particles by asperities burrowing beneath the surface [42, 43].

Therefore, the overall wear volume due to tribocorrosion, W_{tot} , can be defined as follow:

$$W_{tot} = W_{chem(wac)} + W_{mec} \quad (23)$$

where $W_{chem(wac)}$ is the electrochemical contribution to wear; it is termed wear accelerated corrosion and it reflects the material loss due to corrosion in the presence of wear. W_{mec} is the mechanical wear, and it reveals the material loss due to wear in the presence of corrosion, and which can be related to processes as that for the formation-ejection of oxide debris, oxide layers or any corrosion products, and plastically detached metal [3].

W_{tot} can be determined by measuring the volume of the wear scar post-experiment using, for instance, a laser non-contact profilometry or by on-line measurement of the rate of moving down of the counter-body (e.g., a pin) on the surface wear track during sliding. The latter method has the advantage of recording an instantaneous wear rate, but it would only be applicable if no significant amount of solid reaction products (such as third body particles) accumulate in the contact zone during the tribocorrosion experiment [3]. Under potentiostatic control,

the electrochemical term ($W_{chem(wac)}$) can barely be related to the anodic corrosion current ($I_{a,tribocorr}$) measured under mechanical sliding wear (occasionally by subtracting the background current) using Faraday's law. The amount of anodically oxidized metal under such conditions is calculated as follows [14]:

$$W_{chem(wac)} = \frac{Mq}{\rho nF} \quad (24)$$

where $W_{chem(wac)}$ is the volume of the metal transformed by anodic oxidation in a tribo-electrochemical test. q represents the electric charge produced, which results mainly from the integration of the measured current $I_{a,tribocorr}$ under sliding wear conditions over the duration of the tribo-electrochemical test. M , n , and F are the molar mass of the metal, the valence for the anodic oxidation reaction, and the Faraday's constant respectively. ρ is the density of the metal.

The foregoing equation is credible and independent of whether the anodic oxidation leads to the formation of dissolved metal ions or solid reaction products, such as oxide films [3].

It is worthwhile to note that few assumptions must be met in order for Eq. (24) to be used [3, 40], namely:

- The measured current must be equal to the anodic partial current for metal oxidation, which means that cathodic partial currents due to the reaction of oxidizing agents must be negligible. This can be performed by anodic polarization into the passive potential region.
- The charge number “z” for the oxidation reaction must be known [40, 42].

The mechanical wear (W_{mec}) is taken as the difference between the total wear volume W_{tot} and the chemical wear volume $W_{chem(wac)}$ determined from the electric charge.


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