Contents

List of Contributors *XI*
Preface *XIII*

1 Introduction *1*

1.1 History of Batteries *1*
1.2 Development of Cell Technology *3*
1.3 Overview of Lithium Secondary Batteries *3*
1.4 Future of Lithium Secondary Batteries *7*
References *7*

2 The Basic of Battery Chemistry *9*

2.1 Components of Batteries *9*
2.1.1 Electrochemical Cells and Batteries *9*
2.1.2 Battery Components and Electrodes *9*
2.1.3 Full Cells and Half Cells *11*
2.1.4 Electrochemical Reaction and Electric Potential *11*
2.2 Voltage and Current of Batteries *12*
2.2.1 Voltage *12*
2.2.2 Current *14*
2.2.3 Polarization *14*
2.3 Battery Characteristics *15*
2.3.1 Capacity *15*
2.3.2 Energy Density *16*
2.3.3 Power *16*
2.3.4 Cycle Life *17*
2.3.5 Discharge Curves *17*

3 Materials for Lithium Secondary Batteries *21*

3.1 Cathode Materials *21*

3.1.1 Development History of Cathode Materials *21*
3.1.2 Overview of Cathode Materials *23*
3.1.2.1 Redox Reaction of Cathode Materials *23*
3.1.2.2 Discharge Potential Curves *24*
3.1.2.3 Demand Characteristics of Cathode Materials *26*
3.1.2.4 Major Cathode Materials *27*
3.1.3 Structure and Electrochemical Properties of Cathode Materials *27*
3.1.3.1 Layered Structure Compounds *27*
3.1.3.2 Spinel Composites *46*
3.1.3.3 Olivine Composites *52*
3.1.3.4 Vanadium Composites *57*
3.1.4 Performance Improvement by Surface Modification *58*
3.1.4.1 Layered Structure Compounds *60*
3.1.4.2 Spinel Compound *61*
3.1.4.3 Olivine Compounds *64*
3.1.5 Thermal Stability of Cathode Materials *65*
3.1.5.1 Basics of Battery Safety *65*
3.1.5.2 Battery Safety and Cathode Materials *68*
3.1.5.3 Thermal Stability of Cathodes *69*
3.1.6 Prediction of Cathode Physical Properties and Cathode Design *75*
3.1.6.1 Understanding of First-Principles Calculation *77*
3.1.6.2 Prediction and Investigation of Electrode Physical Properties Using First-Principles Calculation *79*
References *84*

3.2 Anode Materials *89*

3.2.1 Development History of Anode Materials *89*
3.2.2 Overview of Anode Materials *90*
3.2.3 Types and Electrochemical Characteristics of Anode Materials *91*
3.2.3.1 Lithium Metal *91*
3.2.3.2 Carbon Materials *92*
3.2.3.3 Noncarbon Materials *118*
3.2.4 Conclusions *137*
References *137*

3.3 Electrolytes *141*

3.3.1 Liquid Electrolytes *142*
3.3.1.1 Requirements of Liquid Electrolytes *142*
3.3.1.2 Components of Liquid Electrolytes *143*

3.3.1.3 Characteristics of Liquid Electrolytes *147*
3.3.1.4 Ionic Liquids *149*
3.3.1.5 Electrolyte Additives *153*
3.3.1.6 Enhancement of Thermal Stability for Electrolytes *157*
3.3.1.7 Development Trends of Liquid Electrolytes *161*
3.3.2 Polymer Electrolytes *162*
3.3.2.1 Types of Polymer Electrolytes *162*
3.3.2.2 Preparation of Polymer Electrolytes *169*
3.3.2.3 Characteristics of Polymer Electrolytes *171*
3.3.2.4 Development Trends of Polymer Electrolytes *173*
3.3.3 Separators *173*
3.3.3.1 Separator Functions *173*
3.3.3.2 Basic Characteristics of Separators *174*
3.3.3.3 Effects of Separators on Battery Assembly *176*
3.3.3.4 Oxidative Stability of Separators *176*
3.3.3.5 Thermal Stability of Separators *178*
3.3.3.6 Development of Separator Materials *179*
3.3.3.7 Separator Manufacturing Process *180*
3.3.3.8 Prospects for Separators *181*
3.3.4 Binders, Conducting Agents, and Current Collectors *181*
3.3.4.1 Binders *181*
3.3.4.2 Conducting Agents *189*
3.3.4.3 Current Collectors *191*
References *192*

3.4 Interfacial Reactions and Characteristics *195*

3.4.1 Electrochemical Decomposition of Nonaqueous Electrolytes *195*
3.4.2 SEI Formation at the Electrode Surface *200*
3.4.3 Anode–Electrolyte Interfacial Reactions *203*
3.4.3.1 Lithium Metal–Electrolyte Interfacial Reactions *204*
3.4.3.2 Interfacial Reactions at Graphite (Carbon) *209*
3.4.3.3 SEI Layer Thickness *211*
3.4.3.4 Effect of Additives *212*
3.4.3.5 Interfacial Reactions between a Noncarbonaceous Anode and Electrolytes *214*
3.4.4 Cathode–Electrolyte Interfacial Reactions *216*
3.4.4.1 Native Surface Layers of Oxide Cathode Materials *217*
3.4.4.2 SEI Layers of Oxide Cathodes *218*
3.4.4.3 Interfacial Reactions at Oxide Cathodes *218*
3.4.4.4 Interfacial Reactions of Phosphate Cathode Materials *223*
3.4.5 Current Collector–Electrolyte Interfacial Reactions *225*
3.4.5.1 Native Layer of Aluminum *225*
3.4.5.2 Corrosion of Aluminum *226*
3.4.5.3 Formation of Passive Layers on Aluminum Surface *228*
References *229*

4 Electrochemical and Material Property Analysis *231*

4.1 Electrochemical Analysis *231*

4.1.1 Open-Circuit Voltage *231*
4.1.2 Linear Sweep Voltammetry *232*
4.1.3 Cyclic Voltammetry *232*
4.1.4 Constant Current (Galvanostatic) Method *234*
4.1.4.1 Cutoff Voltage Control *234*
4.1.4.2 Constant Capacity Cutoff Control *236*
4.1.5 Constant Voltage (Potentiostatic) Method *236*
4.1.5.1 Constant Voltage Charging *236*
4.1.5.2 Potential Stepping Test *236*
4.1.6 GITT and PITT *238*
4.1.6.1 GITT *238*
4.1.6.2 PITT *239*
4.1.7 AC Impedance Analysis *239*
4.1.7.1 Principle *239*
4.1.7.2 Equivalent Circuit Model *241*
4.1.7.3 Applications in Electrode Characteristic Analysis *247*
4.1.7.4 Applications in Al/$LiCoO_2$/Electrolyte/Carbon/Cu Battery Analysis *249*
4.1.7.5 Applications in Al/$LiCoO_2$/Electrolyte/MCMB/Cu Cell Analysis *253*
4.1.7.6 Relative Permittivity *254*
4.1.7.7 Ionic Conductivity *256*
4.1.7.8 Diffusion Coefficient *257*
4.1.8 EQCM Analysis *257*
References *260*

4.2 Material Property Analysis *263*

4.2.1 X-ray Diffraction Analysis *263*
4.2.1.1 Principle of X-ray Diffraction Analysis *263*
4.2.1.2 Rietveld Refinement *265*
4.2.1.3 In Situ XRD *267*
4.2.2 FTIR and Raman Spectroscopy *269*
4.2.2.1 FTIR Spectroscopy *270*
4.2.2.2 Raman Spectroscopy *275*
4.2.3 Solid-State Nuclear Magnetic Resonance Spectroscopy *280*
4.2.4 X-ray Photoelectron Spectroscopy (XPS) *282*
4.2.5 X-ray Absorption Spectroscopy (XAS) *285*
4.2.5.1 X-ray Absorption Near-Edge Structure (XANES) *287*
4.2.5.2 Extended X-ray Absorption Fine Structure (EXAFS) *288*
4.2.6 Transmission Electron Microscopy (TEM) *292*

4.2.7 Scanning Electron Microscopy (SEM) *296*
4.2.8 Atomic Force Microscopy (AFM) *300*
4.2.9 Thermal Analysis *301*
4.2.10 Gas Chromatography-Mass spectrometry (GC–MS) *306*
4.2.11 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) *311*
4.2.12 Brunauer–Emmett–Teller (BET) Surface Analysis *311*
References *315*

5 Battery Design and Manufacturing *319*

5.1 Battery Design *319*
5.1.1 Battery Capacity *320*
5.1.2 Electrode Potential and Battery Voltage Design *321*
5.1.3 Design of Cathode/Anode Capacity Ratio *323*
5.1.4 Practical Aspects of Battery Design *325*
5.2 Battery Manufacturing Process *327*
5.2.1 Electrode Manufacturing Process *328*
5.2.1.1 Preparation of Electrode Slurry *328*
5.2.1.2 Electrode Coating *329*
5.2.1.3 Roll Pressing Process *330*
5.2.1.4 Slitting Process *330*
5.2.1.5 Vacuum Drying Process *331*
5.2.2 Assembly Process *331*
5.2.2.1 Winding Process *331*
5.2.2.2 Jelly Roll Insertion/Cathode Tab Welding/Beading Process *332*
5.2.2.3 Electrolyte Injection Process *334*
5.2.2.4 Cathode Tab Welding/Crimping/X-Ray Inspection/Washing Process *334*
5.2.3 Formation Process *334*
5.2.3.1 Purpose of the Formation Process *334*
5.2.3.2 Procedures and Functions *334*
References *335*

6 Battery Performance Evaluation *337*

6.1 Charge and Discharge Curves of Cells *337*
6.1.1 Significance of Charge and Discharge Curves *337*
6.1.2 Adjustment of Charge/Discharge Curves *339*
6.1.3 Overcharging and Charge/Discharge Curves *340*
6.2 Cycle Life of Batteries *342*
6.2.1 Significance of Cycle Life *342*
6.2.2 Factors Affecting Battery Cycle Life *342*
6.3 Battery Capacity *344*
6.3.1 Introduction *344*
6.3.2 Battery Capacity *345*

6.3.3 Measurement of Battery Capacity *346*
6.4 Discharge Characteristics by Discharge Rate *347*
6.5 Temperature Characteristics *349*
6.5.1 Low-Temperature Characteristics *349*
6.5.2 High-Temperature Characteristics *350*
6.6 Energy and Power Density (Gravimetric/Volumetric) *351*
6.6.1 Energy Density *351*
6.6.2 Power Density *351*
6.7 Applications *351*
6.7.1 Mobile Device Applications *352*
6.7.2 Transportation *352*
6.7.3 Others *353*

Index *355*