# ELECTROCHEMISTRY
# OF METALS
# AND SEMICONDUCTORS

Ashok K. Vijh

# ELECTROCHEMISTRY OF METALS AND SEMICONDUCTORS

## The Application of Solid State Science to Electrochemical Phenomena

Ashok K. Vijh
HYDRO-QUEBEC INSTITUTE OF RESEARCH
VARENNES, QUEBEC, CANADA

MARCEL DEKKER, INC., New York 1973

MARCEL DEKKER, INC.
*95 Madison Avenue, New York, New York 10016*

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 72-97479
ISBN: 0-8247-6064-6

*Printed in the United States of America*

# PREFACE

This book is an attempt to survey those areas of electrochemistry on which solid state materials science has an important bearing. The monograph, although interdisciplinary in nature, has a definite chemical orientation in that the discussion of solid state concepts is presented largely in intuitive and qualitative terms thus bringing the subject within the grasp of those electrochemists (including electroanalytical chemists) who do not have a formal training in solid state physics.

This book deals with a variety of electrode reactions deliberately focusing on the role of the solid in the kinetics of charge transfers at solid-electrolyte interfaces. The reader is presumed to have some familiarity with the general theory and common techniques of electrode processes, a matter which perhaps needs some justification. First, the theory and techniques of interfacial electrochemistry have been treated in various existing books and second, any attempt to describe adequately this large body of information in a chapter or two of the present monograph would have met with a very limited success.

It is important to mention here that a working knowledge of solid state materials science is essential, not just for "semiconductor electrochemistry" as several practicing electrochemists seem to believe. Solid state concepts are also vital for the interpretation of electrode reactions on metals, as is clear from the contents of several chapters in this book.

The literature coverage in this monograph is representative and selective rather than exhaustive. The papers, reviews, and books cited must, therefore, be regarded merely as literature entries and not as complete literature surveys of the topics discussed within various chapters.

It is hoped that the present monograph will be of some interest to investigators in the following areas: electrochemistry; physical chemistry; materials science as understood by workers originating from various conventional disciplines; corrosion science; energy science in general and fuel cells and batteries in particular; electrochemical technology as practiced in a variety of industries such as electropolishing, electromachining, electrolytic capacitors and other electrochemical devices, mineral processing and metallurgy, etc.; and some aspects of semiconductor technology. Since workers in the preceding areas deal, at least partly, with electrode processes on metals and nonmetals, the contents of the monograph should merit their attention. The book should also prove of some value to those about to commence research work in one of the foregoing areas.

Grateful acknowledgement is made to Dr. L. Boulet, the founding Director of the Hydro-Quebec Institute of Research (IREQ) for providing atmosphere, facilities, and inspiration conducive to the pursuit of scientific work. Without Dr. Boulet's active interest and encouragement, the writing of this book could not have been accomplished. The author would like to thank Dr. P. Lenfant, Manager, Electrochemistry Department, IREQ, for his cooperation, advice, and help on matters connected with the writing and development of this book. Dr. G. G. Cloutier, Director of Research, IREQ, is thanked for his kind interest in this project.

Prof. Allen J. Bard of the University of Texas at Austin and Prof. Fred Anson of the California Institute of Technology deserve many thanks for their detailed critical comments on the first draft of the book. Their concrete suggestions for the improvement of the manuscript are gratefully acknowledged. The author has also benefited from the numerous comments on various parts of the manuscript made by the following colleagues: Dr. R. S. Alwitt of the Sprague Electric Co., North Adams, Massachusetts; Dr. G. Bégin and, especially, Dr. G. Bélanger of IREQ; Dr. D. Gilroy of the Electricity Council Research Centre, Capenhurst (U.K.); Dr. W. Mindt of the F. Hoffmann-La Roche and Co., Basle (Switzerland); and Dr. J. L. Weininger of the General Electric Corporate Research and Development Laboratories, Schenectady, N. Y.

Mr. A. Bélanger of the Energy Centre of the National Institute of Scientific Research, University of Quebec helped in the preparation of indexes. Mr. R. Jacques of IREQ assisted in some procedural details. Mr. C. Désy of IREQ carried out the skillful preparation of the final version of drawings.

It is needless to mention that none of the foregoing, to whom the author owes a professional debt in a variety of ways, is responsible for any errors or shortcomings that might be found in this book.

The author's greatest and very personal gratitude, however, is due to his wife Danielle and his son Aldous. Without their understanding and patient attitude, it would have been impossible to undertake this major assignment. Their comforting presence and willingness to sacrifice many hours that in fact belonged to them were indispensable to the execution of the present project.

Ashok K. Vijh
Varennes, Quebec, Canada

# INTRODUCTION

The field of electrochemistry has undergone rapid development in the last twenty years. Touched by the development of advanced instrumentation and computer techniques as well as by the availability of theoretical treatments for electrode reaction mechanisms of great complexity, experimental methods have become available for elucidating the paths of electrode reactions, determining the thermodynamic and kinetic parameters of the reactions, and in some cases, even describing the nature of the interaction of the reactant with the electrode surface. The correlation of molecular properties, such as molecular orbital levels, electron density distributions, and Hammett functions, to electrochemical behavior has also been accomplished. The study of how the electrode material affects the reaction pathway and how correlation of solid state properties and concepts with electrochemical behavior can be used in electrochemistry is also obviously of importance and has been discussed only infrequently in the electrochemical literature.

It is this latter area, a consideration of the nature of the solid state and the application of these concepts to electrode reactions, which Dr. Vijh has addressed in this monograph. Dr. Vijh has been active in the area for several years and has drawn upon his experience as an electrochemist and his background in solid state science to produce a book which should be of interest to most electrochemists, as well as other scientists interested in corrosion, energy conversion, and semiconductors. While this field must still be considered in its infancy, many of the major electrochemical problems that await solution, such as the design of electrocatalysts for oxidation of hydrogen or hydrocarbons and perhaps even the nature of biological membranes, depend upon advances in this area. Indeed solution of what may be the major technological problem for the remainder of this century, conversion of solar or other forms of energy to electricity and the storage of this electricity, may be critically depe[illegible] our understanding of this area.

This book deserves to be widely read. It should stimulate continued research in the correlation of fundamental solid state properties to electrochemical behavior and to the design of new electrode materials and catalysts.

Allen J. Bard
Austin, Texas

# ELECTROCHEMISTRY OF METALS AND SEMICONDUCTORS

## CONTENTS

# Chapter 1

# INTRODUCTION: THE NATURE OF SOLID MATERIALS

## 1.1 INTRODUCTION

The object of the present monograph is to review those electrode processes in which an elementary knowledge of solid state materials science is helpful, even essential, for the complete understanding of electrode phenomena. Although it is realized that all electrochemistry is, in a way, a study of electrochemical behavior of materials, and hence broadly in the domain of materials science, there are some clearly distinguishable areas in which the two disciplines show a rather pronounced intermeshing, e.g., electrode reactions on semiconductors, electrochemistry of solid electrolytes, anodic oxides, electrode processes on film-covered electrodes, electrocatalysis, etc. In these and related areas, the electrochemical reactions are usually examined with particular attention to the role of the solid in processes occurring in solid-electrolyte interphases. The contents are thus concerned with electrode reactions in which the solid surface acts as more than a mere source or sink of electrons. A brief reference is also made to aspects of double-layer work that explore the influence of solid state properties on electrochemical behavior.

It will be assumed that the reader is acquainted with the fundamentals of electrode kinetics and the general techniques used in the study of electrode reactions. However, since many electrochemists (including electroanalytical chemists) are not always as familiar with solid state science, a rudimentary introduction to solid materials is presented here with an adequate list of general references to aid the more avid reader to pursue the subject further.

## 1.2 THE SOLID STATE

Solid state science is concerned with the nature and properties of all types of solid materials. The field thus deals with structure and behavior of a very large variety of substances, e.g., metals, elemental semiconductors like Ge and Si, compound semiconductors and insulators, amorphous and glassy states, and several composite materials of both inorganic and organic origin, some of which (wood, polymers, ceramics, etc...) are frequently encountered in everyday life.

There are virtually countless ways in which atoms can combine among themselves (or be made to combine) to give rise to myriad substances of diverse composition and different types of bonding. In fact, solids may be conveniently classified on the basis of the bonding involved. In chemical compounds formed between atoms which have widely different electronegativity values, such as alkali halides, the nature of bonding is predominantly ionic. A solid of this type, e.g., NaCl, is essentially made up of positive and negative ions which are held together by electrostatic forces. In certain other materials, Ge for example, the constitutent atoms are held together by means of a bond formed by equal sharing of two electrons, one contributed by each of the bound Ge atoms; this type of bond is termed a covalent or homopolar bond. In many of the inorganic materials of practical interest here, e.g., minerals, refractories, ceramics, etc..., the bonding between the constituent atoms is partially ionic and partially covalent so that pure ionic and pure covalent bonds are idealizations seldom present in actual practice. In molecular crystals, e.g., anthracene, the molecules are held together by a type of weak attractive interaction called van der Waals or London forces. These forces are very similar to those involved in the physical adsorption of gases on metals.

In some other solids involving hydrogen atoms, e.g., ice or wood, a type of bond stronger than the van der Waals cohesive force, called a hydrogen bond, is involved. It is usually regarded as an intermediate between the ionic and the covalent bond concerning its electrostatic nature. The strength of its binding, however, is usually smaller in magnitude than that in either the covalent or the ionic bond. The study of the hydrogen bond is of great significance in elucidating the nature of phenomena involved in some organic solids, especially those of biological interest.

In a metal the lattice is usually regarded as consisting of metal ions (i.e., atoms minus one or more electrons) arranged in a certain regular crystalline structure, surrounded by a pervasive electron gas which travels unimpeded through the lattice around the ions and binds them together. The presence of this freely moving electron gas is responsible for high electrical conductivity and other characteristic properties of metals.

In several solids, such as the amorphous materials and a variety of glasses, the nature of bonding is somewhat ill-defined. They are characterized by a range of melting temperatures (instead of a sharp melting point) which reflects the presence of several types of bonds with somewhat different bond energies, bond lengths, and other related parameters.

Solids also exhibit a wide range of electrical resistivities. Compare the low resistivities of some metals ($\simeq 10^{-6}$ ohm-cm) with the enormously high resistivities ($\simeq 10^{16}$ ohm-cm) of certain insulators. The resistivities of semiconducting materials fall between the two.

In the following sections, those aspects of solid state science which are believed to be of interest to the electrochemist will be described. Introductory [1-8], moderately advanced [9-13], and some highly advanced [14-16] accounts of the solid state science are available in the literature.

## 1.3 BAND THEORY OF SOLIDS

In order to explain the origin and nature of electrical conductivity in solids, a knowledge of band theory of solids is essential; a rudimentary and qualitative description of this theory is presented below.

In the band model of solids, the basic underlying concept is the Pauli exclusion principle. This principle states that a given quantum state may not be occupied by more than two electrons (with opposite spins). The shell structures of the atoms (isolated) of the periodic table of elements, of course, are derived on the basis of this principle. The successive shells of an atom are occupied in such a way that the lowest available levels are filled before the higher ones.

Analogous to the shells of an atom are the bands in a solid. The electrons moving through the crystal of a solid possess energies which fall within bands, the latter being derived from the shells of the atoms constituting the crystal. Within the energy band of a solid, there are many permissible levels so closely spaced energetically, that very little energy is expended in exciting an electron from one of these levels to another. For all practical purposes, the energy band, notwithstanding the various levels within it, corresponds roughly to one energy level which usually extends over a fraction of an electron volt. The bands are separated from each other by zones or gaps forbidden to the "intrinsic" electrons, i.e., electrons not originating from an impurity in the solid. The energy band of a solid is thus equivalent to an energy level in an isolated atom. It is clear that the band of a solid will be densely filled with energy levels of the constituent atoms since a solid crystal would be expected to have $10^{20}$ or more atoms per cubic centimeter.

In the case of metals, the uppermost band is only partially populated by electrons. Hence application of even a small field can easily excite some of the electrons to the closely-spaced next higher levels within this band. The electrons thus excited move in the direction of the applied field instead of drifting randomly. In a pure nonmetal, i.e., a semiconductor or an insulator, the uppermost or "conduction" band is empty, whereas all others below it are completely occupied. The uppermost of these completely filled bands is called the valence band. The filled valence band is separated from the empty conduction band by a forbidden region called the band gap. For these nonmetals to conduct, an electron must be made to jump, across the band gap, from the valence band to the conduction band by an external application of energy, e.g., heat or light. For semiconductors, the magnitude of the forbidden gap is small whereas for insulators it has a rather large value (Fig. 1).

In pure semiconductors, when heat or light of suitable intensity is applied, an electron jumps from the valence band to the conduction band, crossing the energy gap. When an electron thus leaves the valence band, it leaves behind a "hole" at the vacated site and both the electron (in the conduction band) and the hole (in the valence band) become the mobile electrical carriers. A hole effectively behaves like a positively charged particle and under the influence of the applied field, it moves in a direction opposite to that of an electron. A semiconducting material in which the electrons and holes originate not from an impurity but from the material itself is called an