

Contents

Chapter 1

Ion Conducting Polymer Sensors

Y. Sakai

1.1	Introduction	1
1.2	Humidity Sensors	1
1.2.1	Humidity Sensors Using Polymers Containing Inorganic Salts	1
1.2.2	Humidity Sensors Using Polymer Electrolytes	2
1.2.2.1	Electrolyte Homopolymers	2
1.2.2.2	Copolymers	4
1.2.2.3	Graft Copolymers	5
1.2.2.4	Hydrophobic Polymers With Added Ionic Groups	7
1.2.2.5	Crosslinked Polymer Electrolytes	8
1.3	Gas Sensors	10
	References	12

Chapter 2

Ultrathin Films for Sensorics and Molecular Electronics

L. Brehmer

2.1	Molecular Electronics and Nanosensorics	15
2.2	Ultrathin Films and Supramolecular Architectures	18
2.2.1	State of the Art	18
2.2.2	Langmuir- and Langmuir-Blodgett Films: Formation and Structure Investigation	19
2.2.2.1	Langmuir Films	19
2.2.2.2	Formation of Langmuir-Blodgett Films	22
2.2.2.3	Structure Investigation of LB-Films	24
2.3	Thin Film Sensorics	28
2.3.1	Advantages of Ultrathin Films for Sensorics	28
2.3.2	Ultrathin Pyrosensors	30
2.3.2.1	State of the Art	30
2.3.2.2	Definitions and Measurements	31
2.3.2.3	Rationale for Using Thin Organic Films for Pyroelectric Devices	35
2.3.2.4	Pyroelectric Cells and Measuring Techniques	36
2.3.2.5	Pyroelectricity of Organic Thin Films	43

2.3.2.6	Polymer Thin Film Pyroelectricity	46
2.3.2.7	Pyroelectric Measurements	47
2.3.2.8	Materials and Experimental Set-Up	47
2.3.2.9	Sample Preparation and Experimental Procedure	49
2.3.2.10	Pyroelectric Response and Long-Term Stability	50
2.3.2.11	Control of Pyroelectric Response	52
2.3.3	Humidity LB Polyelectrolyte Sensors	54
2.3.4	Commercial Application of LB Film Devices	58
2.4	Molecular Electronic Devices	60
2.4.1	Problems and Opportunities	60
2.4.2	Optically Switchable Thin Films	62
2.4.2.1	<i>E-Z</i> -Switching of Azo-Compounds	62
2.4.3	Molecular Rectifier	73
2.4.4	Electroluminescence of Organic Thin Films	77
2.4.5	Ultrathin Films as Electron beam Resists	79
2.5	Outlook	83
	List of Abbreviations	83
	References	85

Chapter 3**Polymers for Optical Fiber Sensors***F. Baldini, S. Bracci*

3.1	Introduction	91
3.2	The Optical Fiber Sensor	92
3.2.1	The Optoelectronic System	92
3.2.2	The Optical Link	93
3.2.3	The Optode	93
3.3	Polymers in Optical Fiber Chemical Sensors	95
3.4	Polymer Functions	97
3.4.1	Polymers as Solid Supports	97
3.4.2	Polymers as Selective Elements	101
3.4.3	Polymers as Chemical Transducers	103
3.5	Conclusions	105
	List of Symbols and Abbreviations	106
	References	106

Chapter 4**Smart Ferroelectric Ceramic/Polymer Composite Sensors***D.-K. Das-Gupta*

4.1	Introduction	109
4.2	Basic Concepts	110
4.2.1	Piezoelectricity	110
4.2.2	Pyroelectricity	114
4.2.3	Ferroelectric Ceramics	115
4.2.4	Ferroelectric Polymers	116

4.3	Ferroelectric Ceramic/Polymer Composites	118
4.3.1	Connectivity	118
4.3.2	0–3 Connectivity Composites and their Fabrication	120
4.3.3	1–3 Connectivity Composite Fabrication	121
4.3.4	3–3 Connectivity Composite Preparation	122
4.3.5	Preparation of Composites with Mixed Connectivity (0–3 and 1–3)	122
4.4	Poling Methods of Ceramic/Polymer Composites	123
4.4.1	D.C. Poling	124
4.4.2	A.C. Poling	125
4.5	Piezoelectric Properties of Ceramic/Polymer Composites	127
4.6	Pyroelectric Properties of Ceramic/Polymer Composites with 0–3 Connectivities	131
4.7	Models of 0–3 and Mixed Connectivity Composites	133
4.7.1	Yamada Model for 0–3 Composites	133
4.7.2	Furukaura Model for 0–3 Composites	134
4.7.3	Parallel and Series Connected Two-Dimensional Structure	135
4.8	Applications of Ceramic/Polymer Composite Sensors	142
4.8.1	Composite Transducers with 1–3 Connectivity	143
4.8.2	Composite Transducers with 0–3 and Mixed Connectivity	143
	References	144

Chapter 5**Sensing Volatile Chemicals Using Conducting Polymer Arrays***R. A. Bailey, K. C. Persaud*

5.1	Introduction	149
5.1.1	Gas Sensor Technologies	152
5.1.1.1	Metal Oxide Semiconductor (MOS) Sensors	152
5.1.1.2	Quartz Crystal Microbalance (QCM) Sensors	152
5.1.1.3	Surface Acoustic Wave (SAW) Sensors	153
5.1.1.4	Amperometric Sensors	153
5.1.1.5	Pellistor Sensors	153
5.1.1.6	Metal-Substituted Phthalocyanine Sensors	153
5.1.1.7	Organic Conducting Polymer (OCP) Gas Sensors	154
5.1.1.8	Other Sensor Technologies	154
5.1.1.9	Combination Gas Sensors	154
5.2	Implementation of a Conducting Polymer Sensor Array	155
5.2.1	Conducting Polymer Sensors	155
5.2.1.1	Preparation of Polypyrrole	156
5.2.1.1.1	Electrochemical Synthesis	157
5.2.1.2	Chemical Synthesis	157
5.2.1.2	Polymerisation Mechanism	158
5.2.1.2.1	Factors Affecting the Polymerisation Process	159
5.2.1.2.1.1	Electrochemical Conditions	159
5.2.1.2.1.2	Counterion Effects	160
5.2.1.2.1.3	Other Effects	160
5.2.2	Structure of Polypyrrole	161

5.2.3	Conductance Mechanism	162
5.2.3.1	Classical Band Theory	162
5.2.3.2	Conducting Polymer Mechanisms	163
5.2.4	Composite Polymers	165
5.3	Gas Sensing	166
5.3.1	Gas Sampling System	167
5.3.2	Data Acquisition Hardware	168
5.3.3	Data Acquisition and Manipulation Software	169
5.3.4	Pattern Recognition Techniques	170
5.4	Linear Solvation Energy Relationships (LSER) and the Investigation of Gas Sensor Responses	170
5.5	Conclusion	177
	References	178

Chapter 6

Molecular Machines Useful for the Design of Chemosensors

S. Shinkai, M. Takeuchi, A. Ikeda

6.1	Introduction	183
6.2	Chromogenic Crown Ethers	184
6.3	Photoresponsive Crown Actuators in Action for Ion and Molecule Recognition	186
6.4	Cyclodextrins Modified as Molecule Sensors	190
6.5	Calixarenes Modified as Ion and Molecule Sensors	193
6.6	New Artificial Sugar Sensing Systems in which the Boronic Acid-Diol Interaction is Combined with Photoinduced Electron-Transfer (PET)	196
6.7	Conclusion	205
	References	205

Chapter 7

Conducting Polymer Actuators: Properties and Modeling

A. Mazzoldi, A. Della Santa, D. De Rossi

7.1	Introduction	207
7.2	Working Principles and Actuator Configurations	209
7.3	Figures of Merit of a CP Actuator	211
7.4	Actuators in the Literature	216
7.5	Materials and Techniques for Fabrication	217
7.5.1	Films	217
7.5.1.1	Film Electrochemical Deposition	217
7.5.1.2	Film Preparation by Casting	218
7.5.2	Fibers	219
7.5.3	All Polymer Actuators	219
7.5.3.1	Dry PANi Fiber Actuator	219
7.5.3.2	Dry PPyClO ₄ Film Actuator	222
7.6	Continuum Electromechanics of CP Actuators	223

7.6.1	Introduction to the Continuum Model	223
7.6.2	The Continuum Approach	224
7.6.3	Configuration of Study	224
7.6.4	Mechanical Equations	224
7.6.5	Electrochemical Equations	227
7.6.5.1	Relations Between the Charges and Equations for the Redox Reactions .	227
7.6.5.2	Motion Equations of Ionic Charges	228
7.6.5.3	Relation Between Current and Potential in the Solid Matrix	229
7.6.5.4	Continuity Equations	229
7.6.5.5	Resolvability	230
7.6.6	Resolution and Validation of the Model in the Passive Case	230
7.6.6.1	Model Resolution	231
7.6.6.2	Experimental Determination of the Parameters Considered in the Passive Case	232
7.6.6.3	Passive Continuum Model Testing	234
7.6.6.3.1	Empirical Corrections	236
7.7	Lumped Parameter Description of a PC Actuator	237
7.7.1	Model	237
7.7.2	Parameters Estimation and Validation	239
7.7.2.1	Passive Condition	239
7.7.2.2	Active Condition	240
7.8	Conclusions	243
	References	244

Chapter 8

Electrically Induced Strain in Polymer Gels Swollen with Non-Ionic Organic Solvents

T. Hirai, M. Hirai

8.1	Introduction	245
8.2	Electrically Induced Strain in PVA-DMSO Gel	245
8.2.1	Electrostrictive Motion of PVA-DMSO Gel	245
8.2.2	Detailed Feature of the Electrically Induced Action of the PVA-DMSO Gel	247
8.2.3	Comparison with PAAM-DMSO Gel	248
8.3	Effect of Crosslinks on the Electrostrictive Strain	249
8.3.1	Preparation Method of the DMSO Gel	249
8.3.2	Effect of Solvent Content on the Performance of the Actuation	249
8.4	Structural Change in PVA-DMSO Gel Induced by Electric Field	251
8.4.1	Orientation of DMSO by Electric Field	251
8.4.1.1	In PVA-DMSO Gel	251
8.4.1.2	Comparison with PVC-DMSO Gel	252
8.4.2	Electrically Induced Structure Change Observed by Small Angle X-Ray Scattering (SAXS)	252
8.4.2.1	Scattering Functions	252
8.4.2.2	Distance Distribution Functions	255
8.4.2.3	Persistence Length and Correlation Length	255

8.5	On the Mechanism of the Electrostrictive Action and Concluding Remarks (for Future Development)	256
	References	257

Chapter 9**Actuating Devices of Liquid-Crystalline Polymers***R. Kishi*

9.1	Introduction	259
9.2	Lyotropic Liquid-Crystalline Polymer Gels	260
9.2.1	Poly(γ -benzyl L-glutamate) Gels Having Cholesteric Liquid-Crystalline Order	260
9.2.2	Poly(γ -benzyl L-glutamate) Gels Having Nematic Liquid-Crystalline Order	263
9.2.3	Optical Anisotropy of Poly(γ -benzyl L-glutamate) Gels Having Cholesteric Liquid-Crystalline Order	265
9.2.4	Poly(L-glutamic acid) Hydrogels Having Liquid-Crystalline Order .	266
9.3	Thermotropic Liquid-Crystalline Polymer Gels	268
9.3.1	Electrical Deformation of Side-Chain Type Liquid-Crystalline Polymer Gels	268
9.3.2	Electrorheological Properties of Thermotropic Liquid-Crystalline Materials	270
9.4	Conclusion	271
	References	272

Chapter 10**Gel Actuators***J. P. Gong, Y. Osada*

10.1	Introduction	273
10.2	Shape Memory Gel	274
10.3	Spontaneous Motion of Polymer Gels on Water	277
10.4	Electrical Contraction and Tactile-Sensing System	280
10.5	Gel Actuator Based on Molecular Assembly Reactions	283
10.5.1	Gel Pendulum	284
10.5.2	Gel Looper	287
10.5.3	Gel-Eel	289
10.6.	Future Prospects	293
	References	294

Chapter 11**Electrochemomechanical Devices Based on Conducting Polymers***T. F. Otero*

11.1	Introduction	295
11.2	Approach Through Electrochemical Systems	297
11.3	Artificial Molecular Muscles in the Literature	299

11.4	Conducting Polymers: a Short Introduction	301
11.5	Redox Processes in Conducting Polymers and Related Properties	302
11.6	Artificial Muscles from Conducting Polymers	306
11.7	Bilayer Devices	307
11.8	Electrochemopositioning Devices	308
11.9	The Working Muscle	309
11.10	Triple Layer Devices	310
11.11	Movement Rate Control	312
11.12	Actuator and Sensor	313
11.13	Lifetime and Degradation Processes	313
11.14	Three-Dimensional Electrochemical Processes and Biological Mimicking	314
11.14.1	Hydro-Organic Batteries	316
11.14.2	Color Mimicking	317
11.14.3	Nerve Interfaces	317
11.14.4	Smart Membranes	318
11.14.5	Mechanochemoelectrical Devices	318
11.15	Theoretical Approaches	319
11.16	Similarities with Natural Muscles	320
11.17	The Future	321
	References	321

Chapter 12**Ion-Exchange Polymer-Metal Composites as Biomimetic Sensors and Actuators***M. Shahinpoor*

12.1	Introduction	325
12.2	Biomimetic Sensing Capability of IPMC	327
12.2.1	General Considerations	327
12.2.2	Theoretical Analysis	329
12.2.3	Experimental Procedures, Results, and Discussion	331
12.2.4	Dynamic Sensing	333
12.2.5	Conclusions	334
12.3	Biomimetic Actuation Properties of IPMCs	335
12.3.1	General Considerations	335
12.3.2	Development of Muscle Actuators	336
12.3.3	Muscle Actuator for Robotic Applications	338
12.3.4	Design of Linear and Platform Type Actuators	339
12.3.5	Conclusions	340
12.4	Large Amplitude Vibrational Response of IPMCs	342
12.4.1	General Considerations	342
12.4.2	Theoretical Model	342
12.4.3	Experimental Observations	343
12.4.4	Conclusions	346
12.5	Load and Force Characterization of IPMCs	347
12.5.1	General Considerations	347
12.5.2	Results and Discussion	347

12.5.3	Conclusions	350
12.5.4	Force vs Displacement	350
12.6	Electromechanical Modeling	351
12.7	Summary	355
	References	356

Chapter 13**Motor Protein Mechanism Coupled with Hydrophobic Hydration/
Dehydration Cycle***M. Suzuki, T. Kodama*

13.1	Introduction	361
13.2	Dielectric Analysis of Hydrated Solute in Water	362
13.3	Dielectric Properties of Motor Protein S1	364
13.4	Hydrophobic Hydration and Accessible Surface Area of S1	365
13.5	Dynamic Change of Hydrophobic Hydration	366
13.6	Discussions	368
	References	369

Chapter 14**Actuating Systems in Biology***J. F. V. Vincent*

14.1	Filamentous Actuators	371
14.1.1	Actin and Myosin	371
14.1.2	Microtubules and Kinesin/Dynein	372
14.1.3	Flagellar Motors	373
14.1.4	Mutable Collagenous Tissues	375
14.1.5	Role of the Collagen Fibrils in Variable Stiffness	377
14.2	Non-Fibrous Actuators	378
14.2.1	The Spasmoneme	378
14.2.2	Outer Hair Cells of the Inner Ear	379
14.3	Pressure Systems	380
14.3.1	Plants	380
14.3.2	Nematocysts	381
	References	383

Chapter 15**Magnetic Field Sensitive Polymeric Actuators***M. Zrinyi, D. Szabó, L. Barsi*

15.1	Introduction	385
15.2	Magnetostriction	385
15.3	Ferrogel: a New Magnetostrictive Soft Material	386
15.4	Magnetic Properties of Ferrogels	387
15.5	Characterisation of Magnetic Field Distribution in One Dimension	390
15.6	Elastic Properties of Ferrogels: Unidirectional Extension	392

15.7	Giant Magnetostriction of Ferrogels as Seen by the Naked Eye	395
15.8	Results of Unidirectional Magnetoelastic Measurements	396
15.9	Ferrogels as Linear Magneto-Elastic Soft Actuators	399
15.10	Interpretation of Noncontinuous Shape Transition	400
15.11	Theoretical Basis for Design of Magnetic Gel Actuators	405
15.12	Kinetics of the Shape Change	406
15.13	Future Aspects	408
	References	408
	Subject Index	409