

Membranes for Membrane Reactors

Preparation, Optimization and Selection

Edited by

ANGELO BASILE

*Institute on Membrane Technology, CNR, c/o University of Calabria,
Rende, CS, Italy*

FAUSTO GALLUCCI

*Chemical Process Intensification, Faculty of Chemical Engineering
and Chemistry, Eindhoven University of Technology, Eindhoven,
The Netherlands*

 **WILEY**

A John Wiley and Sons, Ltd, Publication

Contents

<i>Contributors</i>	xvii
<i>Glossary</i>	xxi
Introduction – A Review of Membrane Reactors	1
<i>Fausto Gallucci, Angelo Basile and Faisal Ibney Hai</i>	
1 Introduction	1
2 Membranes for Membrane Reactors	1
2.1 Polymeric Membranes	2
2.2 Inorganic Membranes	2
2.2.1 Metal Membranes	3
2.2.2 Ceramic Membranes	4
2.2.3 Carbon Membranes	4
2.2.4 Zeolite Membranes	4
2.3 Membrane Housing	4
2.4 Membrane Separation Regime	7
2.4.1 Porous Membrane	7
2.4.2 Dense Metallic Membranes	7
3 Salient Features of Membrane Reactors	10
3.1 Applications of Membrane Reactors	10
3.2 Advantages of the Membrane Reactors	11
4 Hydrogen Production by Membrane Reactors	14
4.1 Methane Steam Reforming	16
4.2 Dry Reforming of Methane	16
4.3 Partial Oxidation of Methane	16
4.4 Water Gas Shift Reaction Performed in Membrane Reactors	17
4.5 Outlines on Reforming Reactions of Renewable Sources in Membrane Reactors	17
5 Other Examples of Membrane Reactors	21
5.1 Zeolite Membrane Reactors	21
5.2 Fluidised Bed Membrane Reactor	22
5.3 Perovskite Membrane Reactors	24
5.4 Hollow Fibre Membrane Reactors	27
5.5 Catalytic Membrane Reactors	29
5.6 Photocatalytic Membrane Reactors	30
6 Membrane Bioreactor	31
6.1 A Brief History of the MBR Technology Development	31
6.2 Market Value and Drivers	34
6.3 Commercially Available MF/UF Membranes for MBR	35
6.3.1 Membrane Geometry	35
6.3.2 Mode of Operation: Inside-Out Versus Outside-In Flow	36

6.3.3	Membrane Materials and Material Properties	36
6.3.4	Features of Commercial MBR Technologies	37
6.4	Advantages of MBR over CAS	38
6.5	Organics and Nutrients Removal in MBR	40
6.5.1	Removal of Organic Matter and Suspended Solids	40
6.5.2	Nutrient Removal	41
6.6	Recalcitrant Industrial Wastewater Treatment by MBR	41
6.6.1	Micropollutants	42
6.6.2	Dye Wastewater	43
6.6.3	Tannery Wastewater	44
6.6.4	Landfill Leachate	44
6.6.5	Oil Contaminated Wastewater	44
6.6.6	Insight into Recalcitrant Compound Removal in MBR	45
6.7	Recent Advances in Membrane Bioreactors Design/Operation	45
6.8	Development Challenges	46
6.8.1	Membrane Fouling	46
6.8.2	Pre-Treatment Requirement	47
6.8.3	Maintaining Membrane Integrity	47
6.9	Future Research	47
7	Conclusion	48
	References	49
1	Microporous Carbon Membranes	63
	<i>Miki Yoshimune and Kenji Haraya</i>	
1.1	Introduction	63
1.2	Transport Mechanisms in Carbon Membranes	64
1.3	Methods for the Preparation of Microporous Carbon Membranes	66
1.3.1	General Preparation and Characterisation	66
1.3.2	Classification of Carbon Membranes	69
1.3.3	The Pyrolysis Process	69
1.3.4	Pretreatment	71
1.3.5	Post-Treatment	72
1.3.6	Polymer Precursors	72
1.3.7	Adjustments of Pore Structures	78
1.3.8	Modification of Porous Substrates	80
1.3.9	Current Status	81
1.3.10	Mixed-Matrix Carbon Membranes	82
1.4	Membrane Modules	85
1.5	Applications of Membranes in Membrane Reactor Processes	87
1.6	Final Remarks and Conclusions	89
	References	90
2	Metallic Membranes by Wire Arc Spraying: Preparation, Characterisation and Applications	99
	<i>Sayed Siavash Madaeni and Parisa Daraei</i>	
2.1	Introduction	99
2.2	Thermal Spraying	100
2.2.1	Definition and Types	100

2.2.2	Applications	100
2.2.3	Wire Arc Spraying	100
2.3	Preparation of Membranes	102
2.3.1	Preparation of Inorganic Membranes Using Thermal Spraying	102
2.3.2	Preparation of Metallic Membranes Using Wire Arc Spraying	103
2.3.3	Advantages and Disadvantages	103
2.4	Characterisation of Prepared Metallic Membrane	104
2.4.1	Metallographic Tests	104
2.4.2	Performance	109
2.5	Applications of Prepared Metallic Membrane	110
2.5.1	Water Treatment	110
2.5.2	Gas Purification	112
2.5.3	Membrane Reactors	112
2.6	Final Remarks and Conclusions	112
	References	113
3	Inorganic Hollow Fibre Membranes for Chemical Reaction	117
	<i>Benjamin F. K. Kingsbury, Zhentao Wu and K. Li</i>	
3.1	Introduction	117
3.2	Preparation of Inorganic Hollow Fibre Membranes	118
3.2.1	Preparation of the Suspension	120
3.2.2	Preparation of the Membrane Precursors	122
3.2.3	Calcination	136
3.3	Coating of Pd/Ag Membranes	140
3.4	Catalyst Impregnation	145
3.5	Application in Chemical Reaction	146
3.6	Final Remarks and Conclusions	151
	References	152
4	Metallic Membranes Prepared by Cold Rolling and Diffusion Welding	155
	<i>Silvano Tosti</i>	
4.1	Introduction	155
4.2	Preparation Method	157
4.2.1	Cold Rolling	157
4.2.2	Diffusion Welding	158
4.3	Applications	161
4.4	Conclusions	165
	References	166
5	Preparation and Synthesis of Mixed Ionic and Electronic Conducting Ceramic Membranes for Oxygen Permeation	169
	<i>Jianhua Tong and Ryan O'Hayre</i>	
5.1	Introduction	169
5.2	Preparation of MIEC Ceramic Powders	170
5.2.1	Conventional Solid-State Reaction	170
5.2.2	Coprecipitation	171
5.2.3	Conventional Sol-Gel Method	172

5.2.4	Polymeric Gelation Method	173
5.2.5	Hydrothermal Synthesis	175
5.2.6	Spray Pyrolysis	175
5.2.7	Combustion Synthesis	176
5.3	Preparation of MIEC Membranes	176
5.3.1	Disk-Shaped Configuration	176
5.3.2	Tubular-Shaped Configuration	177
5.3.3	Hollow Fibre Membrane	180
5.3.4	Asymmetric Thin Film	182
5.4	Example Applications of MIEC Membranes for the Partial Oxidation of Methane	191
5.4.1	Disk-Shaped Membrane Reactor	192
5.4.2	Tubular-Shaped Membrane Reactor	193
5.4.3	Hollow Fibre Membrane Reactor	194
5.4.4	Asymmetric Membrane Reactor	194
5.5	Final Remarks and Conclusions	195
	References	197
6	Nanostructured Perovskites for the Fabrication of Thin Ceramic Membranes and Related Phenomena	201
	<i>V.V. Zyryanov, A.P. Nemudry and V.A. Sadykov</i>	
6.1	Introduction	201
6.2	Support	204
6.3	Selection of Ceramics with High Oxygen Mobility	205
6.4	Synthesis of Ceramics with Required T_s and a High Oxygen Permeability	212
6.5	Combination of Compatible Materials and Operations	219
6.6	Design of Catalyst for Selective Reforming of Methane to Syngas	221
6.7	Conclusion	223
	References	224
7	Compact Catalytic Membrane Reactors for Reforming Applications Based on an Integrated <i>Sandwiched</i> Catalyst Layer	227
	<i>Sreekumar Kurungot and Takeo Yamaguchi</i>	
7.1	Introduction	227
7.2	Experimental	229
7.2.1	Preparation of Silica-Rh- γ -Al ₂ O ₃ Catalytic Membrane	229
7.2.2	Preparation of Redox Modified S-RAL Systems	229
7.2.3	Membrane Reactor	230
7.3	Results and Discussion	231
7.3.1	Physical Characteristics	231
7.3.2	Gas Permeation Properties	232
7.3.3	Hydrothermal Stability	234
7.3.4	Reforming of Methane	235
7.3.5	Stabilisation Effect by CeO ₂ Incorporation	238
7.4	Conclusion	240
	References	241

8 Zeolite Membrane Reactors	243
<i>Carlos Téllez and Miguel Menéndez</i>	
8.1 Introduction	243
8.2 Zeolite Membrane Preparation Outlines	245
8.2.1 Support	245
8.2.2 Zeolite Synthesis by Hydrothermal Synthesis	247
8.2.3 Seeding	248
8.2.4 Improvements and Achievements in Synthesis of Zeolite Membranes	249
8.2.5 Types of Zeolites	250
8.2.6 Post-Treatment of Zeolite Membranes	251
8.3 Detailed Preparation Method of a Zeolite Membrane	251
8.4 Types of Zeolite Membrane Reactors	253
8.4.1 Equilibrium Displacement	254
8.4.2 Product Removal (In Non-Equilibrium Limited Reactors)	259
8.4.3 Reactant Distribution	260
8.4.4 Catalytic Membrane with Product Removal	261
8.4.5 Flow-Through Membrane Reactor	261
8.4.6 Catalytic Membrane Contactor	262
8.4.7 Catalyst Retention	262
8.4.8 Encapsulated Catalyst	263
8.5 Concluding Remarks	263
References	264
9 Metal Supported and Laminated Pd-Based Membranes	275
<i>Silvano Tosti, Angelo Basile and Fausto Gallucci</i>	
9.1 Introduction	275
9.2 Preparation Method	276
9.2.1 Metal Supported Membranes	276
9.2.2 Laminated Membranes	281
9.2.3 Non Pd-Based or Low Pd Content-Based Membranes	283
9.3 Applications	284
9.4 Conclusions	285
References	286
10 PVD Techniques for Metallic Membrane Reactors	289
<i>R. Checchetto, R.S. Brusa, A. Miotello and A. Basile</i>	
10.1 Introduction	289
10.2 Physical Vapour Deposition Techniques	291
10.2.1 Evaporation	291
10.2.2 Pulsed Laser Deposition	296
10.2.3 Sputter Deposition	297
10.3 Pd-Based Metallic Membranes	306
10.3.1 Hydrogen Permeation Through Metallic Membranes	306
10.3.2 Requirements for a Pd-Based Membrane	308
10.3.3 Pd-Based Membranes Prepared by PVD Techniques	308
10.3.4 Pd-Based Membranes Prepared by NonPVD Techniques	310
10.4 Conclusions	311
References	312

11 Membranes Prepared via Electroless Plating	315
<i>M. Broglia, P. Pinacci and A. Basile</i>	
11.1 Introduction	315
11.2 Description of the Electroless Plating Process	316
11.2.1 Introduction	316
11.2.2 Cleaning of the Support	317
11.2.3 Activation of the Support	317
11.2.4 Palladium Deposition	319
11.3 Morphology of Palladium Deposits	321
11.4 Pd-Alloy Preparation	321
11.5 Membrane Performances and Integration in Membrane Reactors	324
11.6 Conclusions	330
References	331
12 Silica Membranes – Preparation by Chemical Vapour Deposition and Characteristics	335
<i>J. Galuszka and T. Giddings</i>	
12.1 Introduction	335
12.2 Fundamentals of Chemical Vapour Deposition	336
12.3 CVD Apparatus	337
12.4 Silica H-Membranes Produced by CVD	338
12.5 Silica Membrane Structure and Transport Mechanism	341
12.6 Hydrothermal Stability of Silica Membranes	346
12.7 Examples of Silica Membrane Application	347
12.7.1 Dehydrogenation of Light Paraffins	347
12.7.2 Water Gas Shift Reaction	349
12.7.3 H ₂ S Decomposition	349
12.8 Conclusions	350
References	351
13 Membranes Prepared via Molecular Layering Method	357
<i>A.A. Malygin, A.A. Malkov, S.V. Mikhaylovskiy, S.D. Dubrovensky, N.L. Basov, M.M. Ermilova, N.V. Orekhova and G.F. Tereschenko</i>	
13.1 Introduction	357
13.2 Molecular Layering: Principles, Synthesis Possibilities and Fields of Application	358
13.3 Optimisation of MR Structure and Catalytic Properties by the ML Method	364
References	367
14 Solvated Metal Atoms in the Preparation of Catalytic Membranes	371
<i>Emanuela Pitzalis, Claudio Evangelisti, Nicoletta Panziera, Angelo Basile, Gustavo Capannelli and Giovanni Vitulli</i>	
14.1 Introduction	371
14.2 Preparation of Catalytic Membranes	373
14.2.1 Platinum on γ -Alumina Membranes	373
14.2.2 Platinum on Silica Membranes	373

14.2.3	Palladium on Alumina Membranes	375
14.2.4	Palladium–Silver on Titania–Alumina Membranes	376
14.2.5	Palladium and Platinum on Polymeric Membranes	376
14.3	Catalytic Exploitation	376
14.4	Conclusions	379
	References	379
15	Electrophoretic Deposition for the Synthesis of Inorganic Membranes	381
	<i>F.J. Varela-Gandía, A. Berenguer-Murcia, A. Linares-Solano, E. Morallón and D. Cazorla-Amorós</i>	
15.1	Introduction	381
15.1.1	Electrophoretic Deposition: Basic Principles	381
15.1.2	Electrophoretic Deposition as a Seeding Technique: Seeding Methods	382
15.1.3	Zeolites as Electrophoretic Species: ‘Role’ of the Templating Agent	383
15.2	State of the Art	383
15.2.1	Methodologies Employed	383
15.2.2	Application of EPD to Aluminium-Free Zeolites	384
15.2.3	Continuous Zeolite Deposits on Different Materials	384
15.3	Experimental	384
15.3.1	Instrumentation and Reactants	384
15.3.2	Procedure	385
15.3.3	Sample Treatment	387
15.4	Discussion and Applications	388
15.4.1	MFI Zeolite Membranes	388
15.4.2	LTA Zeolite Membranes	389
15.4.3	Outlook on Zeolite Membranes	390
15.5	Conclusions	391
	References	392
16	Electrochemical Preparation of Nanoparticle Deposits: Application to Membranes and Catalysis	395
	<i>J. Arias-Pardilla, A. Berenguer-Murcia, D. Cazorla-Amorós and E. Morallón</i>	
16.1	Introduction	395
16.1.1	Principles of Electrochemical Deposition	395
16.1.2	Choice of Methods and Deposited Metals	396
16.2	State of the Art	396
16.2.1	Methodologies for Electrochemical Deposition and Theoretical Models	396
16.2.2	Supports and Deposited Metals: Membrane Reactors	397
16.3	Experimental	398
16.3.1	Instrumentation and Reactants	398
16.3.2	Procedure	398
16.3.3	Sample Treatment	399
16.4	Discussion and Applications	399
16.4.1	Electrodeposition of Platinum on Carbon Materials	399

16.4.2	Influence of Metallic Deposits on Zeolite Membrane Preparation	403
16.5	Conclusions	405
	References	405
17	Electrochemical Preparation of Pd Seeds/Inorganic Multilayers on Structured Metallic Fibres	409
	<i>F. Basile, P. Benito, G. Fornasari, M. Monti, E. Scavetta, M. Tonelli and A. Vaccari</i>	
17.1	Introduction	409
17.2	Brief Review on Preparation Method	410
17.3	Explanation of the Proposed Preparation Method	411
17.4	Multilayer Preparation on Metal Substrates	414
17.5	Final Remarks and Conclusion	417
	References	418
18	Membranes Prepared Via Spray Pyrolysis	419
	<i>Mingtao Li and Liejin Guo</i>	
18.1	Introduction	419
18.2	Spray Pyrolysis Material Preparation Method	420
18.3	Selected Membranes Prepared Via Spray Pyrolysis Coating Method	423
18.3.1	Pd-Ag Alloy Hydrogen Separation Membrane	424
18.3.2	Porous TiO ₂ Membrane	424
18.3.3	Ionic and Electronic Conductive Membrane in SOFCs	425
18.4	Catalyst Synthesis and Spread in PEMFC	431
18.5	Remarks and Perspectives	431
	References	432
19	Preparation and Characterisation of Nanocrystalline and Quasicrystalline Alloys by Planar Flow Casting for Metal Membranes	435
	<i>J.W. Phair and M.A. Gibson</i>	
19.1	Introduction	435
19.2	Properties and Preparation of Nanocrystalline and Quasicrystalline Metals	436
19.2.1	Properties	436
19.2.2	Preparation	437
19.3	Preparation of Nanocrystalline and Quasicrystalline Metal Membranes by Planar Flow Casting	438
19.4	Nanocrystalline and Quasicrystalline Metal Membranes for Hydrogen Separation	444
19.4.1	General	444
19.4.2	Pd-Based Membrane Materials	445
19.4.3	NonPd-Based Alloy Membrane Materials	445
19.4.4	Ni-Ti-Nb-Based Alloy Membrane Materials	445
19.4.5	Ti-Zr-Ni-Based Alloy Membrane Materials	447
19.5	Concluding Remarks	450
	References	450
20	Preparation and Characterisation of Amorphous Alloy Membranes	459
	<i>Shin-ichi Yamaura and Akihisa Inoue</i>	

20.1	Introduction	459
20.2	Brief Review of Preparation Methods	460
20.3	Experimental Procedure	462
20.3.1	Sample Preparation	462
20.3.2	Hydrogen Permeability Measurement	463
20.3.3	Methanol Steam Reforming Experiment	464
20.4	Hydrogen Permeation of Ni-Nb-Zr Amorphous Alloy Membranes	465
20.4.1	Hydrogen Permeation	465
20.4.2	Local Atomic Configuration of the Alloys	467
20.4.3	Long-Term Durability Tests	468
20.5	Hydrogen Production by Methanol Steam Reforming Using Melt-Spun Ni-Nb-Ta-Zr-Co Amorphous Alloy Membrane	469
20.6	Final Remarks and Conclusions	471
	References	472
21	Membranes Prepared Via Phase Inversion	475
	<i>M.G. Buonomenna, S.-H. Choi, F. Galiano and E. Drioli</i>	
21.1	Introduction	475
21.2	Brief Review	476
21.3	Explanation of the Phase Inversion Process	480
21.4	Some Applications	484
21.5	Conclusions	488
	References	488
22	Porous Flat Sheet, Hollow Fibre and Capsule Membranes by Phase Separation of Polymer Solutions	491
	<i>Mathias Ulbricht and Heru Susanto</i>	
22.1	Introduction	491
22.2	Porous Polymeric Membranes Classification	492
22.3	Polymers for Porous Membranes	494
22.3.1	General Considerations	494
22.3.2	Key Characteristics	495
22.4	Polymeric Membrane Preparation Via Phase Separation	495
22.4.1	TIPS Process	497
22.4.2	NIPS Process	497
22.5	Industrial Manufacturing of Porous Polymeric Membranes	502
22.5.1	Flat Sheet Membranes	503
22.5.2	Hollow Fiber/Capillary Membranes	503
22.6	Applications in Membrane Reactor Processes	505
22.7	Conclusions and Outlook	508
	References	509
23	Porous Polymer Membranes by Manufacturing Technologies other than Phase Separation of Polymer Solutions	511
	<i>Mathias Ulbricht and Heru Susanto</i>	
23.1	Introduction	511
23.2	Technologies Based on Extrusion of Polymer Films	512

23.2.1	Pore Formation by Film Stretching	512
23.2.2	Pore Formation by Track Etching	513
23.2.3	Pore Formation by Foaming	515
23.3	Electrospinning of Porous Polymer Membranes	515
23.4	<i>In Situ</i> Polymerisation of Porous Membranes	518
23.5	Surface and Pore Functionalised Membranes	519
23.6	Overview on Technical Porous Polymeric Membranes	523
23.7	Applications in Membrane Reactor Processes	524
23.8	Conclusions and Outlook	526
	References	528
24	Palladium-Loaded Polymeric Membranes for Hydrogenation in Catalytic Membrane Reactors	531
	<i>V.V. Volkov, I.V. Petrova, V.I. Lebedeva, V.I. Roldughin and G.F. Tereshchenko</i>	
24.1	Introduction	531
24.2	Synthesis and Hydrogenation Studies	532
24.2.1	Dense Catalytic Membranes	532
24.2.2	Pd-Loaded Gas Separation Membranes	533
24.2.3	Porous Catalytic Membranes	535
24.3	Characterisation of Palladium Nanoparticles in Catalytic Membranes	539
24.4	Kinetic Studies	542
24.5	Conclusions	545
	References	546
25	Membrane Prepared via Plasma Modification	549
	<i>Marek Bryjak and Irena Gancarz</i>	
25.1	Introduction	549
25.2	Membrane Treatment with Microwave Plasma	550
25.2.1	Membrane Treated by Dielectric Barrier Discharge	550
25.3	Modes of Plasma Use	551
25.4	Plasma of Nonpolymerisable Gas	552
25.4.1	Carbon Dioxide Plasma	552
25.4.2	Case Study on CO ₂ Plasma Action	553
25.4.3	Nitrogen Plasma Action	554
25.4.4	Case Study on Nitrogen Plasma Action	554
25.4.5	Ammonia Plasma	555
25.4.6	Case Study on Ammonia Plasma Action	556
25.4.7	Plasmas of Other Gases	556
25.4.8	Plasma of Nonpolymerisable Species: Summary	558
25.5	Plasma of Polymerisable Species	558
25.5.1	Allyl Alcohol Plasma	559
25.5.2	Case Study on Plasma Polymerisation of Allyl Alcohol	559
25.5.3	Amine Plasma	559
25.5.4	Case Study on Butylamine and Allyloamine Plasma Polymerisation	560
25.5.5	Acid Plasma	561
25.5.6	Other Kinds of Plasma	562
25.5.7	Plasmas of Polymerisable Species: Summary	562

25.6	Plasma-Induced Grafting	562
25.6.1	Case Study on Grafting of Acrylic Acid	563
25.6.2	Plasma Modification of Polymer Membranes: Summary	564
	References	565
26	Enzyme-Immobilised Polymer Membranes for Chemical Reactions	569
	<i>Tadashi Uragami</i>	
26.1	Introduction	569
26.2	Brief Review of the Preparation Method of Enzyme-Immobilised Polymer Membranes	570
26.3	Preparation of Enzyme-Immobilised Polymer Membranes	571
26.3.1	Immobilisation of Enzymes on Polymer Membranes by Adsorption	571
26.3.2	Immobilisation of Enzymes in Polymer Membranes by Covalent Binding	571
26.3.3	Immobilisation of Enzymes in Polymer Membranes by Entrapment	573
26.3.4	Immobilisation of Enzymes in Polyion Complex Membranes with Entrapment and the Formation of Ion Complexes	574
26.3.5	Immobilisation of Enzymes in Ultrafiltration Membranes, Microfiltration Membranes, and Hollow Fibre Membranes	575
26.3.6	Immobilisation of Enzymes in Polymer Membranes by Copolymerisation	577
26.4	Applications of Enzyme-Immobilised Polymer Membranes as Membrane Reactors	578
26.4.1	Polymer Membranes with Enzymes Immobilised by Adsorption	578
26.4.2	Polymer Membranes with Enzymes Immobilised by Covalent Binding	579
26.4.3	Polymer Membranes with Enzymes Immobilised by Entrapment	580
26.4.4	Polymer Membrane with Enzymes Immobilised by Entrapment and Ion Complex	582
26.4.5	Polymer Membranes with Immobilised Enzymes for Ultrafiltration Membranes, Microfiltration Membranes, and Hollow Fibre Membranes	584
26.4.6	Polymer Membranes with Enzymes Immobilised by Copolymerisation	586
26.4.7	Industrial Applications	587
26.5	Final Remarks and Conclusions	587
	References	588
	Final Remarks	591
	<i>Angelo Basile and Fausto Gallucci</i>	
1	Introduction	591
2	Membranes for Membrane Reactors	591
2.1	Inorganic Membranes	592
2.2	Organic Membranes	596
3	Epilogue	597
	References	597
	Index	599