Preface

Lithium-ion (Li-ion) batteries were first introduced into the marketplace by Sony in 1991 to power a video camera. Since then, Li-ion batteries have become part of our daily lives—powering a wide range of mobile electronic devices and power tools. The electrolyte is a key component of a Li-ion battery. Current electrolytes are the result of many years of research and development and play a key role in providing good performance for applications. New and more challenging battery requirements for power tools, hybrid electric vehicles, plug-in electric vehicles, and stand-by power sources for communications and modern airplanes require a significant advance in battery chemistry. The batteries needed are often of higher voltages and higher energy content. Furthermore, they will be exposed to extremes of temperature with the necessity of still providing long cycle and storage life and assured user safety. A new class of electrolytes is needed to meet these demands. The new electrolytes must not only provide good ionic conduction over a wide range of ambient temperatures but also provide good chemical stability and compatibility with the more reactive electrode materials that are required to achieve higher battery-specific energy and power. With the demand for higher energy density Li-ion batteries, recent development trends favor the use of higher voltage cathodes such as 4.7 V for $LiNi_{0.5}Mn_{1.5}O_4$ and 4.8 V $LiCoPO_4$, higher capacity cathodes such as layer–layer composite and layer–spinel composite made of $Li[Ni,Mn,Co]O_2$ with a capacity in the range of 250–300 mA h/g versus 140 mA h/g for $LiCoO_2$ cathodes used today in commercial cells, and higher capacity Li alloy-based anodes such as Li–Sn and Li–Si alloys. Today's state-of-the-art electrolytes made of lithium hexafluorophosphate ($LiPF_6$) dissolved in cyclic carbonate and linear carbonate solvent mixtures with functional additives are not adequate in these new higher energy density electrochemical pairs without losing capacity or power. Looking beyond the horizon, many researchers and institutions intend to utilize sulfur or air as an even higher theoretical capacity cathode and pair with pure Li as an anode pursuing even higher energy density. The need of compatible electrolytes is also imperative for developing such systems.

What we need are better electrolyte materials that are compatible with the chosen electrode materials. The development of better electrolyte materials will require a much better understanding of electrolytes and how they interact with electrode materials. This book provides an overview of electrolyte research and development in the past 10 years as a foundation for thinking about future directions.

A number of books have been devoted to the science and technology of Li-ion batteries in recent years. However, there is no single book giving a comprehensive overview of electrolytes for Li-ion batteries. With the high demand for more robust electrolytes for the improvement of performance and energy density of Li and Li-ion batteries, it is time for a book that covers the electrolyte materials and the understanding of electrolyte and electrode interactions that have been developed in the past 10 years. This book covers the materials' aspects of the electrolytes, the state of the understanding of the electrolyte and electrode interactions, and basic understandings of the electrolytes and electrode/electrolyte interaction through computation. We are pleased to provide a ten-chapter book divided in three parts to cover subjects that we believed would make a good reference for researchers and technologists in the field and also for those who are not working in the field but are interested in understanding the basics, challenges, and progress that have been made in the field.

The first part of the book comprises four chapters focusing on electrolyte materials. In Chap. 1, Professor Wesley A. Pacific Northwest National Laboratory focuses on the various lithium salts that have been developed and compares these salts with $LiPF_6$, which is the salt used in today's Li-ion batteries. A comprehensive review of the physicochemical properties of these salts in nonaqueous solvents is also provided. The developed alternative salts have potential to be useful as additives or substitute for $LiPF_6$ in new Li battery chemistry. Dr. Makoto Ue of Mitsubishi Chemicals together with Emeritus Professor Yukio Sasaki of Tokyo Polytechnic University, Professor Yasutaka Tanaka of Shizuoka University, and Professor Masayuki Morita of Yamaguchi University contribute Chap. 2, which provides a solid review of heteroatom-containing organic solvents—including sulfur, fluorine, boron, and phosphorous—applied to lithium cells in recent years. Dr. Koji Abe of Ube Industries reviews work on additives for Li-ion electrolytes since 1990. Given that the properties of additives vary widely with battery test conditions, Dr. Abe selected additives that were utilized in practical applications and tried to replace those that were less successful; he then organized the additives chronologically. As a result, the cited references are mostly patents. He left the concepts, chemistry, and mechanism for each additive to the cited references as he explained in the Background of his chapter. In Chap. 4, Dr. Hajime Matsumoto of National Institute of Advanced Industrial Science and Technology, Japan, reviews the recent progress on ionic liquids for rechargeable lithium batteries.

The second part of the book focuses on interfacial chemistry at the electrodes and the methods of characterizing the interphases. Dr. Mengqing Xu, Dr. Lidan Xing, and Professor Weishan Li of South China Normal University, China, contribute Chap. 5, a review of the understanding of the interphases between the electrolyte and the anodes including graphite anode and Li–Sn and Li–Si alloy anodes in Li-ion batteries. Dr. Francis Amalraj Susai, Dr. Ronit Sharabi, Dr. Hadar Sclar, and

Professor Doron Aurbach of Bar-Ilan University, Israel, contribute Chap. 6, which provides a review of the surface chemistry of cathode materials including transition metal spinel, transition metal layer, transition metal phosphate, and oxygen cathode materials in nonaqueous electrolytes. Dr. Jordi Cabana of Lawrence Berkeley National Laboratory wrote Chap. 7, which provides an overview of the experimental tools and the kind of information they can offer with representative examples in the literature. It is important to recognize that no single technique can currently provide the answers to these complex interfacial phenomena in Li and Li-ion batteries.

Recent advances in molecular modeling using molecular simulations—and especially density functional theory—show promise of accurate prediction of the electrolyte's electrochemical, structural, and transport properties. The third part of this book is devoted to the understanding of electrolytes and electrolyte/electrode interactions through computational and molecular modeling. In Chap. 8, Dr. Oleg Borodin of the U.S. Army Research Laboratory discusses the applications of quantum chemistry to determine electrolyte oxidative stability and oxidation-induced decomposition reactions. He uses molecular dynamics simulations and density functional theory to predict the structural and transport properties of liquid electrolytes and solid electrolyte interphase (SEI) model compounds; free energy profiles for lithium desolvation from electrolytes; and the behavior of electrolytes at charged electrodes and the electrolyte–SEI interface.

In Chap. 9, Dr. Johan Scheers and Prof. Patrik Johansson of Chalmers University of Technology, Sweden, provide a thorough, historical perspective on the prediction of electrolyte and additive electrochemical stabilities from DFT calculations, a description of the simultaneous computational modeling methods, and materials evolutions. The materials put into reduction and oxidation stability prediction investigation include carbonate solvents, salts with different anions, and additives. In Chap. 10, the final chapter, Dr. Kah Chun Lau, Dr. Rajeev Assary, and Dr. Larry Curtiss of Argonne National Laboratory review the recent progress towards understanding of aprotic electrolytes stability and decomposition mechanisms in Li-Air battery obtained from quantum chemistry calculations that were corroborated with experimental data. They also review the research that has been done on the development of stable aprotic liquid electrolytes for Li-air batteries. One of the key problems is the electrochemical stability of the presently known carbonate- and ether-based nonaqueous electrolyte systems. The Li-air battery is a relatively new system and thus there are great challenges in developing stable electrolytes that are resistant to attack by reduced O_2 species.

The development of higher energy density Li-based batteries, whether they are made of higher voltage cathodes, high capacity cathodes, carbonaceous anodes, higher capacity Li alloy anodes, pure Li anode, or air cathode, all require stable and compatible electrolytes. We need better electrolytes to match the new electrochemical pairs. This cannot be achieved without a good understanding of the electrolyte and electrode interactions in relation to the electrolyte itself. In addition to electrochemical methods, many in situ and ex situ analytical tools need to be applied to the systems. Basic understanding of the stability of the electrolytes—including

electrochemical and chemical interactions with the electrodes through molecular modeling—is much needed. Experimental techniques for the validation of the modeling are also very much in need for advancing the modeling. Research and development of Li and Li-ion batteries are on the rise. New knowledge and new understanding are increasing daily. To advance effectively, synthetic scientists, analytical scientists, and computational scientists need to work together to develop higher energy density electrochemical energy storage systems.

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