

## PREFACE

Advances in science and engineering related to the emerging technologies of lithium-ion batteries (LIBs) have been so spectacular in the past decade that they have become the most popular power source for portable computing and telecommunication equipment. LIBs are simply essential for the constantly increasing demands of our information-rich society. It is expected that LIBs will continue to drive large market shares, and that new applications of LIBs such as powering electric and hybrid electric vehicles will flourish after a series of improvements resulting from current research efforts.

A typical commercial lithium-ion battery system consists of a carbonaceous anode, an organic electrolyte that acts as an ionic path between electrodes and separates the two electrode materials, and a transition metal oxide (such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiNiO}_2$ ) cathode. Recently a variety of novel LIB components have been proposed, like tin-based alloys and disordered carbons as anode materials, and modifications to the conventional transition metal-oxide cathode made by coating it with metal-oxide nanoparticles, most of which are discussed in detail in this book.

One of the most impressive advancements in the chemistry beneath LIBs is the understanding of the electrodes surface chemistry. It is recognized that a passivating layer between an electrode and the electrolyte arises from the reductive decompositions of a small amount of organic electrolytes mostly during the first several cycles of a working cell. This layer, which behaves similarly to a solid electrolyte interphase, was named SEI layer by Peled (*J. Electrochem. Soc.*, **126**, 1979, p. 2047), and it is a determinant factor on the performance of LIBs since the SEI nature and behavior affect the LIBs cycle-life, life time, power capability, and even their safety. Therefore, the build-up of appropriate SEI layers is an essential step in optimizing the combination of anode-electrolyte-cathode for LIBs, either through the screening of existing materials or developing novel ones. To this end, the better understanding of the SEI layer formation and growth for typical LIBs systems is fundamental. This book is designed for this purpose.

The importance of the SEI is well recognized in the scientific community, as reflected by numerous special sessions in battery technology meetings. In Chapters 1 through 9, this book presents the latest developments of the SEI layer formation, growth, and characterization, including its morphology features on various anodes and cathodes, identification of SEI layers by spectral methods,

and insights into SEI formation and growth mechanisms by state-of-the-art experimental techniques as well as first-principles-based molecular theories. Continuum and statistical-mechanics-based macroscopic models are also included for the understanding of SEI growth and that of its effect on the thermodynamics of lithium intercalation in carbon materials. Some long-standing problems and especially new phenomena for LIBs are deeply and extensively discussed by the authors, most of whom have worked in this field for long times and have witnessed many problems associated with the development of LIBs, for example, the failure mechanism of the solvent propylene carbonate (PC) for LIBs employing graphite as anode material and the reasons behind the impressive improvement caused by a small amount of a solvent additive on the SEI layer of PC-based electrolytes.

Peled and Golodnitsky in Chapter 1 begin with a simple introduction to the SEI concept, and the description of the main principles and routes of SEI formation and identification of possible products. It is followed by a discussion of several issues associated with the mechanisms of SEI formation on inert substrates, lithium metal, carbonaceous materials, and tin-based alloys. Attention is focused on the correlation between composition and morphology of the SEI forming on the various planes of highly ordered pyrolytic graphite (HOPG) as well as on different types of disordered electrodes in LIBs.

In Chapter 2, Aurbach and Cohen describe various spectroscopic techniques for SEI layer characterization, classifying these techniques in terms of their ability to providing specific or non-specific identification of SEI species, of enabling *in situ* or *ex situ* electrode characterization, and of being destructive or nondestructive to the electrode surface. Based on careful identifications of the SEI components, Chapter 2 suggests reduction mechanisms for several combinations of common solvents (ethylene carbonate, propylene carbonate, ethers, and  $\gamma$ -butyrolactone) and lithium salts. Based on scanning probe microscopy morphological studies, a novel insight is suggested to explain the major reasons for failure mechanisms of graphite electrodes in PC solutions.

Chapter 3, by Chen and collaborators, concentrates on the spectroscopic investigation of the SEI layer on anodes as well as cathodes of LIBs, including the nanometer-sized SnO anode, and the nano-MgO modified LiCoO<sub>2</sub> cathode. The effect of nano scaled materials on the performance of LIBs is well discussed using combination of spectral techniques, such as scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), surface enhanced Raman scattering (SERS), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS).

Inaba and Ogumi in Chapter 4 focus on the role of solvent co-intercalation in the SEI formation on graphite anodes, and discuss the mechanistic aspects of SEI formation using the images obtained from scanning tunneling microscopy (STM), and atomic force microscopy (AFM).

Chapter 5, by Wang and Balbuena, provides a first-principles-based theoretical avenue for exploring the failure mechanism of PC in LIBs employing graphite as anode, and the functioning mechanism of a solvent additive (vinylene carbonate, VC) in PC-based solutions. The reductive decompositions of EC, PC and VC are investigated in parallel using high-level density functional theory, including their reduction mechanisms, identification of the main reduction products, and their adhesion to the basal and edge planes of graphite.

Ploehn *et al.* in Chapter 6 use both macroscopic continuum and statistical mechanics-based models to simulate the SEI growth and to predict capacity loss in LIBs. Specifically the former model deals with the effects of electronic conductivity and solvent diffusion on SEI growth, while the latter is a lattice-gas model, which describes the thermodynamics of lithium-ion intercalation in carbons under the presence of a SEI.

In Chapter 7, the Raman and near-edge X-ray absorption fine structure (NEXAFS) techniques have been used by Sandi to investigate the electronic and structural properties of carbonaceous materials and those of electrodes made from the synthesized carbons. The electrochemical performance of the carbon anodes is compared and related to the electronic and structural features of the SEI layer.

Thomas and collaborators in Chapter 8 present evidences for the formation of some type of Solid Permeable Interface (SPI) between the electrolyte and the cathode in LIBs. It deals with today's most commonly used cathode materials, such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCo}_2\text{O}_4$ ,  $\text{LiNiO}_2$  and  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  and with the recently introduced  $\text{LiFePO}_4$ .

Chapter 9, by Wang and Balbuena, deals with theoretical studies on the solvent structure and association properties, and on the lithium-ion solvation. SEI layer related phenomena are discussed in relation to lithium-ion solvation in commonly used solvents, co-solvents, and solvent additives.

*Perla B. Balbuena*  
*Yixuan Wang*