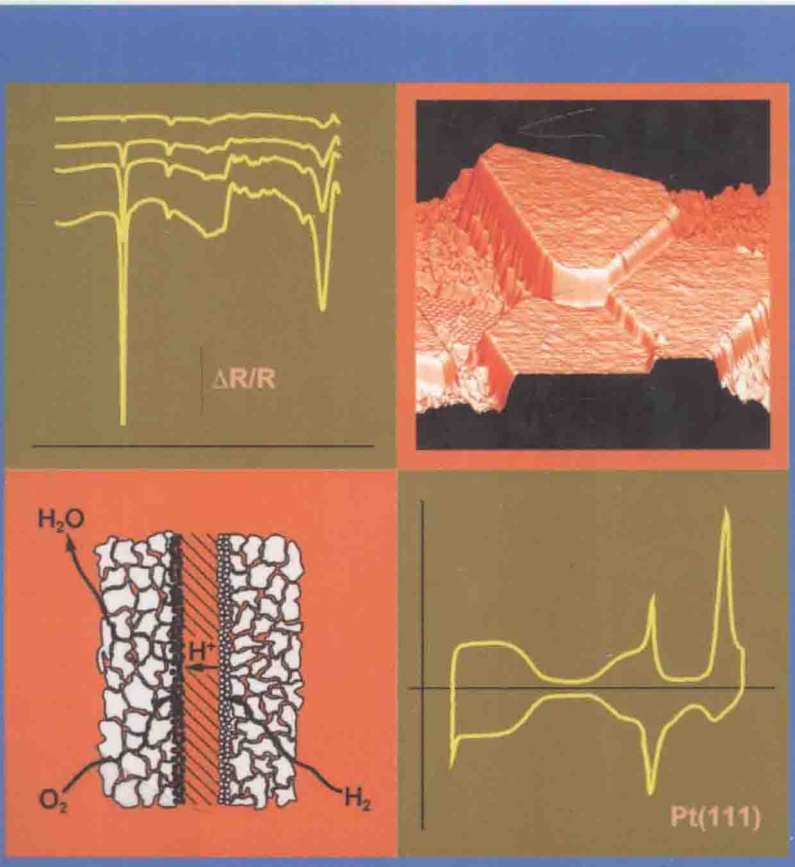
WILEY-VCH

Carl H. Hamann,
Andrew Hamnett, Wolf Vielstich

Electrochemistry



Carl H. Hamann, Andrew Hamnett,
Wolf Vielstich

Electrochemistry

WILEY-VCH

Weinheim · New York · Chichester · Brisbane · Singapore · Toronto

Prof. Dr. Carl Hamann
Fachbereich 9
Angewandte Physikalische Chemie
Carl-von-Ossietzky-Universität Oldenburg
Carl-von-Ossietzky-Straße
Postfach 2503
D-26111 Oldenburg
Germany

Prof. Dr. Andrew Hamnett
University of Newcastle
Pro-Vice-Chancellor
Bedson Building
Newcastle upon Tyne
NE1 7RU
United Kingdom

Prof. Dr. Wolf Vielstich
Fakultät für Elektrotechnik
Institut für Physik
Universität der Bundeswehr München
Werner-Heisenberg-Weg 39
D-85577 Neubiberg
Germany

Cover Illustration: top left: in situ IR spectra; top right: STM image of a semiconductor; bottom left: scheme of a PEM Fuel Cell; bottom right: cyclic voltammogram of Pt(111).

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data:
Hamann, Carl H.:
Electrochemistry / Carl H. Hamann ; Andrew Hamnett ; Wolf Vielstich. – Weinheim ; New York ; Chichester ; Brisbane ; Singapore ; Toronto : Wiley-VCH, 1998
ISBN 3-527-29096-6 (brosch.)
ISBN 3-527-29095-8 (Gb.)

Composition: Mitterweger Werksatz, D-68723 Plankstadt
Printing: Strauss Offsetdruck, D-69509 Mörlenbach
Bookbinding: Wilh. Osswald, D-67433 Neustadt
Cover design: Alicia Riviero, Harry Hoster, Universität der Bundeswehr München
Printed in the Federal Republic of Germany

Carl H. Hamann, Andrew Hamnett, Wolf Vielstich

Electrochemistry

WILEY-VCH

Further Reading from Wiley

Allen J. Bard / Larry F. Faulkner
Electrochemical Methods
Fundamentals and Applications, 2nd Edition
1998, ca. 900 pp., hardcover. Wiley. ISBN 0-471-04372-9.

Preface

Electrochemistry is a component part of physical chemistry, and plays an important role today in many areas of science and technology; examples include:

- the numerous electroanalytical processes now in widespread use;
- the use of measuring devices derived from electrochemical principles in many areas of medicine and biology, and in the control and regulation of a wide range of manufacturing processes;
- the introduction of electrochemical methods into semiconductor fabrication processes, and in particular into the preparation of nanostructures;
- the use of electrochemical processes in the manufacture and refining of many basic chemicals;
- the preparation of potable water from brine through electrodialysis;
- the production and steady improvement of batteries for use in a vast range of consumer goods.

Furthermore, it is becoming increasingly apparent that electrochemistry has the capacity to make an essential contribution to the solution of the energy and environmental problems now facing mankind, through, for example:

- the provision of traction power units for zero-emission and low-noise vehicles using fuel cells or new types of rechargeable batteries;
- the monitoring of traces of harmful emissions in production processes and potentially dangerous gases in the atmosphere through new types of electroanalytical sensors;
- the purification of aqueous waste water from both organic and inorganic impurities and the disinfection of water supplies.

It has been our intention in writing this textbook to provide as wide a coverage of electrochemistry as possible, both in terms of the basics of the subject and its applications. The book should allow all students of the subject, whether from a scientific or engineering background, to gain a working knowledge of the principles of electrochemistry. In spite of its brevity, we believe that the text, in conjunction with suitable lectures and practical classes, should provide the foundation for independent study and work in electrochemistry and facilitate access to the original literature in this area. It should also serve as a textbook to supplement courses in chemistry and engineering, and will, in addition, allow professional scientists and engineers to enter the field for the first time.

The subject-matter of electrochemistry is primarily concerned with charge transfer at the boundary between an electronically conducting or semiconducting phase and an ionically conducting phase, such as a liquid, molten or solid electrolyte. By extension, the subject has traditionally included the study of ionic equilibria and dynamic processes taking place within ionic electrolytes, particularly from the perspective of

those processes determining the concentration of electroactive species at or near the electrode surface.

The structure of this book reflects this subject matter. In Chapter 2, the focus is on the structure of electrolyte solutions, and the equilibria and transport processes in those solutions.

The main focus in Chapter 3 is on the structure of the electrode/liquid-electrolyte interface and on those electron transfer processes that are sufficiently rapid for thermodynamic equilibrium at the interface to be maintained; this chapter covers almost all aspects of traditional electrochemical statics.

Chapter 4 is central to the book: it contains an account of the relationship between current and potential at an electrode surface, and explores the consequence of this relationship in a variety of simple but important electrochemical reactions. This chapter also introduces the ideas of controlled transport of electroactive species to the electrode surface, and covers aspects of semiconductor electrochemistry. The ideas of this chapter are developed further in Chapter 5, in which the rapidly burgeoning area of fundamental mechanistic investigation of multi-step electrochemical reactions is covered in sufficient detail to allow access to more advanced texts.

The remainder of the book is devoted to aspects of applied electrochemistry. Areas covered include major improvements in electrode design and mechanistic understanding that have led to very high enhancement of efficiency in a whole variety of applied electrochemical devices including batteries, fuel cells, electro-organic and inorganic synthetic methods, and modern sensors and analytical devices for a wide variety of medical and environmental applications. These later chapters fuse together fundamental understanding and electrochemical engineering in a manner that we hope will indicate the seamless nature of modern electrochemistry and also illustrate the importance of interaction right across the subject from aspects of quantum chemistry through to the novel design of so-called "zero-gap" cells that have had so great an impact on industrial processes.

In the experimental and technical sections we have been at some pains to describe the actual processes as closely as possible within the over-riding need for clarity of presentation. We have also attempted, as far as possible, to ensure that the necessary physical or physico-chemical background is provided throughout the text, in order to make it as free-standing as we can.

After reflection, it was decided not to include problems at the end of each chapter: particularly in later chapters, such problems would frequently be little more than exercises in algebraic manipulation, and numerical problems covering the material in earlier chapters can be found in a number of published collections of problems and worked examples, such as "Calculations in Advanced Physical Chemistry", 3rd. Ed. by P.D.F. Griffiths and J.D.R. Thomas, Edward Arnold Publishers.

Certain sections of the book are marked within an asterisk: these can be omitted at a first reading, since they contain applications of material covered in more detail in later sections, but they are included for completeness.

The book is the product of a very strong collaborative effort between the three authors, all of whom would wish to acknowledge the very substantial help they have

received from friends and colleagues. In particular, considerable assistance has been received from the Newcastle Electrochemistry Group: from Dr. Paul Christensen, who has read and commented on the whole manuscript, and from Professors Arthur Covington and Keith Scott who made valuable suggestions for Chapters 3 & 8. We would also like to acknowledge the help of P. Schuff, U. Vogel, and especially M. Fabian from Sonnenschein Lithium GmbH and Ch. König from VARTA AG for new data and information on Lithium-ion and nickel/metal hydride batteries.

September 1997 C.H. Hamann, A. Hamnett, W. Vielstich

Contents