

Contents

List of Contributors *XIII*

Series Editors Preface *XIX*

Preface *XXI*

1	Properties of Carbon: An Overview	1
	<i>Shengxi Huang, Johan Ek Weis, Sara Costa, Martin Kalbac, and Mildred S. Dresselhaus</i>	
1.1	Overview of Properties	1
1.2	Different Forms of Carbon	2
1.2.1	Graphene	2
1.2.1.1	Optical Properties	2
1.2.1.2	Electrical Properties and Tunability	4
1.2.1.3	Spectroscopic Properties	5
1.2.2	HOPG	11
1.2.3	Carbon Nanotube	12
1.2.3.1	Structure and Electronic Properties	12
1.2.3.2	Spectroscopy and Spectroelectrochemistry of Carbon Nanotubes	14
1.2.4	Graphene Nanoribbon	18
1.2.5	Diamond	20
1.2.6	Porous Carbon	20
1.3	Outlook	21
	References	21
2	Electrochemistry at Highly Oriented Pyrolytic Graphite (HOPG): Toward a New Perspective	31
	<i>Aleix G. Güell, Sze-yin Tan, Patrick R. Unwin, and Guohui Zhang</i>	
2.1	Introduction	31
2.2	Structure and Electronic Properties of HOPG	33
2.2.1	Structure and Formation	33
2.2.2	Electronic Properties	39
2.2.3	Implications for Electrochemical Studies	44
2.3	Formative Studies of HOPG Electrochemistry	45

2.3.1	Early Macroscopic Voltammetric Measurements and Correlations	45
2.3.2	Macroscopic Voltammetry and Modeling	49
2.3.3	Alternating Current (AC) Voltammetric Methods	50
2.3.4	Critical Comparison of Macroscopic Data	50
2.4	Microscopic Views of Electrochemistry at HOPG	53
2.4.1	Outer-Sphere Redox Systems	53
2.4.1.1	Scanning Micropipette Contact Method	53
2.4.1.2	Nafion Film-Covered HOPG	55
2.4.1.3	Scanning Electrochemical Cell Microscopy (SECCM)	56
2.4.1.4	Scanning Electrochemical Microscopy (SECM)	60
2.4.1.5	SECM–AFM Studies	61
2.4.1.6	Recent Macroscopic Studies	62
2.4.2	Complex Multistep Reactions: Neurotransmitter Oxidation	64
2.4.3	Adsorbed Systems	68
2.4.4	Diazonium Functionalization of HOPG	71
2.5	Conclusions	73
	Acknowledgments	75
	References	75
3	Electrochemistry in One Dimension: Applications of Carbon Nanotubes	83
	<i>Emiliano N. Primo, Fabiana Gutiérrez, María D. Rubianes, Nancy F. Ferreyra, Marcela C. Rodríguez, María. L. Pedano, Aurelien Gasnler, Alejandro Gutierrez, Marcos Eguilaz, Pablo Dalmaso, Guillermina Luque, Soledad Bollo, Concepción Parrado, and Gustavo A. Rivas</i>	
3.1	Carbon Nanotubes: General Considerations	83
3.2	Structure and Synthesis of CNTs	84
3.3	Structure of CNTs versus Electrochemical Properties	86
3.4	Strategies for the Preparation of Carbon Nanotube-Based Electrodes	89
3.4.1	Functionalization	89
3.4.1.1	Covalent Functionalization	90
3.4.1.2	Noncovalent Functionalization	90
3.4.2	Preparation of Carbon Nanotube Paste Electrodes Using Different Binders	106
3.4.2.1	Screen-Printed Electrodes (SPE)	108
3.5	Prospective Work	108
	References	109
4	Electrochemistry of Graphene	121
	<i>Hollie V. Patten, Matěj Velický, and Robert A.W. Dryfe</i>	
4.1	Overview of Graphene Properties	121
4.2	Preparation of Graphene	123

4.2.1	Top-Down Fabrication of Graphene	123
4.2.2	"Bottom-Up" Routes to Graphene Production	128
4.3	Capacitance of Graphene Electrodes	130
4.4	Electron Transfer Kinetics at Graphene Electrodes	137
4.4.1	Modification and Doping of Graphene for Applications in Electrocatalysis	149
4.5	Conclusion and Future Directions	151
	Abbreviations	152
	Symbols	152
	References	153
5	The Use of Conducting Diamond in Electrochemistry	163
	<i>Julie V. Macpherson</i>	
5.1	Introduction	163
5.1.1	Boron-Doped Diamond: Electrical Properties	164
5.1.2	Growth of Synthetic Boron-Doped Diamond for Electrochemical Applications	166
5.1.2.1	High-Pressure High-Temperature (HPHT) Growth	166
5.1.2.2	Chemical Vapor Deposition Growth	167
5.2	Electrode Geometries and Arrangements	170
5.2.1	Characterization of BDD Electrochemical and Material Properties	174
5.2.1.1	Assessment of Surface Morphology	174
5.2.1.2	Extended Solvent Window and Low Capacitance	175
5.2.1.3	Raman Interrogation of sp^2/sp^3 Ratio in BDD	177
5.2.1.4	Outer-Sphere Redox Species Characterization	180
5.3	Effect of Surface Termination on the Electrochemical Response of BDD	182
5.3.1	Inner-Sphere Versus Outer-Sphere Electron Transfer Mechanisms	182
5.3.2	Hydrogen- and Oxygen-Terminated Diamond	183
5.3.2.1	Heterogeneous Electron Transfer Kinetics at Hydrogen- Versus Oxygen-Terminated Electrodes	186
5.4	Polycrystalline Versus Single-Crystal Electrochemistry	190
5.4.1	Electrochemical Imaging of Polycrystalline BDD	191
5.4.2	Single-Crystal BDD Electrochemistry	193
5.5	Imparting Catalytic Activity on BDD	195
5.5.1	Metal Nanoparticle-Coated BDD Electrodes	195
5.5.2	Ion Implantation	197
5.6	Chemical Functionalization of BDD Electrodes	197
5.7	Electroanalytical Applications of BDD	199
5.8	Conclusions	201
	Acknowledgments	202
	References	202

6	Modification of Carbon Electrode Surfaces	211
	<i>Muhammad Tanzirul Alam and J. Justin Gooding</i>	
6.1	Introduction	211
6.2	Covalent Modification	212
6.2.1	Reduction of Diazonium Cation	212
6.2.2	Oxidation of Amine	220
6.2.3	Oxidation of Carboxylate	223
6.2.4	Oxidation of Alcohol	225
6.2.5	Hydrogenation and Halogenation of Carbon	226
6.3	Noncovalent Modification	228
6.3.1	π - π Stacking	228
6.3.2	Surfactant	231
6.4	Future Directions	234
	Acknowledgments	235
	References	235
7	Carbon Materials in Low-Temperature Polymer Electrolyte Membrane Fuel Cells	241
	<i>Michael Bron and Christina Roth</i>	
7.1	Introduction	241
7.1.1	Brief History of the Most Prominent Carbon Materials Applied in Fuel Cell Research	242
7.1.2	Carbon Characterization	246
7.1.2.1	Raman Spectroscopy	247
7.1.2.2	Small-Angle Scattering Techniques	249
7.1.2.3	Surface Chemistry by X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Spectroscopy Fine Structure (NEXAFS)	249
7.1.2.4	Other Methods and In situ Studies	251
7.2	Carbon as Support Material in Fuel Cell Electrocatalysts	251
7.2.1	Carbon Blacks	254
7.2.2	CNTs and Graphene	255
7.2.3	(Ordered) Mesoporous Carbons	257
7.2.4	Graphitization as a Means to Fight Carbon Corrosion	258
7.3	Carbon as Catalytically Active Component in Fuel Cells	259
7.3.1	ORR Activity of Carbons	259
7.3.2	N-Doped Carbons and Functionalized CNTs	260
7.3.3	Modification of Carbon Black and Other Carbon Materials	261
7.3.3.1	CNT-Based Materials	262
7.3.3.2	Graphene	262
7.3.3.3	Nanostructured Carbon Grown over Metal Catalysts	262
7.4	Carbon as Structure-Forming Element in Porous Fuel Cell Electrodes	263
7.4.1	How the Support Material Affects the Electrode Structure	264

7.4.2	How the Chosen Fabrication Step Affects the Electrode Structure	266
7.4.3	How Electrode Structuring Holds Promise to Improve Electrode Performance	267
7.4.4	Classical Electrode Designs	268
7.4.5	Advanced Designs	268
7.4.5.1	Horizontal Structuring by LbL	269
7.4.5.2	Nanostructured Electrodes	270
7.4.6	Novel Concepts	270
7.4.6.1	Electrospinning in Fuel Cell Technology	271
7.4.6.2	“Self-Assembly” by Pickering Emulsions	272
7.5	Summary and Outlook	274
	Acknowledgments	275
	References	275
8	Electrochemical Capacitors Based on Carbon Electrodes in Aqueous Electrolytes	285
	<i>Elżbieta Frąckowiak, Paula Ratajczak, and François Béguin</i>	
8.1	Introduction	285
8.2	Fundamentals on Carbon/Carbon Electrical Double-Layer Capacitors	286
8.3	Carbons and Electrolytes for Electrical Double-Layer Capacitors	290
8.3.1	Electrical Double-Layer Capacitors Based on Carbon Electrodes	290
8.3.2	Electrolytes for Electrical Double-Layer Capacitors	295
8.4	Attractive Electrochemical Capacitors in Aqueous Solutions	296
8.4.1	Extension of Stability Window in Neutral Aqueous Electrolytes	296
8.4.2	Determination of Cell Potential Stability Limits by Floating	300
8.4.3	Capacitance Enhancement through Faradic Reactions at the Carbon–Electrolyte Interface in Aqueous Media	305
8.5	Conclusions and Perspectives	308
	References	309
9	Carbon Electrodes in Electrochemical Technology	313
	<i>Derek Pletcher</i>	
9.1	Introduction	313
9.2	Comments on the Carbons Met in Electrochemical Technology	314
9.3	Manufacture of Chemicals	315
9.3.1	The Chlor-Alkali Industry	316
9.3.2	Aluminum Extraction	317
9.3.3	The Extraction of Group 1 and 2 Metals	318
9.3.4	Fluorine Generation	318
9.3.5	Ozone Generation	319
9.3.6	Hydrogen Peroxide	322

9.3.7	Other Strong Oxidizing Agents	323
9.3.8	Organic Products	323
9.4	Water and Effluent Treatment	327
9.4.1	The Removal of Organics	328
9.4.1.1	Boron-Doped Diamond	328
9.4.1.2	Hydrogen Peroxide Chemistry	329
9.4.1.3	Other Technologies	329
9.4.2	The Removal of Inorganics	330
9.5	Flow Batteries	331
	References	332
10	Carbon Electrodes in Molecular Electronics	339
	<i>Adam Johan Bergren and Oleksii Ivashenko</i>	
10.1	Introduction	339
10.2	Fabrication	344
10.3	Novel Allotropes of Carbon in Molecular Electronics	350
10.3.1	Graphene	350
10.3.1.1	Electrochemistry of Graphene (see also Chapter 4)	350
10.3.1.2	Graphene in Molecular Electronics	351
10.3.2	Carbon Nanotubes	355
10.3.2.1	Electrochemistry of CNT Electrodes	357
10.3.2.2	Electronic Properties of CNTs	357
10.3.2.3	CNT-Based Electronic Devices	357
10.4	Charge Transport	360
10.4.1	Charge Transport Depends on the System	365
10.4.2	Mechanism Transitions	367
10.5	Conclusions and Prospects	367
	Acknowledgments	368
	References	368
11	Carbon Paste Electrodes	379
	<i>Ivan Švancara and Kurt Kalcher</i>	
11.1	Introduction: Carbon Paste Electrodes—The State of the Art	379
11.2	Carbon Paste as the Electrode Material	380
11.2.1	Basic Considerations and Classification	380
11.2.2	Characterization of Two Main Carbon Paste Components	384
11.2.2.1	Carbonaceous Moiety	384
11.2.2.2	Binder/Pasting Liquid Moiety	386
11.2.3	Physicochemical and Electrochemical Characterization of Carbon Pastes and the Respective Carbon Paste Electrodes	387
11.2.3.1	A Few Notes to the Preparation of Common Carbon Paste Mixtures	387
11.2.3.2	Typical Properties and Behavior of Traditional Carbon Paste (Electrode)	388

11.2.3.3	Specific Features of New Types of Two-Component Carbon Pastes	391
11.2.4	Survey of Applications of Two-Component and Unmodified Carbon Pastes	394
11.2.5	Current Trends in Using Carbon Pastes and Some Future Prospects	398
11.3	Modified Carbon Paste Electrodes	399
11.3.1	Modification – How to Alter the Electrode Properties in an Intentional Way	399
11.3.2	Modification Processes	400
11.3.3	Types of Modifiers	401
11.3.4	Carbon Paste Biosensors	406
11.3.5	Applications of CMCPes and CP-Biosensors in Surveys, Facts, and Numbers	408
11.4	Latest Achievements in Electroanalysis with CMCPes and CP-Biosensors and Perspectives for the Future	412
	References	413
12	Screen-Printed Carbon Electrodes	425
	<i>Stephen Fletcher</i>	
12.1	Introduction	425
12.2	Conductivity of Composites	426
12.3	Carbon Polymorphs	427
12.4	Oxygen Functionalities	427
12.5	Activated Carbons	428
12.6	Binder – Solvent Combinations	429
12.7	PVDF Properties	430
12.8	PVDF Solubility	432
12.9	Flexible Substrates	433
12.10	Screen Printing Process	434
12.11	Screen Printing Materials	435
12.12	Ink Flow	436
12.13	Substrate Wetting	436
12.14	Commercial Ink Additives	437
12.15	Binder Percentage	438
12.16	Multilayered Electrodes	438
12.17	IR Drop	439
12.18	Areal Capacitance	439
12.19	Equivalent Circuit	440
	References	441
	Index	445