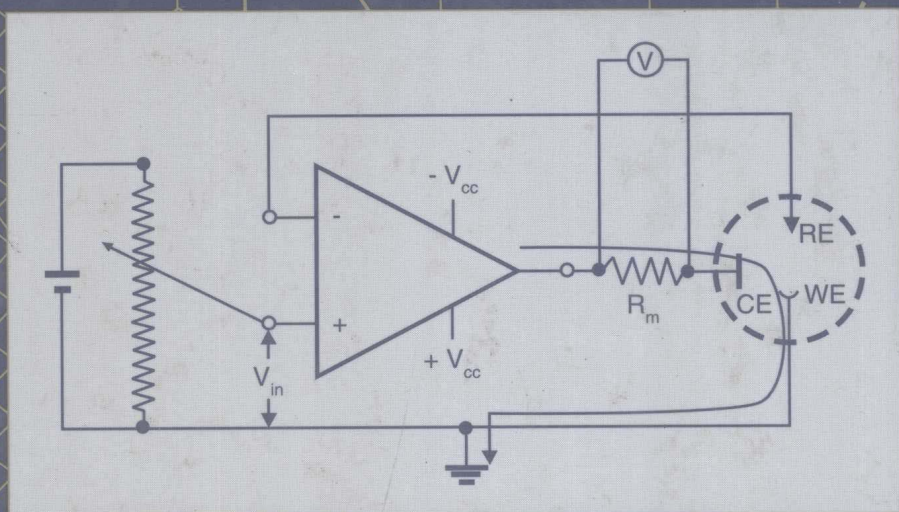


ELECTROCHEMICAL TECHNIQUES IN CORROSION SCIENCE AND ENGINEERING



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Preface

Corrosion science and engineering have benefited tremendously from the explosion in the use of electrochemical methods that can probe the thermodynamic and kinetic aspects of corrosion, including the rate of corrosion. These methods have proved of great utility to corrosion engineers and scientists in predicting the performance of materials and devising corrosion mitigation strategies, understanding the effects of changes in process and environment conditions, and assessing the accuracy of corrosion monitoring techniques. Enhanced prevention and understanding of corrosion has been achieved over the past several decades by applying these methods in both the laboratory and field. Electrochemical methods for corrosion, when used properly, have distinct advantages over exposure techniques. Some of these advantages are speed, nondestructiveness, high resolution, and ability to provide mechanistic information. Unfortunately, few engineers and scientists tasked with corrosion problems have been trained in electrochemical fundamentals and their application to corrosion phenomena.

The goal of this book is to present a framework for understanding the principles of electrochemistry and the methods derived from these principles in a clear manner and ready-to-apply format. The book emphasizes practical fundamentals that make it possible to determine whether electrochemical techniques are of use for a given problem, choose the correct electrochemical method, and intelligently interpret the results, including the limitations of the methods and analyses.

Chapter 1 provides an introduction to some of the basic terms and concepts of electrochemistry and corrosion and provides a detailed overview of the remainder of the book. Chapter 2 provides an overview of the important thermodynamic and kinetic parameters of relevance to corrosion electrochemistry. Chapter 3 focuses on what might be viewed as an aberration from normal dissolution kinetics: passivity. This aberration—or “peculiar condition,” as Faraday referred to it—is critical to the use of stainless steels, aluminum alloys, and all the so-called corrosion resistant alloys (CRAs).

Chapter 4 describes 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. Chapter 5 focuses on how to characterize flow and how to include its effects in the test procedure. Chapter 6 describes the origins of the observed distributions in space and time of the reaction rate. Chapter 7 describes the applications of electrochemical measurements to predictive corrosion models, emphasizing their use in the long-term prediction of corrosion behavior of metallic packages for high-level nuclear waste. Chapter 8 outlines the electrochemical methods that have been applied to develop and test the effectiveness of surface treatments for metals and alloys. The final chapter gives experimental procedures that can be used to illustrate the principles described.

“Electrochemical techniques, when conducted intelligently and interpreted knowledgeably, are valuable tools for solving, understanding, and preventing corrosion problems.” This has been the mantra of a short course on electrochemical methods applied to corrosion that has been conducted annually since 1984. The overall goal of the course is to provide practicing corrosion engineers with an introduction to the use of electrochemical techniques. This book, based on the lectures and laboratories of that short course, shows how to use electrochemical methods to understand corrosion phenomena and solve corrosion problems.

ACKNOWLEDGMENTS

More than 50 people have contributed to the success of the course that spawned this book. These include both faculty members and graduate student assistants who have taken to heart the desire to constantly improve the quality of the instruction. The father of the short course is Pat Moran (U.S. Naval Academy). He not only designed the original course but also served as a mentor for many graduate students in corrosion, including two of the authors of this book. The graduate students listed below have made critical contributions to the experiments described in Chapter 8. The written experimental procedures reflect only a small portion of the time they devoted to designing these labs and making them work during the course. Their influence permeates the book.

The course has enjoyed outstanding support from our sponsors throughout its history. The local sections of NACE International (Baltimore/Washington from 1985–1990; Old Dominion from 1991–present) provided advertising support and their good name. Perkin-Elmer Instruments provided excellent equipment and outstanding technical support from the start. Their steadfast assistance was instrumental in the success of the course.

Many of the figures in Chapters 1 through 5 were created by Jean Reese, who was also critical in the organization of the short course, and the Center for Electrochemical Science and Engineering at the University of Virginia.

The patience and pleasant persistence of the team at Marcel Dekker, Inc., especially Rita Lazazzaro and Eric Stannard, have been instrumental in making this book a reality. Most importantly, we acknowledge our families, who made all the work worthwhile.

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1

Introduction

Corrosion can be defined as the deterioration of a material's properties due to its interaction with its environment. The demands for long-term performance of engineering structures over a wide size scale continue to increase. As microelectronic structures decrease in size, smaller amounts of dissolution on interconnects in integrated circuits can lead to the failure of large computer systems. The long-term storage of nuclear waste may represent man's most compelling engineering challenge: containment of high-level radioactive material for thousands of years. In both cases, as well as in many in between, the corrosion engineer has a primary responsibility to provide guidance throughout the design, construction, and life process in terms of material selection, environment alteration, and life prediction. Over the past thirty years, the use of electrochemical methods for probing corrosion processes has increased to the point where they represent an indispensable set of tools. The overarching goal of this book is to provide the foundation for corrosion engineers to use electrochemical techniques as part of the tool kit they apply to corrosion concerns.

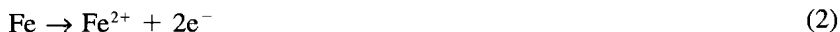
This introduction briefly reviews topics that underlie the remainder of the book. Most of these topics will be familiar from high school or college chemistry. Nonetheless, the topics are generally given short shrift in standard chemistry syllabi, so their importance with respect to corrosion is emphasized here.

I. CHEMICAL VS. ELECTROCHEMICAL REACTIONS

Chemical reactions are those in which elements are added or removed from a chemical species. Purely chemical reactions are those in which none of the species undergoes a change in its valence, i.e., no species is either oxidized or reduced. Electrochemical reactions are chemical reactions in which not only may elements be added or removed from a chemical species but also at least one species undergoes a change in the number of valence electrons. For example, the precipitation of iron hydroxide, $\text{Fe}(\text{OH})_2$, is a pure chemical reaction:



None of the atoms involved have changed its valence; the iron and oxygen are still in the divalent state, and the hydrogen is still univalent. One way to produce the ferrous ion needed in the above reaction is via the oxidation of metallic (zero valent) iron:



In order for this reaction to occur, the two electrons produced must be consumed in a reduction reaction such as the reduction of dissolved oxygen:



If the two reactions are not widely physically separated on a metal surface, the chemical reaction between the hydroxide and ferrous ions can produce a solid on the surface. Thus chemical and electrochemical reactions can be (and often are) coupled.¹ The electrochemical methods described in this book can be used to study directly the wide range of reactions in which electrons are transferred. In addition, some chemical reactions can also be studied indirectly using electrochemical methods.

The vast majority of engineering materials dissolve via electrochemical reactions. Chemical processes are often important, but the dissolution of metallic materials requires an oxidation of the metallic element in order to render it soluble in a liquid phase. In fact, there are four requirements for corrosion: an anode (where oxidation of the metal occurs), a cathode (where reduction of a different species occurs), an electrolytic path for ionic conduction between the two reaction sites, and an electrical path for electron conduction between the reaction sites. These requirements are illustrated schematically in Fig. 1.

All successful corrosion control processes affect one or more of these requirements. For example, the use of oxygen scavengers affects the cathodic reaction rate possible. Isolating dissimilar metals with insulating materials attempts to remove the electrical path. Most organic coatings serve to inhibit the formation of an electrolytic path. Thus, when evaluating a corrosion process or proposed mitigation method, a first-pass analysis of the effects of it on the four requirements can serve to structure one's thinking.

A simple calculation demonstrates the tremendous power of electrochemical reaction rate measurements due to their sensitivity and dynamic range. Dissolution current densities of 10 nA/cm² are not tremendously difficult to measure.

¹ Bard and Faulkner (1) is an excellent source of information on the intricacies of such coupling.

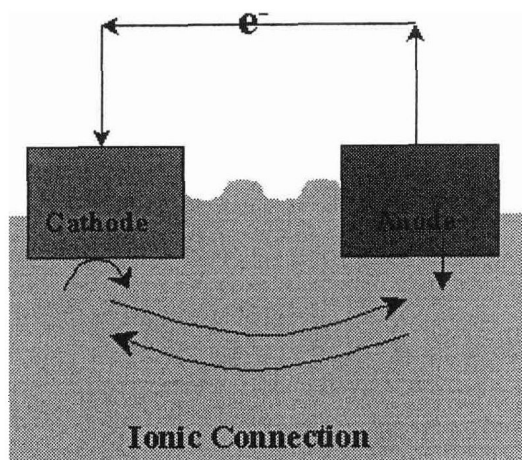


Figure 1 Schematic diagram of four requirements for corrosion. Note that the anode and cathode can be on the same piece of material.

A metal corroding at this rate would lose 100 nm of thickness per year.² On the other end of the spectrum, measurements of reaction rates of several to hundreds of A/cm² are needed in some transient studies of localized corrosion. A dissolution rate of 100 A/cm² corresponds to a penetration rate of 1 km/s. Fortunately for modern society, such penetration rates last in practice for far less than one second! Thus modern instrumentation allows the measurement of dissolution rates over more than 10 orders of magnitude with accuracy on the order of a few percent.

The issues of accuracy and precision are often controversial in discussions of corrosion electrochemistry. Analytical electrochemists can achieve high accuracy and precision through the strict control of variables such as temperature, solution composition, surface condition, and mass transport. Throughout this book, the effects of these and other variables on corrosion processes are highlighted. Unfortunately, in practice, close control of such important parameters is often impossible. In addition, corrosion systems are generally time-varying in practice, further complicating reproducibility. This situation can be disturbing for physical scientists new to electrochemical corrosion measurements who are used to more control and thus more reproducibility in instrumental measurements.

² In most applications, this would be considered outstanding corrosion resistance, but for a nuclear waste storage vessel needing 100,000 years of service, the corrosion allowance would need to be at least 10 cm.

Nonetheless, they become more comfortable with experience, as they realize that in most cases, getting the first digit in the corrosion rate right is both a necessary and a sufficient condition for job security.

II. FARADAY'S LAWS OF ELECTROLYSIS

In the early 1800s, Michael Faraday performed superb quantitative experimental studies of electrochemical reactions. He was able to demonstrate that electrochemical reactions follow all normal chemical stoichiometric relations and in addition follow certain stoichiometric rules related to charge. These additional rules are now known as Faraday's laws. They can be written as follows:

Faraday's First Law: The mass, m , of an element discharged at an electrode is directly proportional to the amount of electrical charge, Q , passed through the electrode.

Faraday's Second Law: If the same amount of electrical charge, Q , is passed through several electrodes, the mass, m , of an element discharged at each will be directly proportional to both the atomic mass of the element and the number of moles of electrons, z , required to discharge one mole of the element from whatever material is being discharged at the electrode. Another way of stating this law is that the masses of the substances reacting at the electrodes are in direct ratio to their equivalent masses.

The charge carried by one mole of electrons is known as 1 faraday (symbol F). The faraday is related to other electrical units because the charge on a single electron is 1.6×10^{-19} C/electron. Multiplying the electronic charge by the Avogadro number 6.02×10^{23} electrons/mole electrons tells us that 1 F equals 96,485 C.

These empirical laws of electrolysis are critical to corrosion as they allow electrical quantities (charge and current, its time derivative) to be related to mass changes and material loss rates. These laws form the basis for the calculations referenced above concerning the power of electrochemical corrosion measurements to predict corrosion rates. The original experiments of Faraday used only elements, but his ideas have been extended to electrochemical reactions involving compounds and ions.

By combining the principles of Faraday with an electrochemical reaction of known stoichiometry permits us to write Faraday's laws of electrolysis as a single equation that relates the charge density (charge/area), q , to the mass loss (per unit area), Δm :

$$\Delta m = \frac{q(AM)}{nF} \quad (4)$$

Taking the time derivative of the equation allows the mass loss rate to be related to the dissolution current density:

$$\dot{m} = \frac{i(\text{AM})}{nF\rho} \quad (5)$$

In many cases, a penetration rate, in units of length/time, is more useful in design. The inclusion of corrosion allowances in a structure requires an assumption of uniform penetration rate. The most common engineering unit of penetration rate is the mil per year (mpy). One mil of penetration equates to a loss in thickness of 0.0001". Corrosion rates of less than 1 mpy are generally considered to be excellent to outstanding, although such adjectives are highly dependent on the details of the engineering scenario. A rule of thumb is that $1\mu\text{A}/\text{cm}^2$ is approximately equivalent to 0.5 mpy for a wide range of structural materials, including ferrous, nickel-, aluminum-, and copper-based alloys. For more exact calculations, the following formula can be used:

$$\text{mpy} = \frac{129(\text{AM})(i)}{n\rho} \quad (6)$$

where

mpy = penetration rate (mils per year)

AM = atomic mass (g)

i = corrosion current density (mA/cm^2)

ρ = density (g/cm^3)

n = number of electrons lost per atom oxidized

Throughout the text, distinctions are made between current, i.e., the rate of a reaction, and current density, i.e., the area-specific reaction rate. The combination of Faraday's laws described above involves current density rather than current. The current, usually symbolized with a capital I , has units of amperes and represents an electrical flux. The current density, usually symbolized with a lower case i , has units of amperes per unit area, e.g., A/cm^2 . Under a given set of conditions (i.e., potential, metal and solution composition, temperature, etc.), the current density is fixed. Thus, although doubling the area of the electrode will double the measured current, the current density will remain unchanged.

The most direct example of the importance of differentiating between i and I is in the application of the conservation of charge to corrosion. In this case, the conservation of charge means that in a isolated system,³ all electrons that are liberated in oxidation reactions (at anodes must be consumed in reduction reac-

³ Isolated means that there are no external sources or sinks of electrons.

tions (at cathodes). In terms of charge, the total anodic charge must equal the total cathodic charge (each in coulombs):

$$\sum_i Q_a = \sum_j Q_c \quad (7)$$

Taking the time derivative converts the law to a rate expression:

$$\sum_i I_a = \sum_j I_c \quad (8)$$

For each reaction, the current density is the current for that reaction divided by the area over which it occurs:

$$i_i = \frac{I_i}{A_i} \quad (9)$$

Thus combining these expressions demonstrates that only in the cases in which the areas on which the anodic and cathodic reactions occur are equal can the anodic and cathodic current densities be equal:

$$\sum_i i_a A_a = \sum_j i_c A_c \quad (10)$$

In other cases, a push-me-pull-you situation arises; the faster (as defined by the current density) reaction cannot produce current any faster than the slower reaction can consume it. Corrosion engineers use this principle in several ways including sacrificial anodes and corrosion inhibitors. Examples can be found throughout the text.

III. OVERVIEW OF THE REMAINDER OF THIS BOOK

A. What Is Covered

This book consists of nine chapters. The second chapter provides an overview of the important thermodynamic and kinetic parameters of relevance to corrosion electrochemistry. This foundation is used in the third chapter to focus on what might be viewed as an aberration from normal dissolution kinetics, passivity. This aberration, or “peculiar condition” as Faraday called it, is critical to the use of stainless steels, aluminum alloys, and all of the so-called corrosion resistant alloys (CRAs). The spatially discrete failure of passivity leads to localized corrosion, one of the most insidious and expensive forms of environmental attack. Chapter 4 explores the use of the electrical nature of corrosion reactions to model the interface as an electrical circuit, allowing measurement methods originating in electrical engineering to be applied to nondestructive corrosion evaluation and

inspection. Convective flow of the environment can have substantial effects on corrosion processes. The fifth chapter focuses on how to characterize flow and how to include its effects in test procedures. In many systems, there are distributions in space and time of the reaction rate due to distributions in the electrochemical potential. The origins of such distributions and their effects on measurements and interpretations are explored in the sixth chapter of the book. Chapter 7 describes the applications of electrochemical measurements to predictive corrosion models, emphasizing their use in the long-term prediction of the corrosion behavior of metallic packages for high-level nuclear waste. Chapter 8 outlines how electrochemical methods have been applied to develop and test the effectiveness of surface treatments for metals and alloys. The final chapter contains descriptions of experimental procedures that can be used to illustrate the principles described. Throughout the book, example from the literature are provided in order to ground the discussions and to provide the interested reader with access to more in-depth discussions of certain topics.

B. What Is Not Covered

We have chosen to focus this text on the use of electrochemical techniques. Thus there are many important areas in corrosion engineering that are excluded. For example, space constraints prevent any direct coverage of environment-assisted cracking, although some of the concepts considered in localized corrosion can be easily extended to the conditions inside occluded cracks. Details of corrosion mechanisms are not described. Fundamental corrosion information is provided only to the extent necessary to understand the origin of signals measured by the electrochemical methods under consideration. Similarly, nonelectrochemical methods are not described in any detail. In general, high-temperature gaseous oxidation does not involve a liquid phase and thus falls outside the purview of this book.

C. Importance of the Motto

The motto found in the front of this book was coined by Pat Moran, currently Chairman of the Department of Mechanical Engineering at the U.S. Naval Academy and the Ph.D. advisor of two of the authors (RGK, JRS). It includes the key elements in electrochemical testing that will be emphasized throughout this book. In order to conduct tests intelligently, one needs to perform the tests in a relevant environment, on a relevant material surface, under relevant experimental conditions. Although this advice sounds obvious, there is always a tension between the proper choices for experimental parameters for accurate simulations and the proper choices for experimental convenience. Such tradeoffs must be carefully

considered. In order to interpret knowledgeably one must be well-read in the appropriate literature, bring one's engineering experience to bear on the results, and use complementary methods for data verification wherever possible. The power of electrochemical methods is substantial as long as their limitations are kept in mind.

REFERENCE

1. A. J. Bard, L. R. Faulkner. *Electrochemical Methods: Fundamentals and Applications*. John Wiley, New York, 1980.

2

Electrochemical Thermodynamics and Kinetics of Relevance to Corrosion

I. ELECTROCHEMICAL THERMODYNAMICS

A. Utility of Thermodynamics in Electrochemistry

Thermodynamic considerations in electrochemistry allow the determination of whether a reaction can occur spontaneously, i.e., without the input of external energy. If metal dissolution is unfavorable thermodynamically in a given set of circumstances, the job of the corrosion engineer is generally done. For example, copper will not corrode in pure, deoxygenated water at any pH. Although this example is one of the few in which corrosion can be excluded on thermodynamic grounds, the use of such principles can be used to understand the effects of some variables on corrosion tendencies. In addition, thermodynamics provides the basis for many of the electrochemical measurements made in corrosion science and engineering.

The three goals of the thermodynamic section are (1) to relate the thermodynamics of corrosion-related electrochemistry to concepts with which the reader may be familiar, (2) to describe the need for and characteristics of reference electrodes, and (3) to describe the origin, use, and limitations of electrochemical phase diagrams (a.k.a., E -pH or Pourbaix diagrams).

B. Relation of ΔG to E_r

All processes in nature that occur spontaneously have a Gibbs free energy change (ΔG) associated with them that is negative. A negative free energy change indicates that the stability of the products is greater than that of the reactants. The nature of the process determines the components of the free energy change that contribute.