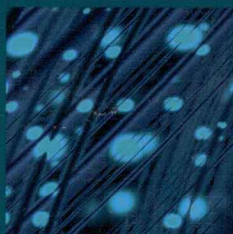


ENGINEERING SCIENCES

*Materials*



# CORROSION AND SURFACE CHEMISTRY OF METALS

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Dieter Landolt

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EPFL Press  
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CORROSION AND  
SURFACE CHEMISTRY  
OF METALS

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## PREFACE

Throughout history, metals have had a decisive effect on human civilization, and they largely condition the way we live today. Electric power, combustion engines, ships, cars, railways, airplanes, production of fertilizers and pharmaceuticals, precision tools, machines, high rise buildings, sanitary systems, home appliances and even computers would not exist without metals. Corrosion and wear limit the useful lifetime of this equipment, reduce their efficiency and often affect their safety. Corrosion control and surface technology are therefore of crucial importance for our technology-based society.

Metals are found in nature in their oxidized state, mostly as oxide or sulfide minerals. The elaboration of metals from minerals requires energy, and, as a consequence, if left alone metals spontaneously return to their natural state; they corrode. The rate at which this occurs varies widely among different metals and as a function of their chemical environment, the prevailing temperature and the concurrent action of mechanical forces. Furthermore, the local corrosion rate of a metallic structure may be affected by electrochemical interactions between different parts of it and by its shape. Often, corrosion rates vary with time due to changing environmental conditions or because corrosion products accumulate on the surface. Corrosion resistance therefore is not an intrinsic property of a material but depends on a given metal-environment system taken as a whole. The prediction of corrosion behavior and the implementation of efficient corrosion control measures requires a good understanding of the underlying reaction mechanisms.

In past years our knowledge about metal surfaces and corrosion mechanisms has advanced greatly, and considerable progress has been achieved in controlling corrosion. Successful examples include multi-year warranties against perforation of car body panels, oil drilling in highly corrosive marine environments or safely operated power plants. Today, at the beginning of the twenty first century, corrosion science and engineering faces many new challenges. First of all, the evident need for sustainability of future development requires that wasting of materials and energy resources due to corrosion be reduced further by developing appropriate technologies. A number of well-established methods of corrosion protection need to be replaced by

more environment-friendly techniques. The development of ever smaller electronic and micromechanical devices and the emerging field of nanotechnology require new approaches to corrosion and wear control on an increasingly finer scale. On the opposite side, installations for energy production, civil engineering structures and transport systems tend to become ever larger and more complex, increasing the requirements for reliable risk analysis and lifetime prediction in relation to corrosion. Corrosion issues are also crucial for safe long-term storage of nuclear waste. Complex physical and chemical interactions between metal surfaces and biological systems govern the lifetime of medical implants and determine the extent to which microbial corrosion damages process equipment and water distribution systems. On a different level, corrosion based chemical and electrochemical shaping and surface treatment processes offer new opportunities for surface engineering and for the fabrication of both microsystems and of new types of nanostructures. To successfully tackle these and other challenges, engineers and scientists need a sound education in the basics of corrosion, electrochemistry and surface chemistry of metals.

The present book is the result of courses that the author has been teaching for many years, mostly to students of materials science and chemical engineering. The original French edition of the book was well received, requiring a second and third printing. For the present English edition the content has been enriched and updated, taking into account recent scientific and technical developments. Among these changes, more space has been given to advanced methods for the characterization of surfaces and interfaces, some sections such as those dealing with dealloying, pitting and tribocorrosion have been rewritten, and a new section on the prevention of microbially influenced corrosion has been added.

This being an introductory textbook, the understanding of principles, rather than technological detail, is emphasized throughout. A careful presentation of the electrochemistry of metals and oxide films is given, and the fundamentals and methods of surface chemistry relevant for corrosion are introduced. Whenever possible, simple quantitative models are used to promote the physical understanding of corrosion and protection phenomena. Because students often experience difficulties in bridging theoretical notions and engineering applications, the practical relevance of theoretical concepts is repeatedly stressed and an entire chapter is dedicated to the presentation of commonly used approaches to corrosion control. Thus the book provides a comprehensive introduction to the principles and methods of modern corrosion science and engineering.

Senior or graduate students in materials science, chemistry and chemical engineering as well as professional scientists and engineers faced with problems of corrosion and surface engineering should profit from this book. It can be used as a textbook in university level courses or for self study. The content is suited for general corrosion courses as well as for introductory courses on the electrochemistry and surface chemistry of metals and oxides. Indeed, the selection of material can be easily adapted to different needs. For example, a corrosion course for engineering students may introduce just the most basic notions of Chapters 2, 4, and 6, with more

emphasis on the practical aspects of corrosion mechanisms of Chapters 7 to 11 and on corrosion prevention discussed in Chapter 12. A science oriented course for students in materials, chemistry or applied physics will focus primarily on the fundamentals and methods exposed in Chapters 2 to 6 and in parts of Chapters 8 and 12. Advanced corrosion courses may study in more detail such topics as high temperature corrosion, stress corrosion cracking and environmental effects on friction and wear presented in Chapters 9 to 11. Homework problems for each chapter complement the material treated in the text.

Dr. Fred Fenter of PPUR carefully translated the original French text which served as a basis for this book, and he was in charge of the production process. The author expresses his gratefulness and thanks to Fred Fenter for encouraging the preparation of this book and for the continuing support and precious collaboration throughout its realization.

Lausanne, December 2006  
Dieter Landolt

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## CHAPTER 1

# INTRODUCTION

## 1.1 THE CORROSION OF METALS

### 1.1.1 Overview of the phenomena

Corrosion, from the Latin *corrodere*, means “to chew away”, “to attack”. It is estimated that corrosion destroys one quarter of the world’s annual steel production, which corresponds to about 150 million tons per year, or 5 tons per second. Of course, corrosion is not limited to steel but affects all materials: metals, polymers and ceramics. It is the result of chemical and/or physical interactions between the material and its environment. Examples of the corrosion phenomena include:

- transformation of steel into rust;
- cracking of brass in the presence of ammonia;
- oxidation of an electrical contact made of copper;
- weakening of high-resistance steel by hydrogen;
- hot corrosion of a super-alloy in a gas turbine;
- swelling of PVC in contact with a solvent;
- chemical attack of a nylon tube by an oxidizing acid;
- alkaline attack on refractory bricks;
- chemical attack of mineral glass by an alkaline solution.

Metals differ from other materials by a number of favorable properties: ductility, high tensile strength, temperature resistance, electrical and thermal conductivity and ease of joining and machining. Critical elements of machines, airplanes, cars, electrical power plants, precision instruments, civil engineering structures and chemical plants are normally made of metal. Electronic components and devices also contain numerous metallic elements to provide electrical connections. Quite generally, the durability and life time of installations, machines and devices is critically dependent on their corrosion and wear resistance. Because of their unique position among engineering materials the study of the corrosion and protection of metals is an important part of materials science and engineering.

Interestingly, most metals and alloys are not thermodynamically stable in contact with the atmosphere and with water and they should spontaneously corrode. Fortunately, for most applications the rate of corrosion can be kept sufficiently small by using adequate preventive measures (choice of materials, surface treatment,

electrochemical protection, etc.). In this way metallic objects can satisfactorily fulfill their function over their projected lifetime.

### Some definitions

From the point of view of the construction engineer **corrosion** is damaging: it destroys a material or degrades its functional properties, rendering it unsuitable for the intended use. **Corrosion damage** is the degradation of a material or of its functional properties through a chemical reaction with the environment. Materials can also be damaged by **wear**, which results from rubbing between solid surfaces or from impingement of fluids or of solid particles. Wear causes a progressive loss of material from a surface by mechanical mechanisms, but chemical interactions between the material and its environment often slow or accelerate the damage. The study of corrosion and protection of metals must also include degradations that arise as a result of combined mechanical and chemical effects.

Sometimes, corrosion is a welcome, even desirable, phenomenon. For example, corrosion destroys metallic objects abandoned in nature and thus eliminates them. Corrosion reactions are also used in industrial manufacturing. A well-known example is the anodizing of aluminum where one applies an anodic voltage to the metal in a suitable electrolyte. Anodizing reinforces the natural oxide film at the surface and thus provides improved corrosion resistance and sometimes also a decorative effect. Similarly, in chemical and electrochemical polishing corrosion reactions are used to produce a smooth surface finish. We can therefore define **corrosion** in a general way as follows [1]: *Corrosion is an irreversible interfacial reaction of a material with its environment, resulting in the loss of material or in the dissolving of one of the constituents of the environment into the material.* This definition includes both the positive and negative effects of corrosion. It also includes material damage due to the absorption of a constituent of the environment, such as hydrogen absorption into steel, which causes embrittlement and thus impairs the mechanical properties of the material.

### 1.1.2 The economic importance of the corrosion

Corrosion affects all areas of the economy, from the integrated circuit to the bridge made of reinforced concrete. The cost of corrosion has been estimated to represent 4% of the gross national product [2]. Even for a small country like Switzerland, this number represents several billion Euros per year. These numbers include:

- direct losses: replacement of corroded materials and of equipment ruined by corrosion;
- indirect losses: cost of repair and loss of production;
- cost of corrosion protection: use of more expensive corrosion-resistant materials, application of surface coatings, cathodic protection systems ;
- cost of corrosion prevention: maintenance, inspections, corrosion prevention by design.

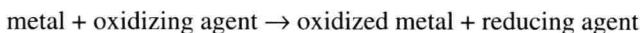
The direct losses represent only part of the total costs of corrosion and are, in fact, often inferior to the indirect costs. If a nuclear power plant, which represents a significant capital investment, has to be stopped for repair or replacement of a corroded heat exchanger, the price of the part is insignificant relative to the cost of the lost production time. Similarly, in order to replace a corroded hot water pipe, buried in the wall of a building, the cost of the repair will usually largely exceed the price of the pipe itself.

The many different types of expenses involved make estimates of the total cost of corrosion difficult and uncertain. There is no doubt, however, that the amounts of money involved are quite elevated. Another important aspect of corrosion concerns safety. Corrosion damage can impair the safe operation of installations or machines and be at the origin of severe accidents and the loss of human life. Furthermore, corrosion is a waste of raw materials and, indirectly, of energy.

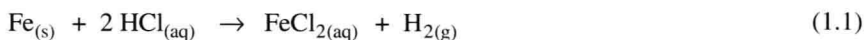
## 1.2 BASIC CONCEPTS

### 1.2.1 Corrosion reactions

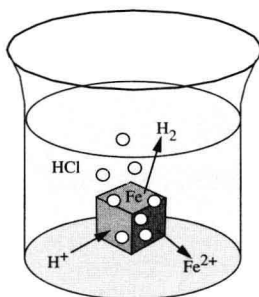
With only a few exceptions (c.f. Chapter 10), the corrosion of metals is due to an irreversible oxidation-reduction (redox) reaction between the metal and an oxidizing agent present in the environment. The oxidation of the metal is inseparably coupled to the reduction of the oxidizing agent:



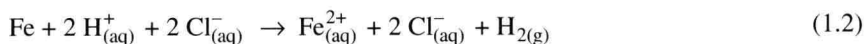
For example, the corrosion of iron in the presence of hydrochloric acid (Figure 1.1) is due to reaction (1.1).



In this equation, the indices (s), (aq), and (g) refer to the solid, aqueous and gaseous phases, respectively. In aqueous phase, hydrochloric acid and ferrous chloride exist in ionic form. We can therefore also write:



**Figure 1.1** The corrosion of iron in acidic solution.



In this case, the oxidizing agent is the solvated proton,  $\text{H}_{(\text{aq})}^{+}$ . The products of the reaction are the solvated ferrous ion  $\text{Fe}_{(\text{aq})}^{2+}$ , and gaseous hydrogen  $\text{H}_{2(\text{g})}$ . To keep the equations simple, the indices that indicate the phase are usually not shown. Because the chloride ions do not undergo a chemical change, the reaction (1.2) can also be expressed as follows.



Under neutral and alkaline conditions, the corrosion of metals is generally due to a reaction of the metal with oxygen. For example, when exposed to air and to humidity iron forms *rust*,  $\text{FeOOH}$ .



Metals also react with oxygen in acidic environments, but under these conditions the concentration of oxygen is usually so much lower than that of protons that its effect can be neglected.

In the absence of humidity, gaseous oxygen is a corrosive agent only at elevated temperatures (at several hundred degrees Celsius). For this reason, a distinction is made between *wet corrosion*, or corrosion at ambient temperatures, and *dry corrosion*, or corrosion at elevated temperatures.

## Oxidizing Agents

In wet corrosion, two principal oxidizing agents are encountered in practice:

- solvated protons;
- dissolved oxygen.

However, other oxidizing agents can also cause corrosion in wet environments, such as:

- oxidizing metal cations:  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sn}^{4+}$ ;
- oxidizing anions:  $\text{NO}_2^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MnO}_4^{-}$ ,  $\text{OCl}^{-}$ ;
- dissolved oxidizing gases:  $\text{O}_3$ ,  $\text{Cl}_2$ ,  $\text{SO}_3$ .

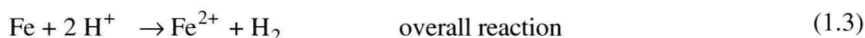
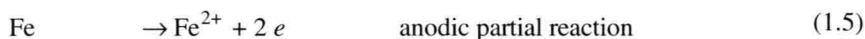
At high temperatures, certain chemical substances, normally inoffensive, become corrosive. Among the oxidizing agents responsible for dry corrosion, one finds:

- gaseous oxygen;
- water vapor;
- carbon dioxide,  $\text{CO}_2$ ;
- sulfur-containing compounds:  $\text{S}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ .

## Partial reactions

All redox reactions consist of two partial reactions, also sometimes called half-cell reactions: the partial oxidation reaction, also referred to as the *anodic partial*

*reaction*; and the partial reduction reaction or *cathodic partial reaction*. Thus for reaction (1.3):



The anodic and cathodic partial reactions show explicitly the electrons that are exchanged during the course of the redox reaction.

Any chemical transformation that implies the transfer of charge across the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte) is referred to as an *electrochemical reaction*. An electrochemical reaction can include one or several *electrode reactions*. For example the reaction (1.3) is an electrochemical reaction: each atom of iron that passes into solution implies the exchange of two electrons between the metal and the protons. Two electrode reactions are involved: the oxidation of the iron and the reduction of the proton. According to the definition given above, *all corrosion reactions that involve metal oxidation are electrochemical reactions*. In order to understand and control corrosion phenomena it is essential to study the thermodynamics and kinetics of electrochemical reactions.

### 1.2.2 Faraday's Law

According to Faraday's Law, when  $n_i$  moles of a given substance react, a proportional electric charge  $Q$  passes across the electrode-electrolyte interface:

$$Q = n \cdot F \cdot n_i \quad (1.7)$$

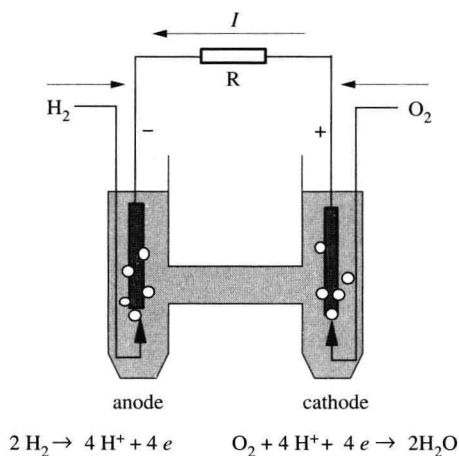
Here,  $F$  designates a universal constant, called *Faraday constant*:  $F = 96,485 \text{ C/mol}$ . The *charge number*  $n$ , without units, expresses the stoichiometric coefficient of the electrons in the equation for the electrode reaction. For example, for the reaction (1.5) describing the anodic dissolution of iron,  $n = 2$ .

By taking the derivative of equation (1.7) with respect to time, one obtains Faraday's law in the form it is most often used:

$$I = n F \frac{dn_i}{dt} \quad (1.8)$$

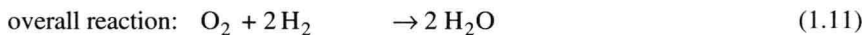
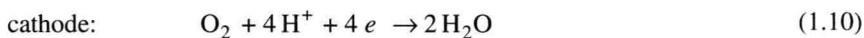
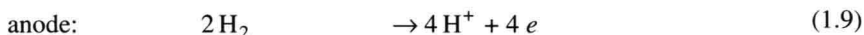
where the electric current, in amperes, is given by  $I = dQ/dt$  and  $dn_i/dt$  represents the rate of reaction in moles per second. Faraday's law thus states that the rate of an electrode reaction is proportional to the magnitude of the electrical current that crosses the electrode-electrolyte interface.

An *electrochemical cell* is a system composed of two electrodes in contact with an electrolyte and connected by an electric conductor. Corrosion cells, batteries and fuel cells are examples of electrochemical cells. As an illustration, Figure 1.2 schematically shows the functioning of an  $\text{H}_2/\text{O}_2$  fuel cell. At the anode, hydrogen is



**Figure 1.2**  $\text{H}_2/\text{O}_2$  fuel cell.

oxidized to  $\text{H}^+$ , whereas at the cathode, oxygen is reduced to  $\text{H}_2\text{O}$ . The overall reaction corresponds to an oxidation-reduction reaction between oxygen and hydrogen.

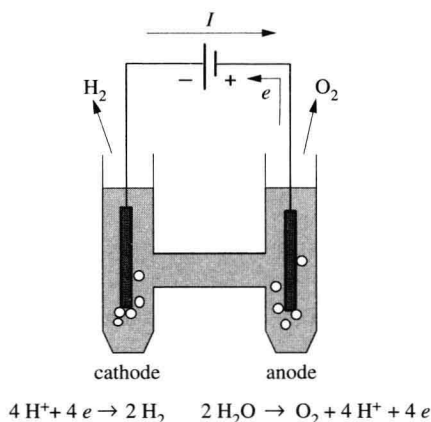


The  $\text{H}_2/\text{O}_2$  fuel cell uses inert electrodes (porous graphite containing platinum as a catalyst, for example). A solution of phosphoric acid, or some other acid, serves as electrolyte. The reaction between oxygen and hydrogen is spontaneous and the fuel cell therefore provides electric power. The current is directly proportional to the number of moles of  $\text{H}_2$  and  $\text{O}_2$  that react at the electrodes, with  $n = 4$  and  $n = 2$  for oxygen and hydrogen, respectively:

$$I = 4 F \frac{dn_{\text{O}_2}}{dt} = 2 F \frac{dn_{\text{H}_2}}{dt} \quad (1.12)$$

In an **electrolysis cell**, also called **electrolyzer**, an external voltage (or current) is applied to the electrodes in order to carry out an electrolysis. For example, in a water electrolysis cell, the current which passes between the anode and the cathode decomposes water into oxygen and hydrogen (Figure 1.3). The number of moles of  $\text{H}_2$  and  $\text{O}_2$  produced during electrolysis is also given by Faraday's law.

In an electrolysis cell, the anode is the positive pole, whereas in a fuel cell or battery it is the negative one. In all cases, however, the partial oxidation reaction takes place at the anode and the partial reduction reaction at the cathode. In other words, the anode is always the site of oxidation, independent of its polarity.



**Figure 1.3** Electrolysis of water.

### 1.2.3 Corrosion rate

The rate of corrosion can be expressed in many different ways depending on the application and personal preferences:

- as a mass loss per unit of surface and per unit of time;
- as the number of moles transformed per unit of surface and per unit of time;
- as corroded depth per unit of time;
- as a current density.

Table 1.4 indicates the conversion factors between units that are frequently used for measuring corrosion rate.

**Table 1.4** Frequently used units for measuring corrosion rate. To obtain the units indicated in the first row, one multiplies the unit in the first column by the corresponding conversion factor.

	$\frac{\text{mole}}{\text{m}^2\text{s}}$	$\frac{\text{mole}}{\text{cm}^2\text{s}}$	$\frac{\text{A}}{\text{m}^2}$	$\frac{\mu\text{A}}{\text{cm}^2}$	$\frac{\text{mg}}{\text{dm}^2\text{day}}$	$\frac{\text{mm}}{\text{year}}$
$\frac{\text{mole}}{\text{m}^2\text{s}}$	1	$10^{-4}$	$9.65 \times 10^4 n$	$9.65 \times 10^6 n$	$8.64 \times 10^5 M$	$3.15 \times 10^4 \frac{M}{\rho}$
$\frac{\text{mole}}{\text{cm}^2\text{s}}$	$10^4$	1	$9.65 \times 10^8 n$	$9.65 \times 10^{10} n$	$8.64 \times 10^9 M$	$3.15 \times 10^8 \frac{M}{\rho}$
$\frac{\text{A}}{\text{m}^2}$	$\frac{1.04 \times 10^{-5}}{n}$	$\frac{1.04 \times 10^{-9}}{n}$	1	100	$8.96 \frac{M}{n}$	$0.327 \frac{M}{n\rho}$
$\frac{\mu\text{A}}{\text{cm}^2}$	$\frac{1.04 \times 10^{-7}}{n}$	$\frac{1.04 \times 10^{-11}}{n}$	0.01	1	$8.96 \times 10^{-2} \frac{M}{n}$	$3.27 \times 10^{-3} \frac{M}{n\rho}$
$\frac{\text{mg}}{\text{dm}^2\text{day}}$	$\frac{1.16 \times 10^{-6}}{M}$	$\frac{1.16 \times 10^{-10}}{M}$	$0.112 \frac{n}{M}$	$11.2 \frac{n}{M}$	1	$\frac{3.65 \times 10^{-2}}{\rho}$
$\frac{\text{mm}}{\text{year}}$	$3.17 \times 10^{-5} \frac{\rho}{M}$	$3.17 \times 10^{-9} \frac{\rho}{M}$	$3.06 \frac{n\rho}{M}$	$306 \frac{n\rho}{M}$	$27.4 \rho$	1

$M$  = atomic mass in g/mol,  $\rho$  = volumetric mass in g/cm<sup>3</sup>,  $n$  = charge number (dimensionless).



### Influence of potential

The prevailing electrode potential determines the direction and rate of the electrode reactions. For example, in a 1 molar solution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions that is in contact with a platinum electrode, the electrode reaction (1.13) takes place.



At an electrode potential of about 0.77 V (c.f. Chapter 2) the above reaction is at equilibrium. The reaction goes from the left to the right if the potential is inferior to this value, and from the right to the left if the potential is more positive. Corrosion reactions take place in an analogous fashion. In hydrochloric acid, for example, iron dissolves less rapidly if one shifts the potential in the negative direction. This effect is used in practice for the protecting metals against corrosion by imposing a sufficiently negative potential.

### Influence of corrosion products

The physical nature of corrosion products often has a major influence on the rate of corrosion. We can divide products into three basic types:

- dissolved ions;
- porous films;
- compact films.

The corrosion of metals in an acidic environment normally produces hydrated cations or complexes that dissolve in the electrolyte and diffuse away from the metal surface. Most often they do not affect the rate of corrosion in an appreciable way.

In neutral or basic environments, but sometimes even in acid solutions, corrosion products are often only slightly soluble. They therefore precipitate at the surface of the metal in the form of hydroxides or metal salts, forming a porous or non-compact surface film. Such films do not protect the metal from corrosion, although they may slow its rate. Rust formed on the surface of steel exposed to a humid atmosphere is an example of this type of corrosion product.

Compact films, in particular oxide films, form a barrier between the metal and its environment, thus protecting the metal. The corrosion of iron in a dry atmosphere stops after the formation of an oxide film that is only a few nanometers thick. On certain metals, compact films also form in humid or liquid environments. These are referred to as *passive films*. They are present on stainless steel in aqueous environments, on aluminum exposed to humid air, and on carbon steel in alkaline surroundings, to cite a few examples. The rate of corrosion of metals coated with a passive film usually is very low.

At high temperatures, under dry corrosion conditions, cations and anions can diffuse more easily through a compact oxide film. The film therefore grows progressively to a greater thickness and this corresponds to a corrosion reaction. Figure 1.5 shows schematically the reaction of a metal with oxygen under these conditions. The metal cations produced by the oxidation reaction at the oxide-metal interface diffuse towards the exterior of the film. At the outer surface, oxygen is