

Contents

Preface xv

Part I Overview of Systems 1

1	System-level Constraints on Fuel Cell Materials and Electrocatalysts 3
	<i>Elliot Padgett and Dimitrios Papageorgopoulos</i>
1.1	Overview of Fuel Cell Applications and System Designs 3
1.1.1	System-level Fuel Cell Metrics 3
1.1.2	Fuel Cell Subsystems and Balance of Plant (BOP) Components 5
1.1.3	Comparison of Fuel Cell Systems for Different Applications 9
1.2	Application-derived Requirements and Constraints 10
1.2.1	Fuel Cell Performance and the Heat Rejection Constraint 10
1.2.2	Startup, Flexibility, and Robustness 13
1.2.3	Fuel Cell Durability 14
1.2.4	Cost 16
1.3	Material Pathways to Improved Fuel Cells 18
1.4	Note 19
	Acronyms 20
	Symbols 20
	References 20
2	PEM Fuel Cell Design from the Atom to the Automobile 23
	<i>Andrew Haug and Michael Yandrasits</i>
2.1	Introduction 23
2.2	The PEMFC Catalyst 27
2.3	The Electrode 32
2.4	Membrane 38
2.5	The GDL 42
2.6	CCM and MEA 46

- 2.7 Flowfield and Single Fuel Cell 50
- 2.8 Stack and System 55
 - Acronyms 57
 - References 58

Part II Basics – Fundamentals 69

- 3 Electrochemical Fundamentals 71**

Vito Di Noto, Gioele Pagot, Ketì Vezzù, Enrico Negro, and Paolo Sgarbossa

 - 3.1 Principles of Electrochemistry 71
 - 3.2 The Role of the First Faraday Law 71
 - 3.3 Electric Double Layer and the Formation of a Potential Difference at the Interface 73
 - 3.4 The Cell 74
 - 3.5 The Spontaneous Processes and the Nernst Equation 75
 - 3.6 Representation of an Electrochemical Cell and the Nernst Equation 77
 - 3.7 The Electrochemical Series 79
 - 3.8 Dependence of the E_{cell} on Temperature and Pressure 82
 - 3.9 Thermodynamic Efficiencies 83
 - 3.10 Case Study – The Impact of Thermodynamics on the Corrosion of Low-T FC Electrodes 85
 - 3.11 Reaction Kinetics and Fuel Cells 88
 - 3.11.1 Correlation Between Current and Reaction Kinetics 88
 - 3.11.2 The Concept of Exchange Current 89
 - 3.12 Charge Transfer Theory Based on Distribution of Energy States 89
 - 3.12.1 The Butler–Volmer Equation 96
 - 3.12.2 The Tafel Equation 100
 - 3.12.3 Interplay Between Exchange Current and Electrocatalyst Activity 101
 - 3.13 Conclusions 103
 - Acronyms 104
 - Symbols 104
 - References 107
- 4 Quantifying the Kinetic Parameters of Fuel Cell Reactions 111**

Viktoriia A. Saveleva, Juan Herranz, and Thomas J. Schmidt

 - 4.1 Introduction 111
 - 4.2 Electrochemical Active Surface Area (ECSA) Determination 114
 - 4.2.1 ECSA Determination Using Underpotential Deposition 115
 - 4.2.1.1 Hydrogen Underpotential Deposition (H_{UPD}) 116
 - 4.2.1.2 Copper Underpotential Deposition (Cu_{UPD}) 117
 - 4.2.2 ECSA Quantification Based on the Adsorption of Probe Molecules 118

4.2.2.1	CO Stripping	118
4.2.2.2	NO_2^-/NO Sorption	119
4.2.3	Double-layer Capacitance Measurements and Other Methods	120
4.2.4	ECSA Measurements in a PEFC: Which Method to Choose?	120
4.3	H_2 -Oxidation and Electrochemical Setups for the Quantification of Kinetic Parameters	121
4.3.1	Rotating Disc Electrodes (RDEs)	122
4.3.2	Hydrogen Pump (PEFC) Approach	124
4.3.3	Ultramicroelectrode Approach	125
4.3.4	Scanning Electrochemical Microscopy (SECM) Approach	125
4.3.5	Floating Electrode Method	127
4.3.6	Methods Summary	128
4.4	ORR Kinetics	129
4.4.1	ORR Mechanism Studies with RRDE Setups	129
4.4.2	ORR Pathway on Me/N/C ORR Catalysts	130
4.4.3	ORR Kinetics: Methods	132
4.4.3.1	Pt-based Electrodes	132
4.4.3.2	Pt-free Catalysts: RDE vs. PEFC Kinetic Studies	133
4.5	Concluding Remarks	133
	Acronyms	134
	Symbols	134
	References	135
5	Adverse and Beneficial Functions of Surface Layers Formed on Fuel Cell Electrocatalysts	149
	<i>Shimshon Gottesfeld</i>	
5.1	Introduction	149
5.2	Catalyst Capping in Heterogeneous Catalysis and in Electrocatalysis	151
5.3	Passivation of PGM/TM and Non-PGM HOR Catalysts and Its Possible Prevention	156
5.4	Literature Reports on Fuel Cell Catalyst Protection by Capping	161
5.4.1	Protection of ORR Pt catalysts Against Agglomeration by an Ultrathin Overlayer of Mesoporous SiO_2 or Me- SiO_2	161
5.4.2	Protection by Carbon Caps Against Catalyst Detachment and Catalyst Passivation Under Ambient Conditions	162
5.5	Other Means for Improving the Performance Stability of Supported Electrocatalysts	166
5.5.1	Replacement of Carbon Supports by Ceramic Supports	166
5.5.2	Protection of Pt Catalysts by Enclosure in Mesopores	167
5.6	Conclusions	170
	Abbreviations	171
	References	171

Part III State of the Art 175

- 6 Design of PGM-free ORR Catalysts: From Molecular to the State of the Art 177**
Naomi Levy and Lior Elbaz
- 6.1 Introduction 177
 - 6.2 The Influence of Molecular Changes Within the Complex 179
 - 6.2.1 The Role of the Metal Center 179
 - 6.2.2 Addition of Substituents to MCs 183
 - 6.2.2.1 Beta-substituents 184
 - 6.2.2.3 Meso-substituents 186
 - 6.2.2.4 Axial Ligands 187
 - 6.3 Cooperative Effects Between Neighboring MCs 190
 - 6.3.1 Bimetallic Cofacial Complexes – “Packman” Complexes 191
 - 6.3.2 MC Polymers 191
 - 6.4 The Physical and/or Chemical Interactions Between the Catalyst and Its Support Material 193
 - 6.5 Effect of Pyrolysis 194
 - Acronyms 196
 - References 196
- 7 Recent Advances in Electrocatalysts for Hydrogen Oxidation Reaction in Alkaline Electrolytes 205**
Indra N. Pulidindi and Meital Shviro
- 7.1 Introduction 205
 - 7.2 Mechanism of the HOR in Alkaline Media 206
 - 7.3 Electrocatalysts for Alkaline HOR 212
 - 7.3.1 Platinum Group Metal HOR Electrocatalysts 212
 - 7.3.2 Non-platinum Group Metal-based HOR Electrocatalysts 214
 - 7.4 Conclusions 220
 - Acronyms 221
 - References 221
- 8 Membranes for Fuel Cells 227**
Paolo Sgarbossa, Giovanni Crivellaro, Francesco Lanero, Gioele Pagot, Afaaf R. Alvi, Enrico Negro, Ketì Vezzù, and Vito Di Noto
- 8.1 Introduction 227
 - 8.2 Properties of the PE separators 228
 - 8.2.1 Benchmarking of IEMs 229
 - 8.2.2 Ion-exchange Capacity (IEC) 229
 - 8.2.3 Water Uptake (WU), Swelling Ratio (SR), and Water Transport 231
 - 8.2.4 Ionic Conductivity (σ) 233
 - 8.2.5 Gas Permeability 234
 - 8.2.6 Chemical Stability 235
 - 8.2.7 Thermal and Mechanical Stability 237

8.2.8	Cost of the IEMs	239
8.3	Classification of Ion-exchange Membranes	240
8.3.1	Cation-exchange Membranes (CEMs)	240
8.3.1.1	Perfluorinated Membranes	240
8.3.1.2	Nonperfluorinated Membranes	245
8.3.2	Anion-exchange Membranes (AEMs)	246
8.3.2.1	Functionalized Polyketones	247
8.3.2.2	Poly(Vinyl Benzyl Trimethyl Ammonium) (PVBtMA) Polymers	248
8.3.2.3	Poly(sulfones) (PS)	249
8.3.3	Hybrid Ion-exchange Membranes	249
8.3.3.1	Hybrid Membranes with Single Ceramic Oxoclusters $[P/(M_xO_y)_n]$	250
8.3.3.2	Hybrid Membranes Comprising Surface-functionalized Nanofillers	254
8.3.3.3	Hybrid Membranes Doped with hierarchical “Core-Shell” Nanofillers	254
8.3.4	Porous Membranes	257
8.3.4.1	Porous Membranes as Host Material	257
8.3.4.2	Porous Membranes as Support Layer	258
8.3.4.3	Porous Membranes as Unconventional Separators	259
8.4	Mechanism of Ion Conduction	259
8.5	Summary and Perspectives	268
	Acronyms	271
	Symbols	272
	References	272

9 Supports for Oxygen Reduction Catalysts: Understanding and Improving Structure, Stability, and Activity 287

Iwona A. Rutkowska, Sylwia Zoladek, and Pawel J. Kulesza

9.1	Introduction	287
9.2	Carbon Black Supports	288
9.3	Decoration and Modification with Metal Oxide Nanostructures	289
9.4	Carbon Nanotube as Carriers	291
9.5	Doping, Modification, and Other Carbon Supports	293
9.6	Graphene as Catalytic Component	293
9.7	Metal Oxide-containing ORR Catalysts	296
9.8	Photodeposition of Pt on Various Oxide-Carbon Composites	299
9.9	Other Supports	301
9.10	Alkaline Medium	302
9.11	Toward More Complex Hybrid Systems	303
9.12	Stabilization Approaches	306
9.13	Conclusions and Perspectives	307
	Acknowledgment	308
	Acronyms	308
	References	308

Part IV Physical–Chemical Characterization 319

- 10 Understanding the Electrocatalytic Reaction in the Fuel Cell by Tracking the Dynamics of the Catalyst by X-ray Absorption Spectroscopy 321**
Ditty Dixon, Aiswarya Bhaskar, and Aswathi Thottungal
- 10.1 Introduction 321
- 10.2 A Short Introduction to XAS 323
- 10.3 Application of XAS in Electrocatalysis 325
- 10.3.1 *Ex Situ* Characterization of Electrocatalyst 325
- 10.3.2 *Operando* XAS Studies 330
- 10.4 $\Delta\mu$ XANES Analysis to Track Adsorbate 334
- 10.5 Time-resolved *Operando* XAS Measurements in Fuel Cells 338
- 10.6 Fourth-generation Synchrotron Facilities and Advanced Characterization Techniques 340
- 10.6.1 Total-reflection Fluorescence X-ray Absorption Spectroscopy 341
- 10.6.2 Resonant X-ray Emission Spectroscopy (RXES) 341
- 10.6.3 Combined XRD and XAS 342
- 10.7 Conclusions 342
- Acronyms 343
- References 344

Part V Modeling 349

- 11 Unraveling Local Electrocatalytic Conditions with Theory and Computation 351**
Jun Huang, Mohammad J. Eslamibidgoli, and Michael H. Eikerling
- 11.1 Local Reaction Conditions: Why Bother? 351
- 11.2 From Electrochemical Cells to Interfaces: Basic Concepts 352
- 11.3 Characteristics of Electrocatalytic Interfaces 355
- 11.4 Multifaceted Effects of Surface Charging on the Local Reaction Conditions 356
- 11.5 The Challenges in Modeling Electrified Interfaces using First-principles Methods 358
- 11.5.1 Computational Hydrogen Electrode 359
- 11.5.2 Unit-cell Extrapolation, Explicit Solvated Protons, and Excess Electrons 360
- 11.5.3 Counter Charge and Reference Electrode 361
- 11.5.4 Effective Screening Medium and mPB Theory 361
- 11.5.5 Grand-canonical DFT 362
- 11.6 A Concerted Theoretical–Computational Framework 362
- 11.7 Case Study: Oxygen Reduction at Pt(111) 364

11.8	Outlook	367
	Acronyms	367
	Symbols	368
	References	368

Part VI Protocols 375

12	Quantifying the Activity of Electrocatalysts	377
	<i>Karla Vega-Granados and Nicolas Alonso-Vante</i>	
12.1	Introduction: Toward a Systematic Protocol for Activity Measurements	377
12.2	Materials Consideration	378
12.2.1	PGM Group	378
12.2.2	Low PGM and PGM-free Approaches	379
12.2.3	Impact of Support Effects on Catalytic Sites	381
12.3	Electrochemical Cell Considerations	382
12.3.1	Cell Configuration and Material	382
12.3.2	Electrolyte	385
12.3.2.1	Purity	385
12.3.2.2	Protons vs. Hydroxide Ions	386
12.3.2.3	Influence of Counterions	388
12.3.3	Electrode Potential Measurements	388
12.3.4	Preparation of Electrodes	391
12.3.5	Well-defined and Nanoparticulated Objects	395
12.4	Parameters Diagnostic of Electrochemical Performance	396
12.4.1	Surface Area	396
12.4.2	Hydrogen Underpotential Deposition Integration	397
12.4.2.1	Surface Oxide Reduction	398
12.4.2.2	CO Monolayer Oxidation (CO Stripping)	400
12.4.2.3	Underpotential Deposition of Metals	401
12.4.2.4	Double-layer Capacitance	402
12.4.3	Electrocatalysts Site Density	402
12.4.4	Data Evaluation (Half-Cell Reactions)	404
12.4.5	The $E_{1/2}$ and $E(j_{Pt}(5\%))$ Parameters	405
12.5	Stability Tests	407
12.6	Data Evaluation (Auxiliary Techniques)	409
12.6.1	Surface Atoms vs. Bulk	410
12.7	Conclusions	411
	Acknowledgments	412
	Acronyms	412
	Symbols	413
	References	414

13	Durability of Fuel Cell Electrocatalysts and Methods for Performance Assessment	429
	<i>Bianca M. Ceballos and Piotr Zelenay</i>	
13.1	Introduction	429
13.2	Fuel Cell PGM-free Electrocatalysts for Low-temperature Applications	431
13.3	PGM-free Electrocatalyst Degradation Pathways	432
13.3.1	Demetallation	432
13.3.2	Carbon Oxidation	436
13.3.3	Micropore Flooding	439
13.3.4	Nitrogen Protonation and Anionic Adsorption	439
13.4	PGM-free Electrocatalyst Durability and Metrics	440
13.4.1	Performance and Durability Evaluation in Air-supplied Fuel Cell Cathode	440
13.4.2	Assessment of Carbon Corrosion in Nitrogen-purged Cathode	443
13.4.3	Determination of Performance Loss upon Cycling Cathode Catalyst in Nitrogen	443
13.4.4	Recommendations for ORR Electrocatalyst Evaluation in RRDE in O ₂ and in an Inert Gas	446
13.4.5	Electrocatalyst Corrosion	447
13.5	Low-PGM Catalyst Degradation	447
13.5.1	Pt Dissolution	449
13.5.2	Carbon Support Corrosion	452
13.5.3	Pt Catalyst MEA Activity Assessment and Durability	454
13.5.4	PGM Electrocatalyst MEA Conditioning in H ₂ /Air	454
13.5.5	Accelerated Stress Test of PGM Electrocatalyst Durability	456
13.6	Conclusion	457
	Acronyms	459
	References	460

Part VII Systems 471

14	Modeling of Polymer Electrolyte Membrane Fuel Cells	473
	<i>Andrea Baricci, Andrea Casalegno, Dario Maggiolo, Federico Moro, Matteo Zago, and Massimo Guarnieri</i>	
14.1	Introduction	473
14.2	General Equations for PEMFC Models	474
14.2.1	Analytical and Numerical Modeling	474
14.2.2	Reversible Electromotive Force	476
14.2.3	Fuel Cell Voltage	477
14.2.4	Activation Overpotential	478
14.2.5	Ohmic Overpotential – PEM Model	479
14.2.6	Concentration Overpotential	480
14.2.7	Examples of Fuel Cell Modeling	482

14.3	Multiphase Water Transport Model for PEMFCs	483
14.4	Fluid Mechanics in PEMFC Porous Media: From 3D Simulations to 1D Models	488
14.4.1	From Micro- to Macroscopic Models	490
14.4.2	Porous Medium Anisotropy	491
14.4.3	Fluid–Fluid Viscous Drag	492
14.4.4	Surface Tension and Capillary Pressure	492
14.5	Physical-based Modeling for Electrochemical Impedance Spectroscopy	496
14.5.1	Experimental Measurement and Modeling Approaches	496
14.5.2	Physical-based Modeling	497
14.5.2.1	Current Relaxation	497
14.5.2.2	Laplace Transform	498
14.5.3	Typical Impedance Features of PEMFC	498
14.5.4	Application of EIS Modeling to PEMFC Diagnostic	500
14.5.5	Approximations of 1D Approach	501
14.6	Conclusions and Perspectives	502
	Acronyms	503
	Symbols	504
	References	507
15	Physics-based Modeling of Polymer Electrolyte Membrane Fuel Cells: From Cell to Automotive Systems	511
	<i>Andrea Baricci, Matteo Zago, Simone Buso, Marco Sorrentino, and Andrea Casalegno</i>	
15.1	Polymer Fuel Cell Model for Stack Simulation	511
15.1.1	General Characteristics of a Fuel Cell System for Automotive Applications	511
15.1.2	Analysis of the Channel Geometry for Stack Performance Modeling	514
15.1.3	Analysis of the Air and Hydrogen Utilization for Stack Performance Modeling	516
15.1.4	Introduction to Transient Stack Models	518
15.2	Auxiliary Subsystems Modeling	519
15.2.1	Air Management Subsystem	519
15.2.2	Hydrogen Management Subsystem	521
15.2.3	Thermal Management Subsystem	522
15.2.4	PEMFC System Simulation	522
15.3	Electronic Power Converters for Fuel Cell-powered Vehicles	525
15.3.1	Power Converter Architecture	527
15.3.2	Load Adaptability	527
15.3.3	Power Electronic System Components	528
15.3.3.1	Port Interface Converters	530
15.3.3.2	The PEMFC Interface Converter	530
15.3.3.3	The Motor Interface Converter	530
15.3.3.4	The Energy Storage Interface	531

15.3.3.5	Supervisory Control	531
15.4	Fuel Cell Powertrains for Mobility Use	532
15.4.1	Transport Application Scenarios	532
15.4.2	Tools for the Codesign of Transport Fuel Cell Systems and Energy Management Strategies	534
15.4.2.1	Automotive Case Study: Optimal Codesign of an LDV FCHV Powertrain	535
	Acronyms	540
	Symbols	541
	References	541
	Index	545