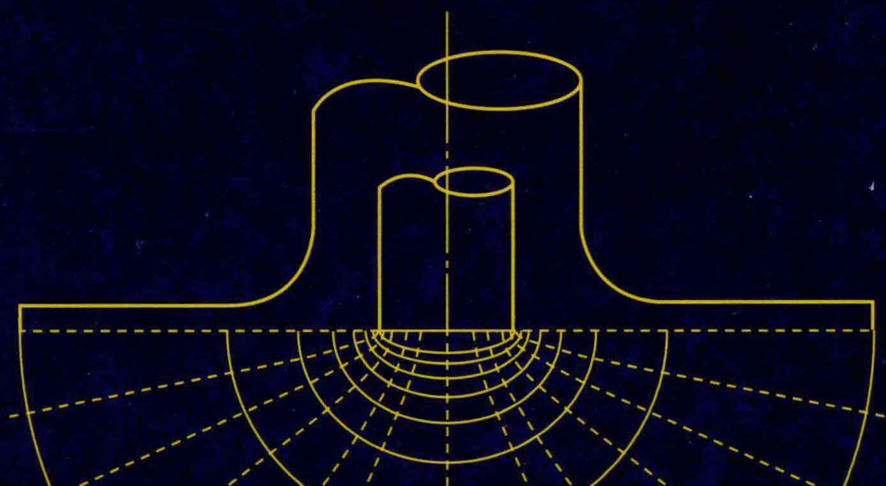
Electrochemical Systems

Third Edition



John Newman
Karen E. Thomas-Alyea

ELECTROCHEMICAL SYSTEMS

Third Edition

JOHN NEWMAN and KAREN E. THOMAS-ALYEA
University of California, Berkeley

WILEY-INTERSCIENCE

A JOHN WILEY & SONS, INC PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Newman, John S., 1938–
Electrochemical systems / John Newman and Karen E. Thomas-Alyea.— 3rd ed.
p. cm.
Includes bibliographical references and index.
ISBN 0-471-47756-7 (cloth)
1. Electrochemistry, Industrial. I. Thomas-Alyea, Karen E. II. Title.
TP255.N48 2004
660′.297—dc22

2004005207

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

PREFACE TO THE THIRD EDITION

This third edition incorporates various improvements developed over the years in teaching electrochemical engineering to both graduate and advanced undergraduate students. Chapter 1 has been entirely rewritten to include more explanations of basic concepts. Chapters 2, 7, 8, 13, 18, and 22 and Appendix C have been modified, to varying degrees, to improve clarity. Illustrative examples taken from real engineering problems have been added to Chapters 8 (kinetics of the hydrogen electrode), 18 (cathodic protection), and 22 (reaction-zone model and flow-through porous electrodes). Some concepts have been added to Chapters 2 (Pourbaix diagrams and the temperature dependence of the standard cell potential) and 13 (expanded treatment of the thermoelectric cell). The exponential growth of computational power over the past decade, which was made possible in part by advances in electrochemical technologies such as semiconductor processing and copper interconnects, has made numerical simulation of coupled nonlinear problems a routine tool of the electrochemical engineer. In realization of the importance of numerical simulation methods, their discussion in Appendix C has been expanded.

As discussed in the preface to the first edition, the science of electrochemistry is both fascinating and challenging because of the interaction among thermodynamic, kinetic, and transport effects. It is nearly impossible to discuss one concept without referring to its interaction with other concepts. We advise the reader to keep this in mind while reading the book, in order to develop facility with the basic principles as well as a more thorough understanding of the interactions and subtleties.

We have much gratitude for the many graduate students and colleagues who have worked on the examples cited and proofread chapters and for our families for their continual support. KET thanks JN for the honor of working with him on this third edition.

JOHN NEWMAN
Berkeley, California

KAREN E. THOMAS-ALYEA
Manchester, Connecticut

PREFACE TO THE SECOND EDITION

A major theme of *Electrochemical Systems* is the simultaneous treatment of many complex, interacting phenomena. The wide acceptance and overall impact of the first edition have been gratifying, and most of its features have been retained in the second edition. New chapters have been added on porous electrodes and semiconductor electrodes. In addition, over 70 new problems are based on actual course examinations.

Immediately after the introduction in Chapter 1, some may prefer to study Chapter 11 on transport in dilute solutions and Chapter 12 on concentrated solutions before entering the complexities of Chapter 2. Chapter 6 provides a less intense, less rigorous approach to the potentials of cells at open circuit. Though the subjects found in Chapters 5, 9, 10, 13, 14, and 15 may not be covered formally in a one-semester course, they provide breadth and a basis for future reference.

The concept of the electric potential is central to the understanding of the electrochemical systems. To aid in comprehension of the difference between the potential of a reference electrode immersed in the solution of interest and the electrostatic potential, the quasi-electrostatic potential, or the cavity potential—since the composition dependence is quite different—Problem 6.12 and Figure 12.1 have been added to the new edition. The reader will also benefit by the understanding of the potential as it is used in semi-conductor electrodes.

PREFACE TO THE FIRST EDITION

Electrochemistry is involved to a significant extent in the present-day industrial economy. Examples are found in primary and secondary batteries and fuel cells; in the production of chlorine, caustic soda, aluminum, and other chemicals; in electroplating, electromachining, and electrorefining; and in corrosion. In addition, electrolytic solutions are encountered in desalting water and in biology. The decreasing relative cost of electric power has stimulated a growing role for electrochemistry. The electrochemical industry in the United States amounts to 1.6 percent of all U.S. manufacturing and is about one third as large as the industrial chemicals industry.[1]

The goal of this book is to treat the behavior of electrochemical systems from a practical point of view. The approach is therefore macroscopic rather than microscopic or molecular. An encyclopedic treatment of many specific systems is, however, not attempted. Instead, the emphasis is placed on fundamentals, so as to provide a basis for the design of new systems or processes as they become economically important.

Thermodynamics, electrode kinetics, and transport phenomena are the three fundamental areas which underlie the treatment, and the attempt is made to illuminate these in the first three parts of the book. These areas are interrelated to a considerable extent, and consequently the choice of the proper sequence of material is a problem. In this circumstance, we have pursued each subject in turn, notwithstanding the necessity of calling upon material which is developed in detail only at a later point. For example, the open-circuit potentials of electrochemical

[1]G. M. Wenglowski, "An Economic Study of the Electrochemical Industry in the United States," J. O'M. Bockris, ed., *Modern Aspects of Electrochemistry*, no. 4 (London: Butterworths, 1966), pp. 251–306.

cells belong, logically and historically, with equilibrium thermodynamics, but a complete discussion requires the consideration of the effect of irreversible diffusion processes.

The fascination of electrochemical systems comes in great measure from the complex phenomena which can occur and the diverse disciplines which find application. Consequences of this complexity are the continual rediscovery of old ideas, the persistence of misconceptions among the uninitiated, and the development of involved programs to answer unanswerable or poorly conceived questions. We have tried, then, to follow a straightforward course. Although this tends to be unimaginative, it does provide a basis for effective instruction.

The treatment of these fundamental aspects is followed by a fourth part, on applications, in which thermodynamics, electrode kinetics, and transport phenomena may all enter into the determination of the behavior of electrochemical systems. These four main parts are preceded by an introductory chapter in which are discussed, mostly in a qualitative fashion, some of the pertinent factors which will come into play later in the book. These concepts are illustrated with rotating cylinders, a system which is moderately simple from the point of view of the distribution of current.

The book is directed toward seniors and graduate students in science and engineering and toward practitioners engaged in the development of electrochemical systems. A background in calculus and classical physical chemistry is assumed.

William H. Smyrl, currently of the University of Minnesota, prepared the first draft of Chapter 2, and Wa-She Wong, formerly at the General Motors Science Center, prepared the first draft of Chapter 5. The author acknowledges with gratitude the support of his research endeavors by the United States Atomic Energy Commission, through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, and subsequently by the United States Department of Energy, through the Materials Sciences Division of the Lawrence Berkeley Laboratory.

CONTENTS

PART A THERMODYNAMICS OF ELECTROCHEMICAL CELLS 27