

Contents

Foreword	xi
Preface.....	xv
Acknowledgments.....	xvii

Chapter 1 Introduction to Electrochemistry and Electroanalysis with Carbon Paste-Based Electrodes.....	1
1.1 Historical Survey and Glossary.....	1
1.1.1 1958: The Very First Report on Carbon Paste Electrodes	2
1.1.2 1959–1963: Proposals of Carbon Pastes, Their Characterization, and Initial Applications	2
1.1.3 1964, 1965: First Modifications of Carbon Pastes	2
1.1.4 1965–1975: Expansion of Carbon Paste Electrodes in Electrochemical Laboratories	3
1.1.5 1976–1980: Pioneering Chemical Modifications of Carbon Paste.....	3
1.1.6 1981–1988: Era of Chemically Modified Carbon Paste Electrodes.....	4
1.1.7 1988–1995: Worldwide Spread of Carbon Pastes with Enzymes as a Novel Type of Biosensor	5
1.1.8 1996–2000: Starting Competition of Traditional Carbon Pastes with Screen-Printed Sensors and Other Carbon Composites	5
1.1.9 2000–2001: Carbon Pastes and New Technologies	6
1.1.10 2002–2003: Carbon Pastes Follow the Concept of Green Chemistry ...	7
1.1.11 2003–2010: Brand New Carbon Pastes and Their Immediate Success	7
1.2 Field in Publication Activities and Literature	9
Chapter 2 Carbon Pastes and Carbon Paste Electrodes.....	11
2.1 Carbon Paste as a Binary Mixture	11
2.1.1 Definitions of Carbon Paste	11
2.1.2 Carbon Powder/Graphite	12
2.1.2.1 Spectroscopic (Spectral) Graphite	12
2.1.2.2 Other Carbonaceous Materials.....	13
2.1.2.3 New Forms of Carbon	14
2.1.3 Pasting Liquid/Binder	16
2.1.3.1 Paraffin (Mineral) Oils	17
2.1.3.2 Aliphatic and Aromatic Hydrocarbons.....	18
2.1.3.3 Silicone Oils and Greases.....	18
2.1.3.4 Halogenated Hydrocarbons and Similar Derivatives	19
2.1.3.5 Other Pasting Liquids and Mixed Binders	19
2.1.3.6 New Types of Carbon Paste Binders	20
2.1.4 Mixing and Preparation of Carbon Pastes	20
2.1.4.1 Carbon-to-Pasting Liquid Ratio	20
2.1.5 Handling and Storage of Carbon Pastes.....	22
2.2 Classification of Carbon Pastes and Carbon Paste Electrodes	23
2.2.1 Traditional Types of Carbon Paste-Based Electrodes	23

2.2.2	Special Types of Carbon Paste–Based Electrodes	26
2.2.2.1	Carbon Paste Electroactive Electrodes	26
2.2.2.2	“Solid,” “Solid-like,” and “Pseudo” Carbon Paste Electrodes	26
2.2.3	New Types of Carbon Paste Electrodes	27
2.2.3.1	Diamond as the Electrode Material and Diamond Paste Electrodes	28
2.2.3.2	Carbon Paste Electrodes and Carbon Nanotubes	29
2.2.3.3	Carbon Paste Electrodes and Ionic Liquids.....	32
2.3	Construction of Carbon Paste Holders	35
2.3.1	Tubings and Rods (Plugs) with Hollow Ends	36
2.3.1.1	Rotated Disc Electrodes for Hydrodynamic Measurements.....	38
2.3.2	Piston-Driven Electrode Holders.....	38
2.3.3	Commercially Available Carbon Paste Electrode Bodies.....	40
2.3.4	Carbon Paste–Based Detectors	40
2.3.5	Planar Constructions of Carbon Paste Electrodes.....	42
2.3.6	Miniaturized Variants of Carbon Paste Electrodes.....	43
2.3.7	Special Constructions of CPEs.....	45
Chapter 3	Carbon Paste as an Electrode Material	49
3.1	Physicochemical Properties of Carbon Pastes	49
3.1.1	Microstructure of Carbon Pastes.....	49
3.1.2	Ohmic Resistance.....	51
3.1.3	Instability of Carbon Pastes in Organic Solvents.....	52
3.1.4	Aging of Carbon Pastes.....	52
3.1.5	Hydrophobicity of Carbon Pastes.....	52
3.2	Electrochemical Characteristics of Carbon Pastes.....	52
3.2.1	Very Low Background	52
3.2.2	Individual Polarizability of Carbon Pastes	53
3.2.3	Specific Reaction Kinetics at Carbon Pastes.....	56
3.3	Testing of Unmodified CPEs	59
3.4	Interactions at Carbon Pastes	62
3.4.1	Interactions at the Carbon Paste Surface	63
3.4.1.1	Electrode Reactions with Charge Transfer (Electrolytic Processes)	63
3.4.1.2	Adsorption and Related Electrode Reactions of Nonelectrolytic Character.....	63
3.4.1.3	Ion Exchange and Ion-Pair Formation.....	64
3.4.1.4	Electrocatalysis-Assisted Detection.....	65
3.4.1.5	Synergistic Processes and Interactions	66
3.4.2	Interactions in Carbon Paste Bulk.....	68
3.4.2.1	Extraction and Reextraction	69
3.4.2.2	Chemical Equilibria in the Bulk and Transport Models	70
Chapter 4	Chemically Modified Carbon Paste Electrodes	73
4.1	Classifications of Chemical Modification	73
4.1.1	Intrinsic Modification.....	74

4.1.2	Extrinsic Modification.....	74
4.1.2.1	Surface Modification	74
4.1.2.2	Bulk Modification.....	76
4.2	Reasons and Strategies for Modification.....	76
4.2.1	Criteria Required for Modifiers.....	76
4.2.2	Activation and Restoration of the Modifier.....	77
4.2.3	Immobilization and Preconcentration: Concepts and Strategies	77
4.2.4	Electrocatalysis.....	78
4.2.5	Other Purposes for Modification.....	81
4.3	Types of Chemical Modifiers	81
4.3.1	Inorganic Materials	82
4.3.1.1	Prussian-Blue Derivatives and Polyoxometallates.....	82
4.3.1.2	Clays and Zeolite-Based Molecular Sieves	83
4.3.1.3	Metal Oxides and Sol-Gel-Derived Inorganic Materials.....	86
4.3.1.4	Other Inorganic Modifiers	87
4.3.2	Organic and Organometallic Compounds.....	89
4.3.2.1	Organic Ligands	89
4.3.2.2	Organic Catalysts.....	91
4.3.2.3	Organometallic Complexes	95
4.3.2.4	Surfactants, Amphiphilic and Lipophilic Modifiers	97
4.3.2.5	Organic Polymers and Macromolecules.....	98
4.3.3	Other Possibilities and Recent Approaches to Chemical Modification	100
4.3.3.1	Organic-Inorganic Hybrid Materials	100
4.3.3.2	Nanomaterials.....	101
4.3.3.3	Surface Treatments and Alterations	103
4.4	Modeling and Testing of Chemically Modified CPEs	104
4.4.1	Basic Procedures and Specifics.....	104
4.4.2	Chemically Modified CPEs versus Bare CPEs	105
4.4.2.1	Sorption Processes at the Bare (Unmodified) Carbon Pastes	105
4.4.2.2	Chemically Modified CPEs	106
Chapter 5	Biologically Modified Carbon Paste Electrodes	109
5.1	Biosensors and Electrodes for Biological Analysis.....	109
5.2	Modifiers and Working Principles	110
5.2.1	Electrocatalysis and Mediation	110
5.2.2	Enzymes	111
5.2.2.1	Oxidases.....	112
5.2.2.2	Dehydrogenases	116
5.2.2.3	Hydrolases	117
5.2.2.4	Auxiliary Enzymes.....	117
5.2.2.5	Enzyme Kinetics.....	118
5.2.3	Nucleic Acids.....	118
5.2.4	Immunosensors	120
5.2.5	Tissues and Cells	120
5.2.6	Other Biomolecules	121
5.3	Modification Strategies (for Biosensors)	121

Chapter 6	Instrumental Measurements with Carbon Paste Electrodes, Sensors, and Detectors.....	123
6.1	Electrochemical Techniques: Fundamentals and Basic Principles	123
6.1.1	Double Layer Concept and Capacitive Current.....	123
6.1.2	Mass Transport.....	124
6.1.3	Faradic Processes	125
6.1.4	Diffusion Layer	127
6.1.4.1	Diffusion Coefficients.....	127
6.1.4.2	Macrosized Stationary Electrodes.....	127
6.1.4.3	Rotating Disk Electrodes	128
6.1.4.4	Microelectrodes	129
6.2	Voltammetry.....	130
6.2.1	Direct Voltammetry	130
6.2.1.1	Voltammetry at Slow Scan Rates	130
6.2.1.2	Voltammetry at Faster Scan Rates.....	131
6.2.2	Stripping Voltammetry.....	133
6.3	Amperometry	134
6.4	Potentiometry	135
6.4.1	Direct Potentiometry and Potentiometric Titrations	135
6.4.2	Chronopotentiometry and Stripping Chronopotentiometry.....	143
6.5	Nonelectrochemical Techniques.....	147
6.5.1	Microscopic Observations.....	147
6.5.2	Other Physicochemical Techniques for Special Characterizations.....	149
Chapter 7	Electrochemical Investigation with Carbon Paste Electrodes and Sensors	151
7.1	Studies on Electrode Reactions and Mechanisms of Organic Compounds in the Early Era of Carbon Pastes	151
7.1.1	Historical Circumstances	151
7.1.2	Adams's Investigation of Aromatic Compounds.....	153
7.1.3	Adams's Legacy	158
7.2	Electrochemistry of Solids	158
7.2.1	Historical Introduction	158
7.2.2	Main Principles, Configurations, Possibilities, and Limitations.....	159
7.2.3	Survey of Practical Applications.....	161
7.3	Electrochemistry <i>in Vivo</i>	162
7.3.1	Rise of the Field and Its Position.....	162
7.3.2	Basic Characterization of <i>in Vivo</i> Measurements	163
7.3.3	Survey of Applications and Some Prospects.....	165
7.4	Special Studies with Carbon Pastes	165
7.4.1	Role of Minor Research	165
7.4.2	Selected Themes across the Field.....	166
7.4.2.1	Carbon Pastes as Substrates for Electropolymerized Films.....	166
7.4.2.2	Carbon Pastes as Electronic Tongues	166
7.4.2.3	Carbon Pastes as CPEEs for Electrochemical Characterization of New Electrocatalysts	167
7.4.2.4	Carbon Pastes in Industrial Use.....	167
7.4.3	Further Examples	168

Chapter 8	Electroanalysis with Carbon Paste–Based Electrodes, Sensors, and Detectors	169
8.1	Determination of Inorganic Ions, Complex Species, and Molecules	170
8.1.1	Noble Metals	171
8.1.2	Heavy Metals.....	172
8.1.3	Metalloids.....	175
8.1.4	Metals of the Iron, Manganese, Chromium, and Vanadium Groups.....	175
8.1.5	Platinum Metals and Uranium	178
8.1.6	Metals of the Fourth and Third Groups, Metals of Rare Earths.....	179
8.1.7	Metals of Alkaline Earths and Alkaline Metals.....	180
8.1.8	Non-Metallic Ions, Complexes, and Neutral Molecules	181
8.1.9	Concluding Remarks	184
8.2	Determination of Organic Substances and Environmental Pollutants	185
8.3	Pharmaceutical and Clinical Analysis	188
8.4	Determination of Biologically Important Compounds	191
8.4.1	Alcohols.....	192
8.4.2	Aldehydes, Ketones, and Acids.....	193
8.4.3	Amino Compounds	194
8.4.3.1	Amides and Amines	194
8.4.3.2	Amino Acids.....	194
8.4.4	Antioxidants and Phenolic Compounds	196
8.4.5	Carbohydrates and Related Compounds	197
8.4.6	Coenzymes, Enzymes, Proteins, and Related Compounds.....	200
8.4.7	Hormones, Phytohormones, and Related Compounds.....	202
8.4.8	Neurotransmitters.....	202
8.4.9	Nucleic Acid, Nucleic Bases, and Related Compounds	204
8.4.10	Purines, Pyridines, and Pyrimidines	205
8.4.11	Vitamins	206
8.4.12	Whole Cells, Microorganisms, Tissues, and Tissue Extracts as Modifiers	208
8.4.13	Survey of Applications of Carbon Paste Mini- and Microelectrodes in Brain Electrochemistry/ <i>in Vivo</i> Voltammetry	209
8.4.14	Miscellaneous.....	209
Chapter 9	In Place of a Conclusion: Carbon Paste Electrodes for Education and Practical Training of Young Scientists	447
Appendix A:	RNA: A Profile of the Carbon Paste Inventor and a Great Scientist	449
Appendix B:	List of Dissertation Theses Defended in the Authors' Countries and Dealing with Carbon Paste–Based Electrodes, Sensors, and Detectors.....	453
Appendix C:	Alternate Titles of Chinese, Japanese, and Korean Journals or Periodicals.....	461
References	463
Authors	601
Author Index	603
Subject Index	643