

# Contents

Preface *xiii*

## Part I Solid Oxide Fuel Cell with Ionic Conducting Electrolyte 1

- 1 Introduction 3  
*Bin Zhu and Peter D. Lund*
- 1.1 An Introduction to the Principles of Fuel Cells 3
- 1.2 Materials and Technologies 5
- 1.3 New Electrolyte Developments on LTSOFC 10
- 1.4 Beyond the State of the Art: The Electrolyte-Free Fuel Cell (EFFC) 20
- 1.4.1 Fundamental Issues 23
- 1.5 Beyond the SOFC 25
- References 28
  
- 2 Solid-State Electrolytes for SOFC 35  
*Liangdong Fan*
- 2.1 Introduction 35
- 2.2 Single-Phase SOFC Electrolytes 37
- 2.2.1 Oxygen Ionic Conducting Electrolyte 37
- 2.2.1.1 Stabilized Zirconia 37
- 2.2.1.2 Doped Ceria 39
- 2.2.1.3 SrO- and MgO-Doped Lanthanum Gallates (LSGM) 42
- 2.2.2 Proton-Conducting Electrolyte and Mixed Ionic Conducting Electrolyte 42
- 2.2.3 Alternative New Electrolytes and Research Interests 44
- 2.3 Ion Conduction/Transportation in Electrolytes 49
- 2.4 Composite Electrolytes 52
- 2.4.1 Oxide–Oxide Electrolyte 52
- 2.4.2 Oxide–Carbonate Composite 53
- 2.4.2.1 Materials Fabrication 54
- 2.4.2.2 Performance and Stability Optimization 57
- 2.4.3 Other Oxide–Salt Composite Electrolytes 60

|          |   |            |
|----------|---|------------|
| 2.4.4    | Ionic Conduction Mechanism Studies of Ceria–Carbonate Composite     | 62         |
| 2.5      | NANOCOFC and Material Design Principle                              | 66         |
| 2.6      | Concluding Remarks  | 67         |
|          | Acknowledgments   | 69         |
|          | References  | 69         |
| <b>3</b> | <b>Cathodes for Solid Oxide Fuel Cell</b>                           | <b>79</b>  |
|          | <i>Tianmin He, Qingjun Zhou, and Fangjun Jin</i>                    |            |
| 3.1      | Introduction  | 79         |
| 3.2      | Overview of Cathode Reaction Mechanism                              | 80         |
| 3.3      | Development of Cathode Materials                                    | 82         |
| 3.3.1    | Perovskite Cathode Materials  | 82         |
| 3.3.1.1  | Mn-Based Perovskite Cathodes  | 83         |
| 3.3.1.2  | Co-Based Perovskite Cathodes  | 85         |
| 3.3.1.3  | Fe-Based Perovskite Cathodes  | 88         |
| 3.3.1.4  | Ni-Based Perovskite Cathodes  | 89         |
| 3.3.2    | Double Perovskite Cathode Materials                                 | 89         |
| 3.4      | Microstructure Optimization of Cathode Materials                    | 94         |
| 3.4.1    | Nanostructured Cathodes   | 94         |
| 3.4.2    | Composite Cathodes  | 97         |
| 3.5      | Summary   | 102        |
|          | References  | 103        |
| <b>4</b> | <b>Anodes for Solid Oxide Fuel Cell</b>                             | <b>113</b> |
|          | <i>Chunwen Sun</i>  |            |
| 4.1      | Introduction  | 113        |
| 4.2      | Overview of Anode Reaction Mechanism                                | 114        |
| 4.2.1    | Basic Operating Principles of a SOFC                                | 114        |
| 4.2.1.1  | The Anode Three-Phase Boundary                                      | 115        |
| 4.3      | Development of Anode Materials                                      | 117        |
| 4.3.1    | Ni–YSZ Cermet Anode Materials                                       | 117        |
| 4.3.2    | Alternative Anode Materials   | 118        |
| 4.3.2.1  | Fluorite Anode Materials  | 118        |
| 4.3.2.2  | Perovskite Anode Materials  | 120        |
| 4.3.3    | Sulfur-Tolerant Anode Materials                                     | 124        |
| 4.4      | Development of Kinetics, Reaction Mechanism, and Model of the Anode | 126        |
| 4.5      | Summary and Outlook   | 135        |
|          | Acknowledgments   | 137        |
|          | References  | 137        |
| <b>5</b> | <b>Design and Development of SOFC Stacks</b>                        | <b>145</b> |
|          | <i>Wanbing Guan</i>   |            |
| 5.1      | Introduction  | 145        |
| 5.2      | Change of Cell Output Performance Under 2D Interface Contact        | 145        |
| 5.2.1    | Design of 2D Interface Contact Mode                                 | 145        |

|       |  |     |
|-------|--|-----|
| 5.2.2 | Variations of Cell Output Performance Under 2D Contact Mode  | 147 |
| 5.2.3 | 2D Interface Structure Improvements and Enhancement of Cell Output Performance                                   | 149 |
| 5.2.4 | Contributions of 3D Contact in 2D Interface Contact  | 151 |
| 5.2.5 | Mechanism of Performance Enhancement After the Transition from 2D to 3D Interface                                | 153 |
| 5.3   | Control Design of Transition from 2D to 3D Interface Contact and Their Quantitative Contribution Differentiation | 156 |
| 5.3.1 | Control Design of 2D and 3D Interface Contact  | 156 |
| 5.3.2 | Quantitative Effects of 2D Contact on the Transient Output Performance of a Cell                                 | 158 |
| 5.3.3 | Quantitative Effects of 2D Contact on the Steady-State Output Performance of the Cell                            | 161 |
| 5.3.4 | Quantitative Effects of 3D Contact on Cell Transient Performance   | 163 |
| 5.3.5 | Quantitative Effects of 3D Contact on the Steady-State Performance of a Cell                                     | 166 |
| 5.3.6 | Differences Between 2D and 3D Interface Contacts   | 169 |
| 5.4   | Conclusions  | 171 |
|       | References   | 172 |

## **Part II Electrolyte-Free Fuel Cells: Materials, Technologies, and Working Principles 173**

|          |   |            |
|----------|---|------------|
| <b>6</b> | <b>Electrolyte-Free SOFCs: Materials, Technologies, and Working Principles</b>        | <b>175</b> |
|          | <i>Bin Zhu, Liangdong Fan, Jung-Sik Kim, and Peter D. Lund</i>                        |            |
| 6.1      | Concept of the Electrolyte-Free Fuel Cell   | 175        |
| 6.2      | SLFC Using the Ionic Conductor-based Electrolyte                                      | 177        |
| 6.3      | Developments on Advanced SLFC   | 179        |
| 6.4      | From SLFCs to Semiconductor-Ionic Fuel Cells (SIFCs)                                  | 184        |
| 6.5      | The SLFC Working Principle  | 196        |
| 6.6      | Remarks   | 204        |
|          | Acknowledgments   | 207        |
|          | References  | 207        |
| <b>7</b> | <b>Ceria Fluorite Electrolytes from Ionic to Mixed Electronic and Ionic Membranes</b> | <b>213</b> |
|          | <i>Baoyuan Wang, Liangdong Fan, Yanyan Liu, and Bin Zhu</i>                           |            |
| 7.1      | Introduction  | 213        |
| 7.2      | Doped Ceria as the Electrolyte for Intermediate Temperature SOFCs                     | 214        |
| 7.3      | Surface Doping for Low Temperature SOFCs  | 216        |
| 7.4      | Non-doped Ceria for Advanced Low Temperature SOFCs                                    | 222        |
|          | References  | 235        |

|          |   |            |
|----------|---|------------|
| <b>8</b> | <b>Charge Transfer in Oxide Solid Fuel Cells</b>  | <b>239</b> |
|          | <i>Jing Shi and Sining Yun</i>  |            |
| 8.1      | Oxygen Diffusion in Perovskite Oxides   | 239        |
| 8.1.1    | Oxygen Vacancy Formation  | 239        |
| 8.1.2    | Oxygen Diffusion Mechanisms   | 242        |
| 8.1.3    | Anisotropy Oxygen Transport in Layered Perovskites  | 244        |
| 8.1.3.1  | Oxygen Transport in Ruddlesden–Popper (RP) Perovskites  | 244        |
| 8.1.3.2  | Oxygen Transport in A-Site Ordered Double Perovskites   | 244        |
| 8.1.4    | Oxygen Ion Diffusion at Grain Boundary  | 246        |
| 8.1.5    | Factors Controlling Oxygen Migration Barriers in Perovskites  | 248        |
| 8.2      | Proton Diffusion in Perovskite-Type Oxides  | 249        |
| 8.2.1    | Proton Diffusion Mechanisms   | 249        |
| 8.2.2    | Proton–Dopant Interaction   | 253        |
| 8.2.2.1  | Influence of Dopants in A-site  | 253        |
| 8.2.2.2  | Influence of Dopants in B-Site  | 254        |
| 8.2.3    | Long-range Proton Conduction Pathways in Perovskites  | 255        |
| 8.2.4    | Hydrogen-Induced Insulation   | 256        |
| 8.3      | Enhanced Ion Conductivity in Oxide Heterostructures   | 259        |
| 8.3.1    | Enhanced Ionic Conduction by Strain   | 259        |
| 8.3.2    | Enhanced Ionic Conductivity by Band Bending   | 263        |
| 8.3.2.1  | Surface State-induced Band Bending  | 263        |
| 8.3.2.2  | Band Bending in p–n Heterojunctions   | 265        |
| 8.3.2.3  | p–n Heterojunction Structures in SOFC   | 265        |
| 8.4      | Summary   | 266        |
|          | Acknowledgments   | 267        |
|          | References  | 267        |
| <b>9</b> | <b>Material Development II: Natural Material-based Composites for Electrolyte Layer-free Fuel Cells</b> | <b>275</b> |
|          | <i>Chen Xia and Yanyan Liu</i>  |            |
| 9.1      | Introduction  | 275        |
| 9.1.1    | Materials Development for EFFCs   | 275        |
| 9.1.2    | Natural Materials as Potential Electrolytes   | 276        |
| 9.2      | Industrial-grade Rare Earth for EFFCs   | 279        |
| 9.2.1    | Rare-earth Oxide LCP  | 280        |
| 9.2.2    | Semiconducting–Ionic Composite Based on LCP   | 281        |
| 9.2.2.1  | LCP–LSCF  | 282        |
| 9.2.2.2  | LCP–ZnO   | 284        |
| 9.2.3    | Stability Operation and Schottky Junction of EFFC   | 288        |
| 9.2.3.1  | Performance Stability   | 288        |
| 9.2.3.2  | In Situ Schottky Junction Effect  | 288        |
| 9.2.4    | Summary   | 290        |
| 9.3      | Natural Hematite for EFFCs  | 291        |
| 9.3.1    | Natural Hematite  | 292        |
| 9.3.2    | Semiconducting–Ionic Composite Based on Hematite  | 295        |

|           |   |            |
|-----------|---|------------|
| 9.3.2.1   | Hematite–LSCF   | 295        |
| 9.3.2.2   | Hematite/LCP–LSCF   | 297        |
| 9.3.3     | Summary   | 300        |
| 9.4       | Natural CuFe Oxide Minerals for EFFCs   | 302        |
| 9.4.1     | Natural $\text{CuFe}_2\text{O}_4$ Mineral for EFFC  | 302        |
| 9.4.2     | Natural Delafossite $\text{CuFeO}_2$ for EFFC   | 305        |
| 9.4.3     | Summary   | 308        |
| 9.5       | Bio-derived Calcite for EFFC  | 308        |
| 9.5.1     | Bio-derived Calcite for EFFC  | 309        |
| 9.5.2     | Summary   | 312        |
|           | References  | 314        |
| <b>10</b> | <b>Charge Transfer, Transportation, and Simulation</b>  | <b>319</b> |
|           | <i>Muhammad Afzal, Mustafa Anwar, Muhammad I. Asghar, Peter D. Lund, Naveed Jhamat, Rizwan Raza, and Bin Zhu</i>                                  |            |
| 10.1      | Physical Aspects  | 319        |
| 10.2      | Electrochemical Aspects   | 320        |
| 10.3      | Ionic Conduction Enhancement in Heterostructure Composites  | 321        |
| 10.4      | Charge Transportation Mechanism and Coupling Effects  | 326        |
| 10.5      | Surface and Interfacial State-Induced Superionic Conduction and Transportation  | 330        |
| 10.6      | Ionic Transport Number Measurements   | 331        |
| 10.7      | Determination of Electron and Ionic Conductivities in EFFCs   | 332        |
| 10.8      | EIS Analysis  | 334        |
| 10.9      | Semiconductor Band Effects on the Ionic Conduction Device Performance   | 335        |
| 10.10     | Simulations   | 339        |
|           | Acknowledgments   | 343        |
|           | References  | 343        |
| <b>11</b> | <b>Electrolyte-Free Fuel Cell: Principles and Crosslink Research</b>  | <b>347</b> |
|           | <i>Yan Wu, Liangdong Fan, Naveed Mushtaq, Bin Zhu, Muhammad Afzal, Muhammad Sajid, Rizwan Raza, Jung-Sik Kim, Wen-Feng Lin, and Peter D. Lund</i> |            |
| 11.1      | Introduction  | 347        |
| 11.2      | Fundamental Considerations of Fuel Cell Semiconductor Electrochemistry  | 353        |
| 11.2.1    | Physics and Electrochemistry at Interfaces  | 353        |
| 11.2.2    | Electrochemistry vs. Semiconductor Physics  | 355        |
| 11.3      | Working Principle of Semiconductor-Based Fuel Cells and Crossing Link Sciences  | 356        |
| 11.4      | Extending Applications by Coupling Devices  | 367        |
| 11.5      | Final Remarks   | 368        |
|           | Acknowledgments   | 372        |
|           | References  | 373        |

### Part III Fuel Cells: From Technology to Applications 377

- 12 Scaling Up Materials and Technology for SLFC 379**  
*Kang Yuan, Zhigang Zhu, Muhammad Afzal, and Bin Zhu*
  - 12.1 Single-Layer Fuel Cell (SLFC) Engineering Materials 379
  - 12.2 Scaling Up Single-Layer Fuel Cell Devices: Tape Casting and Hot Pressing 383
  - 12.3 Scaling Up Single-Layer Fuel Cell Devices: Thermal Spray Coating Technology 386
    - 12.3.1 Traditional Plasma Spray Coating Technology 387
    - 12.3.2 New Developed Low-Pressure Plasma Spray (LPPS) Coating Technology 388
  - 12.4 Short Stack 395
    - 12.4.1 SLFC Cells 395
    - 12.4.2 Bipolar Plate Design 396
    - 12.4.3 Sealing and Sealant-Free Short Stack 396
  - 12.5 Tests and Evaluations 397
  - 12.6 Durability Testing 399
  - 12.7 A Case Study for the Cell Degradation Mechanism 400
  - 12.8 Continuous Efforts and Future Developments 404
  - 12.9 Concluding Remarks 409
  - References 411
- 13 Planar SOFC Stack Design and Development 415**  
*Shaorong Wang, Yixiang Shi, Naveed Mushtaq, and Bin Zhu*
  - 13.1 Internal Manifold and External Manifold 415
  - 13.2 Interface Between an Interconnect Plate and a Single Cell 416
  - 13.3 Antioxidation Coating of the Interconnect Plate 418
  - 13.4 Design the Flow Field of Interconnect Plate 419
    - 13.4.1 Mathematical Simulation 420
    - 13.4.2 Effect of Co-flow, Crossflow, and Counterflow 422
    - 13.4.3 Air Flow Distribution Between Layers in a Stack 424
  - 13.5 The Importance of Sealing 424
    - 13.5.1 Thermal Cycling of the Sealing 428
    - 13.5.2 Durability of Sealing 428
  - 13.6 The Life of the Stack: The Chemical Problems on the Interface 429
  - 13.7 Toward Market Products 431
  - 13.8 Concluding Remarks 443
  - References 443
- 14 Energy System Integration and Future Perspectives 447**  
*Ghazanfar Abbas, Muhammad Ali Babar, Fida Hussain, and Rizwan Raza*
  - 14.1 Solar Cell and Fuel Cell 447
  - 14.2 Fuel Cell–Solar Cell Integration 450
  - 14.3 Solar Electrolysis–Fuel Cell Integration 452
  - 14.4 Fuel Cell–Biomass Integration 453
  - 14.5 The Fuel Cell System Modeling Using Biogas 454

|        |  |     |
|--------|--|-----|
| 14.5.1 | Activation Loss  | 457 |
| 14.5.2 | Ohmic Loss   | 457 |
| 14.5.3 | Concentration Voltage Loss                                 | 458 |
| 14.6   | The Fuel Cell System Efficiency (Heating and Electrical)   | 458 |
| 14.6.1 | The Effect of Different Temperatures on System Efficiency  | 458 |
| 14.6.2 | The Fuel Utilization Factor and Efficiencies of the System | 458 |
| 14.6.3 | The System Efficiencies and Operating Pressure             | 460 |
| 14.7   | Integrated New Clean Energy System                         | 460 |
| 14.8   | Summary  | 462 |
|        | References   | 462 |

|              |            |
|--------------|------------|
| <b>Index</b> | <b>465</b> |
|--------------|------------|