WSPC — COSTED SERIES IN EMERGING TECHNOLOGY

Proceedings of the International Seminar

SOLID STATE IONIC DEVICES

18-23 July 1988, Singapore

Editors
B V R CHOWDARI
S RADHAKRISHNA


World Scientific
Singapore • New Jersey • Hong Kong

COMMITTEE ON SCIENCE & TECHNOLOGY
IN DEVELOPING COUNTRIES

WSPC — COSTED SERIES IN EMERGING TECHNOLOGY

Proceedings of the International Seminar

SOLID STATE IONIC DEVICES

18-23 July 1988, Singapore

Editors

B V R CHOWDARI
National University of Singapore

S RADHAKRISHNA
Indian Institute of Technology, Madras

ASIAN SOCIETY FOR
SOLID STATE IONICS

World Scientific
Singapore • New Jersey • Hong Kong

COMMITTEE ON SCIENCE & TECHNOLOGY
IN DEVELOPING COUNTRIES

Published by

World Scientific Publishing Co. Pte. Ltd.
P. O. Box 128, Farrer Road, Singapore 9128

U. S. A. office: World Scientific Publishing Co., Inc.
687 Hartwell Street, Teaneck NJ 07666, USA

SOLID STATE IONIC DEVICES

ISBN 9971-50-626-2

Printed in Singapore by Utopia Press.

ORGANIZERS

ASIAN SOCIETY FOR
SOLID STATE IONICS

THE DEPARTMENT OF PHYSICS
NATIONAL UNIVERSITY OF SINGAPORE

THE COMMITTEE ON SCIENCE AND TECHNOLOGY
IN DEVELOPING COUNTRIES (COSTED)

INTERNATIONAL ADVISORY COMMITTEE

S. Chandra	India
L. Chen	China
B. V. R. Chowdari	Singapore
P. Hagenmuller	France
S. Radhakrishna	India
Y. Saito	Japan
T. Takahashi	Japan

LOCAL ORGANIZING COMMITTEE

Chairman	:	Y. K. Lim
Co-Chairman	:	B. V. R. Chowdari
Members	:	M. F. Chung
		P. P. Ong
		K. K. Phua
		K. L. Tan
		S. H. Tang

SPONSORS AND SUPPORTERS

Asian Society for Solid State Ionics
Chubu Electric Power Company, Japan
COSTED
Hitachi Central Research Lab., Japan
Institute of Physics, Singapore
Kansai Electric Power Company, Japan
Lee Foundation, Singapore
Matsushita Electric Company, Japan
National University of Singapore
NGK Spark Plug Company, Japan
Osaka Gas Company, Japan
Sanyo Electric Company, Japan
Shell Companies, Singapore
Singapore Turf Club, Singapore
Third World Academy of Sciences
Toa Nenryo Kogyo K.K., Japan
Tokyo Electric Power Company, Japan
Tokyo Gas Company, Japan
Toyota Motor Corporation, Japan
UNESCO
Yuasa Battery Company, Japan

PREFACE

The large number of scientists that have attended the 6th International Conference on Solid State Ionics held at Garmisch-Partenkirchen and the founding of the International Society for Solid State Ionics during that Conference attest to the continued growth of interest in Solid State Ionics. The fundamental goal of all the studies on Solid State Ionics has always been the development of devices based on ionic transport in solids which may be referred to as Solid State Ionic Devices.

A number of Regional/International Conferences, Seminars, Workshops and Advanced Study Institutes have been organised all over the world to discuss either the fundamentals of Solid State Ionic Materials or the development of a specific Solid State Ionic Device. There appears to have been no Seminar/Conference where almost all the Solid State Ionic Devices are discussed together in a single forum. In this context the present International Seminar on Solid State Ionic Devices may stand unique. It is being organised by the Asian Society for Solid State Ionics (ASSSIS) which was founded in Singapore during the Regional Workshop on Materials for Solid State Batteries, 2 - 6 June 1986, the Department of Physics of the National University of Singapore and the Committee on Science and Technology in Developing Countries (COSTED).

With the participation of about 100 scientists from 18 countries, the Proceedings consists of 33 state-of-the-art reviews and 22 short contributions. A few review articles could not be included in the Proceedings as they did not reach us in time. Emphasis has been placed on the physics, chemistry and technology of the following Solid State Ionic Devices:

* Solid state batteries
* Electrochemical sensors
* Fuel cells
* Electrochromic displays.

Fundamental aspects of these devices, their characterization and utility are being highlighted. The scope of the topics ranges from theoretical considerations of ion transport mechanism to the pragmatic realities of actual applications.

Several international organisations such as UNESCO and Third World Academy of Sciences and many Japanese industries have sponsored/supported this Seminar. Some local organisations including Singapore Turf Club, Lee Foundation, Shell Companies and Institute of Physics, Singapore have also generously supported this Seminar. The financial and organisational support received from all the national and international organisations are gratefully acknowledged.

The unique roles played by Prof T Takahashi and Japan Society for Solid State Ionics in supporting this Seminar in particular and the activities of ASSSIS in general are gratefully acknowledged.

The whole-hearted support received from Professor H H Huang, Deputy Vice-Chancellor, Professor Bernard Tan, Dean of Faculty of Science and Prof Y K Lim, Head of the Department of Physics in organizing this Seminar is placed on record with deep gratitude. The hard work of all those who served on the Local Organizing Committee and the International Advisory Committee and the secretarial assistance received from Mrs Pereira and her colleagues are greatly appreciated.

B V R Chowdari
S Radhakrishna

25th June 1988

CONTENTS

II. SHORT CONTRIBUTIONS

I. INVITED PAPERS

THEORETICAL MODELS FOR FAST ION TRANSPORT IN SOLIDS

D. Brinkmann

Physik-Institut, University of Zurich, Zurich, Switzerland

After a brief overview of different solid electrolyte systems several models and theories are discussed which are concerned with the explanation of the high conductivity and diffusion in solid electrolytes. These concepts comprise independent-particle models (single-particle hopping and continuouis diffusion) and many-body models: lattice gas models, density functional approach, liquid-like models, hydrodynamic description, molecular dynamics simulation and models for highly disordered systems (e.g. percolation models).

1. INTRODUCTION

Having reviewed in Lecture 1 several experimental methods used for the study of fast ion transport in solids we now turn to a discussion of theoretical models which have been constructed to explain the phenomena in these solids. Because fast ion conduction takers place in such a variety of substances as crystals, glasses and polymers there does not exist an unique theory applicable to all solid electrolytes. Many theories and models have been made differing by their approach and having different degree of sophistication. For recent and excellent reviews of the theoretical aspects of fast ion conduction we refer to the papers of Dieterich [1] and of Ratner and Nitzan [2], some older reviews are also recommended [3]-[7].

The ultimate goal of a theory is, of course, to calculate material properties in a quantitative and predictive way from microscopic parameters. However, most theories are concerned with conduction and diffusion. We will restrict ourselves to a discussion of these parameters. To facilitate this we start with a short overview of the various classes of solid electrolytes. The remaining sections then will deal with the various models.

2. BRIEF OVERVIEW OF SOLID ELECTROLYTE SYSTEMS

Since the beginning of studies in solid electrolytes several schemes of classification have been used, for instance with respect to the type of defects or disorder present in the material. For the purpose of discussion of theoretical models we use the division into two groups [2]: framework crystalline and highly disordered materials. As the name implies the framework materials consist of a

crystalline skeleton which is more or less rigid and the mobile ions. This group can be subdivided into hard and soft framework crystals. Representatives of the latter crystals are, e.g., AgI, CuI, Ag_2HgI_4. The soft crystals are probably better understood than any other solid electrolyte.

Fig. 1 shows the unit cell of cubic α-AgI as determined by neutron diffraction [8]. The mobile Ag ions are disordered over the available sites because the sites are only partially occupied. The sublattice of the immobile ions exhibits crystalline order. The density profile (taken at 160 °C) for a cube face showed the interesting fact of a

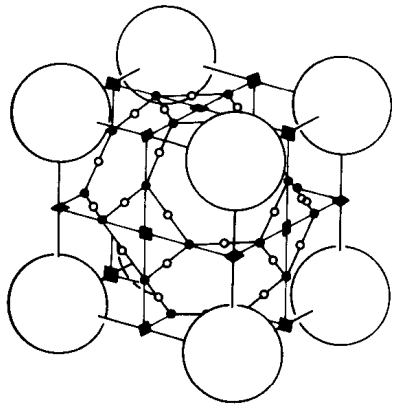

Fig. 1 Unit cell of cubic α-AgI.

continuous density between the tetrahedral sites 1/4,0,1/2 which are the equilibrium sites. Thus pathways exists for the migration of Ag ions. The soft framework crystals are characterized as follows: (i) the bonding is largely ionic; (ii) the mobile ions are, generally, polarizable and heavy (Ag, Cu); (iii) the Debye temperatures are low; (iv) a sharp order-disorder phase transition exists between the low and high conducting phase (147 °C for AgI) accompanied by a large increase of the enthalpy and the Raman linewidth.

The hard framework crystals are usually oxides (e.g. ß-alumina, $LiAlSiO_4$, hollandite) and they are characterized by covalent bonds and consequently high frequencies for local vibrations, high Debye temperatures, low polarizability of the mobile ions, and they generally do not exhibit the ß ⇔ α phase transition. As an example, Fig.2 shows schematicly the hexagonal structure of ß-alumina which has the nominal composition $Na_2O * 11\ Al_2O_3$. The spinel blocks $Al_{11}O_{16}$ are aligned along the c axis and are separated by the conduction plane containing O and the mobile Na which can be positioned in three sites called