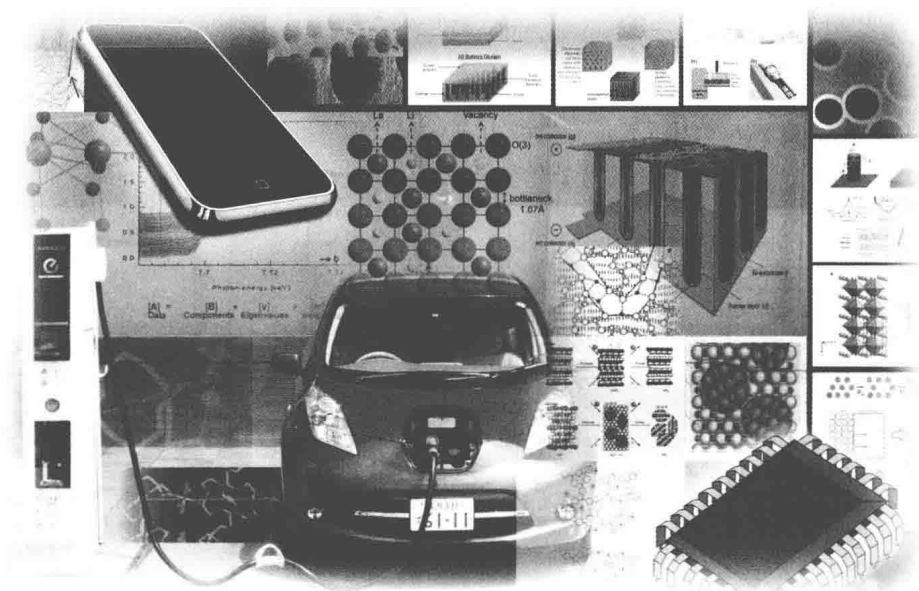


MATERIALS AND ENERGY – Vol. 6

HANDBOOK OF SOLID STATE BATTERIES

Second Edition

Nancy J Dudney
William C West
Jagjit Nanda



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Preface

Solid-state batteries hold the promise of providing energy storage with high specific energy and high power density, yet with far less safety and temperature stability issues relative to those associated with conventional liquid or gel-based lithium-ion batteries. Solid-state batteries are envisioned to be useful for a vast range of energy storage applications, from powering automobiles, stationary storage and load-leveling of renewably generated energy, and powering the wide range of electronics that have become so pervasive in our lives.

Tantalizing evidence of the promise of solid-state battery technology can be found in solid-state thin film batteries which are now commercially produced for specialized low energy applications. These solid-state batteries are capable of tens of thousands of deep discharge cycles at useful charge and discharge rates. The components are highly stable, with no appreciable electrolyte side reactions or electrode dissolution. These cells often incorporate very high specific energy lithium metal anodes resulting in high active-mass basis specific energy.

Since the last edition of this book, significant strides in the field of solid-state batteries have been achieved. In this second edition of this book, we have brought together many subject-matter experts

in the field of solid-state batteries, covering a wide range of topics. Herein, the authors summarize advancements in:

- Very high ionic conductivity sulfide- and oxide-based solid electrolytes with ionic conductivity nearly on-par with liquid lithium-ion electrolytes
- New solid electrolytes for thin film batteries prepared by a number of different techniques
- Adaptation of powerful characterization tools including synchrotron based *in-operando* methods for studies of solid-state batteries
- In-depth characterization and modeling of the nature of the critical solid electrolyte-electrode interface
- Development of advanced *in-situ* and *in-operando* electron microscopy methods
- Incorporation of solid-state batteries into multi-functional and structural components
- Advanced *ab initio* modeling capabilities to predict structure and performance of solid electrolytes and solid-state batteries
- New cell designs incorporating three-dimensional structures
- New solid electrolytes for conduction of lithium, fluoride, and silver ions
- Advanced polymer electrolytes with a wide range of compositions, structural motifs, and additives for improved ionic conductivity and mechanical stability

Yet many scientific and technological challenges remain. Many research activities focus on the ionic transport and electrochemical reactions of a single material, yet the challenge for devices hinge on the stability and unimpeded motion of ions across interfaces between the electrode-electrolyte and in some cases between multiple electrolytes. Cell designs utilizing thick, energy dense electrodes with a relatively small electrolyte contact area will be particularly challenging due to the high current density. The community also needs to investigate and provide avenues for practical industrial processing and mass production.

While a commercially viable solid-state battery competitive with conventional lithium-ion batteries has yet to be fully realized, we anticipate further advancements that will soon bring this exciting new technology to fruition.

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14 June 2015

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Part 1

**Enabling Techniques
and Fundamentals
of Solid State Systems**

Chapter 1

Fundamental Aspects of Ion Transport In Solid Electrolytes

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1. Introduction

Solid electrolytes (also termed as superionic solids or fast ion conductors) are characterized by high ionic conductivity, sometimes comparable to concentrated liquid electrolytes or even molten salt electrolytes, made possible by rapid transport of ions in the solid lattice. The electronic conductivity is small with an electron transfer number (t_e) of less than 10^{-4} . A semi-empirical rule formulated by Heyne¹ stipulates the allowable values for the electronic band-gap in good solid electrolytes to be higher than $T/300$ eV, i.e. a low electronic conductivity of 10^{-6} S/cm at any temperature — a necessary but not sufficient condition. Such superionic solids

paved the way for the development of solid-state electrochemistry or solid-state ionics and also furthered progress in related technologies such as galvanic cells (batteries), fuel cells, capacitors, electrochromic devices and sensors.

The conductivity of superionic solids (e.g. RbAg_4I_5 — 0.27 S/cm at room temperature) is typically many orders of magnitude higher than that of commonly known ionic solids, (e.g. NaCl , KCl — 10^{-16} S/cm). Many ionic solids exhibit such high electrical conductivity above a certain temperature, often associated with distinct structural change (e.g. AgI). Furthermore, structures that permit rapid ion transport are generally disordered, channeled, or layered.²

Microscopically, the ionic conductivity in solids is caused by the existence of defects or disorder. A perfect crystal of an ionic compound would be an insulator.³ Based on the types of defects or disorder, the superionic solids can be classified as follows:

Point defect (zero dimensional) type: Here, the concentration of the point defects is in the order of 10^{20} cm^{-3} .

Molten-sub-lattice type: a case of liquid-like sub-lattice, in which the number of ions of a particular type is less than the number of sites available for them. The number of mobile ionic charge carriers is 10^{22} cm^{-3} . These materials are often marked by a channeled or layered structure or amorphous liquid-like regions as in polymeric materials.

Despite the fact that cations as well as anions can move in the solid lattice, mobility of cations is generally favored due to their small ionic size. Many of the known superionic solids are cationic conductors and especially of small size, e.g. Li^+ , Na^+ , K^+ . Also many of the solid electrolytes involve a monovalent ion, owing to the relatively strong coulombic interactions between divalent or trivalent ions within the lattice. A rigorous correlation between the ionic conduction and the structural aspects of the solid electrolytes has been reported.^{2,4-6} Anion conduction is represented largely by oxide ion conductors as in defect oxides with the perovskite structure⁷ and fluoride ion conduction occurs in doped-lanthanum fluoride.⁸⁻¹¹ Ion conduction is encountered in solid polymeric electrolytes in the