Contents

Preface *xv*
Acknowledgments *xix*

Part I Introduction *1*

1 Introduction *3*
References *5*

Part II Natural Carbon Cycle *7*

2 Natural Carbon Cycle and Anthropogenic Carbon Cycle *9*
2.1 Definition and General Process *9*
2.2 From Inorganic Carbon to Organic Carbon *10*
2.3 From Organic Carbon to Inorganic Carbon *11*
2.4 Anthropogenic Carbon Cycle *11*
2.4.1 Anthropogenic Carbon Emissions *12*
2.4.2 Capture and Recycle of CO_2 from the Atmosphere *13*
2.4.3 Fixation and Conversion of CO_2 *14*
2.4.3.1 Photochemical Reduction *14*
2.4.3.2 Electrochemical Reduction *15*
2.4.3.3 Chemical/Thermo Reforming *16*
2.4.3.4 Physical Fixation *16*
2.4.3.5 Anthropogenic Carbon Conversion and Emissions Via Electrochemistry *17*
References *18*

Part III Electrochemical Catalysis Process *21*

3 Electrochemical Catalysis Processes *23*
3.1 Water Splitting *23*
3.1.1 Reaction Mechanism *23*
3.1.1.1 Mechanism of OER *23*
3.1.1.2 Mechanism of ORR *24*
3.1.1.3 Mechanism of HER *26*
3.1.2 General Parameters to Evaluate Water Splitting *27*
3.1.2.1 Tafel Slope *27*
3.1.2.2 TOF *27*
3.1.2.3 Onset/Overpotential *28*
3.1.2.4 Stability *28*
3.1.2.5 Electrolyte *28*
3.2 Electrochemistry CO_2 Reduction Reaction (ECDRR) *29*
3.2.1 Possible Reaction Pathways of ECDRR *29*
3.2.1.1 Formation of $HCOO^-$ or HCOOH *29*
3.2.1.2 Formation of CO *30*
3.2.1.3 Formation of C_1 Products *30*
3.2.1.4 Formation of C_2 Products *31*
3.2.1.5 Formation of CH_3COOH and CH_3COO^- *33*
3.2.1.6 Formation of *n*-Propanol (C_3 Product) *33*
3.2.2 General Parameters to Evaluate ECDRR *34*
3.2.2.1 Onset Potential *34*
3.2.2.2 Faradaic Efficiency *34*
3.2.2.3 Partial Current Density *34*
3.2.2.4 Environmental Impact and Cost *35*
3.2.2.5 Electrolytes *35*
3.2.2.6 Electrochemical Cells *36*
3.3 Small Organic Molecules Oxidation *36*
3.3.1 The Mechanism of Electrochemistry HCOOH Oxidation *36*
3.3.2 The Mechanism of Electro-oxidation of Alcohol *37*
References *40*

Part IV Water Splitting and Devices *43*

4 Water Splitting Basic Parameter/Others *45*
4.1 Composition and Exact Reactions in Different pH Solution *45*
4.2 Evaluation of the Catalytic Activity *47*
4.2.1 Overpotential *47*
4.2.2 Tafel Slope *48*
4.2.3 Stability *49*
4.2.4 Faradaic Efficiency *49*

4.2.5 Turnover Frequency *50*
References *50*

5 H_2O Oxidation *53*
5.1 Regular H_2O Oxidation *53*
5.1.1 Noble Metal Catalysts *53*
5.1.2 Other Transition Metals *64*
5.1.3 Other Catalysts *72*
5.2 Photo-Assisted H_2O Oxidation *76*
5.2.1 Metal Compound-Based Catalysts *76*
5.2.2 Metal–Metal Heterostructure Catalysts *80*
5.2.3 Metal–Nonmetal Heterostructure Catalysts *86*
References *88*

6 H_2O Reduction and Water Splitting Electrocatalytic Cell *91*
6.1 Noble-Metal-Based HER Catalysts *91*
6.2 Non-Noble Metal Catalysts *93*
6.3 Water Splitting Electrocatalytic Cell *96*
References *99*

Part V H_2 Oxidation/O_2 Reduction and Device *101*

7 Introduction *103*
7.1 Electrocatalytic Reaction Parameters *104*
7.1.1 Electrochemically Active Surface Area (ECSA) *104*
7.1.1.1 Test Methods *104*
7.1.2 Determination Based on the Surface Redox Reaction *104*
7.1.3 Determination by Electric Double-Layer Capacitance Method *105*
7.1.4 Kinetic and Exchange Current Density (j_k and j_0) *105*
7.1.4.1 Definition *105*
7.1.4.2 Calculation *106*
7.1.5 Overpotential HUPD *106*
7.1.6 Tafel Slope *108*
7.1.7 Halfwave Potentials *108*
References *108*

8 Hydrogen Oxidation Reaction (HOR) *111*
8.1 Mechanism for HOR *111*
8.1.1 Hydrogen Bonding Energy (HBE) *111*
8.1.2 Underpotential Deposition (UPD) of Hydrogen *112*
8.2 Catalysts for HOR *112*
8.2.1 Pt-based Materials *112*
8.2.2 Pd-Based Materials *120*
8.2.3 Ir-Based Materials *121*

8.2.4 Rh-Based Materials *121*
8.2.5 Ru-Based Materials *121*
8.2.6 Non-noble Metal Materials *122*
References *130*

9 Oxygen Reduction Reaction (ORR) *133*
9.1 Mechanism for ORR *133*
9.1.1 Battery System and Damaged Electrodes *133*
9.1.2 Intermediate Species *134*
9.2 Catalysts in ORR *134*
9.2.1 Noble Metal Materials *134*
9.2.1.1 Platinum/Carbon Catalyst *138*
9.2.1.2 Pd and Pt *145*
9.2.2 Transition Metal Catalysts *145*
9.2.3 Metal-Free Catalysts *149*
9.3 Hydrogen Peroxide Synthesis *154*
9.3.1 Catalysts Advances *154*
9.3.1.1 Pure Metals *154*
9.3.1.2 Metal Alloys *156*
9.3.1.3 Carbon Materials *157*
9.3.1.4 Electrodes and Reaction Cells *158*
References *161*

10 Fuel Cell and Metal-Air Battery *167*
10.1 H_2 Fuel Cell *167*
10.2 Metal-Air Battery *170*
10.2.1 Metal-Air Battery Structure *171*
References *181*

Part VI Small Organic Molecules Oxidation and Device *183*

11 Introduction *185*
11.1 Primary Measurement Methods and Parameters *186*
11.1.1 Primary Measurement Methods *186*
11.1.2 Primary Parameter *193*
References *197*

12 C1 Molecule Oxidation *199*
12.1 Methane Oxidation *199*
12.1.1 Reaction Mechanism *199*
12.1.1.1 Solid–Liquid–Gas Reaction System *199*
12.1.2 Acidic Media *199*
12.1.3 Alkaline or Neutral Media *201*
12.2 Methanol Oxidation *203*

12.2.1 Reaction Thermodynamics and Mechanism *203*
12.2.2 Catalyst Advances *204*
12.2.2.1 Pd-Based Catalysts *204*
12.2.2.2 Pt-Based Catalysts *208*
12.2.2.3 Platinum-Based Nanowires *208*
12.2.2.4 Platinum-Based Nanotubes *210*
12.2.2.5 Platinum-Based Nanoflowers *212*
12.2.2.6 Platinum-Based Nanorods *214*
12.2.2.7 Platinum-Based Nanocubes *215*
12.2.3 Pt–Ru System *217*
12.2.4 Pt–Sn Catalysts *218*
12.3 Formic Acid Oxidation *219*
12.3.1 Reaction Mechanism *219*
12.3.2 Catalyst Advances *220*
12.3.2.1 Pd-Based Catalysts *220*
12.3.2.2 Pt-Based Catalysts *223*
References *226*

13 C_{2+} Molecule Oxidation *235*
13.1 Ethanol Oxidation *235*
13.1.1 Reaction Mechanism *235*
13.1.2 Catalyst Advances *235*
13.1.2.1 Pd-Based Catalysts *235*
13.1.2.2 Pt-Based Catalysts *239*
13.1.2.3 Pt–Sn System *243*
13.2 Glucose Oxidase *250*
13.3 Ethylene Glycol Oxidation *251*
13.4 Glycerol Oxidation *251*
References *254*

14 Fuel Cell Devices *257*
14.1 Introduction *257*
14.2 Types of Direct Liquid Fuel Cells *258*
14.2.1 Acid and Alkaline Fuel Cells *258*
14.2.2 Direct Methanol Fuel Cells (DMFCs) *260*
14.2.3 Direct Ethanol Fuel Cells (DEFCs) *261*
14.2.4 Direct Ethylene Glycol Fuel Cells (DEGFCs) *261*
14.2.5 Direct Glycerol Fuel Cells (DGFCs) *262*
14.2.6 Direct Formic Acid Fuel Cells (DFAFCs) *262*
14.2.7 Direct Dimethyl Ether Fuel Cells (DDEFCs) *263*
14.2.8 Other DLFCs *263*
14.2.9 Challenges of DLFCs *264*
14.2.10 Fuel Conversion and Cathode Flooding *264*
14.2.11 Chemical Safety and By-product Production *265*

14.2.12 Unproven Long-term Durability *265*
References *267*

Part VII CO_2 Reduction and Device *271*

15 Introduction *273*
15.1 Basic Parameters of the CO_2 Reduction Reaction *276*
15.1.1 The Fundamental Parameters to Evaluate the Catalytic Activity *276*
15.1.1.1 Overpotential (η) *276*
15.1.1.2 Faradaic Efficiency (FE) *276*
15.1.1.3 Current Density (j) *277*
15.1.1.4 Energy Efficiency (EE) *277*
15.1.1.5 Tafel Slope *278*
15.1.2 Factors Affecting ECDRR *278*
15.1.2.1 Solvent/Electrolyte *278*
15.1.2.2 pH *280*
15.1.2.3 Cations and Anions *281*
15.1.2.4 Concentration *282*
15.1.2.5 Temperature and Pressure Effect *282*
15.1.3 Electrode *283*
15.1.3.1 Loading Method *283*
15.1.3.2 Preparation *284*
15.1.3.3 Experimental Process and Analysis Methods *284*
References *285*

16 Electrocatalysts-1 *289*
16.1 Heterogeneous Electrochemical CO_2 Reduction Reaction *289*
16.2 Thermodynamic and Kinetic Parameters of Heterogeneous CO_2 Reduction in Liquid Phase *289*
16.2.1 Bulk Metals *293*
16.2.2 Nanoscale Metal and Oxidant Metal Catalysts *294*
16.2.2.1 Gold (Au) *295*
16.2.2.2 Silver (Ag) *296*
16.2.2.3 Palladium (Pd) *297*
16.2.2.4 Zinc (Zn) *298*
16.2.2.5 Copper (Cu) *299*
16.2.3 Bimetallic/Alloy *301*
References *306*

17 Electrocatalysts-2 *309*
17.1 Single-Atom Metal-Doped Carbon Catalysts (SACs) *309*
17.1.1 Nickel (Ni)-SACs *309*
17.1.2 Cobalt (Co)-SACs *311*
17.1.3 Iron (Fe)-SACs *311*

17.1.4 Zinc (Zn)-SACs *314*
17.1.5 Copper (Cu)-SACs *314*
17.1.6 Other *316*
17.2 Metal Nanoparticles-Doped Carbon Catalysts *317*
17.3 Porous Organic Material *320*
17.3.1 Metal Organic Frameworks (MOFs) *320*
17.3.2 Covalent Organic Frameworks (COFs) *321*
17.3.3 Metal-Free Catalyst *322*
17.4 Metal-Free Carbon-Based Catalyst *322*
17.4.1 Other Metal-Free Catalyst *324*
17.5 Electrochemical CO Reduction Reaction *324*
17.5.1 The Importance of CO Reduction Study *324*
17.5.2 Advances in CO Reduction *326*
References *327*

18 Devices *331*
18.1 H-Cell *331*
18.2 Flow Cell *333*
18.3 Requirements and Challenges for Next-Generation CO_2 Reduction Cell *338*
18.3.1 Wide Range of Electrocatalysts *338*
18.3.2 Fundamental Factor Influencing the Catalytic Activity for ECDRR *339*
18.3.3 Device Engineering *340*
References *342*

Part VIII Computations-Guided Electrocatalysis *345*

19 Insights into the Catalytic Process *347*
19.1 Electric Double Layer *347*
19.2 Kinetics and Thermodynamics *349*
19.3 Electrode Potential Effects *350*
References *352*

20 Computational Electrocatalysis *355*
20.1 Computational Screening Toward Calculation Theories *356*
20.2 Reactivity Descriptors *358*
20.2.1 d-band Theory Motivates Electronic Descriptor *359*
20.2.2 Coordination Numbers Motives Structure Descriptor *361*
20.3 Scaling Relationships: Applications of Descriptors *361*
20.4 The Activity Principles and the Volcano Curve *363*
20.5 DFT Modeling *366*
20.5.1 CHE Model *367*
20.5.2 Solvation Models *368*

20.5.3 Kinetic Modeling *371*
References *374*

21 Theory-Guided Rational Design *377*
21.1 Descriptors-Guided Screening *377*
21.2 Scaling Relationship-Guided Trends *380*
21.2.1 Reactivity Trends of ECR *380*
21.2.2 Reactivity Trends of O-included Reactions *382*
21.2.3 Reactivity Trends of H-included Reactions *385*
21.3 DOS-Guided Models and Active Sites *386*
References *388*

22 DFT Applications in Selected Electrocatalytic Systems *391*
22.1 Unveiling the Electrocatalytic Mechanism *391*
22.1.1 ECR Reaction *393*
22.1.2 OER Reaction *394*
22.1.3 ORR Reaction *396*
22.1.4 HER Reaction *397*
22.1.5 HOR Reaction *398*
22.1.6 CO Oxidation Reaction *400*
22.1.7 FAOR Reaction *402*
22.1.8 MOR Reaction *402*
22.1.9 EOR Reaction *404*
22.2 Understanding the Electrocatalytic Environment *406*
22.2.1 Solvation Effects *406*
22.2.2 pH Effects *409*
22.3 Analyzing the Electrochemical Kinetics *410*
22.4 Perspectives, Challenges, and Future Direction of DFT Computation in Electrocatalysis *413*
References *414*

Part IX Potential of In Situ Characterizations for Electrocatalysis *421*
References *422*

23 In Situ Characterization Techniques *423*
23.1 Optical Characterization Techniques *423*
23.1.1 Infrared Spectroscopy *423*
23.1.2 Raman Spectroscopy *424*
23.1.3 UV–vis Spectroscopy *426*
23.2 X-Ray Characterization Techniques *427*
23.2.1 X-Ray Diffraction (XRD) *429*
23.2.2 X-Ray Absorption Spectroscopy (XAS) *429*
23.2.3 X-Ray Photoelectron Spectroscopy (XPS) *431*
23.3 Mass Spectrometric Characterization Techniques *431*

23.4 Electron-Based Characterization Techniques *432*
23.4.1 Transmission Electron Microscopy (TEM) *434*
23.4.2 Scanning Probe Microscopy (SPM) *434*
References *436*

24 In Situ Characterizations in Electrocatalytic Cycle *441*
24.1 Investigating the Real Active Centers *441*
24.1.1 Monitoring the Electronic Structure *442*
24.1.2 Monitoring the Atomic Structure *444*
24.1.3 Monitoring the Catalyst Phase Transformation *446*
24.2 Investigating the Reaction Mechanism *449*
24.2.1 Through Adsorption/Activation Understanding *450*
24.2.2 Through Intermediates In Situ Probing *451*
24.2.3 Through Catalytic Product In Situ Detections *454*
24.3 Evaluating the Catalyst Stability/Decay *457*
24.4 Revealing the Interfacial-Related Insights *460*
24.5 Conclusion *462*
References *462*

Part X Electrochemical Catalytic Carbon Cycle *465*
References *466*

25 Electrochemical CO_2 Reduction to Fuels *467*
References *479*

26 Electrochemical Fuel Oxidation *483*
References *495*

27 Evaluation and Management of ECC *499*
27.1 Basic Performance Index *499*
27.2 CO_2 Capture and Fuel Transport *500*
27.3 External Management *500*
27.4 General Outlook *502*
References *505*

Index *507*