MATERIALS SCIENCE SERIES

INTERCALATION CHEMISTRY

EDITED BY
M. STANLEY WHITTINGHAM
ALLAN J. JACOBSON

Intercalation Chemistry

Edited by

M. Stanley Whittingham

Technology Department
Exxon Research and Engineering Company
Florham Park, New Jersey

Allan J. Jacobson

Corporate Research
Exxon Research and Engineering Company
Linden, New Jersey

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List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

G. Alberti (147), Department of Chemistry, University of Perugia, 06100 Perugia, Italy
J. S. Anderson[1] (503), University College of Wales, Aberystwyth, Dyfed, Wales
Neil Bartlett (19), Department of Chemistry, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
K. H. J. Buschow (405), Philips Research Laboratories, Eindhoven, The Netherlands
John D. Corbett (361), Ames Laboratory-DOE, Department of Chemistry, Iowa State University, Ames, Iowa 50011
U. Costantino (147), Department of Chemistry, University of Perugia, 06100 Perugia, Italy
E. G. Derouane (101), Laboratoire de Catalyse, Facultés Universitaires de Namur, B-5000-Namur, Belgium
F. J. Di Salvo (573), Bell Laboratories, Murray Hill, New Jersey 07974
P. G. Dickens (539), Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, England
Thomas R. Halbert (375), Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036
Tjipke Hibma (285), Brown Boveri Research Center, CH-5405 Baden-Dättwil, Switzerland
Allan J. Jacobson (229), Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036
Jack W. Johnson (267), Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036
Robert L. Jones (445), Department of Chemistry, Laboratory for Microbial and Biochemical Sciences, Georgia State University, Atlanta, Georgia 30303

[1] Present address: Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia

B. W. McQuillan[2] (19), Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
D. W. Murphy (563), Bell Laboratories, Murray Hill, New Jersey 07974
M. F. Pye (539), Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, England
R. Schöllhorn (315), Anorganisch-Chemisches Institut der Universität, 4400 Münster, West Germany
J. M. Thomas (55), Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, England
A. H. Thompson[3] (573), Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036
B. C. Tofield (181), Materials Development Division, A. E. R. E. Harwell, Didcot, Oxon, OX11 ORA, England
M. Stanley Whittingham (1), Exxon Research and Engineering Company, Technology Department, Florham Park, New Jersey 07932
W. David Wilson (445), Department of Chemistry, Laboratory for Microbial and Biochemical Sciences, Georgia State University, Atlanta, Georgia 30303
H. H. van Mal[4] (405), Philips Research Laboratories, Eindhoven, The Netherlands

[2] Present address: Instituto Technologico de Tijuana, Tijuana, BC Mexico.
[3] Present address: Exxon Production Research Company, Houston, Texas 77001
[4] Present address: University of Technology, Eindhoven, 560 MB Eindhoven, The Netherlands.

Preface

The study of reactions between guest molecules or ions and solid host lattices, which retain the major features of their structures, has continued since 1841 when Schauffautl first reported the intercalation of graphite by sulfate ions. However, it was not until the 1960s that interest in intercalation chemistry began to grow significantly and to extend into many scientific disciplines. Although the term intercalation has been used widely to describe reactions of guests with layered host lattices, many other reactions have characteristics in common. We decided to draw together in this volume a number of these related areas in which host lattices maintain some essential structural features during the reaction. The volume therefore aims to introduce the specialist reader to the breadth of intercalation chemistry and the newcomer to the diverse research opportunities and challenges available in synthetic and reaction chemistry and also in the controlled modification of physical properties.

After an introductory paper, the next chapter describes the intercalation chemistry of graphite. Graphite is perhaps the simplest host lattice structure but shows varied chemistry due to its ability to react with both oxidants and reductants and to incorporate neutral molecules. Its chemistry is further complicated by staging, which is more prevalent than in any other layered system. The second group of materials described are complex oxides with both two(clays and acid phosphates)- and three(zeolites)-dimensional structures. These systems are currently of considerable interest, because of technological applications in heterogeneous catalysis, as sorbents and inorganic ion exchangers. Their chemistry is dominated primarily by the intercalation of neutral molecules and by ion exchange rather than by the redox chemistry observed in both graphite and the layered chalcogenides. The β-aluminas (Chapter 6) have been mostly studied for applications as solid ion conductors in electrochemical cells, but much of their chemistry is analogous to that of the clays, though

limited to small molecules and ions by the fixed interlayer separation imposed by the bridging oxygen.

Four chapters describe the intercalation chemistry of layered chalcogenides and halides with simple and hydrated cations and organic and organometallic ions. The reactions are mainly characterized by reduction of the host lattice; unlike graphite, no host oxidations accompanied by anion insertions have been observed, though attempts have been made to intercalate electron-accepting molecules, such as TCNQ, into the filled d-band group-VI dichalcogenides, for example, MoS_2. Once formed, these intercalation compounds show ion-exchange behavior that is similar to clays. In the redox systems, however, the ion-exchange capacity is set by the degree of host reduction, whereas in clay and zeolite chemistry, it is determined by cation substitution, e.g., Si for Al, in zeolites.

The next two chapters discuss areas that are not normally considered by the inorganic chemist. The first of these is concerned with the chemistry, thermodynamics, and applications of intermetallic compounds that incorporate hydrogen. The reader will observe many similarities and differences in behavior when compared with lithium intercalation in the dichalcogenides and oxides. Chapter 14 discusses intercalation in the context of biological systems and shows how the intercalation model was developed for the interaction of molecules with DNA. Crystallographic shear structures (Chapter 15) are not usually considered as related to intercalation compounds. However, there are important similarities, particularly in the way in which the structure imposes constraints on reactions. Reduction reactions, for example, leave the main part of the crystal lattice unperturbed and are accommodated by rearrangements of small numbers of atoms on specific sites. In the following two chapters, intercalation reactions of oxides and chalcogenides of vanadium, molybdenum, and tungsten are described. The final chapter touches on the physical properties of some intercalation compounds of the dichalcogenides.

In collecting these contributions, we have not attempted to cover all the aspects of intercalation chemistry, nor to describe, in any detail, their technological applications. Rather, we have concentrated on the chemistry and structural principles of a wide range of systems. It is our hope thereby to stimulate wider interactions among researchers in the various materials science disciplines.

M. Stanley Whittingham
Allan J. Jacobson

MATERIALS SCIENCE AND TECHNOLOGY

EDITORS

A. S. NOWICK
Henry Krumb School of Mines
Columbia University
New York, New York

G.G. LIBOWITZ
Solid State Chemistry Department
Materials Research Center
Allied Corporation
Morristown, New Jersey

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D. W. MURPHY