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Preface

The field of solid state ionics is multidisciplinary in nature. Chemists, physicists, electrochimists, and engineers all are involved in the research and development of materials, techniques, and theoretical approaches. This science is one of the great triumphs of the second part of the 20th century. For nearly a century, development of materials for solid-state ionic technology has been restricted. During the last two decades there have been remarkable advances: more materials were discovered, modern technologies were used for characterization and optimization of ionic conduction in solids, trial and error approaches were deserted for defined predictions. During the same period fundamental theories for ion conduction in solids appeared.

The large explosion of solid-state ionic material science may be considered to be due to two other influences. The first aspect is related to economy and connected with energy production, storage, and utilization. There are basic problems in industrialized countries from the economical, environmental, political, and technological points of view. The possibility of storing a large amount of utilizable energy in a comparatively small volume would make a number of non-conventional intermittent energy sources of practical convenience and cost. The second aspect is related to huge increase in international relationships between researchers and exchanges of results make considerable progress between scientists; one find many institutes joined in common search programs such as the material science networks organized by EEC in the European countries.

Moreover, one of the most intriguing perspectives for application of the recently discovered solid-state ionic materials is represented by the development of either inexpensive high-power-density secondary batteries or rechargeable microbatteries. The former systems would also have a highly positive environmental impact through the replacement of gasoline engines with electric motors, which would dramatically reduce atmospheric pollution, acid rains, and background noise. Immediate examples are given by the USABC project in the USA and the LIBES project in Japan. The objectives of microbattery research are to combine the technologies of solid-state ionics and electronics. A solid-state microbattery deposited on the same chip carrier can provide memory backup power. It can also be used as power supply in sensors and biomedical implantable devices. One of the best examples is the lithium-iodide battery which has been successfully used during the past decade in cardiac pacemakers.

Although experimental and theoretical results on solid-state ionic materials have appeared extensively in the original scientific literature and in research monographs, there does not exist at the present time, to our knowledge, a reference work in which a wide variety of chemical, physical, and electrochemical properties of these materials are treated in a unified manner emphasizing the ionic conduction aspects in electrolytes and electrodes. In this situation, there is a need for a broad introductory text for the use of students and research workers. It is this void that we attemped to fill by writing this volume. Our objective is to illustrate how detailed information on the actual behavior of ionic solids can be extracted for the design of microbatteries, taking into consideration the different properties that are involved in such devices.

This volume therefore aims to introduce the reader to the breadth of solid-state ionics, i.e., electrolytes and electrodes, which are the electrochemically active components in microbatteries, and the newcomer to the various research opportunities and challenge available in this branch of the material science.

The general plan which we have adopted is the following. The fundamental concepts in solid-state ionics involving ion and electron motions in a specific medium are developed in detail with the main goal to design and optimize materials used for microbatteries. We rationalized our choice of subject material in the following way. As it is indicated by the foregoing summary, we restricted ourselves to those materials which are concerned with lithium-ion conduction because lithium is the highest electroactive and the lowest dense metal and lithium contained systems are considered as the most promising materials for advanced batteries. Electrolyte and electrode materials are considered in the crystalline and amorphous states. Thin-film materials are also presented.

We have not hesitated to include some basic considerations on the electrochemical systems; we hope that this part will be useful to graduate scientists and those who have newly joined the solid-state ionic field. Some sections will be also helpful to technical assistants regularly undertaking measurements of solid-state ionic properties, and many parts of the text should be helpful to final-year undergraduates following a specialist course or undertaking a project. While prior knowledge of the concept of solid-state ionic technology is desirable for the use of this book, the mathematical treatment we use is elementary.

The order of presentation is as follows. In the introductory chapter, we describe the theoretical background of the basic processes involved in cell operation, and in some detail the electrochemical insertion process of intercalant species in host structures is given. Different theoretical models for ion transport are presented. The second part of chapter 1 is devoted to quality criteria for thin-film materials; the transport limitations are analyzed in both electrode and electrolyte thin-films. This is followed by four chapters on solid electrolyte phases, i.e., crystalline, vitreous, or amorphous, thin-films and plastic or polymeric materials. In chapter 2, the basic definitions and phenomenological analysis of conduction in crystalline phase are presented. A simplified overview of the theoretical models normally used in the study of transport phenomena in solid electrolytes is given with emphasis to the discrete and continuous models. Thus, the different classes of solid electrolytes are treated: anionic and cationic fast-ion conductors. Fluorine, oxygen, alkali, silver, and copper ion conductors are presented with their theoretical understanding. Composite electrolytes are also examined here. Amorphous electrolytes are introduced in chapter 3, where silver, sodium, and lithium fast-ion conducting glasses are presented.

Structure-composition relations are examined and special attention is given to cationic-conducting materials that are lithium-ion conducting glasses, which are the most promising materials for microbatteries. The different models for conduction in glasses, which are the strong-electrolyte, the weak-electrolyte, and the decoupling approaches, are briefly presented at the beginning of this chapter. Chapter 4 covers the description of various fast-ion conducting materials grown by thin-film technologies. The fabrication and electrical properties of thin-films of fast-ionic conducting lithium-borate glasses are reviewed. In chapter 5, there is a survey on polymeric electrolytes. Our aim is to present a brief informative overview on these materials, and provide some keynotes and references that may be useful for further bibliographic researches. The final three chapters are devoted to cathode materials and applications. Chapter 6, where the crystalline cathode materials are treated is organized as follows: after a short introduction describing the different classes of cathodes, the structural, physical, and electrochemical properties of inorganic chalcogenides and oxides are largely described. Properties of transition metal dichalcogenides, non-transition metal chalcogenides, composite electrodes, and high-voltage cathodes are widely treated. The aim of chapter 7 is to report the properties of amorphous cathode active compounds. The material parameters of different classes of cathodes are reviewed and comparison, with crystalline phases are indicated as far as possible. The properties of cathodic glasses and a description of different mechanisms of conduction involved in them are given. There is an attempt to summarize the literature survey on thin-film cathode materials. Much attention is given to the transition metal dichalcogenide and non-transition metal chalcogenide thin-films. Some applications of solid-state ionic materials are presented in the final chapter. Various designs of working devices are outlined with the emphasis on all solid-state configurations. Lithium metal-free rechargeable batteries, also called rocking-chair batteries, and recently developed microbatteries are treated.

It is with great pleasure that we express our thanks to Professor Harry Tuller, who provided encouragements and had given us the opportunity to contribute, under his direction, in the series Electronic Materials: Science and Technology. We are indebted to friends who have read and commented on some sections of the manuscript. Our special thanks go to Dr. H.S. Mavi for his important help in the manuscript preparation, running the literature search. One of us (C.J) would like to acknowledge his graduate students I. Samaras, S.I. Saikh, P. Dzwonkowski, A. Khelfa, and N. Benramdane, who spent long hours practicing the art of solid-state ionics. We wish to acknowledge Mr. Amar for help on many phases of the production of the manuscript. Effort has been made to trace the owners of copyright material in a few cases this has proved impossible and we take this opportunity to offer our apologies to any copyright holders whose rights we may have unwittingly infringed. Last, but not least, we are grateful to our respective spouses, Dominique and Pari, for their patience in putting up with rather unsociable authors during the time that it has taken to write this book.

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