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CORROSION MECHANISMS IN THEORY AND PRACTICE

e d i t e d b y

**P. Marcus
J. Oudar**

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CORROSION MECHANISMS IN THEORY AND PRACTICE

edited by

P. Marcus
J. Oudar

江苏工业学院图书馆

藏书章

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Université Pierre et Marie Curie
Ecole Nationale Supérieure de Chimie de Paris
Paris, France*

Marcel Dekker, Inc.

New York • Basel • Hong Kong

Library of Congress Cataloging-in-Publication Data

Corrosion mechanisms in theory and practice / edited by P. Marcus and J. Oudar.

p. cm. — (Corrosion technology ; 8)

Includes bibliographical references and index.

ISBN 0-8247-9592-X (hardcover : acid-free paper)

I. Corrosion and anti-corrosives. I. Marcus, P. (Philippe)

II. Oudar, J. (Jacques). III. Series: Corrosion technology

(New York, N.Y.) ; 8.

TA462.C65575 1995

620.1'1223—dc20

95-7009

CIP

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Marcel Dekker, Inc.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

The degradation of metallic materials under the effect of corrosion is a costly problem which nearly every industry is confronted with.

We believe that solving existing corrosion problems and preventing future problems requires a detailed understanding of the mechanisms of corrosion. The aim of this book is to review recent advances in the understanding of corrosion and protection mechanisms. Dealing with fundamental and practical aspects, we hope to provide the readers with a detailed view of the surface reactions that govern corrosion and of the link between microscopic forces and macroscopic behavior.

The book is organized into 16 chapters. Chapters 1 to 10 cover the basic phenomena in corrosion: adsorption, anodic dissolution, passivation, passivity breakdown, and localized corrosion as well as stress corrosion cracking. Chapters 11 to 16 provide the connection between the theoretical aspects of corrosion mechanisms and practical applications in industry: corrosion inhibition, atmospheric corrosion, microbially induced corrosion, corrosion in nuclear systems, corrosion of microelectronic and magnetic-storage devices, and the technologically important area of corrosion protection by surface coatings.

This book is based on the results of intensive worldwide research efforts in materials science, surface science, and corrosion science over the past few years. The contributors, from leading academic and industrial research institutes, are highly recognized scientists in these disciplines.

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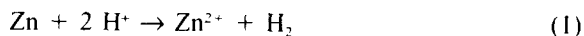
Introduction to Surface Reactions: Electrochemical Basis of Corrosion

DIETER LANDOLT

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INTRODUCTION

Most corrosion phenomena are of electrochemical nature. They imply two or more electrode reactions: the oxidation of a metal (anodic partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction). To understand corrosion reactions one needs to study electrochemical thermodynamics and electrochemical kinetics of the partial reactions. For example, the corrosion of zinc in an acid environment proceeds according to the overall reaction:



This reaction includes the anodic partial reaction (2) and the cathodic partial reaction (3):



The corrosion rate depends on the electrode kinetics of both partial reactions.

In principle, it can be predicted if all electrochemical parameters of the anodic and cathodic partial reactions are known. According to Faraday's law, there is a linear relationship between the metal dissolution rate at any potential, v_M , and the partial anodic current density for metal dissolution $i_{a,M}$:

$$v_M = \frac{i_{a,M}}{nF} \quad (4)$$

In this equation n is the charge number (dimensionless), which indicates the number of electrons exchanged in the dissolution reaction, and F is the Faraday constant, $F = 96,485 \text{ C/mol}$. In the absence of an external polarization a metal in contact with an oxidizing electrolytic environment acquires spontaneously a certain potential, called the corrosion potential, E_{cor} . The partial anodic current density at the corrosion potential is equal to the corrosion current density i_{cor} . Equation (4) thus becomes:

$$v_{M(E=E_{\text{cor}})} = v_{\text{cor}} = \frac{i_{\text{cor}}}{nF} \quad (5)$$

The corrosion potential lies always between the equilibrium potentials of the respective anodic and cathodic partial reactions. Its exact value is determined by the kinetics of the partial reactions.

ELECTROCHEMICAL THERMODYNAMICS

Electrochemical thermodynamics predicts the equilibrium potential of the partial reactions. The overall stoichiometry of any chemical reaction can be expressed by eq. (6).

$$0 = \sum \nu_i B_i \quad (6)$$

Here the symbol B_i designates the reactants and products. The stoichiometric coefficients ν_i of the products are positive and of the reactants negative. The free enthalpy of reaction ΔG is:

$$\Delta G = \sum \nu_i \mu_i \quad (7)$$

Here μ_i is the chemical potential of the participating species. If reaction (6) is carried out in an electrochemical cell, the corresponding equilibrium potential E_{rev} is given by

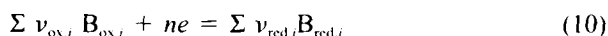
$$\Delta G = -nFE_{\text{rev}} \quad (8)$$

By analogy, under standard conditions (all activities equal to one) one gets

$$\Delta G^0 = -nFE^0 \quad (9)$$

where ΔG° represents the standard free enthalpy and E° represents the standard potential of the reaction.

It is common to write electrode reactions in the general form



Here $\nu_{\text{ox},i}$ represents the stoichiometric coefficient of the “oxidized” species, $\text{B}_{\text{ox},i}$ appearing on the left side of the equality sign together with the free electrons, and $\nu_{\text{red},j}$ indicates the stoichiometric coefficients of the reduced species, $\text{B}_{\text{red},j}$, appearing on the right side of the equality sign, opposite to the electrons. Equation (10) corresponds to a partial reduction reaction and the stoichiometric coefficients $\nu_{\text{ox},i}$ and $\nu_{\text{red},j}$ are both positive.

By setting the standard chemical potential of the solvated proton and of molecular hydrogen equal to zero, $\mu_{\text{H}^+}^\circ = 0$, $\mu_{\text{H}_2}^\circ = 0$, one can define the standard potential of the partial reduction reaction (10) with respect to the standard hydrogen electrode. The standard potential of an electrode reaction thus corresponds to the overall reaction:

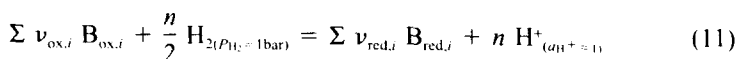


Table 1 indicates the standard potential of selected electrode reactions. Extensive compilations of data can be found in Refs. 1 and 2.

TABLE 1 Standard Potentials of Electrode Reactions at 25°C

Electrode	E°/V
$\text{Li}^+ + e = \text{Li}$	-3.045
$\text{Mg}^{2+} + 2e = \text{Mg}$	-2.34
$\text{Al}^{3+} + 3e = \text{Al}$	-1.67
$\text{Ti}^{2+} + 2e = \text{Ti}$	-1.63
$\text{Cr}^{2+} + 2e = \text{Cr}$	-0.90
$\text{Zn}^{2+} + 2e = \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.44
$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.257
$2\text{H}^+ + 2e = \text{H}_2$	0
$\text{Cu}^{2+} + 2e = \text{Cu}$	0.340
$\text{Ag}^+ + e = \text{Ag}$	0.799
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	1.229
$\text{Au}^{3+} + 3e = \text{Au}$	1.52

The chemical potential of a species B is defined by (12), where a_B represents its activity.

$$\mu_B = \mu_B^\circ + RT \ln a_B \quad (12)$$

Introducing (12) into (7) applied to reaction (11), one obtains for the free enthalpy of reaction

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{H^+}^{n_+} \prod a_{red,i}^{v_{red,i}}}{P_{H_2}^{n_2} \prod a_{ox,i}^{v_{ox,i}}} \quad (13)$$

With (8) and using $a_{H^+} = 1$, $P_{H_2} = 1$ bar for the standard hydrogen electrode, one obtains the Nernst equation (14) of an electrode reaction. It expresses the variation of the equilibrium potential E_{rev} with respect to the standard hydrogen electrode as a function of the activities of the participating species $B_{ox,i}$ and $B_{red,i}$.

$$E_{rev} = E^\circ + \frac{RT}{nF} \ln \frac{\prod a_{ox,i}^{v_{ox,i}}}{\prod a_{red,i}^{v_{red,i}}} \quad (14)$$

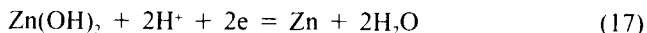
In Eq. (14) the activity of pure substances is equal to one. The activity of dissolved ions cannot be determined unless nonthermodynamic assumptions are made. In corrosion one usually replaces the ionic activities by the respective concentrations. Thus for the electrode reaction (2) one obtains

$$E_{rev} = E_{Zn^{2+}/Zn}^\circ + \frac{RT}{2F} \ln c_{Zn^{2+}} \quad (15)$$

Using the data of Table 1 and replacing the natural logarithm by the logarithm base 10, this yields for 25°C

$$E_{rev} = -0.76 + \frac{0.059}{2} \log c_{Zn^{2+}} \quad (16)$$

In a similar way, for the reaction



the Nernst equation reads

$$E_{rev} = E_{Zn(OH)_2/Zn}^\circ + \frac{RT}{F} \ln a_{H^+} \quad (18)$$

At 25°C this becomes

$$E_{rev} = -0.439 - 0.059 \text{ pH} \quad (19)$$

In this Equation $E_{Zn(OH)_2/Zn}^\circ = -0.439$ is the standard potential for the formation of a hydrated zinc oxide [2].

Pourbaix Diagrams:

The graphical representation of the reversible potential as a function of pH is called potential-pH diagram or Pourbaix diagram. In order to trace such diagrams one must fix the concentration of the dissolved species. Figure 1 shows a simplified Pourbaix diagram for zinc [2]. The numbers indicate different concentrations of dissolved species, for example, 10^{-2} , 10^{-4} mol/l. The diagram shown takes into account the formation of zinc hydroxide, of Zn^{2+} and of the zincate ions HZnO_2^- and ZnO_2^{2-} . At high potentials ZnO_2 may possibly be formed, but because the corresponding thermodynamic data are uncertain they

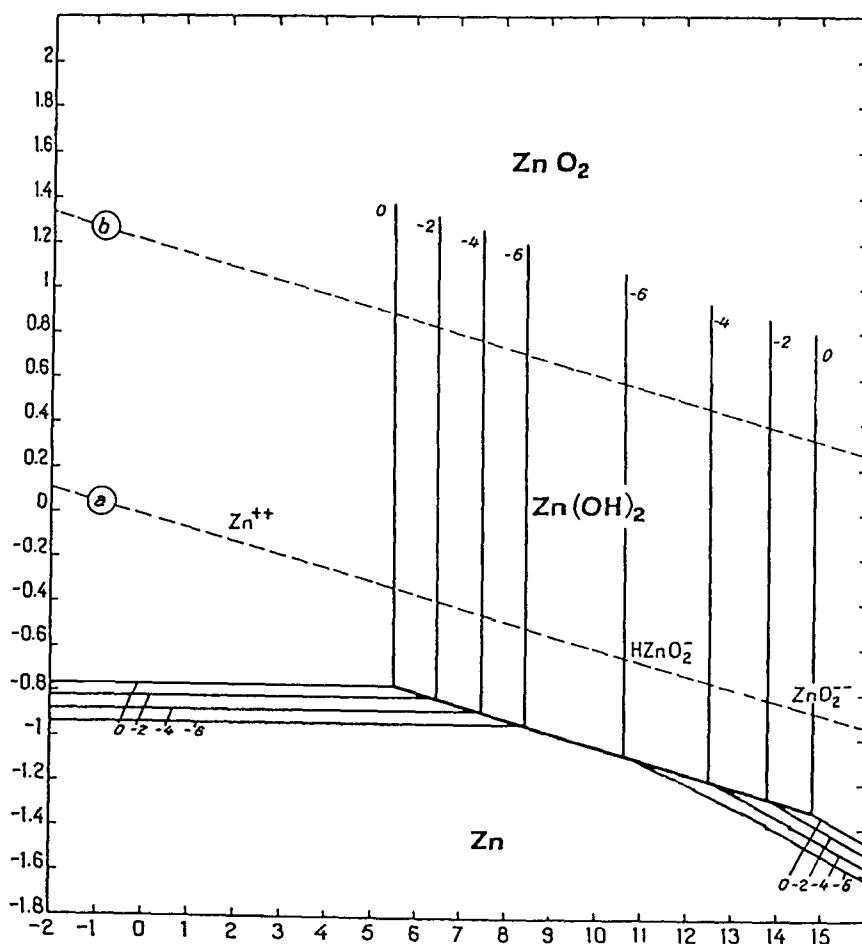


FIGURE 1 Potential-pH diagram of zinc. (From Ref. 2.)

are not presented in the diagram. The broken lines indicate the domain of thermodynamic stability of water. Pourbaix diagrams are widely used in corrosion because they easily permit one to identify the predominant species at equilibrium for a given potential and pH. On the other hand, being based on thermodynamic data, they give no information on the rate of possible corrosion reactions.

KINETICS OF CHARGE TRANSFER REACTIONS

At the electrode-electrolyte interface a charge separation between the metal surface and the electrolyte occurs. The spatial region corresponding to the charge separation is called the electrical double layer. It is usually separated into two parts, the Helmholtz layer or compact double layer and the Gouy-Chapman layer or diffuse double layer. The relative importance of the diffuse double layer increases with decreasing concentration. In very dilute solutions it may extend over a distance of several nanometers, whereas the compact layer never exceeds two to three tenths of a nanometer. The charges at the interface establish an electric field. Within the compact double layer the electric field reaches values of the order of 10^8 to 10^9 V/m. Charge transfer reactions occur across the compact double layer and the influence of the diffuse double layer is usually neglected.

Let us consider the transfer of n electrons between two species, B_{ox} and B_{red} .



According to Faraday's law, the current density across the interface corresponding to this reaction is equal to the difference of the anodic rate v_a and the cathodic rate v_c multiplied by nF .

$$i = nF (v_a - v_c) = k'_{a(E)} c_{red,s} - k'_{c(E)} c_{ox,s} \quad (21)$$

Here $k'_{a(E)}$ and $k'_{c(E)}$ are potential-dependent rate constants and $c_{red,s}$ and $c_{ox,s}$ represent the surface concentrations of B_{red} and B_{ox} , respectively. The rate constants k'_a and k'_c obey the Arrhenius equation.

$$k'_{a(E)} = k'_{a,0} \exp\left(-\frac{\Delta G_a^\ddagger}{RT}\right) \quad (22)$$

$$k'_{c(E)} = k'_{c,0} \exp\left(-\frac{\Delta G_c^\ddagger}{RT}\right) \quad (23)$$

Here ΔG_a^\ddagger and ΔG_c^\ddagger represent the activation energies for the anodic and cathodic partial reactions, respectively, and $k'_{a,0}$ and $k'_{c,0}$ are preexponential factors. The presence of an electric field at the electrode-electrolyte interface modifies the

activation energy of the partial oxidation and reduction reactions as shown schematically in Figure 2. The electric field in this case diminishes the activation energy of the anodic partial reaction and increases that of the cathodic partial reaction.

$$\Delta G^\#_a = \Delta G^\#_{a, \text{ch}} - \alpha F \Delta \Phi \quad (24)$$

$$\Delta G^\#_c = \Delta G^\#_{c, \text{ch}} + (1 - \alpha) F \Delta \Phi \quad (25)$$

Here $\Delta G^\#_{a, \text{ch}}$ and $\Delta G^\#_{c, \text{ch}}$ represent the potential independent parts of the activation energies and $\Delta \Phi$ represents the potential difference across the interface. The proportionality factor α is called the charge transfer coefficient. Its value is usually close to 0.5 [3]. The absolute value of $\Delta \Phi$ is not measurable. It differs from the electrode potential E measured with respect to the standard hydrogen reference electrode by a constant.

$$E = \Delta \Phi + \text{constant} \quad (26)$$

Combining all potential independent terms in the rate constants k_a and k_c one gets

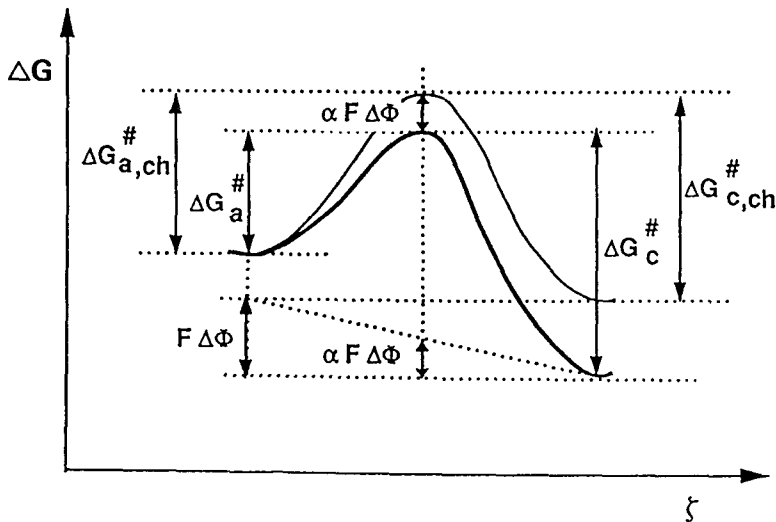


FIGURE 2 Free enthalpy as a function of the reaction coordinate showing the influence of the electric potential on the activation energy of a charge transfer process.

$$k'_{a(E)} = k_a \exp\left(\frac{\alpha n F}{RT} E\right) \quad (27)$$

$$k'_{c(E)} = k_c \exp\left(-\frac{(1 - \alpha)nF}{RT} E\right)$$

With Eqs. (21) and (27) one obtains Eq. (28).

$$i = nFk_a c_{\text{red},s} \exp\left(\frac{\alpha n F}{RT} E\right) - nFk_c c_{\text{ox},s} \exp\left(-\frac{(1 - \alpha)nF}{RT} E\right) \quad (28)$$

The current density i corresponds to the sum of the partial anodic and cathodic current densities:

$$i = i_a + i_c \quad (29)$$

The anodic and cathodic partial current densities, i_a and i_c , respectively, are given by

$$i_a = nFk_a c_{\text{red},s} \exp\left(\frac{\alpha n F}{RT} E\right) \quad (30)$$

$$i_c = -nFk_c c_{\text{ox},s} \exp\left(-\frac{(1 - \alpha)nF}{RT} E\right) \quad (31)$$

At the reversible potential, $E = E_{\text{rev}}$, the current density i is zero and the surface concentration of the reacting species is equal to the bulk concentration: $c_{\text{red},s} = c_{\text{red},b}$, $c_{\text{ox},s} = c_{\text{ox},b}$. This allows one to define the exchange current density of a reaction by the relation:

$$i_{a(E=E_{\text{rev}})} = -i_{c(E=E_{\text{rev}})} = i_0 \quad (32)$$

With (32) and (28) one gets

$$i_0 = nFk_a c_{\text{red},b} \exp\left(\frac{\alpha n F}{RT} E_{\text{rev}}\right) = nFk_c c_{\text{ox},b} \exp\left(-\frac{(1 - \alpha)nF}{RT} E_{\text{rev}}\right) \quad (33)$$

This expression shows that the value of the exchange current density depends on the concentration of the participating species. Defining the overvoltage $\eta = E - E_{\text{rev}}$, Eqs. (33) and (28) yield (34).

$$i = i_0 \frac{c_{\text{red},s}}{c_{\text{red},b}} \exp\left(\frac{\alpha n F}{RT} \eta\right) - i_0 \frac{c_{\text{ox},s}}{c_{\text{ox},b}} \exp\left(-\frac{(1 - \alpha)nF}{RT} \eta\right) \quad (34)$$

If the rate of an electrode reaction is entirely controlled by charge transfer the concentrations of reactants and products at the electrode surface are equal to the bulk concentrations. Equation (34) then reads

$$i = i_0 \exp\left(\frac{\alpha n F}{RT} \eta\right) - i_0 \exp\left(-\frac{(1 - \alpha) n F}{RT} \eta\right) \quad (35)$$

This is the usual form of the Butler-Volmer equation which describes the relationship between current density and potential for a simple electrode reaction controlled by charge transfer.

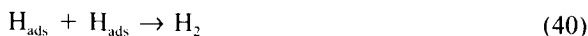
Normally, multielectron transfer reactions proceed in subsequent one-electron transfer reaction steps. For $n > 1$, Eq. (35), therefore, does not describe the physical mechanism. Indeed, depending on which reaction step is rate limiting, the value of the exponential terms may change. For example, the cathodic reduction of protons corresponding to the overall reaction



proceeds in two steps. The Volmer-Heyrovsky mechanism applies to most metal substrates:



On certain noble metals of the platinum group, however, the so-called Volmer-Tafel mechanism applies:



In this case the second step is a chemical recombination reaction of adsorbed hydrogen atoms produced in the first step, which according to the reaction stoichiometry must proceed twice. The two mechanisms presented here and the rate-determining steps can be distinguished by measuring Tafel slopes. For a more detailed discussion of this point the reader may refer to the literature [3–6].

In corroding systems the detailed mechanisms of the partial electrode reactions are frequently not known. Therefore, it has been found useful to introduce the empirical Tafel coefficients β_a and β_c defined by

$$\beta_a = \frac{dE}{d \ln i_a} \quad (42)$$

$$\beta_c = \frac{dE}{d \ln |i_c|} \quad (43)$$

Comparing these definitions with Eqs. (30) and (31), one finds $\beta_a = RT/\alpha n F$ and $\beta_c = RT/(1 - \alpha) n F$. Equation (35) thus becomes: