

Edited by Suzana Pereira Nunes,
Klaus-Viktor Peinemann

 WILEY-VCH

Membrane Technology in the Chemical Industry

Second, Revised and Extended Edition



Contents

Part I	Membrane Materials and Membrane Preparation	
	<i>S. P. Nunes and K.-V. Peinemann</i>	
1	Introduction	3
2	Membrane Market	5
3	Membrane Preparation	9
3.1	Phase Inversion	10
4	Presently Available Membranes for Liquid Separation	15
4.1	Membranes for Reverse Osmosis	15
4.2	Membranes for Nanofiltration	18
4.2.1	Solvent-resistant Membranes for Nanofiltration	20
4.2.2	NF Membranes Stable in Extreme pH Conditions	22
4.3	Membranes for Ultrafiltration	23
4.3.1	Polysulfone and Polyethersulfone	23
4.3.2	Poly(vinylidene fluoride)	26
4.3.3	Polyetherimide	28
4.3.4	Polyacrylonitrile	30
4.3.5	Cellulose	32
4.3.6	Solvent-resistant Membranes for Ultrafiltration	32
4.4	Membranes for Microfiltration	34
4.4.1	Polypropylene and Polyethylene	34
4.4.2	Poly(tetrafluorethylene)	36
4.4.3	Polycarbonate and Poly(ethylene terephthalate)	37
5	Surface Modification of Membranes	39
5.1	Chemical Oxidation	39
5.2	Plasma Treatment	40
5.3	Classical Organic Reactions	41
5.4	Polymer Grafting	41

6	Membranes for Fuel Cells	45
6.1	Perfluorinated Membranes	46
6.2	Nonfluorinated Membranes	48
6.3	Polymer Membranes for High Temperatures	51
6.4	Organic-Inorganic Membranes for Fuel Cells	52
7	Gas Separation with Membranes	53
7.1	Introduction	53
7.2	Materials and Transport Mechanisms	53
7.2.1	Organic Polymers	55
7.2.2	Background	55
7.2.3	Polymers for Commercial Gas-separation Membranes	57
7.2.4	Ultrahigh Free Volume Polymers	58
7.2.5	Inorganic Materials for Gas-separation Membranes	62
7.2.6	Carbon Membranes	62
7.2.7	Perovskite-type Oxide Membranes for Air Separation	64
7.2.8	Mixed-matrix Membranes	67
7.3	Basic Process Design	69
	Acknowledgments	75
	References	75

Part II Current Application and Perspectives

1	The Separation of Organic Vapors from Gas Streams by Means of Membranes	93
	<i>K. Ohlrogge and K. Stürken</i>	
	Summary	93
1.1	Introduction	94
1.2	Historical Background	94
1.3	Membranes for Organic Vapor Separation	96
1.3.1	Principles	96
1.3.2	Selectivity	96
1.3.3	Temperature and Pressure	97
1.3.4	Membrane Modules	98
1.4	Applications	100
1.4.1	Design Criteria	100
1.4.2	Off-gas and Process Gas Treatment	102
1.4.2.1	Gasoline Vapor Recovery	103
1.4.2.2	Polyolefin Production Processes	109
1.5	Applications at the Threshold of Commercialization	111
1.5.1	Emission Control at Petrol Stations	111
1.5.2	Natural Gas Treatment	113
1.5.3	Hydrogen/Hydrocarbon Separation	114
1.6	Conclusions and Outlook	116
	References	116

2	Gas-separation Membrane Applications	119
	<i>D. J. Stookey</i>	
2.1	Introduction	119
2.2	Membrane Application Development	120
2.2.1	Membrane Selection	120
2.2.2	Membrane Form	123
2.2.3	Membrane Module Geometry	125
2.2.4	Compatible Sealing Materials	129
2.2.5	Module Manufacture	130
2.2.6	Pilot or Field Demonstration	130
2.2.7	Process Design	132
2.2.8	Membrane System	133
2.2.9	Beta Site	135
2.2.10	Cost/Performance	136
2.3	Commercial Gas-separation Membrane Applications	136
2.3.1	Hydrogen Separations	137
2.3.2	Helium Separations	140
2.3.3	Nitrogen Generation	140
2.3.4	Acid Gas-Separations	143
2.3.5	Gas Dehydration	144
2.4	Developing Membrane Applications	146
2.4.1	Oxygen and Oxygen-enriched Air	146
2.4.2	Nitrogen Rejection from Natural Gas	147
2.4.3	Nitrogen-enriched Air (NEA)	147
	References	147
3	State-of-the-Art of Pervaporation Processes in the Chemical Industry	151
	<i>H. E. A. Brüscke</i>	
3.1	Introduction	151
3.2	Principles and Calculations	153
3.2.1	Definitions	153
3.2.2	Calculation	155
3.2.3	Permeate-side Conditions	163
3.2.4	Transport Resistances	166
3.2.5	Principles of Pervaporation	168
3.2.6	Principles of Vapor Permeation	171
3.3	Membranes	175
3.3.1	Characterization of Membranes	180
3.4	Modules	182
3.4.1	Plate Modules	183
3.4.2	Spiral-wound Modules	185
3.4.3	"Cushion" Module	185
3.4.4	Tubular Modules	186
3.4.5	Other Modules	187

- 3.5 Applications 188
- 3.5.1 Organophilic Membranes 188
- 3.5.2 Hydrophilic Membranes 189
 - 3.5.2.1 Pervaporation 189
 - 3.5.2.2 Vapor Permeation 191
- 3.5.3 Removal of Water from Reaction Mixtures 194
- 3.5.4 Organic–Organic Separation 197
- 3.6 Conclusion 200
- References 200

- 4 Organic Solvent Nanofiltration 203**
A. G. Livingston, L. G. Peeva and P. Silva
Summary 203
- 4.1 Current Applications and Potential 203
- 4.2 Theoretical Background to Transport Processes 205
 - 4.2.1 Pore-flow Model 205
 - 4.2.2 Solution-Diffusion Model 206
 - 4.2.3 Models Combining Membrane Transport with the Film Theory of Mass Transfer 207
- 4.3 Transport of Solvent Mixtures 210
 - 4.3.1 Experimental 210
 - 4.3.1.1 Filtration Equipment and Experimental Measurements 210
 - 4.3.2 Results for Binary Solvent Fluxes 210
 - 4.4 Concentration Polarization and Osmotic Pressure 213
 - 4.4.1 Experimental 213
 - 4.4.2 Results for Concentration Polarization and Osmotic Pressure 214
 - 4.4.2.1 Parameter Estimation 214
 - 4.4.2.2 Nanofiltration of Docosane-Toluene Solutions 216
 - 4.4.2.3 Nanofiltration of TOABr-Toluene Solutions 219
- 4.5 Conclusions 224
- Nomenclature 225
- Greek letters 225
- Subscripts 226
- References 226

- 5 Industrial Membrane Reactors 229**
M. F. Kemmere and J. T. F. Keurentjes
- 5.1 Introduction 229
- 5.2 Membrane Functions in Reactors 232
 - 5.2.1 Controlled Introduction of Reactants 232
 - 5.2.2 Separation of Products 238
 - 5.2.3 Catalyst Retention 241
- 5.3 Applications 242
 - 5.3.1 Pervaporation-assisted Esterification 242
 - 5.3.2 Large-scale Dehydrogenations with Inorganic Membranes 248

5.3.3	OTM Syngas Process	250
5.3.4	Membrane Recycle Reactor for the Acylase Process	251
5.3.5	Membrane Extraction Integrated Systems	253
5.4	Concluding Remarks and Outlook to the Future	254
	References	255
6	Electromembrane Processes	259
	<i>T. A. Davis, V. D. Grebenyuk and O. Grebenyuk</i>	
6.1	Ion-exchange Membranes	259
6.2	Ion-exchange Membrane Properties	262
6.2.1	Swelling	262
6.2.2	Electrical Conductivity	263
6.2.3	Electrochemical Performance	267
6.2.4	Diffusion Permeability	268
6.2.5	Hydraulic Permeability	269
6.2.6	Osmotic Permeability	269
6.2.7	Electroosmotic Permeability	270
6.2.8	Polarization	271
6.2.9	Chemical and Radiation Stability	273
6.3	Electromembrane Process Application	274
6.3.1	Electrodialysis	274
6.3.2	Electrodeionization	280
6.3.3	Electrochemical Regeneration of Ion-exchange Resin	282
6.3.4	Synthesis of New Substances without Electrode Reaction Participation: Bipolar-membrane Applications	283
6.3.5	Isolation of Chemical Substances from Dilute Solutions	285
6.3.6	Electrodialysis Applications for Chemical-solution Desalination	285
6.4	Electrochemical Processing with Membranes	286
6.4.1	Electrochemistry	286
6.4.2	Chlor-alkali Industry	291
6.4.3	Perfluorinated Membranes	291
6.4.4	Process Conditions	293
6.4.5	Zero-gap Electrode Configurations	294
6.4.6	Other Electrolytic Processes	295
6.4.7	Fuel Cells	297
6.4.8	Electroorganic Synthesis	299
6.4.9	Electrochemical Oxidation of Organic Wastes	300
	Acknowledgments	300
	List of Symbols	300
	References	301

7	Membrane Technology in the Chemical Industry: Future Directions	305
	<i>R. W. Baker</i>	
7.1	The Past: Basis for Current Membrane Technology	305
7.1.1	Ultrathin Membranes	305
7.1.2	Membrane Modules	306
7.1.3	Membrane Selectivity	308
7.2	The Present: Current Status and Potential of the Membrane Industry	309
7.2.1	Reverse Osmosis	309
7.2.2	Ultrafiltration	313
7.2.3	Microfiltration	314
7.2.4	Gas Separation	315
7.2.4.1	Refinery Hydrogen Applications	317
7.2.4.2	Nitrogen (and Oxygen) Separation from Air	319
7.2.4.3	Natural Gas Separations	323
7.2.4.4	Vapor/Gas, Vapor/Vapor Separations	326
7.2.5	Pervaporation	329
7.2.6	Ion-conducting Membranes	330
7.3	The Future: Predictions for 2020	332
	References	333
	Subject Index	337