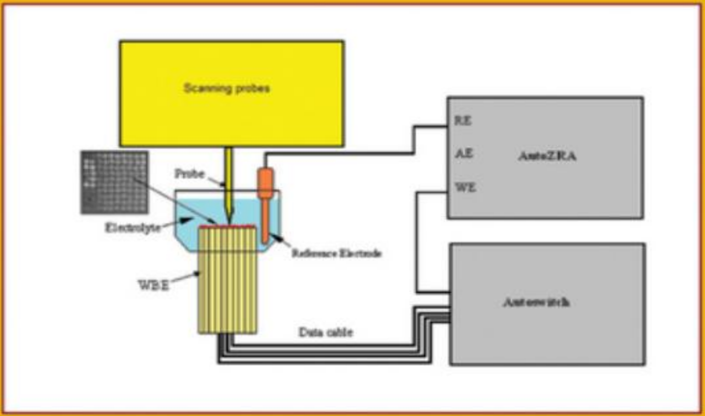
Wiley Series in Corrosion
R. Winston Revie, Series Editor

HETEROGENEOUS ELECTRODE PROCESSES AND LOCALIZED CORROSION



YONGJUN TAN

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Heterogeneous Electrode Processes and Localized Corrosion

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Preface

Electrochemistry is an enabling science that since Galvani's 1780s experiment on frog legs and Volta's nineteenth-century invention of the battery has facilitated a wide spectrum of scientific discoveries and industrial processes. These include electrolysis, electroplating, metal winning, hydrometallurgy, corrosion prevention, passivation, batteries, fuel cells, solar cells, environmental and biological sensors, organic and inorganic electrosynthesis, electrophoresis, effluent remediation, and neurochemistry. Electrochemical theories and models have also been developed, including the most fundamental relationships, such as Faraday's law, the Nernst equation, and the Bulter–Volmer formulation. However, traditional electrochemistry has a major weakness—there is a “missing link” between its ideal uniform electrode model and practical heterogeneous electrode processes because of the phenomenon of electrochemical heterogeneity.

Electrochemical heterogeneity refers to the localization of chemical and electrochemical reactions over an electrode surface. In electrochemical reactions the reactants do not need to be near each other spatially as normal chemical reactions do; they collide separately with spatially separated electronic conductors. This characteristic permits distinct separation of electrode reactions over an electrode surface, leading to the localization of electrode chemistry, reaction thermodynamics, and kinetics. Most frequently, Electrochemical heterogeneity is initiated from preexisting electrode inhomogeneity (i.e., spatial, physical, compositional, metallurgical, or chemical nonuniformities existing on electrode surfaces). It could also be initiated from an ideally homogeneous surface, especially if the surface were exposed to a nonuniform environment.

Electrochemical heterogeneity is a ubiquitous phenomenon that plays critical roles in many difficult but important issues in electrochemical science and engineering, such as localized corrosion, porous electrodeposition, uneven electrodissolution, electrochemical noise, and various forms of dispersion in voltammetry.

Electrochemical heterogeneity has not been confronted effectively in traditional electrochemical science research and has not been covered sufficiently in the electrochemical and corrosion science literature. It is evident that classical theories describing the Faradaic electron transfer processes in dynamic electrochemistry and traditional methods of electrochemical measurement are based on the assumption that the electrode surface is homogeneous. Initial experimental studies used to validate traditional electrochemical theories and methods commonly employed mercury drop electrodes, where a truly homogeneous surface is indeed likely to be achieved. However, solid electrodes that are in practical use today generally have inhomogeneous surfaces, where electrochemical heterogeneity could initiate, propagate, or terminate dynamically. Indeed, there is a major theoretical and technological gap between conventional electrochemistry over uniform surfaces and heterogeneous electrochemistry over inhomogeneous surfaces.

I was first attracted to the issue of electrochemical heterogeneity in 1988 when I was mystified by difficulties in repeating my impedance spectra of coated electrodes. Over the past two decades I have been fortunate to be able to continue my thinking and research on this issue, leading to the development and application of an electrochemically integrated multielectrode array: the wire beam electrode. My colleagues and I have carried out numerous experiments to study a variety of heterogeneous electrode processes. Our experimental findings indicate that electrochemists may need to recognize more widely the fundamental significance of electrode inhomogeneity and electrochemical heterogeneity.

This book is probably the first to focus on electrode inhomogeneity, electrochemical heterogeneity, and their effects on nonuniform electrode processes. Attempts are made to critically review various forms of techniques that have been applied for probing localized electrode–electrolyte interfaces, in particular scanning probe techniques such as the scanning Kelvin probe, the scanning Kelvin probe force microscopy, the scanning vibrating electrode technique, local electrochemical impedance spectroscopy, and scanning electrochemical microscopy. Special attention is focused on localized corrosion experiments designed using the wire beam electrode as a key tool. Case studies presented in this book to illustrate innovative experiments are based primarily on published data with which I have substantial firsthand experience. I acknowledge work by several other research groups that have reported innovative and interesting experiments using various forms of electrode arrays.

I express my sincere thanks to colleagues and co-workers who have collaborated with me over the past two decades, especially (in chronological order) Cuilan Wu, Xuejun Zhou, Shiti Yu, Stuart Bailey, Yadran Marinovich, Brian Kinsella, Alex Lowe, Tie Liu, Naing Naing Aung, Ting Wang, Kim Yong Lim, Bernice Zee, Alan Bond, Chong Yong Lee, Mauro Mocerino, Tristan Paterson, Young Fwu, Kriti Bhardwaj, Bruce Hinton, and Maria Forsyth. I thank them and many other colleagues who have taught me patiently over the years. I also thank my family for giving me encouragement, time, and support throughout the years.

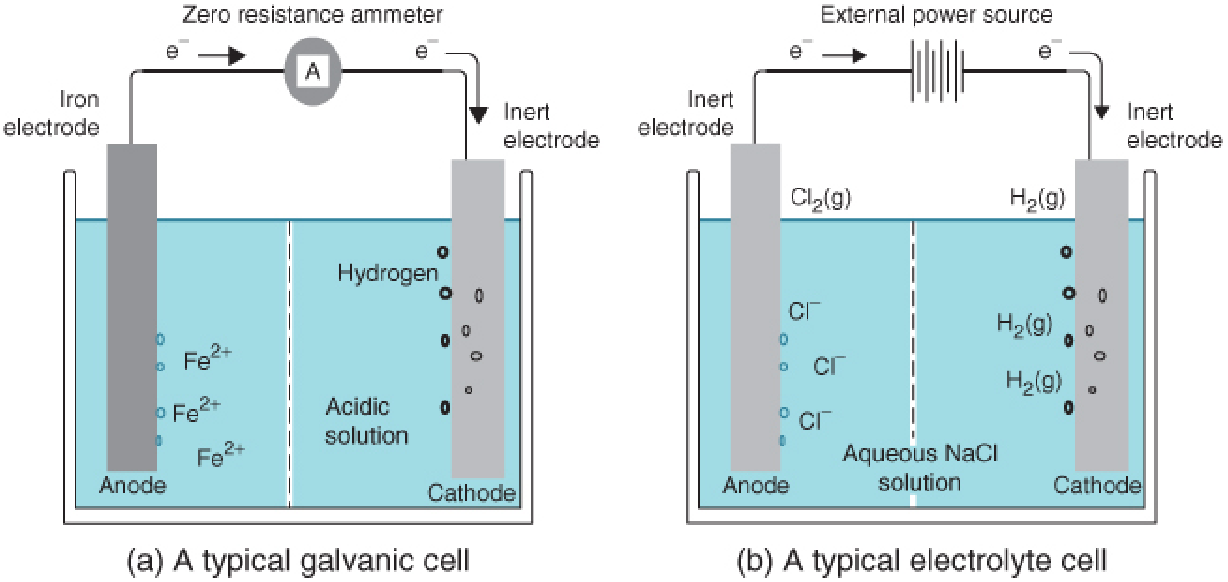
Youngjun Tan

Chapter 1: Homogeneous Electrode Models and Uniform Corrosion Measurements

Electrochemical reaction is a special form of chemical reaction that occurs in reaction devices: that is, electrochemical cells. Since Galvanis' 1780's experiment on frog legs and Volta's nineteenth-century invention of the voltaic pile, numerous types of electrochemical cells, such as batteries, fuel cells, solar cells, galvanic cells, and electroplating and electrowinning baths, have been invented by electrochemists, facilitating a wide spectrum of industrial processes and scientific discoveries. Many electrochemistry-based technologies, including electrolysis, electrosynthesis, electrocatalysis; electroplating, metal winning, hydrometallurgy, electrophoresis, effluent remediation, electrochemical energy conversion and storage, cathodic and anodic protection, and environmental, biological, and corrosion sensors, have been developed for various industrial applications. Electrochemistry also provides a theoretical basis for understanding and explaining natural phenomena in scientific fields such as corrosion science and neurochemistry.

Fundamentally, electrochemical cells are based on two basic electrochemical devices: the galvanic cell (Figure 1.1a) and the electrolytic cell (Figure 1.1b). All electrochemical cells consist of an anode, a cathode, an electrically conductive path, and an ionically conductive path. Electrodes are basic components that provide the interface between an electronic conductor, usually a metal, and an ionic conductor, usually an electrolytic solution.

Figure 1.1 Basic electrochemical devices.



(a) A typical galvanic cell

(b) A typical electrolyte cell

Electrochemical reactions in a galvanic or electrolytic cell always involve two half-cell reactions occurring simultaneously over separated anode and cathode surfaces. Anodic oxidation reactions occur at the anode–solution interface across which species lose electrons, while cathodic reduction reactions occur at the cathode–solution interface across which species gain electrons. The mass transfer, chemical reaction, and physical state change are the sequential steps of electrochemical processes occurring at the anodic and cathodic half-cells. In a *galvanic cell* (Figure 1.1a), electrochemical reactions occur spontaneously at the anodes and cathodes when they are connected externally by a conductor. Galvanic cells are often employed as batteries and fuel cells to convert chemical energy into electrical energy. A galvanic cell also provides a starting point for the development of metal corrosion theories and corrosion prevention technologies. In an *electrolytic cell* (Figure 1.1b), electrochemical reactions are driven by the imposition of an external voltage greater than the open-circuit potential of the cell. Electrolytic cells are widely employed in such industrial processes as electrolysis, metal winning, electroplating, and cathodic protection.

An electrochemical reaction is a chemical reaction in nature, and therefore all factors affecting normal chemical reactions, such as the chemical nature of reactants, the concentrations of the reactants, the temperature, the ability of reactants to come into contact with each other, and the availability of rate-accelerating or rate-decelerating agents, affect electrochemical reactions. However, it should be pointed out that there is a fundamental difference between normal chemical reactions and electrochemical reactions. An electrochemical reaction occurs at the electrode–solution interface, often driven by voltage applied externally. In an electrochemical reaction the reactants do not need to be near each other spatially as normal chemical reactions do; they collide individually with spatially separated anodes and cathodes. For this reason, electrochemical reactions are affected significantly by the structure and property of electrode–solution interfaces, movements of ions and electrons between electrodes, and the voltage applied externally.

In this chapter we provide an overview of models illustrating homogeneous electrode–solution interfacial structure and theories describing electrode processes with and without the effects of voltage applied externally. Particular focus is on a mixed electrode model that explains uniform corrosion. Electrochemical and corrosion principles are reviewed; however, a detailed description of traditional electrochemical and corrosion theories is not attempted because these have already been discussed by many authors, among them Bard and Faulkner [1], Bockris et al. [2], Fontana [3], Mansfeld [4], and Evans [5]. Attempts are made to discuss limitations in traditional electrochemical methods and factors that may cause a change from a uniform corrosion mechanism to a localized form, leading to the concepts of electrode inhomogeneity and electrochemical heterogeneity.

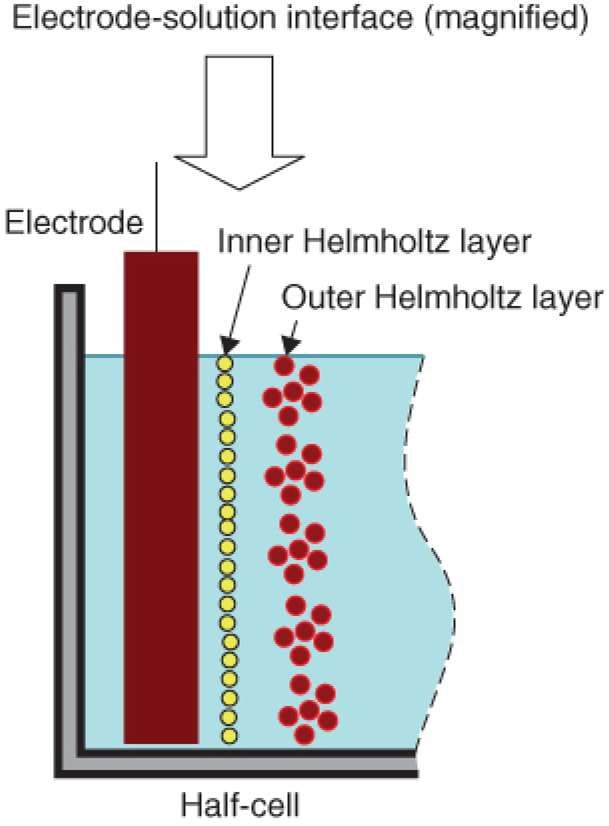
Carbon dioxide (CO_2) corrosion of iron in sodium chloride (NaCl)-containing solutions under ambient temperature and atmospheric pressure conditions is used as a case to illustrate typical uniform corrosion processes occurring in practical industrial systems. Electrochemical measurements are described through their applications in investigating the rates and interfacial structures of steel electrodes in CO_2 corrosion environments, with and without the present of corrosion inhibitors.

1.1 Homogeneous electrodes and traditional electrochemical methods

Electrochemical reactions occur at the interface of an electrode and a solution. Knowledge of the structure and property of an electrode–solution interface is critical for understanding electrochemical reactions and their thermodynamics and kinetics. It is well known that the electrode–solution interface is affected by electrode surface roughness and scratches, impurities, mill scales, surface flaws, metallurgical defects, precipitated phases, grain boundaries, dislocation arrays, localized stresses, selective dissolution, and damage to passive films. It is also understood that an electrode–solution interface is affected by factors such as surface chemical adsorption and desorption, mass transfer, and liquid flow. However, unfortunately, direct observation of an electrode–solution interface is very difficult, if not impossible. Instead, theoretical models are employed to help in addressing issues relating to the structure, properties, and reactivity of an electrode–solution interfacial region and its components.

Figure 1.2 is a simplified model of a conventional uniform electrode–solution interface. In this model it is assumed that an electrochemical double layer exists in the vicinity of an electrode surface, consisting of inner and outer Helmholtz layers. It is also assumed that the electrode surface is chemically and electrochemically homogeneous and that electrode reactions are distributed uniformly over the electrode surface.

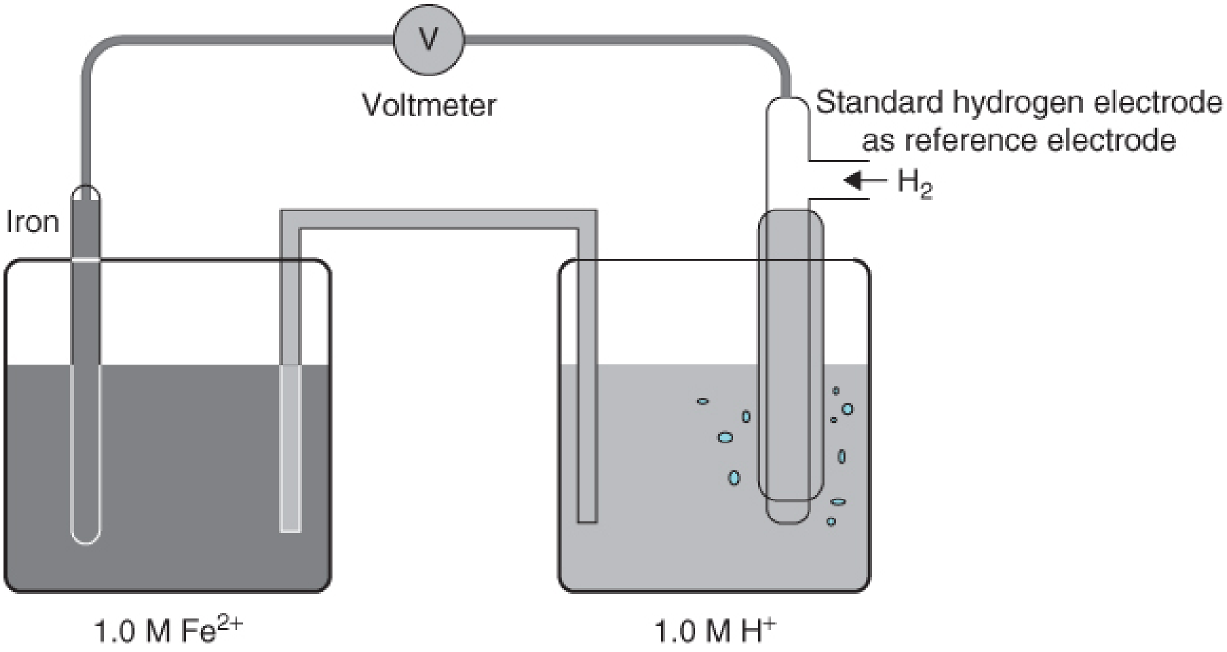
Figure 1.2 Simplified electrode–solution interface model.



This homogeneous electrode–solution interface model significantly simplifies the analysis of electrochemical processes. Under this homogeneous electrode assumption, electrochemical properties at any location of an electrode surface can be considered to be identical to that of the entire electrode surface. For example, it allows the application of Faraday's law of electrolysis [1] to determine the thickness of electrodeposits because electrodeposition current can be considered as being uniformly distributed over an electrode surface. This assumption is also employed as a prerequisite for fundamental electrochemical thermodynamic and kinetic relationships, including the Nernst equation and the Bulter–Volmer formulation and also for traditional electrochemical methods such as electrode potential and polarization measurements [1–5].

This electrode–solution interface model is applicable to both the anode and cathode of a galvanic cell or an electrolytic cell. In a galvanic cell, such as the iron corrosion cell shown in Figure 1.1a, actual reactions occurring at its anodic and cathodic interfaces are determined by the electrochemical thermodynamics of chemical species in the cell. Electrode potential is a thermodynamic parameter that reveals the tendency of a chemical species to be reduced in an electrochemical reaction. Figure 1.3 illustrates a traditional setup for determining the standard reduction potential of an iron electrode in 1.00 M Fe^{2+} solution using a standard hydrogen reference electrode and a high-resistance voltmeter. This laboratory method determines the reduction potential of 1.00 M Fe^{2+} against the reduction potential of 1.00 M H^+. Under standard conditions this value would be − 0.44 V, indicating a lower tendency of 1.00 M Fe^{2+} to be reduced than 1.00 M H^+. For this reason, in this system, H^+ would be reduced, $H^+ + 2e^- \rightarrow H_2$, while Fe would be forced to oxidize, $Fe \rightarrow Fe^{2+} + 2e^-$. As a consequence, iron corrodes in the galvanic cell.

Figure 1.3 Electrode potential measurement.



The potential measured using the experimental setup shown in Figure 1.3 is a reversible equilibrium potential of the half-cell electrode reaction, $Fe^{2+} + 2e^{-} \Leftrightarrow Fe$. This electrode potential can be related to the fundamental electrode thermodynamic equation, the *Nernst equation* [equation (1.1)], which gives an electrode potential for any reversible half-cell reaction, $Ox + ne^{-} \Leftrightarrow Red$, as a function of nonstandard ionic concentrations:

1.1
$$E = E^{o} + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$

where *E* is the nonstandard half-cell reduction potential of interest, E^{o} the standard half-cell reduction potential, [Ox] the concentration of oxidant Ox, [Red] the concentration of reductant Red, *F* is Faraday's constant, *R* the universal gas constant, *T* the absolute temperature, and *n* the number of electrons transferred in the reaction.

For an iron electrode reaction, $Fe^{2+} + 2e^{-} \Leftrightarrow Fe$, the Nernst equation gives the relationship between its reduction potential and the Fe^{2+} concentration:

1.2 $$E = E^{\circ} + \frac{RT}{2F}\ln[\mathrm{Fe}^{2+}]$$

The potential measurement method illustrated in Figure 1.3 is valid only under the assumption that the iron electrode–solution interface is homogeneous, and therefore that the iron electrode potential measured can be considered to be equal to the potential at any location of the iron electrode surface. This homogeneous electrode assumption is also essential for the relationship in equation (1.2) because the Nernst equation is valid only when the concentration of Fe^{2+} is distributed uniformly over the electrode–solution interface, and therefore the electrode potential calculated can be considered to be equal to the potential at any location of the iron electrode surface.

Classical theory describing the kinetics of Faradaic electron transfer processes in dynamic electrochemistry is also based on this homogeneous electrode–solution interface model. The most fundamental electrode reaction kinetic relationship, the *Bulter–Volmer* equation [1, 6, 7], is used to describe the kinetics of anodic and cathodic half-cell reactions:

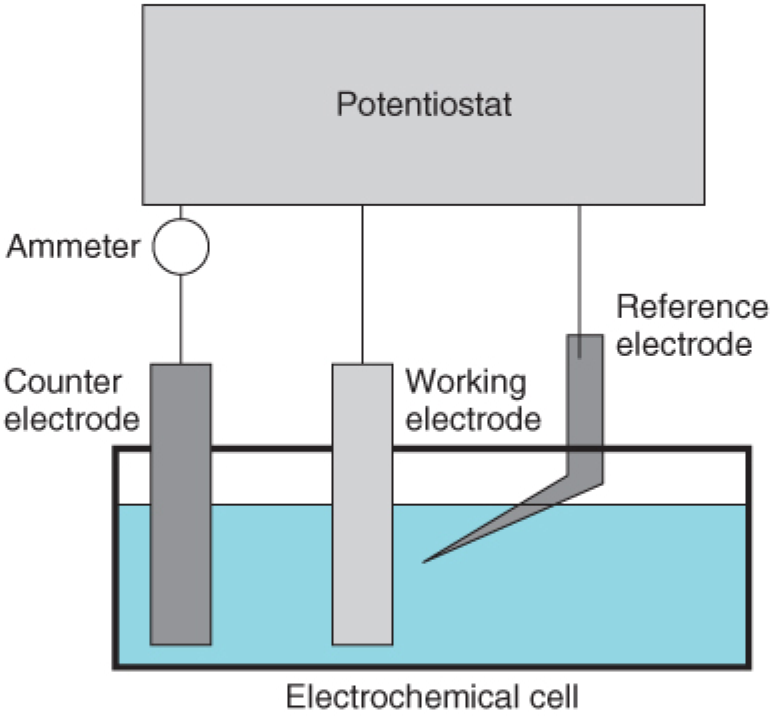
1.3 $$i = i_{\mathrm{o}}\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(\frac{-\beta nF}{RT}\eta\right)\right]$$

where η is the overpotential ($= E - E_{eq}$), the amount by which a potential deviates from equilibrium potential; i the measured or applied current density; i_o the exchange current density, F is Faraday's constant, R the universal gas constant, T the absolute temperature, n the number of electrons transferred in the reaction, and α and β are anodic and cathodic charge transfer coefficients that are related to the potential drop through the electrochemical double layer.

The Bulter–Volmer equation suggests that the kinetics of an electrochemical reaction depends on various factors, including overpotential and exchange current density.

Positive overpotentials enhance oxidation reactions on the electrode, whereas negative overpotentials induce reduction reactions to occur. For a given overpotential, the magnitude of reaction current flow is affected particularly by the charge transfer rate between solution species and the electrode. The charge transfer rate is a key parameter indicating the kinetics of an electrochemical reaction. It is usually measured by the exchange current density, i_O, using the electrochemical polarization measurement setup shown in Figure 1.4.

Figure 1.4 Experimental setup for polarization measurement.



In polarization measurements, a potentiostat is used to perturb the working electrode by injecting or extracting electrons to or from the electrode, causing the electrode potential to change from its equilibrium potential E_{eq} to a new electrode potential, E. The overpotential, $\eta = E - E_{eq}$, is a response to the applied current, which can be adjusted to any value desired. The electrode potential can be measured using a voltmeter and a reference electrode, while the applied current can be measured using a zero-resistance ammeter. The measured potential vs. current (or log *i*) data are usually presented as polarization curves. Experimental polarization curves contain information on electrode reaction kinetics and factors affecting electrochemical processes and mechanisms.

Apparently, the Butler–Volmer equation and the polarization measurement are also based on the assumption that an electrode–solution interface is homogeneous and therefore that electrode potential and currents can be considered to be distributed uniformly over the electrode surface. It should also be noted that the Butler–Volmer equation describes only an idealized active controlled electrode. That is, the electrode kinetics limits the current flow; it is not applicable to situations where electrochemical kinetics are controlled by mass transport of reactant molecules or ions from the bulk electrolyte. More detailed descriptions of traditional electrochemical thermodynamic and kinetic theories and methods may be found in books by Bard and Faulkner [1], Bockris et al. [2], and Mansfeld [4].

1.2 Mixed electrodes and uniform corrosion models

Unlike the ideal electrode–solution interface shown in Figure 1.2 and the ideal half-cells shown in Figure 1.3, practical electrode processes such as aqueous metal corrosion involve at least two electrode–solution interfaces and two half-cell reactions occurring simultaneously at the anodic and cathodic half-cells. A typical example is the galvanic corrosion cell shown in Figure 1.1a, which involves an anodic metal dissolution reaction ($Fe \rightarrow Fe^{2+} + 2e^{-}$) and a cathodic hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2$) occurring over two separate electrode–solution interfaces. Other examples of galvanic cells include cells made up of electrodes of two dissimilar metals that are connected electrically, and cells containing electrodes of the same electrode material exposed to different oxygen concentrations [3].

In most practical cases, aqueous corrosion reactions occur over a single piece of metal surface rather than over two separate electrodes in a galvanic cell. Such a corroding metal surface is often referred to as a *mixed electrode* [8] since several different redox reactions with different kinetics and reduction potentials occur simultaneously over the same electrode surface. A microelectrochemical cell model is proposed to explain the uniform corrosion phenomenon, based on the following assumptions:

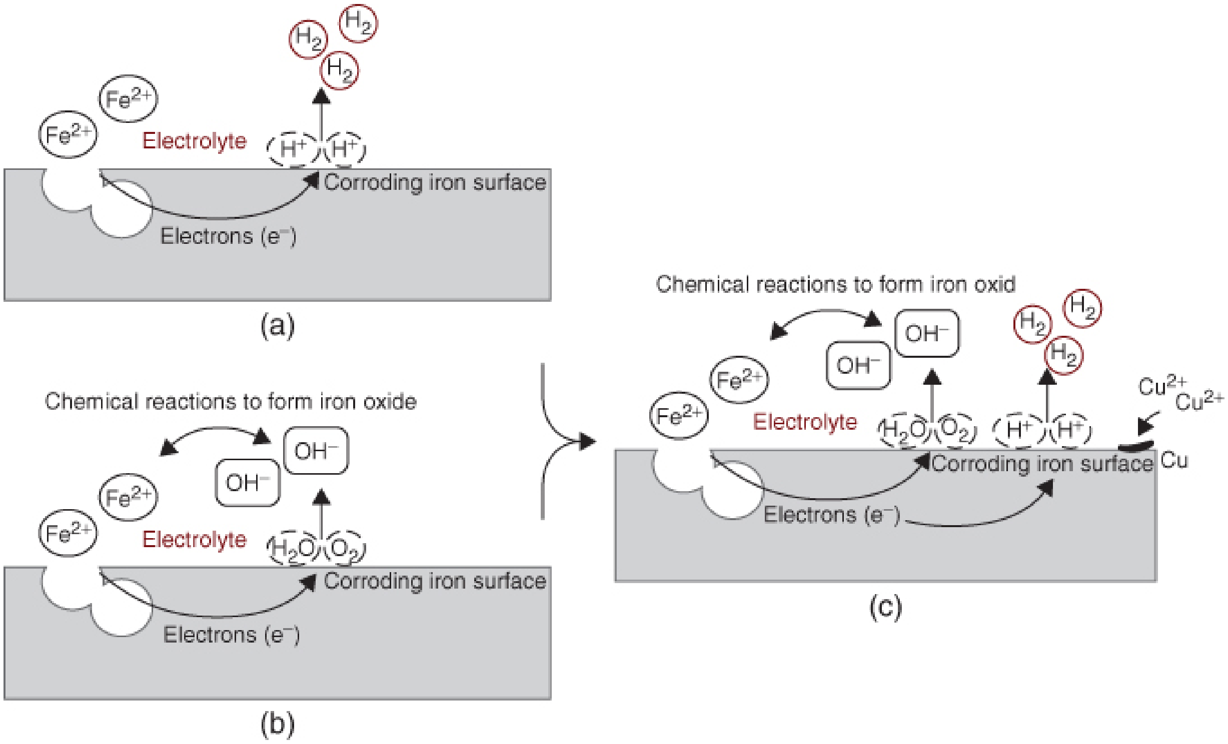
1. Many tiny microscopic anodes and cathodes form on a single piece of corroding metal surface. Anodes and cathodes are distributed randomly over areas of the metal surface with different electrochemical potentials.

2. Individual half-reactions occur in these microscopically separated half-cells, causing an anode to corrode and an electron transfer to the cathode through an internal electrical circuit. Ions flow through a conducting solution on the metal surface.

3. Anode and cathode locations change dynamically, and a given area on a metal surface acts as both an anode and a cathode over any extended period of time. The averaging effect of these shifting local electrochemical cells results in a rather uniform attack and general loss of material and roughening of the surface.

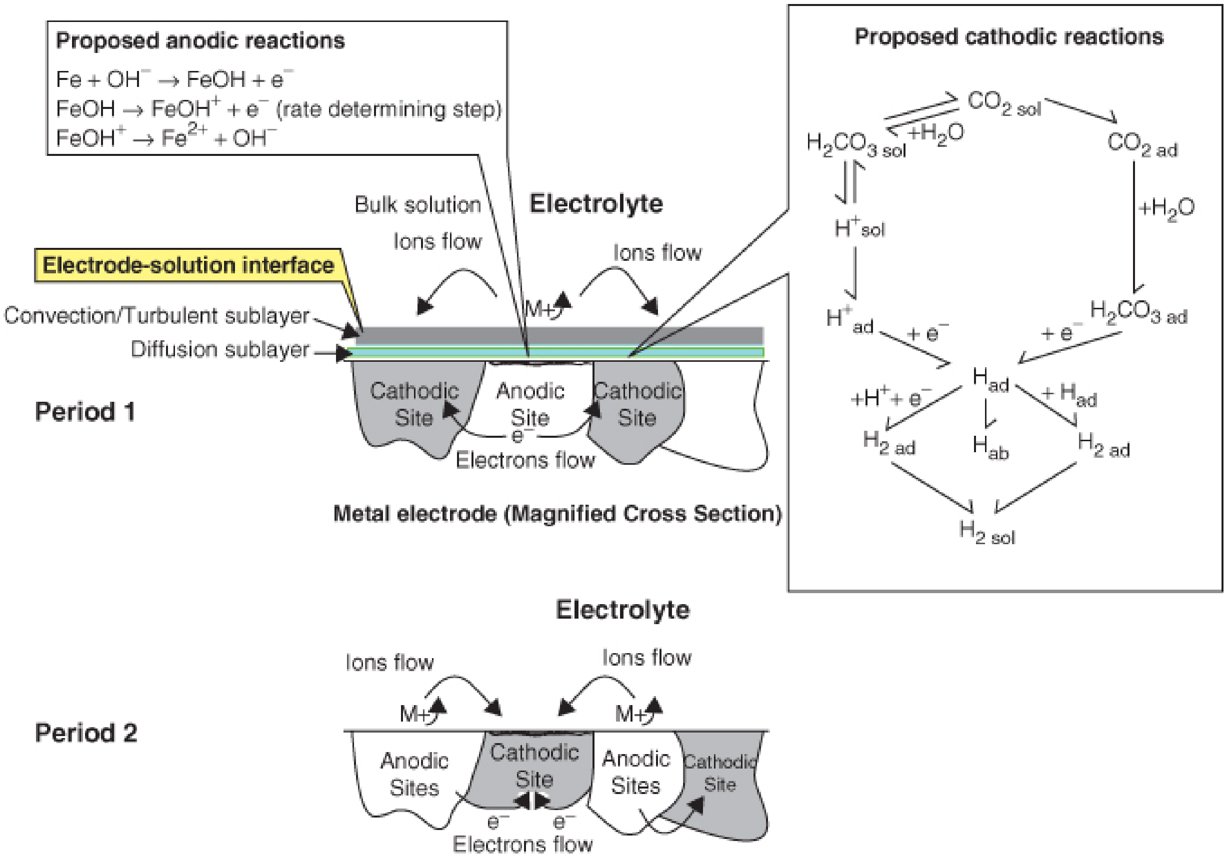
Figure 1.5 shows magnified representations of typical corroding iron surfaces exposed to three different environmental conditions. Figure 1.5a shows a typical iron electrochemical corrosion cell in acidic media where hydrogen evolution is the predominate cathodic reaction. Figure 1.5b shows a magnified corrosion cell under neutral pH or alkaline conditions where oxygen reduction ($O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$) is the predominate cathodic reaction. Figure 1.5c shows a more complex corrosion system, where more than one reduction reaction occurs simultaneously over an electrode surface. In these microscopic corrosion cells the major corrosion anodic reaction is determined by which species is most easily oxidized, while the major cathodic reaction is the one with the highest reduction potential (i.e., the one with the greater tendency to undergo reduction). In the corrosion system shown in Figure 1.5a, the oxidation of iron has the lowest reduction potential and is therefore forced to undergo oxidation, $Fe \rightarrow Fe^{2+} + 2e^{-}$($E^0 = -0.44$ V vs. SHE, iron corrosion), and the reduction of hydrogen is the major cathodic reaction because it is the most easily reduced species in an oxygen-free environment, $2H^{+} + 2e^{-} \rightarrow H_2$($E^0 = 0$, hydrogen evolution). If other oxidizing agents, such as oxygen and cupric ion (Cu^{2+}), exist in the corrosion environment, as shown in Figure 1.5c, there will be competing cathodic reactions, $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$ ($E^0 = +1.23$, oxygen reduction) and $Cu^{2+} + 2e^{-} \rightarrow Cu$($E^0 = +0.34$, copper plating).

Figure 1.5 Magnified representation of electrochemical corrosion cells over iron electrodes exposed to various environmental conditions.



More complex mixed electrode–solution interfacial models are often needed to describe practical industrial corrosion processes. Figure 1.6 illustrates a mixed electrode–solution interfacial model illustrating corrosion of iron in a CO_2-containing aqueous solution under ambient temperature and atmospheric pressure conditions. Corrosion of iron in a CO_2-containing aqueous environment is a typical electrochemical corrosion case that commonly occurs in oil and gas pipelines. CO_2 is a naturally occurring component in many oil and gas fields, where CO_2 is associated with water, oil, and gas production. In aqueous environments, CO_2 dissolves and forms carbonic acid, leading to various forms of steel pipeline corrosion. It is known that CO_2 is significantly more corrosive than normal weak acid and that at a given pH, more corrosion of steel is caused by aqueous CO_2 solution than by hydrochloric acid [9]. This experimental fact suggests that hydrogen ion is unlikely to be the major corrosive species in CO_2 corrosion (i.e., the reduction of H^+ is unlikely to be the main cathodic reduction reaction in CO_2 corrosion). De Waard and Milliams concluded that the cathodic hydrogen evolution in CO_2 corrosion proceeds in a “catalytic” manner by direct reduction of undissociated adsorbed carbonic acid [10]. This mechanism is now generally accepted as the explanation for the strong corrosivity of carbonic acid. The detailed process of the cathodic reduction reaction of CO_2 corrosion was reported by Schmitt [11], and the cathodic reaction mechanism proposed is shown in Figure 1.6.

Figure 1.6 Electrode–solution interfacial model illustrating electrochemical and chemical reactions leading to uniform iron corrosion in CO_2-containing aqueous solution.



As shown, in CO_2 corrosion processes, anode and cathode locations change from period 1 to period 2. A given area on a metal surface would act as both an anode and a cathode over any extended period of time, and the averaging effect of these shifting local reactions results in a rather uniform dissolution of metal surfaces; therefore, this corrosion model would lead to uniform corrosion.

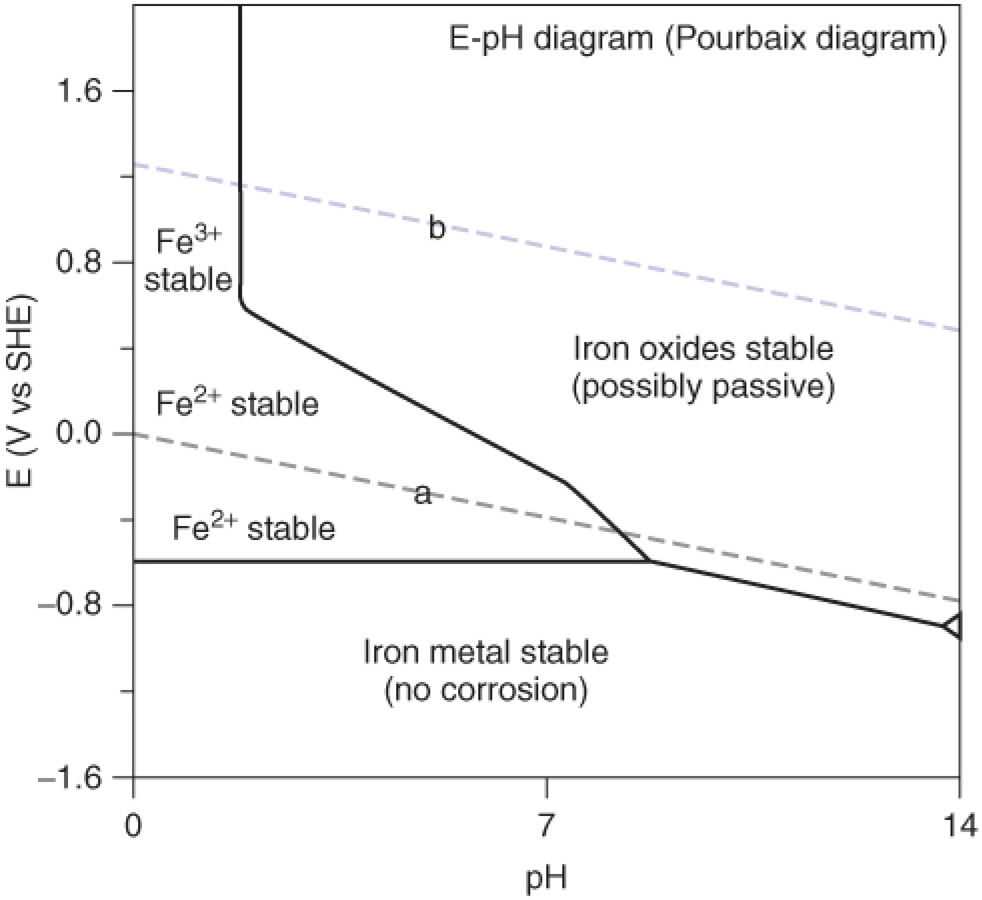
If a more careful investigation of the electrode–solution interface is carried out, it can be found that the uniform CO_2 corrosion of iron also involves transport processes occurring simultaneously over an electrode–solution interface. Since electrochemical and chemical reactions would cause the concentration of certain species in the solution (e.g., Fe^{2+}) to increase whereas others will be depleted (e.g., H^+), the established concentration gradients will lead to the movement of reactants and products toward and away from the electrode surface. If the transportation of reaction species due to diffusion and convection processes is unable to sustain the speed of the electrochemical reactions, the concentration of species at the electrode–solution interface can become very different from those in the bulk solution [12]. In this case, the electrode–solution model needs to accommodate a two-way coupling between the electrochemical corrosion processes at the metal surface and the diffusion and electromigration processes in the adjacent solution layer. Many corrosion models described in the literature have been developed to illustrate various forms of uniform or general corrosion in more complex environmental conditions.

Mixed potential theory and electrochemical corrosion measurement

Wagner–Truad proposed mixed potential theory to explain the operation of mixed electrode cells operating at a mixed potential [8]. According to this theory, any electrochemical reaction can be divided algebraically into separate oxidation and reduction reactions with no net accumulation of electrical charge. In the absence of an externally applied potential, the oxidation of a metal and the reduction of species in solution occur simultaneously at a metal–electrolyte interface. Under these circumstances, the net measurable current is zero and the corroding metal is charge neutral, with no net accumulation of charge. For metals, the electrochemical potential of a metal at the anodic site is assumed equal to that at the cathodic site, due to its very low resistance [8].

Corrosion is a typical mixed electrode process operating at a mixed potential: the corrosion potential. The corrosion potential can be measured using an experimental setup similar to that shown in Figure 1.3, by recording the potential difference between a corroding electrode where both anodic and cathodic reactions occur, and a stable reference electrode. The corrosion potential is commonly used in conjunction with an *E–pH diagram* (often referred to as a *Pourbaix diagram*) as an indicator of the corrosion thermodynamic status to predict if corrosion will occur, to estimate the composition of corrosion products, and to predict environmental changes that would prevent or reduce corrosion attack. The *E*–pH diagram is a graphical representation of the thermodynamics of common electrochemical and chemical equilibria between metal and water, indicating thermodynamically stable phases as a function of electrode potential and pH [13]. An *E*–pH diagram can be constructed through application of the Nernst equation to each of these electrode reactions as a function of pH. Many *E*–pH diagrams have already been constructed for common material-environment systems by corrosion scientists, including those in Pourbaix's laboratory [14]. In many cases, an *E*–pH diagram can be found from the literature for a particular material environment, although we may need to construct *E*–pH diagrams for less common systems. Figure 1.7 shows a typical version of the *E*–pH diagram for an iron–water system at ambient temperature.

Figure 1.7 Simplified *E*–pH diagram for an iron–water system.



An *E*–pH diagram visualizes the thermodynamics of corrosion processes and gives information about a metal surface, whether it is in a region of immunity where the tendency for corrosion is nil, in a region where the tendency for corrosion is high, or in a region where the tendency for corrosion may still exist but where there is also a tendency and possibility for a protective or passive film to exist.