

Contents

Preface XI

List of Contributors XIII

- 1 Electropolymerized Films of π -Conjugated Polymers. A Tool for Surface Functionalization: a Brief Historical Evolution and Recent Trends** 1
Gérard Bidan
- 1.1 Introduction 1
- 1.2 Electropolymerization: Epistemological Analysis within the ICP Saga 2
- 1.3 Electropolymerization: from Pristine Heterocyclic to Sophisticated Functional and Conjugated Architectures 4
- 1.3.1 Electropolymerization of Pristine Aromatic Heterocycles 5
- 1.3.2 Electropolymerization of Substituted Heterocycles 7
- 1.3.3 Electropolymerization as a Tool to Elaborate Functional Conjugated Architectures 10
- 1.4 Conclusion 12
- References 13
- 2 Mechanisms of Electropolymerization and Redox Activity: Fundamental Aspects** 27
Mikhail A. Vorotyntsev, Veronika A. Zinov'yeva, and Dmitry V. Konev
- 2.1 Electropolymerization: General Aspects 27
- 2.2 Redox Activity of Polymer Films 32
- 2.3 Effect of Polymerization Parameters on Properties of Deposited Polymer Films 38
- 2.4 Conclusions 47
- References 47
- 3 Electrochemical Impedance Spectroscopy (EIS) for Polymer Characterization** 51
György Inzelt and Győző G. Láng
- 3.1 Introduction 51

3.2	Experimental Arrangements	53
3.3	Impedance Spectra of Polymer Films	55
3.3.1	Effect of the Film Thickness and Thickness Distribution of Polymer Films	56
3.3.2	Characteristic Quantities for Modified Electrodes	57
3.3.3	Impedance Associated with Polymer Films in Contact with Media Allowing both Ionic and Electronic Interfacial Exchange	60
3.4	Analysis of the Impedance Spectra	61
3.5	Models of Polymeric Layers	63
3.5.1	“Homogeneous” or “Uniform” Models	63
3.5.2	“Heterogeneous” or “Porous Layer” Model	64
3.5.3	Theories Dealing with Two or Three Charge Carriers	65
3.5.4	Brush Model	66
3.6	Summary	70
	Acknowledgment	70
	References	70
4	Recent Trends in Polypyrrole Electrochemistry, Nanostructuration, and Applications	77
	<i>Pierre Audebert</i>	
4.1	Introduction	77
4.2	Advances in Synthetic Procedures – New Polymers	78
4.2.1	New Monomers and Polymers	78
4.2.2	Fundamental Research	78
4.2.3	New Polymerization Methods	79
4.3	Nanostructuration of Polypyrrole	80
4.3.1	Nanostructuration of Polypyrrole	80
4.3.2	Polypyrrole Nanocomposites	80
4.4	Applications	83
4.4.1	Batteries and Supercapacitors	84
4.4.2	Actuators	85
4.4.3	Anticorrosion	85
4.4.4	Miscellaneous	86
4.5	Conclusion	87
	References	87
5	Electropolymerized Azines: a New Group of Electroactive Polymers	93
	<i>Arkady A. Karyakin</i>	
5.1	Introduction	93
5.2	Electropolymerized Azines as a New Group of Electroactive Polymers	93
5.2.1	Electropolymerization of Azines	94
5.2.2	Hypothesis of Polyazine Structure	96
5.3	Polyazines in Electroanalysis	98
5.3.1	Electrocatalysis by Polyazines	98

5.3.2	Electropolymerized Azines as Advanced Electrocatalysts for NAD ⁺ NADH Regeneration	99
5.3.2.1	Dehydrogenase Enzymes and Electrocatalysis of NAD ⁺ NADH Regeneration	99
5.3.2.2	Mimetics of Enzyme Catalysis	100
5.3.2.3	Electropolymerized Azines as NADH Transducers	101
5.3.2.4	Electroreduction of NAD ⁺ to Enzymatically Active NADH at Poly(Neutral Red)-Modified Electrodes	102
5.3.2.5	Observation of the Equilibrium NAD ⁺ NADH Potential at Poly(Neutral Red) Electrodes	103
5.4	Electropolymerized Azines as Promoters for Bioelectrocatalysis	105
5.4.1	Attempts to Involve Glucose Oxidase in Mediator Free Bioelectrocatalysis	105
5.4.1.1	Bioelectrocatalysis by Hydrogenase and Peroxidase	106
5.4.2	Bioelectrocatalysis by Cellobiose Dehydrogenase on Polyazines	106
5.5	Conclusion	108
	References	108
6	Electropolymerization of Phthalocyanines	111
	<i>Ninel M. Alpatova and Elena V. Ovsyannikova</i>	
6.1	Introduction	111
6.2	Immobilization of Transition-Metal Phthalocyanines on Conducting and Nonconducting Substrates	111
6.2.1	Phthalocyanines in Electron-Conducting Polymers	111
6.2.2	Phthalocyanines in Matrices of Artificial Lipids	113
6.2.3	Composites of Ultrathin Layers of Oppositely Charged Ions	115
6.3	Electropolymerization of Phthalocyanines	117
6.3.1	Electropolymerization of Phthalocyanines with Ligands Bonded to Radicals of Electron-Conducting Polymer Precursors	118
6.3.2	Electropolymerization of Tetra-Amino-Substituted Phthalocyanines	119
6.3.3	Electrochemical Modification of Electrodes with Nickel Tetra-Sulfonated Phthalocyanine	125
6.4	Conclusion	128
	References	130
7	Imprinted Polymers	133
	<i>Michael J. Whitcombe and Dhana Lakshmi</i>	
7.1	Introduction	133
7.1.1	What is Molecular Imprinting?	133
7.2	Molecular Imprinting in Conjugated Polymers	135
7.3	Solgel Imprinted Films Prepared by Electropolymerization	138
7.4	Integration of MIPs with the Surface of Transducers	139
7.5	Nanostructured Materials	140
7.6	Other MIP-Based Sensors	143

7.6.1	Piezoelectric Sensors	144
7.6.2	Capacitive Sensors	144
7.6.3	Amperometric and Voltammetric/Potentiometric Sensors	145
7.6.4	Miscellaneous Sensing Systems	146
7.7	Conclusion	147
	References	148
8	Gas Sensing with Conducting Polymers	153
	<i>Karin Potje-Kamloth</i>	
8.1	Introduction	153
8.2	Electronic Properties of Conducting Polymers	153
8.3	Preparation of Polymer Gas-Sensing Layers	155
8.3.1	Solvent Casting	155
8.3.2	<i>In situ</i> Electrochemical Deposition	155
8.3.3	Tuning of Electronic Properties of Conducting Polymers	156
8.3.3.1	Effect of Primary Doping on Work Function	156
8.3.3.2	Electrochemical Work Function Tuning	156
8.4	Mechanism of Gas/Polymer Interactions	157
8.4.1	Secondary Doping by Donor/Acceptor Interactions	157
8.4.2	Work Function Modulation – Modulation of Carrier Density	157
8.4.3	Bulk Resistance Changes	158
8.4.4	Contact Resistance Changes (Schottky Barrier)	158
8.5	Types of Conducting Polymer-Based Gas Sensors	159
8.5.1	Potentiometric (Zero-Current) Sensors	159
8.5.1.1	Kelvin Probe	159
8.5.1.2	CHEMFET	159
8.5.1.3	Examples of Kelvin Probe and CHEMFET Gas Sensors	160
8.5.2	Conductometric (Nonzero-Current) Sensors	163
8.5.2.1	Chemiresistors – Bulk Resistance Modulation	163
8.5.2.2	Schottky Barrier Diodes – Contact Resistance Modulation	165
8.5.2.3	OFETs – Field-Modulated Chemiresistors	168
8.5.2.4	Examples of Conductometric Gas Sensors	168
8.5.2.5	Examples of Polymer Schottky Diode Gas Sensors	168
8.6	Conclusion	169
	References	169
9	Chemical Sensors Based on Conducting Polymers	173
	<i>Johan Bobacka and Ari Ivaska</i>	
9.1	Introduction	173
9.2	Electrochemical Signal Transduction	174
9.2.1	Potentiometric Sensors	175
9.2.2	Amperometric and Voltammetric Sensors	179
9.2.3	Conductimetric Sensors	181
9.2.4	Chemically Sensitive Transistors	182
9.3	Optical Signal Transduction	184

9.4	Conclusions	184
	Acknowledgments	185
	References	185
10	Biosensors Based on Electropolymerized Films	189
	<i>Serge Cosnier and Michael Holzinger</i>	
10.1	Introduction	189
10.2	Chronological Evolution of the Concept of Biosensors Based on Electropolymerized Films: Principal Stages	190
10.3	Formation of Polymer Films by Direct Electropolymerization of the Biomolecule	191
10.4	Adsorption on Electrogenerated Polymers	194
10.5	Mechanical Entrapment within Electropolymerized Films	195
10.6	Covalent Binding at the Surface of Electropolymerized Films	200
10.7	Noncovalent Binding by Affinity Interactions with the Electropolymerized Films	203
10.8	Outlook	205
	References	206
11	Inherently Conducting Polymers via Electropolymerization for Energy Conversion and Storage	215
	<i>Gordon G. Wallace, George Tsekouras, and Caiyun Wang</i>	
11.1	Introduction	215
11.1.1	Electrochemical Techniques	216
11.1.2	Substrates	217
11.1.3	The Electrolyte	217
11.2	Energy Conversion	218
11.2.1	Polythiophenes via Electropolymerization of Simple Precursors	219
11.2.2	Polythiophenes via Electropolymerization of Precursors Functionalized with Electron Accepting/Withdrawing Moieties	222
11.2.3	Polythiophenes via Electropolymerization of Precursors Functionalized with Light-Harvesting Moieties	225
11.3	Energy Storage	227
11.3.1	Application of Inherently Conducting Polymers in Rechargeable Batteries	228
11.3.2	Application of Conducting Polymers in Supercapacitors	229
11.4	Electropolymerization to Form Electrodes for Energy Storage Applications	230
11.4.1	PPy	230
11.4.2	PANi	231
11.4.3	PTh and Derivatives	232
11.5	Nanostructured Conducting Polymers	233
11.5.1	Template-Assisted Electropolymerization	233
11.5.2	Direct Electropolymerization	233
11.6	Conducting Polymer Composites	234

11.7	Conclusions	236
	References	236
12	Electrochemomechanical Devices: Artificial Muscles	241
	<i>Toribio F. Otero and Joaquín Arias-Pardilla</i>	
12.1	Introduction	241
12.2	Conducting Polymers as Reactive Materials: Electrochemical Reactions	242
12.2.1	Oxidation	242
12.2.1.1	Prevailing Anion Interchange	243
12.2.1.2	Prevailing Cation Interchange	243
12.2.2	Reduction of Neutral Chains	244
12.2.3	Complex Actual Ionic Interchanges and Polymeric Structure	244
12.2.4	Giant Nonstoichiometry	245
12.3	Electrochemical Properties: Multifunctionality and Biomimetism	246
12.3.1	Electrochemomechanical Properties and Artificial Muscles	246
12.3.2	Basic Molecular Motor	247
12.4	Macroscopic Dimensional Changes and Mechanical Properties	248
12.5	Anisotropy Obtained from Isotropic Changes: Macroscopic Devices	248
12.5.1	Electrochemical Transducer	249
12.5.2	Efficiency	251
12.5.3	Bending Structures	252
12.5.3.1	Asymmetrical Monolayers	252
12.5.3.2	Bilayers	253
12.5.3.3	Triple Layers	253
12.5.4	Structures Giving Lineal Movements	254
12.5.4.1	Fibers and Films	254
12.5.4.2	Tubes and Films with Metal Support	254
12.5.5	Combination of Bending Structures	255
12.5.6	Microdevices and Microtools	255
12.6	Electrochemical Characterization	257
12.7	Sensing Capabilities of Artificial Muscles	258
12.8	Tactile Sensitivity	259
12.9	Intelligent Devices	263
12.10	Muscles Working in Air	264
12.11	Advantages, Limitations, and Challenges	264
12.12	Artificial Muscles as Products	265
	References	266
	Index	273