

## Contents

<b>Preface</b>	<i>xv</i>
<b>Acknowledgments</b>	<i>xvii</i>
<b>1 Introduction</b>	<b>1</b>
<i>Yiran Zhang, Zhicheng Zhang</i>	
1.1	Origins and Evolution of Small-molecule Catalysis for Electrochemical Energy Conversion 1
1.2	Current State of Small-molecule Catalysis in Electrochemical Energy Conversion 2
1.2.1	Hydrogen Evolution and Oxygen Evolution Reactions 2
1.2.2	Oxygen Reduction Reaction 2
1.2.3	CO <sub>2</sub> Reduction 2
1.2.4	Nitrogen Fixation 3
1.3	Challenges in Small-molecule Catalysis for Electrochemical Energy Conversion 3
1.4	Opportunities and Future Outlook 4
	Acknowledgment 4
<b>2 Electrochemical Energy Conversion Techniques</b>	<b>7</b>
<i>Zhongxin Chen, Huaiguang Li</i>	
2.1	Introduction: The Future Is Electrifying 7
2.2	Fuel Cells and Electrolyzers 9
2.2.1	Water Splitting Reaction (Water Electrolyzer) 9
2.2.2	Chlor-alkali Process 12
2.2.3	CO <sub>2</sub> Electrolyzers 13
2.2.4	Fuel Cells 14
2.2.4.1	Proton Exchange Membrane Fuel Cells 15
2.2.4.2	Alkaline Fuel Cells 16
2.2.4.3	Phosphoric Acid Fuel Cells 17
2.2.4.4	Molten Carbonate Fuel Cells 17
2.2.4.5	Solid Oxide Fuel Cells 18
2.3	Batteries and Supercapacitors 18
2.4	Summary 20

<b>3</b>	<b>Constant-potential Modeling in Electrochemical CO<sub>2</sub> Reduction</b>	<b>23</b>
	<i>Yaqiong Su</i>	
3.1	Introduction	23
3.2	Principle of Constant-potential Modeling	24
3.3	Constant-potential Modeling of Electrochemical CO <sub>2</sub> RR	25
3.3.1	Single-atom Catalysis for Electrochemical CO <sub>2</sub> RR	25
3.3.2	Cu-based Surface Catalysis for Electrochemical CO <sub>2</sub> RR	29
3.3.3	Cation Effect for Electrochemical CO <sub>2</sub> RR	32
3.3.4	Surface-modified Species for Electrochemical CO <sub>2</sub> RR	34
3.4	Conclusion and Outlook	37
	Acknowledgment	37
<b>4</b>	<b>Advanced In Situ Characterization Techniques for Direct Observation of Gas-involved Electrochemical Reactions</b>	<b>43</b>
	<i>Yue Zhai, Jiamin Zhu, ShuHui Li, Luohua Liu, Li An</i>	
4.1	Introduction	43
4.2	In Situ Infrared Technique	44
4.2.1	Example Study	45
4.2.2	In Situ Characterization of Catalyst Reaction Mechanism	45
4.2.3	In Situ Infrared Spectrum Analysis	46
4.2.4	In Situ FT-IR Characterization of the Electrode Reaction Process of Calcium Ion Batteries	46
4.3	Electrochemical Quartz Crystal Microbalance	48
4.3.1	EQCM System Diagram	48
4.3.2	Development History of EQCM	49
4.3.3	Monitoring the Ion Transport Mode of Supercapacitors	49
4.3.4	Monitor the Ion Solvation Number of Supercapacitors	50
4.3.5	Combination of EQCM and Other Detection Methods	51
4.3.6	Summary and Prospect	52
4.4	X-ray Powder Diffraction	53
4.5	In Situ Differential Electrochemical Mass Spectrometer	56
4.6	In Situ Raman Spectroscopy	60
4.7	In Situ Fluorescence Spectrum	65
4.8	X-ray Photoelectron Spectrometer	67
4.8.1	Theory of XPS	67
4.8.2	X-ray Photoelectron Spectrometer	68
4.8.3	Characteristic	68
4.8.4	In Situ X-ray Photoelectron Spectroscopy	69
4.9	Ultraviolet Photoelectron Spectrometer	71
4.9.1	Theory of Ultraviolet Photoelectron Spectrometer	71
4.9.2	Ultraviolet Photoelectron Spectroscopy	72
4.9.3	Characteristic	72
4.9.4	In Situ UPS	72

<b>5</b>	<b>Dynamic Structural Evolution Identification via X-ray Absorption Fine Structure</b>	<b>77</b>
	<i>Chengyi Liu, Shibo Xi</i>	
5.1	Introduction	77
5.2	Fundamentals of XAFS	78
5.2.1	Principles of XAFS	79
5.2.1.1	XANES	80
5.2.1.2	EXAFS	80
5.2.2	Key Concepts in XAFS	81
5.2.2.1	Absorption Coefficient $\mu$	81
5.2.2.2	Local Probing Capability	81
5.2.2.3	Element-specific Nature	82
5.2.3	Experimental Setup for XAFS	82
5.2.3.1	Synchrotron Radiation	82
5.2.3.2	Data Acquisition	82
5.2.4	Applications of XAFS	84
5.3	XAFS Data Analysis and Interpretation	84
5.3.1	Key Components of XAFS Analysis	85
5.3.1.1	Data Preprocessing	85
5.3.1.2	Background Subtraction	85
5.3.1.3	Normalization	86
5.3.2	EXAFS Analysis	86
5.3.2.1	Fourier Transform	86
5.3.2.2	Curve Fitting	87
5.3.2.3	Wavelet Transform	88
5.3.3	XANES Analysis	88
5.3.3.1	Pre-edge Analysis	89
5.3.3.2	Edge Position and Shape	89
5.3.3.3	Multiple Scattering Contributions	89
5.3.4	Integration with Computational Methods	89
5.3.5	Challenges and Future Directions	89
5.3.5.1	Noise and Artifacts	89
5.3.5.2	Model Dependency	89
5.3.5.3	High-throughput and Automation	90
5.4	In Situ and Operando XAFS Techniques	90
5.4.1	Key Concepts	90
5.4.1.1	In Situ versus Operando XAFS	90
5.4.2	Applications of In Situ and Operando XAFS	92
5.4.2.1	Catalysis	92
5.4.2.2	Energy Conversion and Storage	92
5.4.2.3	Environmental Studies	93
5.4.3	Methodologies and Experimental Considerations	94
5.4.4	Challenges and Future Directions	95

5.4.4.1	Technical Challenges	95
5.4.4.2	Future Directions	95
5.5	Advanced XAFS Methods	95
5.5.1	Key Techniques	96
5.5.1.1	High-energy Resolution Fluorescence Detected XAFS (HERFD-XAFS)	96
5.5.1.2	Grazing-Incidence XAFS (GI-XAFS)	96
5.5.1.3	Quick-scanning XAFS	97
5.5.2	Applications in Electrocatalysis	98
5.5.2.1	Single-atom Catalysts	98
5.5.2.2	Multi-component Systems	98
5.5.2.3	Reaction Mechanisms	98
5.5.3	Challenges and Future Directions	98
5.5.3.1	Technical Limitations	98
5.5.3.2	Integration with Complementary Techniques	99
5.5.3.3	Computational Approaches	99
5.6	Dynamic Structural Evolution in Catalysts	99
5.6.1	Role of Surface and Bulk Dynamics	100
5.6.2	Dynamic Effects in Nanostructured Catalysts	100
5.7	Application of XAFS in Electrochemical Energy Conversion	101
5.7.1	Hydrogen Evolution Reaction	101
5.7.2	Oxygen Evolution Reaction	102
5.7.3	Oxygen Reduction Reaction	102
5.7.4	Carbon Dioxide Reduction Reaction (CO <sub>2</sub> RR)	102
5.7.5	Nitrogen Reduction Reaction	103
5.8	Conclusion and Outlook	104
	Acknowledgment	105
<b>6</b>	<b>Electrochemical Hydrogen Evolution Reaction</b>	<b>111</b>
	<i>Xinran Sun, Boxin Xiao, Jiaqing Liu, Xue Feng Lu</i>	
6.1	Introduction	111
6.2	Performance Evaluation Criteria and Methods	114
6.2.1	Overpotential	115
6.2.2	Onset Potential	115
6.2.3	Electrochemical Impedance Spectroscopy	116
6.2.4	Tafel Slope and Exchange Current Density	116
6.2.5	Electrochemically Active Surface Area	116
6.2.6	Mass and Specific Activities	117
6.2.7	Turnover Frequency	117
6.2.8	Faraday Efficiency	118
6.2.9	Stability and Durability	118
6.3	Advanced Electrocatalysts for HER	118
6.3.1	Noble Metal-based Electrocatalysts for Acidic HER	119
6.3.1.1	Alloying	119
6.3.1.2	Heteroatom Doping	119
6.3.1.3	Size and Dimension Regulation	121

6.3.1.4	Lattice Strain Engineering	121
6.3.1.5	Surface and Interface Engineering	122
6.3.2	Transition Metal-based Electrocatalysts for Alkaline HER	123
6.3.2.1	Transition Metal Carbides	125
6.3.2.2	Transition Metal Nitrides	125
6.3.2.3	Transition Metal Phosphides	125
6.3.2.4	Transition Metal Dichalcogenides	126
6.3.2.5	Other Transition Metal-based Electrocatalysts	126
6.3.3	Neutral HER	127
6.4	Summary and Perspective	129
6.4.1	Strengthen Fundamental Theories	130
6.4.2	Develop High-throughput Technology	130
6.4.3	Synthesis High-efficiency Catalysts	130
6.4.4	Standardize Performance Assessment	131
6.4.5	Monitor Deactivation Mechanism	131
6.4.6	Reduce Hydrogen Production Costs	131
	Acknowledgment	132
<b>7</b>	<b>Electrochemical Oxygen Evolution Reaction</b>	<b>139</b>
	<i>Yifan Ma, Junhua Li, Ying Tang, Hang An, Xiaopeng Wang</i>	
7.1	Introduction	139
7.2	The State-of-the-art Characterization Techniques	141
7.3	OER Mechanisms	143
7.3.1	Adsorbate Evolution Mechanism	143
7.3.2	Lattice Oxygen Oxidation Mechanism	145
7.3.3	Oxide Path Mechanism	145
7.3.4	Coupled Oxygen Evolution Mechanism	146
7.4	The Mechanism and Development Status of Some Typical Energy Conversion Reactions	147
7.4.1	Photocatalytic Water Splitting	147
7.4.2	Electrolysis	148
7.4.3	Photoelectrochemical Water Splitting	149
7.5	Catalysis Evaluation and Prediction	149
7.6	Conclusion	150
	Acknowledgment	150
<b>8</b>	<b>Electrochemical Hydrogen/Liquid Fuel Oxidation Reaction</b>	<b>157</b>
	<i>Ran Wang, Huan Pang</i>	
8.1	Introduction	157
8.2	Hydrogen Fuel Oxidation Reaction	158
8.2.1	Hydrogen Oxidation Reaction Mechanism	158
8.2.1.1	HOR Reaction Kinetics	160
8.2.1.2	HBE Theory	161
8.2.2	HOR Catalyst Research Progress	162
8.2.2.1	Catalysts in Acidic Media	162
8.2.2.2	Catalysts in Alkaline Media	163

8.3	Liquid Fuel Oxidation Reaction	164
8.3.1	Liquid Fuel Oxidation Mechanism	164
8.3.1.1	Methanol Oxidation Reaction Mechanism	164
8.3.1.2	Ethanol Oxidation Reaction Mechanism	166
8.3.1.3	Formic Acid Oxidation Reaction Mechanism	167
8.3.2	Liquid Fuel Oxidation Catalyst Research Progress	168
8.3.2.1	Pt-based and Pd-based Electrocatalysts	168
8.3.2.2	Transition Metal-based Catalysts	170
8.3.2.3	Nonmetal Doped Carbon-based Catalysts	172
8.4	Conclusion and Outlook	172
	Acknowledgment	173
<b>9</b>	<b>Catalysts for Electrocatalytic Oxygen Reduction Reaction</b>	<b>183</b>
	<i>An-Liang Wang</i>	
9.1	Introduction	183
9.2	The ORR Mechanism	183
9.3	ORR Catalyst Characterization Techniques	185
9.4	The Category of ORR Catalyst	186
9.4.1	Pt-based Metal Catalysts	186
9.4.1.1	Pt Monometallic, Bimetallic, and Trimetallic Catalysts	186
9.4.1.2	Pt-based High-entropy Alloy Catalysts	188
9.4.1.3	Pt-based Heterostructures	189
9.5	Pd-based Metal Catalysts	190
9.6	Non-platinum Group Metal Catalysts	192
9.7	Metal-free Catalysts	194
9.8	Single-atom Catalysts	195
9.8.1	Pt-based Single-atom Catalysts	196
9.8.2	Fe Single-atom Catalysts	197
9.8.3	Co Single-atom Catalysts	198
9.8.4	Other Single-atom Catalysts	199
9.9	Conclusion and Outlook	200
	Acknowledgment	201
<b>10</b>	<b>Electrochemical Conversion of Biomass Derivatives</b>	<b>209</b>
	<i>Tao Zhang, Jing Peng</i>	
10.1	Introduction	209
10.2	Fundamentals of Electrooxidation of Biomass Derivatives	210
10.2.1	Principle and Mechanism	210
10.2.2	Descriptors of Performance	211
10.2.3	Catalogs of Biomass Derivatives	212
10.2.3.1	Monomer/Polyol	213
10.2.3.2	Furan Compounds	215
10.2.3.3	Glucose	215
10.2.3.4	Lignin	217
10.3	Cathodic Reaction in Biomass Electrooxidation System	218
10.3.1	Coupled Cathodic HER	218

- 10.3.2 Coupled Cathodic CO<sub>2</sub>RR 220
- 10.3.3 Coupled Cathodic NRR 222
- 10.4 Challenges and Future Perspectives 224
  - 10.4.1 Challenges 224
  - 10.4.2 Future Perspectives 224
- 11 Electrochemical CO<sub>2</sub> Reduction and Conversion 231**  
*Jiapeng Ji, Xiaolong Zhang*
  - 11.1 Introduction 231
    - 11.1.1 Importance of CO<sub>2</sub> Reduction in Climate Change and Sustainable Energy Production 231
    - 11.1.2 Brief History and Current State of Electrochemical CO<sub>2</sub> Reduction Research 232
  - 11.2 Fundamentals of ECR 233
    - 11.2.1 Thermodynamics and Kinetics of the CO<sub>2</sub> Reduction Reaction 233
    - 11.2.2 Overview of Different Electrochemical Setups and Electrolytes Used for CO<sub>2</sub> Reduction 234
    - 11.2.3 Introduction to the Concept of Overpotential and Its Significance in Electrochemical Reactions 235
      - 11.2.3.1 Faradaic Efficiency 235
      - 11.2.3.2 Overpotential 235
      - 11.2.3.3 Current Density 236
  - 11.3 Catalysts for ECR 236
    - 11.3.1 Metal-based Catalysts: Discussing the Role of Metals Such as Copper, Silver, and Gold in CO<sub>2</sub> Reduction 236
    - 11.3.2 Nonmetal Catalysts: Exploring the Use of Carbon-based and Other Nonmetallic Materials 238
    - 11.3.3 Hybrid and Nanocomposite Catalysts: Combining Different Materials to Enhance Catalytic Activity 239
  - 11.4 Mechanisms and Pathways of ECR 240
    - 11.4.1 Detailed Description of the Reduction Process, Including Intermediate Steps and Possible Products 241
    - 11.4.2 Factors Influencing the Selectivity of the Reaction Towards Different Products (e.g., Methane, Ethylene, Ethanol) 245
      - 11.4.2.1 Catalyst Properties 245
      - 11.4.2.2 Reaction Conditions 246
      - 11.4.2.3 Electrolyte Composition 246
  - 11.5 Challenges and Opportunities 246
    - 11.5.1 Challenges and Opportunities for the Future Development of ECR 246
    - 11.5.2 Challenges in ECR 247
      - 11.5.2.1 Catalyst Development and Selectivity 247
      - 11.5.2.2 Reaction Conditions and Energy Efficiency 247
      - 11.5.2.3 Scale-up and Commercialization 247
    - 11.5.3 Opportunities for Future Development 248
      - 11.5.3.1 Advanced Catalyst Design and Materials Science 248
      - 11.5.3.2 Electrolyte Engineering and Reaction Engineering 248

- 11.5.3.3 Interdisciplinary Collaboration and Innovation 248
- 11.5.3.4 Sustainability and Environmental Benefits 249
- 11.5.4 Technical Challenges: Addressing Issues Such as Catalyst Deactivation, Product Separation, and Energy Efficiency 249
  - 11.5.4.1 Catalyst Deactivation 250
  - 11.5.4.2 Product Separation 250
  - 11.5.4.3 Energy Efficiency 250
- 11.5.5 Economic Considerations: Cost–Benefit Analysis of ECR Compared to Traditional Chemical Processes 250
  - 11.5.5.1 Raw Material Costs 250
  - 11.5.5.2 Energy Consumption 251
  - 11.5.5.3 Product Separation and Purity 251
  - 11.5.5.4 Sustainability and Environmental Costs 252
  - 11.5.5.5 Equipment Investment and Maintenance 252
- 11.5.6 Environmental Sustainability Evaluation of Electrochemical Conversion Systems 253
  - 11.5.6.1 Energy Source Optimization and Conversion Efficiency 253
  - 11.5.6.2 Catalytic System Selection and Durability Considerations 253
  - 11.5.6.3 Resource Utilization and Output Management 253
  - 11.5.6.4 Comprehensive Life Cycle Analysis 253
- 11.6 Case Studies and Applications 254
  - 11.6.1 Examples of ECR Systems in Laboratory and Pilot Scales 254
    - 11.6.1.1 Laboratory Scale Example 254
    - 11.6.1.2 Pilot and Industrial Scale Examples 256
  - 11.6.2 Discussion on the Potential Industrial Applications and Integration with Existing Chemical Processes 257
    - 11.6.2.1 Potential Industrial Applications 257
    - 11.6.2.2 Integration with Existing Chemical Processes 257
- 11.7 Future Perspectives 257
  - 11.7.1 Exploring New Catalyst Materials and Reaction Conditions to Improve Efficiency and Selectivity 257
  - 11.7.2 Prospects for Scaling Up ECR Technology 258
  - 11.7.3 Policy Frameworks and Economic Incentives for Advancing Industrial ECR Sectors 258
- 11.8 Conclusion 258
  - 11.8.1 Summarizing the Key Points Discussed in this Chapter 258
  - 11.8.2 Highlighting the Importance of ECR in Achieving Sustainability Goals 259
  - 11.8.3 Outlook on the Future of ECR Technology 259
    - 11.8.3.1 Technological Innovation 260
    - 11.8.3.2 Commercial Applications 260
    - 11.8.3.3 Integration with Other Technologies 260
    - 11.8.3.4 Global Cooperation and Policy Support 260

<b>12</b>	<b>Electrochemical Nitrogen Fixation and Conversion</b>	<b>269</b>
	<i>Rong Zhang, Shaoce Zhang, Ying Guo</i>	
12.1	Introduction	269
12.2	Electrocatalytic N <sub>2</sub> Reduction Reaction	271
12.2.1	Electrochemistry of NRR	271
12.2.2	Reaction Pathways of NRR	272
12.2.3	Criteria for the NRR	274
12.2.4	Cathodic NRR Catalyst Materials	277
12.2.4.1	Metal-based NRR Catalysts	278
12.2.4.2	Nonmetal-based NRR Catalysts	283
12.2.5	Challenges and Prospects of the NRR	289
12.3	Electrocatalytic N <sub>2</sub> Oxidation Reaction	289
12.3.1	Development of Nitric Acid Production	289
12.3.2	Electrochemistry of NOR	291
12.3.3	Anodic NOR Catalyst Materials	293
12.3.4	Summary and Challenges of the NOR	294
12.4	Conclusion and Outlook	295
	Acknowledgment	296
<b>13</b>	<b>Recent Progress in Electrochemical C–N Coupling Reactions</b>	<b>311</b>
	<i>Chu Zhang, Chunyuan Feng, Lixiang Zhong, Chade Lv</i>	
13.1	Introduction	311
13.2	Milestones in Electrocatalytic C–N Coupling	312
13.3	Fundamentals of Electrocatalytic C–N Coupling	313
13.3.1	Detection Techniques	314
13.3.2	Key Evaluation Index	316
13.3.3	Reactors	318
13.4	Electrocatalytic C–N Coupling for Urea Synthesis	320
13.4.1	C–N Coupling with CO <sub>2</sub> and N <sub>2</sub>	321
13.4.2	C–N Coupling with CO <sub>2</sub> and Nitric Oxide	324
13.4.3	C–N Coupling with CO <sub>2</sub> and Nitrate/Nitrite	324
13.4.4	C–N Coupling with CO and NH <sub>3</sub>	329
13.5	Electrocatalytic C–N Coupling for Amide Synthesis	330
13.5.1	C–N Coupling with CO <sub>2</sub> and Nitrate/Nitrite	330
13.5.2	C–N Coupling with CO and NO	332
13.5.3	C–N Coupling with CO <sub>2</sub> and NH <sub>3</sub>	333
13.6	Mechanistic Understanding of Electrocatalytic C–N Coupling	335
13.6.1	Theoretical Calculations	335
13.6.2	Operando Studies	337
13.6.3	Other Advanced Techniques	340
13.7	Summary	341
	Acknowledgment	341

<b>14</b>	<b>Electrochemical Fluorination</b>	<b>347</b>
	<i>Meng Li, Chuang Fan, Gengtao Fu</i>	
14.1	Introduction	347
14.2	Electrochemically Driven Fluoroalkylation	348
14.2.1	Electrochemical Trifluoromethylation	348
14.2.2	Electrochemical Difluoromethylation	351
14.3	Electrochemical Selective Fluorination of Alkenes	352
14.3.1	Regioselectivity of Alkenes	353
14.3.2	Stereoselective of Alkenes	354
14.3.3	Chemoselectivity of Alkenes	354
14.4	Ionic Liquids-facilitated Electrofluorination	356
14.4.1	Electrochemical Fluorination in Amine-HF Composite ILs	356
14.4.2	Electrochemical Fluorination in Using Mediators in ILs	358
14.5	Electrochemical Fluorination Using Alkali Metal Fluorides	360
14.6	Conclusion and Outlook	362
	Acknowledgment	363
<b>15</b>	<b>Electrochemical Polymerization: Synthesis of Functional Films for Energy Devices</b>	<b>367</b>
	<i>Yansong Zhou, Shuangyin Wang</i>	
15.1	Introduction	367
15.2	General Principles of Electrochemical Polymerization	368
15.2.1	Definition	368
15.2.2	Characteristics of Electrochemical Polymerization	369
15.2.3	Types of Electrochemical Polymerization	369
15.2.4	Mechanisms of Electrochemical Polymerization	369
15.2.5	Stages of Electrochemical Polymerization	370
15.2.6	Setup, Electrolytes, and Electrochemical Methods	370
15.3	Advanced Electrochemical Polymerization Technology	371
15.4	Electrochemical Polymerization in the Fabrication of Functional Films	372
15.4.1	Electrochemical Polymerization-fabricated Polymers in Optical Devices	372
15.4.2	Electrochemical Polymerization-fabricated Polymers in Energy Conversion Devices	373
15.4.3	Electrochemical Polymerization-fabricated Polymers in Energy Storage Devices	374
15.5	Concluding Remarks	375
	Acknowledgment	376
<b>16</b>	<b>Summary and Perspective</b>	<b>383</b>
	<i>Yuanmiao Sun</i>	
16.1	Summary	383
16.2	Perspective	384