Design and fabrication of nanofibrous thin film composite membranes by electrospinning for osmotically driven membrane processes

Tian, Miao

2015

Tian, M. (2015). Design and fabrication of nanofibrous thin film composite membranes by electrospinning for osmotically driven membrane processes. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65646>

<https://doi.org/10.32657/10356/65646>

**DESIGN AND FABRICATION OF NANOFIBROUS THIN
FILM COMPOSITE MEMBRANES BY
ELECTROSPINNING FOR OSMOTICALLY DRIVEN
MEMBRANE PROCESSES**

TIAN MIAO

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2015

**DESIGN AND FABRICATION OF NANOFIBROUS THIN
FILM COMPOSITE MEMBRANES BY
ELECTROSPINNING FOR OSMOTICALLY DRIVEN
MEMBRANE PROCESSES**

TIAN MIAO

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2015

ACKNOWLEDGEMENTS

This thesis would not have been possible without the guidance and help of many people who contributed and extended their valuable assistance in the preparation and completion of this study.

First of all, I would like to express my deep gratitude to my academic supervisor, Professor Wang Rong, for her support, guidance, encouragement, patience and advice. Also, my sincere thanks are given to Dr. Qiu Changquan, Dr. Wang Yining, Mr. Goh Kunli, Dr. Liao Yuan and Dr. Chou Shuren for their valuable advices and academic contribution to my research. I would like to express my sincere thanks to my colleague Dr. Miles Edward Rzechowicz for his help to correct the grammar and polish the writing for the whole thesis with seven chapters.

I sincerely thank my qualification exam reviewer committee, Associate Professor Dong Zhili, Associate Professor Tang Chuyang and Assistant Professor Chang Wei-Chung, for their kind suggestions and comments.

This research was supported by a grant from the Singapore National Research Foundation under its Environmental and Water Technologies Strategic Research Programme and administered by the Environment and Water Industry Programme Office (EWI) of the PUB (#1102-IRIS-07-01). I am grateful to Nanyang Technological University for awarding me with the research student scholarship, the School of Civil and Environmental Engineering (CEE), and the Singapore Membrane Technology Centre (SMTTC) for providing me with safe and comfortable workplaces.

I would also like to express my sincere thanks to the project team members: Dr. Laurentia E.K. Setiawan, Dr. Wei Jing, Dr. She Qianhong, and Mr. Zhang Lizhi for their valuable discussions. I thank Assistant Professor Chong Tzyy Haur and Dr.

Shi Lei for their involvement and guidance in laboratory safety and equipment purchasing.

I am thankful to Mrs. Lim-Tay Chew Wang and Ms. Chan Wai Yee for their kind support and help for the purchase of consumables and equipment used in my study, Ms. Maria Chong Ai Shing and Ms. See Shen Yen Pearlyn for their assistance in equipment usage, and other staff in CEE Environment Laboratory for their help.

I also want to express my appreciation to my friends and colleagues for their companionship, support and help. Special thanks go to my office and lab buddies as well as my group mates: Dr. Wu Bing, Dr. Loh Chunheng, Ms. Loo Siew Leng, Ms. Yao Lei, Mr. Zeng Zhiping, Dr. Qi Saren, Dr. Zhang Jingsong, Dr. Zhang Yuan, Dr. Liu Chang, Dr. Fang Wangxi, Dr. Li Tian, Dr. Sunee Wongchitphimon and other friends. It is my pleasure to be part of SMTC family.

Lastly, I would like to express my sincere gratitude to my parents, my elder brother and his family for their love, encouragement and support. Without their constant moral support and concern, it would be impossible for me to complete my PhD work.

TIAN MIAO

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
TABLE OF CONTENTS	III
LIST OF PUBLICATIONS	VII
LIST OF FIGURES	IX
LIST OF TABLES	XIV
LIST OF SYMBOLS	XVI
ABSTRACT.....	XX
CHAPTER 1. INTRODUCTION	1
1.1 Background	1
1.2 Research objectives.....	3
1.3 Thesis outlines	5
CHAPTER 2. LITERATURE REVIEW	8
2.1 Osmotically driven membrane processes (ODMPs).....	8
2.1.1 Introduction of ODMPs	8
2.1.2 ODMPs transport theory	12
2.1.3 Challenges in ODMPs	17
2.2 Development of ODMPs membranes	17
2.2.1 Requirements of ODMPs membranes	17
2.2.2 Thin film composite (TFC) membranes	18
2.2.3 State of the art of current ODMPs membranes	21
2.3 Electrospun nanofibrous membranes (ENMs).....	32
2.3.1 Electrospinning	32
2.3.2 Electrospun nanofibrous membranes applications.....	35
2.3.3 Electrospun membrane development for ODMPs applications.....	37

2.3.4 Reinforcement of the nanofiber membrane	38
CHAPTER 3. PREPARATION OF POLYAMIDE TFC FORWARD OSMOSIS MEMBRANES USING ELECTROSPUN POLYVINYLIDENE FLUORIDE (PVDF) NANOFIBERS AS SUBSTRATES	40
3.1 Introduction	40
3.2 Experiments	41
3.2.1 Materials and chemicals	41
3.2.2 Preparation of nanofibrous substrates	42
3.2.3 Synthesize of polyamide selective layer.....	43
3.2.4 Characterization of nanofiber substrates and TFC membranes.....	43
3.2.5 Intrinsic permeability evaluation of nanofiber-based TFC membranes ...	45
3.2.6 FO performance test of nanofiber-based TFC membranes	46
3.3 Results and discussion	48
3.3.1 Structure of nanofiber substrates	48
3.3.2 Interfacial polymerization on nanofiber substrates	50
3.3.3 Characteristics of nanofiber-based TFC Membranes	53
3.3.4 FO performance of nanofiber-based TFC membranes	60
3.4 Conclusions	64
CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF TFN FO MEMBRANES WITH NANOFIBROUS SUPPORT INCORPORATED WITH SILICA	65
4.1 Introduction	65
4.2 Experiments	66
4.2.1 Materials and chemicals	66
4.2.2 Preparation of nanofibrous substrates	67
4.2.3 Preparation of polyamide selective layer	68
4.2.4 Morphology and structure characterization.....	68
4.2.5 Intrinsic separation properties characterization.....	69
4.2.6 FO performance evaluation	69
4.3 Results and discussion	69

4.3.1 Characterization of silica-filled PEI nanofibrous substrates.....	69
4.3.2 Characterization of the silica-filled TFN FO membrane	76
4.3.3 FO performance of TFN membranes	78
4.4 Conclusions.....	81
CHAPTER 5. SYNTHESIS AND CHARACTERIZATION OF TFN FO MEMBRANES WITH NANOFIBROUS SUBSTRATE REINFORCED BY FUNCTIONALIZED CARBON NANOTUBES	83
5.1 Introduction.....	83
5.2 Experiments	84
5.2.1 Materials and chemicals.....	84
5.2.2 Nanofibrous substrate via electrospinning.....	84
5.2.3 Synthesis of polyamide skin by interfacial polymerization.....	86
5.2.4 Membrane characterization.....	86
5.3 Results and discussion	88
5.3.1 Characterization of f-CNTs	88
5.3.2 Characterization of nanofibrous substrates	89
5.3.3 High FO performance of TFN membranes	92
5.4 Conclusions.....	97
CHAPTER 6. SYNTHESIS AND CHARACTERIZATION OF TFN PRO MEMBRANES WITH TIERED NANOFIBER SUPPORT REINFORCED BY FUNCTIONALIZED CARBON NANOTUBES	98
6.1 Introduction.....	98
6.2 Experiments	99
6.2.1 Materials and chemicals.....	99
6.2.2 Fabrication of tiered nanofibrous composite substrates.....	100
6.2.3 Polyamide selective skin by interfacial polymerization	100
6.2.4 Membrane characterization.....	102
6.2.5 Pressure retarded osmosis tests	102
6.3 Results and discussion	105

6.3.1 Characteristics of nanofibrous supports incorporated with f-CNTs.....	105
6.3.2 Characteristics of nanofibrous TFN membranes	109
6.3.3 Osmosis performance of TFN membranes	112
6.4 Conclusions	117
CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS.....	118
7.1 Overall conclusions	118
7.2 Recommendations for future research	122
REFERENCES	124

LIST OF PUBLICATIONS

- **JOURNALS**

- **M. Tian**, C. Qiu, Y. Liao, S. Chou, R. Wang, Preparation of polyamide thin film composite forward osmosis membranes using electrospun polyvinylidene fluoride (PVDF) nanofibers as substrates, *Separation and Purification Technology*, 118 (2013) 727-736.
- **M. Tian**, R. Wang, KL. Goh, Y. Liao, A. G. Fane, Synthesis and characterization of high-performance novel thin film nanocomposite PRO membranes with tiered nanofiber support reinforced by functionalized carbon nanotubes, *Journal of Membrane Science*, 486 (2015) 151-160.
- **M. Tian**, YN. Wang, R. Wang, Synthesis and characterization of high-performance novel thin film nanocomposite (TFN) FO membranes with nanofiber support reinforced by functionalized carbon nanotubes, *Desalination*, 370 (2015) 79-86.
- **M. Tian**, YN. Wang, R. Wang, Design of silica-incorporated thin-film nanofibrous composite polyethylenimine (PEI) membranes with high performance for forward osmosis, *Journal of Membrane Science*, to be submitted.
- Y. Liao, R. Wang, **M. Tian**, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, *Journal of Membrane Science*, 425–426 (2013) 30-39.
- S. T. Sim, R. Wang, **M. Tian**, A. G. Fane, 2013. Membranes for Osmotic Power. *Encyclopedia of Membrane Science and Technology*. 1–13.
- Y. Liao, C. H. Loh, **M. Tian**, R. Wang, A.G. Fane, Fabrication of electrospun composite nanofiber membrane for water applications: a review, to be submitted (2014).

- **CONFERENCE PRESENTATIONS**

- **M. Tian**, R. Wang, “Design of Novel Thin Film Nanofibrous Composite Polyetherimide (PEI) Membrane for Osmotically Driven Processes” (Oral Presentation) The North American Membrane Society 24th Annual Meeting, May 31-June 4, 2014, Houston, TX, USA.

LIST OF FIGURES

Figure 2-2 Schematic representation of the PRO process for power generation.....	10
Figure 2-3 Illustration of osmotic driving force for a membrane in active layer facing draw solution (AL-DS) orientation in ODMPs.	14
Figure 2-4 Thin film formation via interfacial polymerization (Vankelecom, De Smet <i>et al.</i> 2005; Vandezande, Gevers <i>et al.</i> 2008).....	19
Figure 2-5 Schematic diagram of the possible mechanism of nanofiber formation in electrospinning process. The effects of intrinsic properties of solution are marked in orange test box, operational conditions are marked in the olive text box and surrounding conditions in purple box (Loh, Liao <i>et al.</i> 2015).	33
Figure 3-1 Schematic diagram of electrospinning process	42
Figure 3-2 Schematic of customized FO system	48
Figure 3-3 FE-SEM images of electrospun PVDF nanofibrous substrates. (a) top view of substrate S1 at 5,000X; (b) top view of S1 enlarged at 20,000X; (c) cross-sectional view of S1 at 10,000X; (d) top view of S2 at 5,000X; (e) top view of S2 enlarged at 20,000X;(f) cross-sectional view of S2 at 10,000X. (All scale bars in picture represent 1 μ m).....	49
Figure 3-4 Interfacial polymerization reaction scheme of polyamide based on TMC and MPD. (The x in polymer chain represents the crosslinked part of the resulting polymer, y represents the linear part. $x+y=1$. If $x=1$, the resulting polyamide is fully crosslinked, if $y=1$, the resulting polyamide is fully linear)	51
Figure 3-5 Intrinsic properties of the nanofibrous TFC membranes fabricated with varied MPD concentrations and fixed TMC concentration (0.15 wt%). (RO testing conditions: 1000 ppm NaCl as feed solution at 5 bar applied pressure and 23 °C.).	52

Figure 3-6 Intrinsic properties of TFC membranes fabricated with varied TMC concentrations and fixed MPD concentration (5 wt%). (RO testing conditions: 1000 ppm NaCl as feed solution at 5 bar applied pressure and 23 °C)	53
Figure 3-7 FE-SEM images of electrospun nanofiber based TFC membrane. (a) top view of TFC-1# at 20,000X; (b) cross sectional view of TFC-1# at 10,000X; (c) top view of TFC-2# at 20,000X; (d) cross sectional view of TFC-2# at 10,000X. (All scale bars in picture represent 1µm).....	54
Figure 3-8 Schematic of polyamide layers formed on different supports.	57
Figure 3-9 AFM images of the two electrospun nanofiber substrates (S1 and S2) and nanofiber based TFC membrane (TFC-1# and TFC-2#). (R _a values of the sample are calculated based on three different positions of the samples)	58
Figure 3-11 Experimental results of water flux (solid symbols) and salt flux (open symbols) as a function of DS concentration for TFC-1# membrane. (AL-FW: circle symbol; AL-DS: square symbol; FW: DI water; temperature: 23 °C)	62
Figure 3-12 Experimental results of water flux (solid symbols) and salt flux (open symbols) as a function of DS concentration for TFC-2# membrane. (AL-FW: circle symbol; AL-DS: square symbol; FW: DI water; temperature: 23 °C)	62
Figure 4-1 EDX images showing the silicon and carbon element in the nanofibrous substrates (a) #1S, (b) #2S, and (c) #3S; and (d) the silicon carbon molar ratio in these substrates.	71
Figure 4-2 Surface morphologies of the membrane substrates (a) #Control, (b) #1S, (c) #2S and (d) #3S. The insets show a higher magnification.....	72
Figure 4-3 AFM topography images of the nanofibrous substrates (a) #Control; (b) #1S; (c) #2S and (d) #3S, and (e) the root mean square	

roughness along the individual nanofiber (red line) for the four substrates. The error bars were based on analysis of at least 6 nanofibers.	72
Figure 4-4 FESEM micrographs showing the cross-sections of the membrane substrates (a) #Control, (b) #1S, (c) #2S and (d) #3S.	73
Figure 4-5 The FESEM micrographs showing the polyamide active surfaces of (a) TFC#C, (b) TFN#1, (c) TFN#2 and (d) TFN#3	77
Figure 4-6 FO flux performance at 1 M NaCl draw solution in both AL-FW and AL-DS orientations. Error bars were based on 2-3 replicates.	78
Figure 4-7 A comparison of (a) reversed solute flux, J_s and (b) specific solute flux, J_s/J_v during FO process with 1 M NaCl DS. DI water was used as the FW. Error bars were based on 2-3 replicates.	80
Figure 4-8 Effect of DS concentration on FO water flux for membrane TFN#3. 0.5-2.0 M NaCl solutions were used as DS. DI water was used as FW. Error bars were based on 2-3 replicates.	81
Figure 5-1 Comparison of MWCNTs and functionalized MWCNTs (f-CNTs) via (a) dispersion stability in PEI/NMP/DMF dope solution; and (b) Raman spectra. (Photographs were taken 7 days after preparation).	89
Figure 5-2 Characterization of nanofibrous substrates. (a) Photo images of the PEI-0 (Left) and CNT-PEI (Right). FE-SEM micrographs of (b) PEI-0, (c) CNT-PEI (inset is TEM image) and (d) CNT-PEI-L.	90
Figure 5-3 FE-SEM micrographs showing the active surfaces of (a) TFC-0, (b) TFN-1 and (c) TFN-2 and the cross-sections of (d) TFC-0, (e) TFN-1 and (f) TFN-2.	92
Figure 5-4 Pure water permeability and solute permeability of the three FO membranes. They were obtained from RO tests at applied pressure of 7 bar. DI water was used as feed for determining A value, while 10 mM NaCl was used for the calculation of B value.	93

Figure 5-5 Performance of the synthesized FO membranes (A) water flux and (B) specific solute flux (J_s/J_v). (Milli-Q water was used as the feed and 1 M NaCl solution were employed as the draw solution. Error bars were based on 2-3 replicate tests.)	94
Figure 5-6 Effect of draw solution concentration on FO water flux in (a) AL-DS and (b) AL-FW orientations. DI water was used as the feed. Error bars were based on 2-3 replicate tests.	95
Figure 6-1 Schematic diagram of the lab-scale setup for PRO.	105
Figure 6-2 PEI nanofibrous support T3 with tiered structure. Note that the sample was prepared with the non-woven support peeled off.....	106
Figure 6-3 Nanofiber diameter distribution of the designed layers.(A) finer fiber layer without CNT (B) finer fiber layer with CNT; (C) coarse fiber layer with CNT; (D) Mechanical properties of pure PEI nanofibrous support with various diameter distribution.....	107
Figure 6-4 (A) TEM image proves the existence of functionalized multi-walled carbon nanotubes (f-CNTs) inside the PEI nanofiber; (B) enlarged TEM image confirms the dark tubular have the typical structure of multi-walled carbon nanotubes.	108
Figure 6-5 (A) Surface morphology of the top finer fiber layer before interfacial polymerization with average contact angle of 130° (inset picture); (B) Surface morphology after interfacial polymerization with average contact angle of $66 \pm 7^\circ$ (inset picture) ; (C) FE-SEM image of nanofibrous TFC membrane cross-sections; (D) Enlarged image of nanofiber layer underneath the polyamide layer; (E) Enlarged images of top finer fiber layer (inset top, scale bar 100 nm) and bottom coarse fiber layer (inset bottom, scale bar 100 nm), and the rejoin between these two layers.	110
Figure 6-6 Images of polyamide selective layer before and after PRO testing. (The finer fiber is the surface of T3 and coarse fiber is a control sample made from coarse fibers).....	112

Figure 6-7 PRO performance versus different hydraulic pressures for three membranes (A) water flux; (B) power density. The data in the figures simply illustrate the trend using one set experiment result but the replicates have been done to ensure reproducibility. (Testing conditions: 1.0 M NaCl as draw solution and DI water as feed water, flow rate at 400 ml/min in the cell)	113
Figure 6-8 (A) Hypothetical deduction of the deformation of the nanofibrous support under PRO testing. (B) PRO water flux of the membranes before and after pressurized at 15 bar.....	115
Figure 6-9 PRO performance versus different hydraulic pressures of IP-T3 after compact at 15 bar under RO condition for 2~4 hour. (A) water flux, (B) power density. (Testing conditions: 1.0 M NaCl as draw solution and DI water as feed water, flow rate at 400 ml/min in the cell).....	116
Figure 6-10 Long term PRO performance of nanofibrous TFC membrane IP-T3. (A) water flux and power density; (B) J_s/J_v (salt back diffusion flux/water flux) (Testing condition: 1.0 M NaCl as draw and MilliQ as feed, $23 \pm 2^\circ\text{C}$, and dosing every 0.5~1 hour to regulate the conductivity of DS and FW)	116

LIST OF TABLES

Table 2-1 Reported commercial FO membranes performance.....	25
Table 2-2 Reported commercial PRO membranes performance	26
Table 2-3 Typical lab-made FO membranes developed on phase inversion support layers.....	27
Table 2-4 Typical lab-made PRO membranes developed on phase inversion support layers.....	30
Table 2-5 Summary of nanofibrous FO membranes.....	31
Table 2-6 Summary of nanofibrous PRO membranes.....	31
Table 3-1 Properties of PVDF nanofibrous supports.....	50
Table 3-2 Separation properties of PVDF nanofiber based TFC membranes.....	56
Table 3-3 Element concentration from XPS analysis	59
Table 3-4 FO performances of various flat-sheet TFC membranes	63
Table 4-1 Dope composition of membrane substrates before electrospinning	68
Table 4-2 Characterization of the nanofibrous substrates.....	75
Table 4-3 Intrinsic separation properties of FO membranes.	77
Table 5-1 Electrospun conditions for preparation of the three nanofibrous supports.	85
Table 5-2 Properties of nanofibrous substrates PEI-0, CNT-PEI and CNT-PEI-L	91
Table 5-3 Comparison of nanofibrous FO membranes	96
Table 6-1 Summary of the characteristics of the three PEI nanofibrous supports.....	101
Table 6-2 Properties of nanofibrous substrates T1, T2 and T3.	109

Table 6-3 Intrinsic separation prosperities of prepared membranes	113
--	-----

LIST OF SYMBOLS

A	water permeability coefficient ($\text{L}/\text{m}^2 \text{ h} \cdot \text{bar}$, $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)
AFM	Atomic force microscope
$AL-DS$	active layer facing draw solution
$AL-FW$	active layer facing feed water
B	NaCl salt permeability coefficient ($\text{L}/\text{m}^2 \text{ h}$, $\text{L m}^{-2} \text{ h}^{-1}$)
C	Ionic molar concentration
CA	Cellulose acetate
$C_{d,b}$	Draw solution salt concentration at the bulk solution
$C_{d,m}$	Draw solution salt concentration at the membrane surface
$C_{f,b}$	Feed water salt concentration at the bulk solution
$CNTs$	Carbon nanotubes
CP	Concentration polarization
CTA	Cellulose triacetate
d_h	Hydraulic diameter
D_i	Isopropyl alcohol density
DI	Deionised water
d_m	Maximum pore size
DMF	N, N-Dimethylformamide
d_p	Mean pore size
D_p	Polymer density
DS	Draw solution
DS	Draw solution
EDX	Energy-dispersive X-ray spectroscopy
$ENMs$	Electrospun nanofibrous membranes

E_t	Tensile modulus
$f\text{-CNTs}$	Functionalized carbon nanotubes
$FE\text{-SEM}$	Field emission scanning electron microscope
FO	Forward osmosis
FS	Flat sheet
FW	Feed water
HF	Hollow fiber
ICP	Internal concentration polarization
IP	Interfacial polymerization
IPA	Isopropyl alcohol
J	Permeate flux, $\text{L}/\text{m}^2\text{h}$, LMH, $\text{L m}^{-2} \text{h}^{-1}$)
J_s	solute flux, $\text{g m}^{-2} \text{h}^{-1}$ (gMH)
J_v	volumetric flux, $\text{L m}^{-2} \text{h}^{-1}$ ($\text{L}/\text{m}^2\text{h}$)
k	Mass transfer coefficient in the draw solution
K_m	Mass transfer coefficient in the membrane substrate,
L	Critical length of the straight jet
l	Radius of the jet
LbL	Layer-by-layer assembly
$LiCl$	Lithium chloride
MD	Membrane distillation
MF	Microfiltration
MPD	M-Phenylenediamine
M_w	molecular weight of the solute, g/mol
$MWCNTs$	Multi-walled carbon nanotubes
NF	Nanofiltration

<i>ODMPs</i>	Osmotic driven membrane processes
π ,	Osmotic pressure
<i>PAI</i>	Polyamide-imide
<i>PAN</i>	Poly acrylonitrile
<i>PBI</i>	Polybenzimidazole
<i>PDA</i>	Poly-dopamine
<i>PEG</i>	Polyethylene glycol
<i>PEI</i>	Polyetherimide
<i>PES</i>	Polyethersulfone
<i>PET</i>	Polyethylene terephthalate
<i>ppm</i>	Part per million
<i>PRO</i>	Pressure retarded osmosis
<i>PSf, PSF</i>	Polysulfone
<i>PVDF</i>	Poly (vinylidene fluoride)
<i>Q</i>	volumetric permeation flow rate, l h^{-1}
<i>R</i>	General gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
<i>R_a</i>	Arithmetic mean of the surface roughness, nm
<i>RC</i>	Regenerated cellulose
<i>RH</i>	Relative humidity
<i>RO</i>	Reverse osmosis
<i>R_s</i>	Salt/Solute rejection, %
<i>S_s</i>	Substrate structure parameter, m
<i>SEM</i>	Scanning electron microscopy
<i>Sh</i>	Sherwood number
<i>SPEK</i>	Sulphonated poly(ether ketone)

<i>sPPSU</i>	Sulphonated polyphenylenesulfone
<i>T</i>	Absolute temperature, K
<i>TEM</i>	Transmission electron microscopy
<i>TDS</i>	Total dissolved solids
<i>TFC</i>	Thin film composite
<i>TFN</i>	Thin film nanocomposite
<i>TMC</i>	1, 3, 5-Benzenetricarboxylic acid chloride
<i>UF</i>	Ultrafiltration
<i>XPS</i>	X-ray photoelectron spectroscopy
δ	Strain at break
ω_1	Weight of the wet membrane
ω_2	Weight of the dry membrane
<i>wt%</i>	Weight percentage

ABSTRACT

Nowadays, high water demands due to fast global population growth and rapid economic development call for new technologies to provide clean water with less energy consumption. The serious environmental pollution caused by fossil fuel usage also require us to develop environmentally friendly technologies to harvest energy. As an emerging technology, osmotically driven membrane processes (ODMPs) including forward osmosis (FO) and pressure retarded osmosis (PRO) processes, are considered to be attractive technologies to treat waste water, recycle used water and harvest energy from salinity-gradients. However, FO and PRO technologies are still in the development stage. Developing osmotic membranes with both high water permeation and excellent ion rejection is a challenging task. The desired osmotic membrane may be a thin film composite (TFC) membrane consisting of an ultrathin polyamide layer with high water permeability and low solute permeability, and a highly porous support layer for low internal concentration polarization (ICP), which is one of the obstacles to improving FO/PRO membrane performance. In addition, high mechanical properties are essential for the membrane to withstand high hydraulic pressures in PRO processes. Fortunately, electrospun nanofibrous membranes have great potential to fulfil all the requirements of an ideal membrane support layer due to their open and porous structural features and ease with which nanomaterials can be incorporated to increase the mechanical properties of the nanofibers. Additionally, interfacial polymerization can be carried out on electrospun nanofibrous membrane surfaces to obtain an ultrathin polyamide selective layer. After incorporating nanomaterials in either the polyamide selective layer or the support layer, thin film nanocomposite (TFN) membranes may have great potential to exhibit excellent performance in ODMPs.

The objectives of this research are to design and develop novel nanofiber-based composite membranes for ODMPs. Specifically, this thesis presents the development of novel nanofiber-supported polyamide TFC and TFN membranes with high water permeation, good selectivity, and excellent mechanical properties for FO and PRO processes. Electrospinning was utilized to fabricate a variety of

highly porous nanofibrous substrates while interfacial polymerization was exploited to form the thin polyamide rejection layer on the substrate.

In the beginning, we explored the feasibility of using electrospun polyvinylidene fluoride (PVDF) nanofibers as the substrate to make high-performance FO membranes. polyamide thin films were successfully formed via interfacial polymerization directly on two electrospun PVDF nanofiber substrates, S1 and S2, having different surface properties in terms of pore size and surface roughness. Experimental results revealed that a denser and less permeable polyamide layer was formed on the S1 substrate which possessed relatively smaller pore sizes (mean pore size: $0.32 \pm 0.07 \mu\text{m}$; maximum pore size: $0.50 \pm 0.10 \mu\text{m}$), while a looser polyamide layer with higher water permeability was attained on the S2 substrate with larger pore size (mean pore size: $0.40 \pm 0.02 \mu\text{m}$; maximum pore size: $0.59 \pm 0.04 \mu\text{m}$). The difference in polyamide layer structure was believed to be associated with the substrate structure, leading to different cross-linking degrees during the interfacial polymerization. The basic FO performance of resulting TFC membranes has been investigated. A water flux of $30.4 \text{ L/m}^2\text{h}$ was achieved when the active layer was oriented towards the 1.0 M NaCl draw solution while the ratio of reverse salt flux to water flux could be kept as low as 0.21 g/L .

Following the success of the PVDF nanofiber composite FO membrane, some nanomaterials were proposed for incorporation in the nanofibrous substrates to provide more water channels and improve the substrate's hydrophilicity. We fabricated a novel TFN membrane consisting of a polyetherimide (PEI) nanofibrous substrate incorporating silica nanoparticles and an ultrathin polyamide skin layer. PEI was also chosen in this research as it is a versatile polymer with a wide range of applications due to its excellent thermal, mechanical and solvent-resistance properties. It was verified that the incorporation of silica nanoparticles assisted in reducing the structure parameter of the substrate in terms of porosity, increasing additional water channels and hydrophilicity, and improving membrane performance significantly in the FO process.

To further enhance both the performance and mechanical properties of the composite membrane, we proposed and fabricated a novel TFN membrane consisting of a PEI nanofibrous support reinforced by functionalized multi-walled carbon nanotubes (f-CNTs) and an ultrathin polyamide rejection layer. In addition to the superior inter-connected porous structure of the nanofibrous support, the well-distributed f-CNTs in the nanofibers increased the substrate porosity by 18%, reduced the structure parameter by 30%, and significantly improved the substrate tensile strength by 53%. The high mechanical strength provided by the embedded f-CNTs enabled us to further increase the substrate porosity to reduce the ICP, which was demonstrated by the high performance of TFN-2 FO membrane with a structure parameter of 310 μm . Its water flux at 1.0 M NaCl draw solution was 61 and 33 $\text{L}/\text{m}^2\text{h}$ in the active layer-facing-DS (AL-DS) and active layer-facing-feed water (AL-FW) orientations, respectively. To the best of our knowledge, it is the first time that the CNTs incorporation increases both water flux and membrane mechanical strength. It is believed that this novel design strategy has great implications for PRO membrane fabrication.

In the last part of this study, we have successfully fabricated a novel TFN membrane consisting of a tiered structure of f-CNTs-reinforced PEI nanofibrous support and an ultrathin polyamide-based selective skin layer for PRO process. The tiered support was made by fine and coarse PEI nanofiber layers. The fine fiber reinforced with well dispersed f-CNTs has been found to increase mechanical stability of the polyamide selective layer, allowing the support to withstand high hydraulic pressure in the PRO system. The optimized membrane can endure a trans-membrane pressure up to 24 bar and generate a peak power density as high as 17.3 W/m^2 at 16.9 bar using synthetic seawater brine (1.0 M NaCl) as the draw solution against de-ionized (DI) water. In addition, the long term PRO results show that this membrane can generate a stable power density of $15.0 \pm 0.5 \text{ W}/\text{m}^2$ for a test period of 10 hours. This demonstrates that the membrane holds great potential to be used in the PRO process.

In conclusion, this thesis presents the design and development of novel nanofibrous TFC and TFN membranes based on studies of the fundamental mechanisms of interfacial polymerization on a variety of nanofibrous substrates, fabrication of highly porous nanofibrous TFN FO membrane by incorporation of silica nanoparticles, development of robust and highly porous nanofibrous TFN FO membrane by incorporation of f-CNTs, and the design of a PRO membrane with a tiered structure. This work contributes to the development of membrane fabrication technology and facilitates practical applications of nanofibrous membranes in ODMPs.

CHAPTER 1.

Introduction

1.1 Background

One of the most pervasive problems affecting people throughout the world is the shortage of water and energy. It is well known that clean and safe water is a prerequisite for all organisms in nature including human beings. However, only 2.5% of all earth's water is fresh water (Oki and Kanae 2006). More than 80 countries suffer from water scarcity and nearly 80% of the world's population has inadequate access to a satisfactory quality and quantity of fresh water (Karagiannis and Soldatos 2008; Vorosmarty *et al.* 2010). Due to population growth and economic development, more exploitation of aquifers has reduced groundwater levels and availability of fresh water sources. Thus, more fresh water resources need to be found to meet the increasing demand.

Over the years, energy has been widely supplied by power stations, most of which burn fossil fuels to power their generators. However, fossil fuels have a number of drawbacks (Armaroli and Balzani 2007; Post *et al.* 2007), such as emissions of greenhouse gases, the non-renewable nature of the resource and its uneven distribution depending on geographical location. To make matters worse, the United Nations projects global population to grow from about 7 billion today to 9.3 billion in 2050 and 10.1 billion by 2100 (Lee 2011). Consequently, demand for water and energy are increasing significantly. Additionally, Japan's nuclear crisis after the earthquake in March 2011 has prompted many countries to reconsider the safety of

nuclear energy. Thus, there is an urgent requirement for sustainable and environmentally friendly energy conversion technology.

Possible alternative methods for providing both clean and safe water and sustainable and environmentally friendly energy are the osmotically driven membrane process (ODMPs) including forward osmosis (FO) and pressure retarded osmosis (PRO). These technologies exploit the natural phenomenon of osmosis. The driving force of these processes is osmotic pressure, which drives the transport of water across a semi-permeable membrane from a solution with a low salt concentration into a high concentration solution.

Specifically, FO can be adapted to treat many complex feed solutions, including industrial streams (Coday *et al.* 2014; Lutchmiah *et al.* 2014; Zhang *et al.* 2014), seawater (Li *et al.* 2012), nutrient-rich liquid streams (Holloway *et al.* 2007), activated sludge (Cornelissen *et al.* 2008), wastewater effluents (Linares *et al.* 2013), simulated wastewaters (Cath *et al.* 2005; Cartinella *et al.* 2006; Su *et al.* 2012), and even nuclear wastewaters (Zhao *et al.* 2012). As an upgraded application of FO, PRO could be potentially employed to generate electric power from the mixing of a high concentration salt solution under high hydraulic pressure with a low concentration salt solution without hydraulic pressure via a robust FO membrane. This salinity-gradient energy, also called blue energy, is available worldwide where there are natural or industrial salt brines (Pattle 1954; Norman 1974; Loeb and Norman 1975; Loeb 1976; Wick 1978; Isaacs and Schmitt 1980; Reali 1981; Bemporad 1992; Loeb 1998; 2001; 2002; Post *et al.* 2007; Nijmeijer and Metz 2010). The benefits of salinity energy include: (1) it is completely renewable and less intermittent than other renewable energy like wind and solar energies; (2) there is no significant hazardous waste discharging to the environment (Thorsen and Holt 2009); (3) the estimated energy cost is comparable and competitive with other renewable energy sources (Thorsen and Holt 2009). These all qualify ODMPs for green certificates and other supportive policy measures for renewable energy.

As for other membrane processes, the membranes play a significant role in ODMPs. Commercial reverse osmosis (RO) membranes, due to their inherent transport limitations, are ineffective in ODMPs. Their thick support layers cause severe internal concentration polarisation (ICP) leading to poor performance in ODMPs. To make a breakthrough and commercialize the ODMPs on a large scale, novel membranes need to be designed and fabricated for ODMPs. The membrane support structure needs to be further optimized to increase membrane porosity, reduce ICP, and enhance membrane performance. However, the mechanical properties of the porous supports usually cannot withstand the high hydraulic pressure during PRO operation. Thus, design and fabrication of porous and robust supports for ODMPs membranes is highly desirable.

A number of techniques including sintering, stretching, track-etching and phase inversion have been employed to fabricate membranes with different materials and structures for various kinds of membrane processes. Electrospinning, as a widely known method for producing nanofibers with diameters as small as a few nanometers, could be applied to fabricate nanofibrous mats with layered, highly porous and interconnected structures. Many additives can be incorporated into nanofibers to enhance mechanical strength. These key features make nanofibrous membranes a great candidate to serve as supports for ODMPs membranes. In this work, the nanofiber supported polyamide thin film composite (TFC) and thin film nanocomposite (TFN) membranes have been designed, fabricated and optimized for ODMPs. The mechanical properties of the electrospun nanofibrous membranes have been enhanced to satisfy the requirements for PRO processes.

1.2 Research objectives

This research aims to design and fabricate nanofiber supported TFC and TFN membranes for ODMPs by electrospinning. More specifically, the main objectives of the study are:

- To fabricate polyvinylidene fluoride (PVDF) nanofiber supported polyamide TFC membranes for ODMPs and to:
 - Investigate the impact of monomer concentration on the intrinsic separation property of the polyamide rejection layer synthesised by interfacial polymerization on a PVDF nanofibrous support;
 - Demonstrate the effect of nanofiber morphology, *e.g.*, fiber diameter (pore size), on the formation of a polyamide layer on PVDF nanofibrous supports;
 - Fabricate PVDF nanofibrous TFC membranes with competitive osmotic water flux and low reverse salt flux, which could be suitable for use in a harsh chemical environment.

- To engineer highly porous nanofibrous support layers by incorporating silica nanoparticles in polyetherimide (PEI) nanofibers in order to increase the support porosity and reduce support structure parameter thus improving water flux in ODMPs:
 - Fabricate PEI nanofiber support layers with different silica nanoparticles embedding ratios;
 - Reveal the effects of silica nanoparticles on nanofiber surface morphology, topology and the resulting effects on pure water flux and porosity of support layer;
 - Compare the osmotic performance of designed PEI nanofibrous TFC membranes incorporating silica nanoparticles with a control membrane.

- To design nanomaterial reinforced nanofibrous supports with a balance of high porosity and high mechanical strength for FO membranes. This nanomaterialsreinforcement strategy could be further extended to PRO membrane design.
 - Graft –COOH groups onto multi-walled carbon nanotubes (designed as f-CNTs) in order to have a good dispersion and interaction with polymer dope solution;
 - Incorporate the f-CNTs in PEI nanofibers via electrospinning method;

- Demonstrate that the newly developed composite fibrous mats have enhanced mechanical properties and increased porosity;
- Fundamentally understand the effect of the structure of nanofibrous mats on FO performance.
- To create tiered nanofibrous support structures for PRO membranes:
 - Fabricate two PEI nanofiber layers with different fiber diameters: fine fiber layer (smaller fiber diameter: ~100 nm) and coarse fiber layer (large fiber diameter: ~200 nm);
 - Strengthen each PEI nanofiber layer with f-CNTs
 - Develop three different TFC membranes on three various supports with tiered structure;
 - Evaluate morphology, pore size, mechanical properties as well as porosity of the supports;
 - Conduct PRO testing to evaluate the membranes' efficiency in generating electric power.

1.3 Thesis outline

Seven chapters are presented in this thesis, which are outlined as follows:

Chapter 1: *Introduction* – Background information, challenges in this research area and the objectives of the study are provided.

Chapter 2: *Literature review* – A brief literature review is categorized into three parts. In the first part, the concepts, theory and challenges regarding ODMPs are reviewed. In the second part, the requirements and state-of-the-art of ODMPs membranes are summarized. Membrane materials and configuration, current status of commercial and lab-scale membranes used in ODMPs are reviewed. Finally, the electrospinning process is introduced together with the development of composite nanofibrous membranes. Mechanisms of electrospinning and the influences of parameters during the electrospinning process are briefly discussed, followed by the

review of the development and application of composite nanofibrous membranes in conventional filtration applications as well as ODMPs. Additionally, investigations of the reinforcement of nanofibers are also reviewed here.

Chapter 3: *Preparation of Polyamide Thin Film Composite Forward Osmosis Membranes Using Electrospun Polyvinylidene Fluoride (PVDF) Nanofibers as Substrates*—We explored the feasibility of using electrospun PVDF nanofibers as substrates to make high-performance FO membranes. Polyamide thin films were successfully formed via interfacial polymerization directly on two electrospun PVDF nanofiber substrates having different surface properties in terms of pore size and surface roughness. The surface structure, water permeability and salt rejection of the resultant TFC FO membranes were characterized by a series of measurements including field emission scanning electron microscope (FE-SEM) imaging, X-ray photoelectron spectroscopy (XPS) characterization and inherent separation property tests.

Chapter 4: *Synthesis and characterization of high-performance novel thin film nanocomposite (TFN) FO membranes with polyethylenimine (PEI) nanofibrous support incorporating silica*—A TFN FO membrane consisting of a polyamide skin layer and silica incorporated PEI nanofibrous support was developed in this work. Membrane morphology and structure were characterized with FE-SEM and Energy-dispersive X-ray spectroscopy (EDX). The effects of silica on the nanofibrous support morphology, structure and FO performance were evaluated.

Chapter 5: *Synthesis and characterization of high-performance novel thin film nanocomposite (TFN) FO membranes with nanofiber support reinforced by functionalized carbon nanotubes*—TFN FO membranes, which consist of a polyamide skin layer formed on PEI nanofibrous support reinforced by f-CNTs, were developed in this study. Transmission electron microscopy (TEM) was utilized to characterize the f-CNTs in the membranes. The effects of incorporation of f-CNTs in nanofibers on membrane mechanical properties and FO performance were evaluated.

Chapter 6: *Synthesis and characterization of high-performance novel thin film nanocomposite (TFN) PRO membranes with tiered nanofiber support reinforced by functionalized carbon nanotubes* – Tiered nanofiber supports were designed and fabricated by electrospinning to serve as supports for PRO membranes. The individual nanofiber used to construct the nanofibrous supports were reinforced by f-CNTs and bonded via heat-press to provide high mechanical properties to endure high pressures in the PRO process. The morphology, mechanical properties, and PRO performance of the membranes thus developed are thoroughly investigated.

Chapter 7: *Conclusions and recommendations* – The important findings of this study and recommendations for future work are summarized in this chapter.

CHAPTER 2.

Literature review

2.1 Osmotically driven membrane processes (ODMPs)

2.1.1 Introduction of ODMPs

Osmosis occurs when two solutions with different concentrations are separated by a semipermeable membrane (*i.e.*, osmotic membrane) which is ideally only permeable to the solvent, not the solute. In the ODMPs, the solvent is forced by osmotic pressure through a membrane from the diluted solution to the more concentrated one. Compared with traditional pressure-driven processes, the ODMPs have become increasingly popular in recent years in many fields such as wastewater treatment (Holloway *et al.* 2007; Cornelissen *et al.* 2008; Achilli *et al.* 2009b; Lay *et al.* 2011; Zhang *et al.* 2011b), seawater desalination (Elimelech 2007; Choi *et al.* 2009; Tan and Ng 2010; Hancock *et al.* 2011; Ge *et al.* 2012), the food industry (Garcia-Castello and McCutcheon 2011), pharmaceutical applications (Jin *et al.* 2012a; Xie *et al.* 2012), and green electric power (Chou *et al.* 2013; Li *et al.* 2013b; Song *et al.* 2013).

The osmotic pressure of sodium chloride solution, π , is given by the well-known Van't Hoff equation (Enomoto *et al.* 2010):

$$\pi = iCRT \quad 2-1$$

where i is the van't Hoff factor (2 for a doubly monovalent electrolyte), C is the molar concentration of the solute, R is the general gas constant, and T is the absolute temperature.

Figure 2-1 Schematic diagram illustrating the three osmotic processes through an ideal membrane. The blue arrows and red arrows represent the water flow direction and salt flow direction respectively. $\Delta\pi$ represents the osmotic pressure difference of the two solutions separated by the membrane, Δp represents the hydrostatic pressure difference along the membrane (Xu *et al.* 2010).

There are three osmotic processes: forward osmosis (FO), pressure retarded osmosis (PRO) and reverse osmosis (RO), as illustrated in **Figure 2-1**. The RO process uses hydraulic pressure as the driving force for separation, which serves to counteract the osmotic pressure gradient. Thus, the net driving force for a RO process is defined as $(p-\pi)$. In an RO process, the water and solute flow in the same direction. By comparison, the net driving force in FO and PRO is from osmotic pressure. Therefore, FO and PRO processes are classified into ODMs. The net driving force for FO and PRO processes are π and $(\pi-p)$, respectively. In PRO and FO processes, the water and solute flow in opposite directions.

In detail, FO is a natural or spontaneous process that uses an osmotic pressure gradient across a semi-permeable membrane to effectively separate water from dissolved solutes. As little or no hydraulic pressure is required for the FO process, significantly lower energy consumption is expected compared to the RO process.

The PRO process can be utilized to generate electric power. Usually, the process allows the water to permeate through a semipermeable membrane from a low-pressure diluted solution (feed solution) to a high-pressure concentrated salt

solution (draw solution), producing electric power by depressurizing a portion of the permeate via a hydro-turbine. The process scheme of PRO has been proposed by Loeb (Loeb 1976) and then Jellinek (Jellinek and Masuda 1981). The working mechanism of the PRO process is illustrated in **Figure 2-2**.

Figure 2-2 Schematic representation of the PRO process for power generation.

It can be seen from **Figure 2-2**, that V cubic meters of concentrated solution (Brine), with the osmotic pressure π_{high} , is pressurized to a hydraulic pressure P atmospheres (atm), which requires a work input of PV cubic meter atmospheres (m^3 atm). Then the pressurized stream is delivered to the high pressure side of a membrane unit. Simultaneously a diluted solution (Fresh water), with the osmotic pressure π_{low} , is fed into the low pressure side of the membrane unit. It is assumed that a volume of ΔV m^3 of diluted solution will permeate through the membrane to the concentrated solution against the hydraulic pressure, P , which is less than the osmotic pressure difference across the membrane. A total volume of $(V + \Delta V)$ m^3 of mixed solution is delivered to a hydro-turbine at a pressure P atm. Thus $P (V + \Delta V)$ m^3 atm work is generated by depressurizing the solution to zero atm. The net work of PRO process is $P \Delta V$ m^3 atm, namely the difference between the output from hydro-turbine and the input to the pump.

The motivation for adopting ODMPs for water treatment and energy generation comes from their potential advantages over current technologies (Lutchmiah *et al.* 2014):

- 1) FO membranes reject particles, pathogens, emerging substances, and salt due to their mean pore radii of 0.25-0.37 nm. Compared to other membrane processes,

FO demonstrates a higher total dissolved solids (TDS) removal rate with a lower energy consumption.

- 2) FO has shown excellent durability, reliability and water quality during operation with highly polluted water in emergency situations.
- 3) Extremely highly saline streams (pressure higher than 83 bar) can be treated by FO.
- 4) FO can be used for dewatering feeds for effective anaerobic digestion of wastewater, which is simpler, greener and is more effective than traditional dewatering systems.
- 5) Extensive pre-treatment systems for FO may be redundant when treating complex feeds. RO and NF, in contrast, are prone to fouling and require pre-treatment to improve operation sustainability and reduce operating costs.
- 6) Unlike the RO process, FO is a natural or spontaneous process that uses the osmotic pressure gradient across a semi-permeable membrane to effectively separate water from dissolved solutes. As little or no hydraulic pressure is employed, FO requires less energy input than RO. This enables FO to be applied in areas where access to electricity is limited.
- 7) FO has demonstrated flexibility and applicability due to: a) scalability of the membrane system; b) reduced fouling tendency and simple cleaning compared to RO.
- 8) PRO could generate environmental friendly electric power from osmotic energy.

2.1.2 ODMs transport theory

Due to the complexity and variability of wastewater, it is difficult to address the mass transport models in consideration of fouling. Most of the existing models are based on solution-diffusion and convection-diffusion equations, which incorporate concentration polarization (CP) phenomena but neglect the effect of fouling on the transport model. Before giving the theoretical derivations of the water flux in ODMs, the basic permeability constants/coefficients (A , B) of the TFC membrane are introduced.

- **Membrane intrinsic permeability coefficients (A , B)**

The simplified equation from solution-diffusion model which gives the water flux through a membrane as a function of the pressure difference was presented as below (Mulder 1996; Wijmans and Baker 2006):

$$J_w = \frac{D_w \cdot c_{w,1}^m}{l} \left(\left[\frac{V_w (\Delta P - \Delta \pi)}{RT} \right] \right) \quad 2-2$$

Where the D_w is the diffusivity of water in polymer fixed frame; l is the membrane thickness; $c_{w,1}^m$ represents the water concentration inside the membrane near the feed phase; V_w is the molar weight of water. This equation can also be written in a simple form as:

$$J_w = A \cdot (\Delta P - \Delta \pi) \quad 2-3$$

with $A = D_w \cdot c_{w,1}^m \cdot V_w / (RTl)$. A is called the water permeability coefficient and can be measured by RO tests with ultrapure water ($\Delta \pi = 0$) as feed (Wang *et al.* 2010a; Wei *et al.* 2011b), and is defined as below:

$$A = \frac{J}{\Delta P} \quad 2-4$$

where ΔP is the applied trans-membrane pressure and J represents the permeate water flux.

Most of ODMs membranes are not ideally semi-permeable and a small amount of salt can permeate through the membrane. This salt leakage will cause two effects: 1)

reverse salt diffusion, and 2) concentration polarization. Together these reduce the effective osmotic pressure difference across the membrane.

Reverse salt diffusion occurs when a small amount of salt penetrates the membrane from the draw solution to the feed solution due to the concentration gradient across the membrane. The simplified solute flux (J_s) derived from solution-diffusion model can be written as

$$J_s = \frac{D_s \cdot K_s \cdot \Delta c}{l} \quad 2-5$$

Where $B = D_s K_s / l$ and is called the solute permeability coefficient. D_s is the diffusivity of solute in polymer fixed frame; K_s is the solubility constant. The salt permeability coefficient of a membrane can be obtained using RO experiments and is expressed as below:

$$B = \frac{A(1 - R)(\Delta P - \Delta \pi)}{R_s} \quad 2-6$$

where R_s represents the salt rejection and is given by:

$$R_s = 1 - \frac{C_p}{C_f} \quad 2-7$$

where C_p and C_f represent the salt concentrations in the permeate and feed solutions, respectively. In general, unless the membrane has a very salt selectivity, salt leakage is not a serious problem when compared with concentration polarization.

- **Concentration polarization (CP)**

A schematic of the salt concentration profile across a membrane employed in an ODMP is shown in **Figure 2-3** to help illustrate CP.

Concentration polarization is the accumulation or depletion of salt near the interface boundary. There are two types of concentration polarization existing in ODMP applications. External concentration polarization (ECP) occurs at the surface of the selective layer of the membrane and occurs in RO, FO and PRO processes. The salt concentration at the membrane surface ($C_{d,m}$ in **Figure 2-3**) is lower than the bulk

solution ($C_{d,b}$ in **Figure 2-3**) which reduces the osmotic water flux. Fortunately, the ECP can be mitigated by optimization of the shear rate and turbulence of the flow along the membrane surface. The dilutive ECP could be calculated based on film theory. Thus, the osmotic pressure at the membrane interface is derived from the bulk osmotic pressure as below:

Figure 2-3 Illustration of osmotic driving force for a membrane in active layer facing draw solution (AL-DS) orientation in ODMPs.

$$\pi_{d,m} = \pi_{d,b} \times \exp\left(-\frac{J_w}{k}\right) \quad 2-8$$

where k is the mass transfer coefficient in the draw solution and can be calculated as follows:

$$k = \frac{ShD}{d_h} \quad 2-9$$

where D is the salt diffusion coefficient, Sh is the Sherwood number, and d_h is hydraulic diameter.

As shown in **Figure 2-3**, the direction of water flow is opposite to the salt flow. Consequently, the water flow will carry the salt in the feed solution back towards the selective layer, causing it to accumulate at the interface between the support layer and the selective layer. Consequently, the effective osmotic pressure is given by $(C_{d,m}-C_{f,m})$ and is much smaller than the apparent osmotic pressure $(C_{d,m}-C_{f,b})$. This phenomenon is described as internal concentration polarization (ICP). ICP is a phenomenon specific to ODMPs which occurs inside the support layer of the membrane. Both ECP and ICP can reduce the effective osmotic pressure gradient across the membrane. However, ICP can reduce the driving force drastically and cannot be mitigated by altering flow turbulence. Additionally, the ICP is proven to be more severe than ECP in ODMP systems. Consequently, the main objective for ODMP membrane fabrication is to reduce the ICP as far as possible.

- **ODMPs performance (J_w and J_s)**

Most ODMP membranes have an asymmetric structure with two distinct layers: an active layer providing selectivity and a support layer providing mechanical strength. The membrane can be configured with the active layer facing either the draw solution (AL-DS orientation) or the feed water (AL-FW orientation). Models of the water flux in both orientations are given below (Xu *et al.* 2010; Chou *et al.* 2012):

$$\text{AL-DS:} \quad \frac{J_w}{K_m} = \ln \left[\frac{(A\pi_d - A\Delta P - J_w) + B(\frac{A\Delta P}{J_w} + 1)}{A\pi_f + B(\frac{A\Delta P}{J_w} + 1)} \right] \quad 2-10$$

$$\text{AL-FW:} \quad \frac{J_w}{K_m} = \ln \left[\frac{A\pi_d + B(\frac{A\Delta P}{J_w} + 1)}{(A\pi_f + J_w + A\Delta P) + B(\frac{A\Delta P}{J_w} + 1)} \right] \quad 2-11$$

Here the water flux is related to the intrinsic membrane parameters (A and B), the mass transfer coefficient (K_m), and the hydraulic pressure across the membrane (ΔP).

If the hydraulic pressure, ΔP , equals 0, Equations 2-10 and 2-11 simplify to describe the FO process, as shown below.

$$\text{AL-DS: } \frac{J_w}{K_m} = \ln \left[\frac{A\pi_d - J_w + B}{A\pi_f + B} \right] \quad 2-12$$

$$\text{AL-FW: } \frac{J_w}{K_m} = \ln \left[\frac{A\pi_d + B}{A\pi_f + J_w + B} \right] \quad 2-13$$

Note that the membrane orientation affects water flux and fouling significantly. Extensive research has shown that higher water fluxes are obtained in AL-DS orientation due to less severe concentrative ICP (Tang *et al.* 2010; Lutchmiah *et al.* 2014). Generally, when wastewater rich in foulants serves as the feed water, these foulants would be entrapped in the support layer, accelerating ICP (Tang *et al.* 2010; Jin *et al.* 2012b). Thus, in most applications, *e.g.*, osmotic membrane bioreactors, the AL-FW orientation is preferred in order to minimise fouling issues (Lutchmiah *et al.* 2014).

The mass transfer coefficient K_m is given by the ratio of the solute diffusion coefficient (D) to the membrane structure parameter (S):

$$K_m = \frac{D}{S} \quad 2-14$$

- **Structure parameter (S)**

The structure parameter is an important intrinsic parameter of the membrane support layer; The S value is expressed by

$$S = \frac{\tau\delta}{\varepsilon} \quad 2-15$$

where τ , δ , ε are the membrane thickness, tortuosity and porosity, respectively.

In other words, S can reflect the degree of ICP in a membrane support layer in a length scale. A larger structure parameter (*e.g.*, thicker membrane support) leads to a lower K_m , which can significantly reduce permeate flux due to the exponential dependence of concentration polarization on K_m .

- **Power density (W)**

Power density, W , is the major performance indicator in PRO processes because it determines the membrane area and therefore the size of the PRO plant required for a given capacity of energy production. Power density is defined as the power generated per unit of membrane area

$$W = J_v \times \Delta P \quad 2-16$$

where J_v is the water flux through the membrane, ΔP is the applied hydraulic pressure difference across the membrane. As the power density of the membrane increases it becomes more economically effective.

2.1.3 Challenges in ODMPs

As described above, one of the major challenges in ODMPs is the undesired ICP, which tends to reduce the effective osmotic driving force, and hence the water flux. To reduce the ICP, highly porous support layers with smaller structure parameters need to be designed and fabricated for ODMPs. Additionally, another challenge of membrane design for ODMPs, specifically for PRO processes, is the mechanical stability of the membrane under high applied hydraulic pressure. In the next section, the requirements and current state of the art of ODMP membranes are reviewed and discussed.

2.2 Development of ODMPs membranes

2.2.1 Requirements of ODMPs membranes

As mentioned above, membranes are critical for advancing the field of ODMPs. In order to design and fabricate ODMP membranes, the desired characteristics of membranes for ODMPs need to be considered, which are summarized as follows (Cath *et al.* 2006):

- ❖ Rejection layers with high water permeability and low salt permeability;

- ❖ Thin and highly porous support layer (smaller structure parameter) with high mechanical stability to sustain long-term operation and reduce ICP, therefore maximizing the effective osmotic pressure driving force, resulting in higher water fluxes;
- ❖ High hydrophilicity to enhance flux and reduce membrane fouling;
- ❖ High mechanical stability to sustain hydraulic pressure when used for PRO processes;
- ❖ Good chemical and mechanical stabilities during long term operation.

It was reported that TFC membranes consisting of an ultrathin rejection layer and a porous support layer can remarkably reduce ICP and lead to excellent performance in ODMPs (Yip *et al.* 2010; Wei *et al.* 2011b). This is possible because both the rejection layer transport properties and support layer structure parameter can be separately designed and optimized to meet their different requirements.

2.2.2 Thin film composite (TFC) membranes

- **Introduction of TFC membranes**

Usually, the substrate of TFC membranes is fabricated via a phase inversion method which is based on thermodynamic principles. The pore structure of the substrate can be controlled by varying, for example, the polymer dope composition, the bore fluid solution composition and the coagulation bath temperature among other parameters. The pore structure of the substrate (*e.g.*, porosity, tortuosity, thickness) governs the structure parameter. The structure, porosity, and substrate's surface hydrophobicity have been demonstrated to influence the permeability and selectivity properties of the polyamide rejection layer formed on top of the substrate via interfacial polymerization.

In addition to the porous substrate structure, the characteristics of the selective layer are also crucial for membrane functionality. Interfacial polymerization is extensively utilized to deposit a thin layer upon a porous substrate. In this process, a polymerisation reaction occurs between two very reactive monomers at the interface of two immiscible solvents with the schematic shown in **Figure 2-4**.

Figure 2-4 Thin film formation via interfacial polymerization (Vankelecom *et al.* 2005; Vandezande *et al.* 2008)

The advantage of interfacial polymerisation is that the reaction is self-inhibiting due to the limited supply of reactants through the already formed layer, resulting in an extremely thin film with typical thicknesses in the order of 50 nm.

- **Selection of membrane materials**

To design a membrane you need to first determine the membrane materials to be used in the support layer. Membrane material selection allows control over the nature of permeate-membrane physicochemical interactions. The separation of liquid mixtures is strongly influenced by both the effective molecular size of the permeates and the chemical interactions which occur within the membrane phase. Lloyd and Meluch (Lloyd and Meluch 1985), followed by Hoehn (Hoehn H 1985),

have discussed membrane material selection in terms of physicochemical interactions for liquid mixture separations. In addition, Lloyd and co-workers (Lloyd and Meluch 1985) presented twenty-seven polymers, copolymers and blends currently being used for liquid separation membranes.

Prior to developing membranes, it is beneficial to have a comprehensive understanding of the characteristics of the polymers in terms of the following: molecular architecture or bulk properties (molecular weight characteristics, degree of branching, chemical functionality, copolymer or blend composition), polymer solution properties (polymer swellability, solubility and solution viscosities), thermal properties (glass transition temperature and crystal melting temperature), chemical stability, and biocompatibility (Lloyd 1985). Polymer physical properties, such as mechanical strength and extent of crystallization, are strongly influenced by preparation procedures. Ultimately, these considerations will determine the long-term properties of the membrane. All these intrinsic properties of the polymers as well as the fabrication procedures have a great impact on the lifetime and transport properties of the membrane in its practical application.

Susceptibility to membrane fouling is also material dependant. To date, most substrate materials used for ODMPs membranes are hydrophilic, mainly because of the concern of the high fouling tendencies of membranes composed of hydrophobic materials. The widely used hydrophilic asymmetric cellulose triacetate (CTA) membranes from Hydration Technology Innovations (HTI) are less prone to fouling than alternative, more hydrophobic materials, making them more suitable for treatment of high fouling wastewaters. However, in harsh environments, the hydrolysis of cellulosic materials is still a matter for concern.

Materials that have been utilized for ODMPs membrane support fabrication include, but are not limited to: polyethersulfone (PES) (Wang *et al.* 2010a; Song *et al.* 2011), polysulfone (PSF) (Tiraferri *et al.* 2012; Hoover *et al.* 2013), poly acrylonitrile (PAN) (Qi *et al.* 2012; Bui and McCutcheon 2013), cellulose acetate (CA) (Sairam *et al.* 2011), nylon 6,6 (Huang *et al.* 2013a), sulphonated polyphenylenesulfone

(sPPSU) (Zhong *et al.* 2013), polyamide-imide (PAI), polyimide (PI) (Han *et al.* 2013b), and polyetherimide (PEI) (Chou *et al.* 2013).

Due to the technical requirements for PRO processes, there is a demand for a new category of materials with high mechanical and thermal stabilities, low-fouling characters, and good chemical stability.

- **Membrane orientation**

Most ODMPs membranes have an asymmetric structure with two different layers: an active layer and a support layer. Due to this asymmetry, these membranes can be configured with the active layer facing either the feed water side (AL-FW) or the draw solution side (AL-DS). The membrane orientation significantly affects FO performance in terms of both water flux and fouling. Extensive studies have reported that a higher water flux is observed in AL-DS orientation, attributed to the less severe ICP. However, this orientation is inclined to cause membrane fouling due to foulants becoming entrapped in the support layer, further reducing the membrane porosity and increasing ICP (Tang *et al.* 2010; Jin *et al.* 2012b). Thus, it is preferable to arrange the membrane with the polyamide skin layer facing the solution with the higher fouling propensity, *e.g.*, in an osmotic membrane bioreactor, the active layer will normally face the bioactive feed (Lutchmiah *et al.* 2014).

2.2.3 State of the art of current ODMPs membranes

- **Commercial ODMPs membranes**

Since the 1970s, commercial hollow fiber and flat-sheet membrane modules that are not particularly suited to ODMP applications have been used for experimental testing of ODMPs for theoretical development and analysis (Loeb *et al.* 1976; Mehta and Loeb 1978; Loeb and Mehta 1979; Mehta 1979; Gerstandt *et al.* 2008; Skilhagen *et al.* 2008; Arena *et al.* 2011). The water fluxes and power densities achieved by the commercial membranes in earlier studies are far below those

required for economic feasibility, due to the thick support layers and therefore large structure parameters of the membranes. In recent studies, the only reported commercial flat sheet membranes particularly designed for ODMPs, including asymmetric CTA and TFC membranes, were manufactured by HTI. The CTA membrane contains an embedded support screen and has a dense rejection layer far thicker (10-20 μm) than commercially available TFC RO membranes. However, this membrane has performed much better in ODMPs than other commercially available RO membranes and has been extensively used in the research of ODMPs due to its small structure parameter.

According to a press release from HTI (Alsvik and Hägg 2013), a new TFC FO membrane has been developed that delivers a water flux more than double that of their previous CTA membrane, which is tolerant to pH values ranging from 2-12 and has a salt rejection of 99.3%. This membrane shows an average flux of 20 $\text{L}/\text{m}^2\text{h}$ in AL-FW orientation and 49 $\text{L}/\text{m}^2\text{h}$ in AL-DS orientation at a test conditions of 1 M NaCl as DS, DI water as FW, an operating temperature of 23 °C and a cross flow velocity of 30 cm/s. This membrane has also been tested in a PRO process and achieved a power density of 3.5 W/m^2 at 1034 kPa. By comparison, HTI's CTA FO membrane has a flux of 9 $\text{L}/\text{m}^2\text{h}$. The FO and PRO performances of these commercial membranes are shown in **Table 2-1** and **Table 2-2**.

The HTI TFC membranes have a smaller support structure parameter to mitigate ICP and thus to enhance their FO water flux. However, the relatively low water permeability and low salt rejection of these membranes means that further improvement is still necessary.

- **Lab-made ODMPs membranes development for FO**

During the last few years a number of handmade laboratory FO membranes have been reported. These are tabulated in **Table 2-3**. According to the permeability and selectivity of the rejection layer, the FO membranes could be categorized into two classes: RO-like FO membranes and NF-like FO membranes. If classified by the

membrane structures, they could be categorized into asymmetric FO membranes and TFC FO membranes. Little research has been focused on asymmetric FO membrane development due to its limitations in separately designing the rejection layer and the support layer, thus resulting in low FO performances (Wang *et al.* 2007; Su *et al.* 2010).

TFC FO membranes (Wang *et al.* 2010a; Yip *et al.* 2010; Wei *et al.* 2011b; Han *et al.* 2012), either in hollow fiber or flat-sheet configuration, consist of a rejection layer on top of a support layer. Both the rejection and support layer can be tailored separately. The literature reveals that most of the methods for preparing TFC FO membranes still employ the traditional techniques for the development of RO membranes: fabrication of the support layer by phase inversion and the rejection layer by interfacial polymerization. For a TFC FO membrane, the membrane support layer prepared by phase inversion determines the ICP and thus water flux in FO while the active layer governs the water permeability and salt selectivity. TFC membranes prepared by interfacial polymerization could achieve a very high solute rejection and small back diffusion of solute.

Another approach to of TFC FO membrane fabrication is layer-by-layer (LbL) assembly or charged NF-like FO membranes (Qi *et al.* 2011; Setiawan *et al.* 2011). PAI can provide both cationic and anionic repulsion to salt transfer through the membrane and produce NF-like selective layers (Qiu *et al.* 2012). These membranes tend to have high water permeability and good retention of divalent ions. However, the high cost for large scale production and low retention of sodium chloride limits their performance.

A number of studies have been carried out on the improvement of FO membranes in the following areas:

- ❖ Support structure designed to minimize the undesired ICP (Tiraferri *et al.* 2011; Dumée *et al.* 2013; Hoover *et al.* 2013; Huang *et al.* 2013a; Emadzadeh *et al.* 2014a);

- ❖ Support hydrophilicity modification to improve support wetting properties (Han *et al.* 2012; Saraf *et al.* 2014);
- ❖ Selective layer design to achieve higher water permeability and further improve FO water flux (Yip *et al.* 2011; Ma *et al.* 2012);
- ❖ Selective layer antifouling modification (Tiraferri *et al.* 2012);
- ❖ Biomimetic FO membranes (Wang *et al.* 2012);

Although, great progress has been made in FO membrane design and fabrication, it is still far below academic and industrial expectations. Techniques used in developing membranes strongly influence membrane behaviour and filtration efficiency. New technologies and concepts are required to further improve the membrane performance.

Table 2-1 Reported commercial FO membranes performance

Sample	Configuration	Materials	Water Flux (L/m ² h) (AL-DS / AL-FW)	Salt Flux (g/m ² h) (AL-DS / AL-FW)	FW	DS	Ref.
CTA-HW	FS	CTA	15.4 / 9.0	9.4 / 5.3	10mM NaCl	0.5M NaCl	(Wei <i>et al.</i> 2011b)
CTA-W	FS	CTA	6.6 / 5.0	4.8 / 2.9	10mM NaCl	0.5M NaCl	(Wei <i>et al.</i> 2011b)
CTA-NW	FS	CTA	8.2 / 4.4	2.8 / 0.6	10mM NaCl	0.5M NaCl	(Wei <i>et al.</i> 2011b)
HTI	FS	CTA	20 / 12*	8.8 / 6.1*	DI	1.5 M NaCl	(Bui and McCutcheon 2013)

*The data were derived from the figures in the references.

Table 2-2 Reported commercial PRO membranes performance

Configuration	Materials	Hydraulic pressure (bar)	Spacer	Water flux (L/m ² h)	Power density (W/m ²)	FW	DS	Ref.
			Spacer B	3.45	1.22	DI	0.5 M NaCl	(Kim and Elimelech 2012)
FS	Cellulose-based (HTI)	12.5	Spacer B	14.54	5.18	DI	1.0 M NaCl	(Kim and Elimelech 2012)
			Spacer B	27.08	9.66	DI	2.0 M NaCl	(Kim and Elimelech 2012)
FS	CTA-HTI	17.2	RO permeate carrier	12.5	5.8	10 mM NaCl	1.0 M NaCl	(She <i>et al.</i> 2013)
FS	CTA-HTI	9.72	Mesh spacer	18.8	5.06	DI	60 g/L NaCl	(Achilli <i>et al.</i> 2009a)
FS	HTI-TFC	20.7	Customized tricot	24.5	14.1	DI	1.0 M NaCl	(Straub <i>et al.</i> 2014)
HF	Asymmetric PSf	19.3	-	2.9	1.56	≤ 0.02 Π_{draw}	101 bar	(Loeb and Mehta 1979; Achilli <i>et al.</i> 2009a)
HF	Permasep B-10	40.5	-	2.9	3.27	0	8.6% NaCl	(Mehta 1979; Achilli <i>et al.</i> 2009a)
HF	Permasep B-10	40.5	-	2.8	3.12	0	78 bar	(Mehta and Loeb 1978; Achilli <i>et al.</i> 2009a)

- No data were reported in the references.

Table 2-3 Typical lab-made FO membranes developed on phase inversion support layers.

Configuration	Materials	Water Flux (L/m ² h) (AL-DS / AL-FW)	Salt Flux (g/m ² h) (AL-DS / AL-FW)	FW	DS	Ref.
TFC-FS	PA-PSF /SPEK	50 / 35	9 / 7	DI	2.0M NaCl	(Han <i>et al.</i> 2012)
TFC-FS	PA-PSF	- /18.16 ± 0.96	-/-	DI	1.5M NaCl	(Yip <i>et al.</i> 2010)
TFC-FS	PA-PSF	20.5 / 12.0	5.9 / 4.9	10mM	0.5M NaCl	(Wei <i>et al.</i> 2011b)
TFC-FS	PA-PSF	- / 25.0 ± 4.1	- / -	DI	1.0M NaCl	(Tirafferri <i>et al.</i> 2011)
Double skinned-FS	CA	17.3 ± 0.4 / 10.3 ± 0.3	1.2 ± 0.2 / 0.8 ± 0.1	DI	2.0M MgCl ₂	(Zhang <i>et al.</i> 2010)
FS	Cellulose ester	89.5 ± 4.9 / 56.9 ± 1.8	10.8 ± 1.2 / 7.8 ± 0.6	DI	1.0 M NaCl	(Ong <i>et al.</i> 2015)
FS	SW30-XLE	19 [*] / -	3.2 [*] / -	DI	1.0 M NaCl	(Arena <i>et al.</i> 2011)
TFC-HF	PA-PES	12.9 / 5.0	5.0 / 2.12	DI	0.5M NaCl	(Wang <i>et al.</i> 2010a)
TFC-HF	PA-PES	32.2 / 14	3.5 / 1.75	DI	0.5M NaCl	(Saraf <i>et al.</i> 2014)
TFC-HF	PA-PES	32.9 / -	2.9 / -	8.6	0.5M NaCl	(Chou <i>et al.</i> 2010)
TFC-HF	PA-PES	49 / 28	5.9 / 5.1	DI	1.5 M NaCl	(Sukitpaneenit and Chung 2012)
TFC-HF	PA-sPPSU	82 / 30.6	14.8 / 7.0	DI	2.0 M NaCl	(Zhong <i>et al.</i> 2013)
TFC-HF	PA-PES	55.2 ± 4.5 / -	4.5 ± 0.2 / -	DI	0.5 M NaCl	(Li <i>et al.</i> 2015a)
Charged HF	PAI-PEI	6.34 / 4.15	3.0 / 1.9	DI	1.5 M MgCl ₂	(Setiawan <i>et al.</i> 2011)
Charged HF	PAI-PEI	17.3 / 11.7	16.9 / 3.9	DI	1.5 M MgCl ₂	(Setiawan <i>et al.</i> 2011)
Charged HF	PAI-PEI	17.2 / 12.9	37.7 / 4.8	DI	1.5 M MgCl ₂	(Setiawan <i>et al.</i> 2011)
HF	CA	7.3 / 5.0	- / -	DI	2.0M MgCl ₂	(Su <i>et al.</i> 2010)
HF	PBI	3.84 / -	- / -	DI	2.0M NaCl	(Wang <i>et al.</i> 2007)
HF	PBI	9.02 / -	- / -	DI	2.0M MgCl ₂	(Wang <i>et al.</i> 2007)

- No data were reported in the references.

- **Lab-made ODMF membrane development for PRO**

A desired application for FO membranes is the PRO process, which has the potential to convert salinity gradient energy into electric energy via a robust FO membrane operating under hydraulic pressures up to 25 bar. Since the invention of the PRO process by Prof. Sidney Loeb in 1973, practical application has been prevented by the lack of a suitable membrane. A number of commercial RO membranes were employed in PRO processes in 1980s, but these generated power densities far below the 5 W/m^2 estimated to be required for economic feasibility. In recent years, PRO has again attracted a lot of interest both in academic research and industry communities with more and more novel PRO membranes successfully fabricated. The performance of lab-made PRO membranes is summarized in **Table 2-4**.

Commercial HTI CTA membranes could achieve a power density of 5.18 W/m^2 when using 1.0 M NaCl as DS against DI FW with a specially designed spacer at 12.5 bar hydraulic pressure (Kim and Elimelech 2012). By comparison, a newly developed TFC hollow fiber membrane with PES finger-like support layer was developed and achieved a high power density of 11.0 W/m^2 in PRO using 1.0 M NaCl DS against 10 mM NaCl FW at 8.4 bar operating pressure (Chou *et al.* 2012). Further efforts have been made to improve the operating pressure and power density of hollow fiber membranes using PES (Zhang and Chung 2013) and PEI (Chou *et al.* 2013) support layers with a more sponge-like structure.

Significant progress has also been reported for TFC flat-sheet membranes. A flat-sheet TFC membrane developed on a PI support achieved a power density of 12 W/m^2 at 15 bar utilizing 1.0 M NaCl DS against DI FW (Han *et al.* 2013b). The significant improvements made in PRO membranes depend upon either new material selection or support layer structure design. So far, long term operational results for PRO membranes have not been reported. Further research could focus on investigation and improvement of the long term operation stability of the developed

membranes in PRO processes. Membrane fouling mechanisms in PRO should also be studied in the future.

Table 2-4 Typical lab-made PRO membranes developed on phase inversion support layers.

Configuration	Materials	Hydraulic pressure (bar)	Power density (W/m ²)	FW	DS	Ref.
FS	PA reject layer/PAN support	10	2.6	DI	3.5 wt% NaCl	(Zhang <i>et al.</i> 2013)
FS	PA reject layer/PDA modified PAI support	6	2.84	DI	3.5 wt% NaCl	(Li <i>et al.</i> 2013b)
FS	PA reject layer /PI support	15	12	DI	1.0 M NaCl	(Han <i>et al.</i> 2013b)
FS	PA reject layer/ PEI support	17.2	16.7	DI	1.0 M NaCl	(Li <i>et al.</i> 2015b)
HF	PA reject layer /PES support	20.0	24.3	DI	1.0 M NaCl	(Zhang and Chung 2013)
HF	PA reject layer /PES support	9	10.6	40 mM NaCl	1.0 M NaCl	(Chou <i>et al.</i> 2012)
HF	PA reject layer /PEI support	15	20.9	1 mM NaCl	1.0 M NaCl	(Chou <i>et al.</i> 2013)
HF	PA reject layer /PI support	16	14	DI	1.0 M NaCl	(Han <i>et al.</i> 2013a)
HF	PA reject layer /PI support	22.0	18.1	DI	1.0 M NaCl	(Cui <i>et al.</i> 2014)
HF	PA reject layer /PI support	9.0	6.0	DI	1.0 M NaCl	(Li <i>et al.</i> 2013a)
HF	PA reject layer /PI support	15	16.5	DI	1.0 M NaCl	(Han and Chung 2014)
HF	PA reject layer /PES support	20	27	DI	1.0 M NaCl	(Wan and Chung 2015)
HF	PA reject layer /PES support	20	4.6	Wastewater retentate	1.0 M NaCl	(Wan and Chung 2015)
HF	PA reject layer /PES support	20	21	DI	Seawater brine	(Wan and Chung 2015)

Table 2-5 Summary of nanofibrous FO membranes.

Configuration	Materials	Structure Parameter (μm)	Water Flux ($\text{L}/\text{m}^2\text{h}$) (AL-DS / AL-FW)	Salt Flux ($\text{g}/\text{m}^2\text{h}$) (AL-DS / AL-FW)	FW	DS	Ref.
FS	PVDF(1#)	812	30.4 / 11.6	6.4 / 3.5	DI	1.0 M NaCl	(Tian <i>et al.</i> 2013)
FS	PVDF(2#)	325	47.6 / 28.0	21.6 / 12.9	DI	1.0 M NaCl	(Tian <i>et al.</i> 2013)
FS	PAN*	290.7 ± 53.1	52 ± 7 / 29 ± 4	3.2 ± 1.5 / 8.6 ± 3	DI	1.5 M NaCl	(Bui and McCutcheon 2013)
FS	PSF	-	24 / -	8.63 / -	DI	1.5 M NaCl	(Bui <i>et al.</i> 2011)
FS	PES	80 ± 6	- / 37.8	- / -	DI	0.5 M NaCl	(Song <i>et al.</i> 2011)
FS	PES	106 ± 8	33.9 / 33.9	- / -	DI	0.5 M NaCl	(Song <i>et al.</i> 2011)

- No data were reported in the references.

Table 2-6 Summary of nanofibrous PRO membranes.

Configuration	Materials	Hydraulic pressure (bar)	Power density (W/m^2)	FW	DS	Ref.
FS	PA reject layer/PAN support	11.5	8	DI	0.5 M NaCl	(Bui and McCutcheon 2014)
FS	PA reject layer/PAN support	15.2	15.2	0.9 mM	1.09 M NaCl	(Song <i>et al.</i> 2013)

2.3 Electrospun nanofibrous membranes (ENMs)

2.3.1 Electrospinning

Electrospinning was first reported in the 1930s, and have regained the interest since 1990s due to the significant progress that has been made in understanding the complex electrospinning process and controlling fiber formation. This allowed an expansion of electrospinning applications in membrane fabrication, drug delivery, tissue engineering, security, and energy storage (Ramakrishna *et al.* 2006; Sill and von Recum 2008; Chen *et al.* 2013; Liao *et al.* 2013a). **Figure 2-5** shows a schematic drawing of a typical electrospinning setup which constitutes three basic parts: a high voltage supply, a capillary spinneret (connected with syringe pump), and a grounded metal collector (Sun *et al.* 2014). Essentially, an electrospinning process begins with the extrusion of a precursor solution to form a small droplet at tip of the spinneret, then from where the charged solution jets are ejected. The fluid extension starts in uniform filaments, followed by vigorous whipping due to fluid and electrically driven bending instabilities, and finally deposits on the grounded collector (Reneker and Yarin 2008).

In the electrospinning process, polymeric nanofibers are prepared by creation and elongation of an electrified fluid jet. Forces, including Coulombic repulsion force, electrostatic force, surface tension, viscoelastic force, gravity, and drag force, are act on the charged fluid jet as shown in **Figure 2-5**. It has been demonstrated that the electrospinning process generally consists of the following three stages (Reneker and Fong 2006; Loh *et al.* 2015): (1) onset of jetting and rectilinear jet development; (2) bending deformation with looping and spiraling trajectories; (3) solidification and deposition on the collector.

Figure 2-5 Schematic diagram of the possible mechanism of nanofiber formation in electrospinning process. The effects of intrinsic properties of solution are marked in orange test box, operational conditions are marked in the olivine text box and surrounding conditions in purple box (Loh *et al.* 2015).

First of all, in the electrospinning process, an electrical potential difference is applied between a polymer droplet at the tip of the spinneret and the grounded collector (Fong and Reneker 2000). As the applied voltage increases, the droplet adopts a conical shape named Taylor Cone, from which a jet emanates (Taylor 1964). This cone shape is stable as long as sufficient solution is flowing in and replacing the droplet during the electrospinning process. The critical voltage, beyond which nanofibers can be generated from a given dope solution, is determined by the dope surface tension, spinneret radius, and distance between spinneret tip and collecting screen (Taylor 1969).

After the nanofiber is initiated, the jet of polymer solution will follow a nearly straight line for a certain distance away from the tip (Reneker *et al.* 2002; He *et al.* 2005). The critical length of this distance is proportional to the applied electric field, conductivity, and dope flow rate but inversely proportional to the liquid density and the current passing through the jet. After the path as a straight segment, the jet is elongated driven by electrical forces. This causes the onset of bending instability, characterized by a series of successively bending coils rotating at increasing radius (Reneker *et al.* 2000; Yarin *et al.* 2001; Reneker *et al.* 2002). It has been

demonstrated that a non-axisymmetric or electrically driven bending instability plays the key role in causing stretching/bending of jet at high frequencies and reducing the jet diameter from micrometers to nanometers (Huebner and Chu 1971; Fong *et al.* 1999; Shin *et al.* 2001a; 2001b). During the elongation and bending of the polymer jet, the solvent evaporates simultaneously, which consequently produces dry polymer fibers on the grounded collector (Yarin *et al.* 2001). These fibers overlap to form electrospun nanofibrous membranes (ENMs) with interconnected pores.

It has been extensively demonstrated that the structure and morphology of ENMs, as well as the fiber diameter, are influenced by the viscosity of polymer dope solutions (Deitzel *et al.* 2001; Huang *et al.* 2003; Lee *et al.* 2003; Ryu *et al.* 2003). For a given combination of a polymer and a solvent, there exists a threshold of polymer concentration for successful fabrication of nanofibers. Polymer solutions with lower viscosity (*i.e.*, lower concentration) produce bead-on-string fibers while polymer solutions with higher viscosity (*i.e.*, higher concentration) tends to change the shape of the beads from spherical to spindle-like and then forming uniform fiber shapes (Reneker and Chun 1996; Bhardwaj and Kundu 2010). With further increases in viscosity, the diameter of fibers increases.

In addition, electrical conductivity of the dope solution can also determine rheological behavior and considerably influences spinnability of the dope solution (Subbiah *et al.* 2005; Rutledge and Fridrikh 2007). Solution conductivity is mainly determined by the type of polymer and solvent, as well as the availability of ionisable salts (Bhardwaj and Kundu 2010). During electrospinning process, highly conductive solutions tend to generate thinner fibers with dramatic bending and fast drying (Sill and von Recum 2008; Liao *et al.* 2013a). Further enhancement of dope conductivity can cause instability of Taylor cone, which consequently produces more micro-sized droplets and dense-nets (Wongchitphimon *et al.* 2011). The addition of ions to the polymer solution can improve conductivity dramatically and it has been illustrated that the ions with smaller atomic radii can impose a stronger elongation force on the jet due to their higher charge density and higher mobility

(Zong *et al.* 2002; Barakat *et al.* 2009; Yang *et al.* 2011; Liao *et al.* 2013a). Thus, in order to obtain ultrathin nanofibers and ENMs with small pore sizes, the conductivity of polymer dope needs to be optimized.

It was revealed that selection of solvents and surface tension of solutions also played roles in regulating the morphology of nanofibers (Lin *et al.* 2004; Talwar *et al.* 2010; Hu *et al.* 2011; Wang *et al.* 2011). Evidently, the intrinsic properties of solutions are critical to the successful preparation of ENMs.

2.3.2 Electrospun nanofibrous membranes applications

Nanofibrous membranes have gained popularity in gas filtration, affinity membranes, membrane distillation, and liquid filtration due to their unique pore structure, high porosity, low tortuosity, large surface area, and light weight. Gibson *et al.* (Gibson *et al.* 2001) demonstrated the use of nanofibrous membranes for gas separation applications. Ma *et al.* (Ma *et al.* 2005) reported the fabrication of an cellulose nanofibrous affinity membrane. Investigation of the water-filtration properties of a regenerated cellulose (RC) membrane revealed a higher water permeability than commercial microfiltration (MF) membranes. They demonstrated the potential of the novel RC nanofibrous membrane as an alternative tool for affinity membrane applications. Electrospun PVDF nanofibrous membranes were demonstrated to perform well in producing drinking water from saline water via membrane distillation (Feng *et al.* 2008; Liao *et al.* 2013b). It is believed that this new approach could enable the membrane distillation process to compete with conventional seawater desalination processes such as distillation and RO.

Applicability of nanofibrous membranes could be increased by formation of a separative surface layer. In pressure driven liquid filtration processes including MF, ultrafiltration (UF) and nanofiltration (NF), the nanofibrous membranes are also presented priority to traditional phase inversion based-membranes. For the first time, a novel high-flux UF membrane was reported consisting of a polyvinyl alcohol (PVA) nanofibrous substrate and a PVA hydrogel coating selective layer (Wang *et*

al. 2006). The UF test indicated that the flux rate of PVA nanofibrous composite membranes is several times higher than that of existing commercial TFC membranes. Meanwhile, the rejection rate ($> 99.5\%$) was similar to that of commercial membranes. Its performance could be further improved by a reduction in the selective layer thickness or changes in the layer composition.

A high-flux nanofibrous UF membrane was designed, consisting of a thin selective layer of a hydrophilic but water-resistant chitosan coating, an electrospun PAN nanofibrous mid-layer support, and a nonwoven polyethylene terephthalate (PET) substrate (Yoon *et al.* 2006). A mixed solution of vegetable oil, a surfactant, and deionized water was used as the feed solution for testing. Compared with a commercial NF filter (NF 270 from Dow), the nanofibrous composite membrane, even without optimization, exhibited a flux an order of magnitude higher after 24 h of operation and rejection ratios better than 99.9%. Later, they (Yoon *et al.* 2009) fabricated high flux PAN nanofibrous thin film composite membranes for NF applications. The top polyamide selective layer was synthesized by interfacial polymerization of piperazine and bipiperidine. The nanofiber TFC membranes exhibited at least 2.4 times more water flux than the conventional TFC membranes with the same chemical compositions, while maintaining the same rejection rate ($\sim 98\%$).

In addition, a nanofibrous composite membrane for NF was fabricated by interfacial polymerization of piperazine using ionic liquids (Yung *et al.* 2010). A comparison was made to illustrate the advantage of using a highly porous electrospun PES nanofibrous scaffold versus a typical UF membrane as the support for the piperazine-based polyamide barrier layer. Compared with those of commercial NF membranes, the nanofibrous TFC membrane exhibited a permeation flux twice that of NF-90 membranes and comparable permeation flux to NF-270. The three membranes have similar salt rejection ratios.

Kaur *et al.* (Kaur *et al.* 2012) explored the applicability of polyamide layer synthesis on PVDF electrospun nanofibrous supports for NF applications through a

reverse interfacial polymerization. The reverse interfacial polymerization allowed the separation of 80.7% of 2000-ppm MgSO_4 and 67.0% of 2000-ppm NaCl at a pressure of 482 kPa under a dead-end filtration mode with fluxes of 0.51 and 0.52 $\text{L/m}^2\text{h}$, respectively.

2.3.3 Electrospun membrane development for ODMs applications

Due to its unique pore structures and high porosity, a nanofibrous support layer can reduce the ICP and maximize the effective osmotic pressure and efficiency of ODMs. **Table 2-5** and **Table 2-6** summarize the reported nanofibrous FO and PRO membranes reported in the literature. PSF nanofiber supported polyamide composite membranes exhibited two to five times higher flux with up to 100 times lower salt flux than a standard commercial HTI CTA osmotic membrane (Bui *et al.* 2011). This promising improvement in water flux is due to the greatly reduced structure parameter of nanofibrous support, typically 80~290 μm (Song *et al.* 2011; Bui and McCutcheon 2013), compared with 350~960 μm for a phase inversion based support (Yip *et al.* 2010; Wei *et al.* 2011b; Hoover *et al.* 2013) and 600~1380 μm for commercial HTI-CTA membrane (Yip *et al.* 2010; Wei *et al.* 2011b).

A very recent work reports that a nanofiber supported TFC membrane achieved a peak power density of 15.2 W/m^2 when a synthetic seawater brine (1.06 M NaCl) and a synthetic river water (0.9 mM NaCl) were used as the draw and feed solutions respectively (Song *et al.* 2013). In this work, tetraethylorthosilicate was used as a source of SiO_2 to reinforce the electrospun PAN nanofibrous support, followed by additional reinforcement with poly(vinyl alcohol) crosslinking before a polyamide selective layer was formed. The resultant membrane was then subject to chlorine modification. These complex steps appeared to make the membrane lose its flexibility. In another study, a tiered PAN nanofibrous TFC membrane with nanofibers layers of different diameters was fabricated. Compared with a commercial membrane (as a control) in the same experimental conditions, these membranes demonstrated their superiority in reducing ICP in PRO process and achieved a power density of 8.0 W/m^2 at 11.5 bar using 0.5 M NaCl and DI water as

the draw and feed solutions, respectively (Bui and McCutcheon 2014). Additionally, these two reported works utilized PAN purchased from Sigma-Aldrich as a source material rather than industrial engineering plastics, due to the critical polymer requirement for electrospinning. This results in an economically uncompetitive membrane if utilized in large scale production.

In summary, compared with phase inversion supported ODMPs membranes, only a few studies have focused on the field of nanofibrous membrane design for ODMPs. Some fundamental work still needs to be done to further improve the nanofibrous TFC membrane performance before its employment in large scale applications.

2.3.4 Reinforcement of the nanofiber membrane

Although electrospun nanofiber based TFC membranes possess great potential in ODMPs, their drawbacks, including the low rate of membrane production and poor mechanical properties, have limited their practical applications (Subbiah *et al.* 2005). Therefore, enhancing their mechanical properties is an important objective from an industrial point of view (Huang *et al.* 2003). In order to meet the above requirement, several approaches such as heat treatment, solvent induced interfiber bonding, adhesion (Baek *et al.* 2012), and a nano-composite strategy (Homaieghar and Elbahri 2012) have been used by the researchers to reinforce the mechanical strength of electrospun nanofibrous mats.

Zhang *et al.* (Zhang *et al.* 2011a) demonstrated that a robust pH sensitive membrane (pHS-M) was synthesized firstly by two-nozzle electrospinning to combine indicative nanofibers from a 9% PAN solution and micro-sized fibers from a 20% Nylon 6-6 solution simultaneously. The pH indicative property of composite electrospun membrane can be achieved by first aminating PAN nanofibers with ethylenediamine and then immobilizing phenolphthalein covalently through a Mannich reaction, while micro-sized Nylon 6-6 fibers provided mechanical support due to their elastic and flexible behavior. The tensile strength was enhanced from

1.3 MPa to 6.90 MPa by generous addition of microfiber which is beneficial for the practical uses of the membranes.

Lin *et al.* (Lin *et al.* 2012) reported a robust thermally tolerant nanofibrous hydrophilic membrane was produced by single step electrospinning. It was showed that the membrane had high rejection for silica nanoparticles from aqueous solution, which revealed its potential for application in liquid filtration. In addition, the high break strength of the nanofibrous membrane is believed to be due to the inherent properties of the material and the entanglement and point-bonded structures among this nanofibers. The good mechanical properties of nanofibrous membranes would make them good candidates for applications requiring high strength and high thermal resistance.

The weak mechanical properties of extraordinary porous electrospun nanofibrous membranes are a key challenge for their industrial development. To address this, Homaeigohar *et al.* (Homaeigohar and Elbahri 2012) reinforced an PES nanofibrous membrane using zirconia nanoparticles. The compaction resistance of the electrospun nanofibrous membranes was improved significantly as long as no nanoparticle agglomeration occurred. In addition to obtaining a desired mechanical performance, the hydrophilicity of the membrane was enhanced. The combination of promising properties including optimal mechanical strength and surface hydrophilicity led to the relatively high water permeability and high rejection of the aforesaid nanofibrous membranes.

CHAPTER 3.

Preparation of Polyamide TFC Forward Osmosis Membranes Using Electrospun Polyvinylidene Fluoride (PVDF) Nanofibers as Substrates

3.1 Introduction

As described in Chapter 2, one of the major barriers impeding FO membrane development is lack of suitable highly porous supports with low structure parameter. Electrospun nanofibrous membranes have much higher porosity due to their unique interconnected fiber structure as compared with membranes made by phase inversion. So far, polyethersulfone (PES), polyacrylonitrile (PAN)/cellulose acetate (CTA), and Polysulfone (PSf) nanofibrous mats have been used as scaffold-like porous substrates to fabricate FO membranes. It was reported that this uniquely interconnected structure could facilitate the mixing of accumulated solutes with a dilute feed stream to overcome the problem of ICP. It was also demonstrated that due to their superior porosity and pore interconnectivity, electrospun nanofiber supported TFC membranes have potential for osmotic process. However, electrospun nanofiber-based FO/PRO membranes are still in the early stages of development. Since electrospun nanofiber fabrication is not strictly constrained by the materials used, as is the case for phase inversion, it provides an opportunity to explore the applicability of different types of polymers for making electrospun nanofibrous mats which can be used as substrates for FO/PRO membrane preparation.

To date, most substrate materials used for FO membranes are hydrophilic, mainly because of concern about the high membrane fouling tendency of hydrophobic materials. However, hydrophobic materials such as polyvinylidene fluoride (PVDF) normally possess good chemical resistance, which could extend the use of FO process to some harsh environments with chemical wastes such as aromatic hydrocarbons, ketones, ethers, and esters (Kim *et al.* 2009). For example, wastewater effluents from chemical/pharmaceutical manufacturing plants often contain these contaminants, including pesticides (Geise *et al.* 2010). However, PVDF membranes made by the phase inversion method normally possess limited porosity. In this current study, we intend to make PVDF nanofiber membranes as substrates for subsequent interfacial polymerization to make TFC FO membranes. The effect of the surface structure of the PVDF ENMs on the formation of the selective layer will be investigated. The preparation conditions of the TFC polyamide layer on the intrinsic separation properties of the resultant FO membranes will also be examined. Finally, we will evaluate the FO performance of the prepared membranes in two orientations. This study is expected to provide an insight into the interaction of PVDF ENM surface properties with the polyamide layer to guide ENM-based TFC FO membrane development.

3.2 Experiments

3.2.1 Materials and chemicals

PVDF (HSV900, Solvay Advanced Polymers, Alpharetta GA), were used without further purification to prepare the electrospun fibrous mats. N, N-dimethylformamide (DMF, > 99.5%, CAS # 68-12-2) was purchased from Merck Chemicals, Singapore. Lithium chloride (LiCl, CAS#7447-41-8, Merck Chemicals) was used as the additive. M-Phenylenediamine (MPD, > 99%, CAS#108-45-2, ACROS) and 1, 3, 5-Benzenetricarboxylic acid chloride (TMC, 98%, CAS # 4422-95-1, ACROS) were also used directly as received. For filtration experiments, sodium chloride (NaCl, $\geq$ 99%) was purchased from Merck.

3.2.2 Preparation of nanofibrous substrates

8 wt% of PVDF polymer powder was dissolved in DMF by stirring at 60 °C for 24 hours. The viscous solution was placed into a syringe pump and electrospun with a laboratory-scale electrospinning apparatus shown in **Figure 3-1**. By controlling the spinning parameters, two nanofiber supports, S1 and S2, were fabricated.

S1 and S2 substrates were fabricated by applying a voltage of 27 and 30 kV between the spinneret and collector with a working distance of 12 and 15 cm, respectively. The polymer solution was delivered to the spinneret via a step syringe pump at a fixed rate of 30 $\mu\text{L min}^{-1}$. The use of different voltages and working distances resulted in different fiber diameters for the two substrates.

The experimental air humidity was 70%. The electrospun fibrous mats were kept in a vacuum oven over night at 50 °C to remove residual solvent. Then the nanofiber support was heat-pressed at 150 °C for 1 hour at a pressure less than 138 kPa.

Figure 3-1 Schematic diagram of electrospinning process

3.2.3 Synthesize of polyamide selective layer

An ultrathin polyamide separation layer was formed on the as-prepared nanofibrous substrates via interfacial polymerization between MPD and TMC monomers. Reaction formula investigation was conducted to optimize the concentrations of the two monomers. Two series of nanofiber-based TFC membranes were prepared. In the first series (the MPD series), the aqueous solutions contained MPD with a concentration ranging from 1 to 10 wt%, while the organic solutions had a fixed TMC concentration of 0.15 wt% in n-hexane. In the second series (the TMC series), the MPD concentration was kept constant at 5.0 wt%, while the TMC concentration varied from 0.1 to 0.5 wt%.

The PVDF nanofiber substrates were pre-wetted thoroughly with ethanol for 2 hours, followed by washing with DI water. Then the nanofiber substrates were soaked in a MPD solution for 5 min. A rubber roller was applied to remove the excess MPD solution on the substrate surface. A TMC solution was gently poured onto the substrate surface to react with the residual MPD for 1 min to form the polyamide layer. The nanofiber based TFC membrane was washed with tap water and stored in DI water for further use.

3.2.4 Characterization of nanofiber substrates and TFC membranes

The surface morphologies of the substrate samples were observed by a field emission scanning electron microscope (FE-SEM, JSM7600F, JEOL Asia Pte Ltd, Japan). The FE-SEM measurements were carried out at an accelerating voltage of 5 kV. The membrane cross sections were obtained by fracturing wet membranes in liquid nitrogen. A JEOL JFC-1600 sputter coater was utilized to coat the samples with platinum for 30 seconds at 20 mA.

The topography of the substrate surfaces was characterized by atomic force microscopy (AFM, XE 100, Park Systems, Korea). Each sample was scanned three times using tapping mode and an arithmetic mean of the surface roughness (Ra) was

calculated from the roughness profile determined by AFM. The sampling area was 5 μm X 5 μm and testing was performed in air at 26 °C.

Water contact angles on the nanofiber substrates were measured by the sessile drop method, using a goniometer (Contact Angle System OCA, Data Physics Instruments GmbH). One 5 μl water droplet was dropped onto a levelled membrane surface and the images of the water drop on membrane surface were captured by the system to calculate the contact angle. Each sample was tested more than 5 times.

The bubble point test is a method to determine the minimum and maximum diameters of the membrane pores. The bubble point test was conducted on a porometer (CFP 1500A) manufactured by Porous Material. Inc. (PMI).

The membrane porosity is defined as the volume of the pores divided by the total volume of the membrane. The average overall porosity (ε) of the substrate can be determined by gravimetric method which measures the weight of isopropyl alcohol (IPA) as the wetting solvent contained in membrane pores. The following equation (Wang *et al.* 2010a) was used to calculate the porosity of membrane.

$$\varepsilon = \frac{(W_{wet} - W_{dry}) / \rho_{IPA}}{W_{dry} / \rho_{polymer} + (W_{wet} - W_{dry}) / \rho_{IPA}} \quad 3-1$$

where W_{dry} is the weight of dry membrane, W_{wet} is the total weight of membrane and IPA. ρ_{IPA} and $\rho_{polymer}$ are the IPA density and polymer density, respectively.

The thickness of the membranes was determined by a Swiss style outside inch micrometer (0-1 inch Measuring Range, ± 0.00016 inch Accuracy, 0.0001 inch Graduation, Fowler). The tensile strength of the nanofiber substrates was determined using a Zwick 0.5 kN Universal Testing Machine at room temperature. The specimen sizes for the evaluation were 50 mm X 10 mm (length X width).

X-ray photoelectron spectroscopy (XPS) tests, using a Theta Probe XPS provided by Thermo Fisher Scientific (Singapore), were conducted to analyze the chemical composition of the thin selective polyamide layer. The core-level signals were obtained at a photoelectron take off angle of 50° with respect to the sample surface. Binding energies were calibrated with respect to C1s hydrocarbon bond at 284.6 eV.

3.2.5 Intrinsic permeability evaluation of nanofiber-based TFC membranes

The intrinsic separation properties of nanofibrous FO membranes were measured in a cross-flow filtration setup in the RO testing mode (*i.e.*, pressurized mode) described elsewhere (Tang, She *et al.* 2010). The membrane samples with an area of 42 cm² were placed in the cell with the active layer facing the incoming feed. Compaction using DI water was carried out at 5 bar for 1 h prior to measurement.

The membrane water permeability, A , was evaluated by RO tests over an applied pressure range of 5 bar with ultrapure water as feed. The A value was calculated according to following equation (Wang *et al.* 2010a; Wei *et al.* 2011b):

$$A = \frac{J}{\Delta P} \quad 3-2$$

where, ΔP is the applied trans-membrane pressure and J represents the permeate water flux.

The salt rejection, R_s , and salt permeability, B , were carried out in the RO setup using a 1000 ppm NaCl solution as feed solution under a constant pressure of 5 bar and temperature of 23 ± 2 °C.

Rejection was determined based on conductivity measurement of the feed and permeate (Wang *et al.* 2010a; Wei *et al.* 2011b):

$$R_s = \frac{C_f - C_p}{C_f} \times 100\% \quad 3-3$$

where C_f and C_p represent the salt concentration in the feed and permeate, respectively.

The salt permeability was calculated using following equation (Tang *et al.* 2010):

$$B = J \times \left(\frac{1}{R_s} - 1 \right) \quad 3-4$$

3.2.6 FO performance test of nanofiber-based TFC membranes

Osmotic water flux and reverse salt flux through the nanofibrous FO membranes were measured with a lab-scale cross-flow FO system (**Figure 3-2**). The configuration of the FO cell channel is 95 mm in length, 38 mm in width and 1 mm in depth on both sides of the membrane. The effective membrane area is 0.00361 m². Diamond-patterned spacers were located on both sides of the membrane. Two variable-speed peristaltic pumps were used to recirculate and control the cross-flow velocities of the feed and draw solutions.

Various sodium chloride solutions ranging from 0.5 M to 2.0 M were used as the draw solution while DI water was used as the feed solution. The cross flow rates of the feed and draw solutions were both kept at 20.8 cm/s. The temperatures of the feed and draw solutions were maintained at 23 ± 2 °C. The conductivity of the feed solution was measured to evaluate the reverse salt leakage through the membrane. Membrane volumetric flux was determined by measuring the mass changes of the feed solution by a balance. The osmotic water flux under active layer facing feed water (AL-FW) and active layer facing draw solution (AL-DS) orientations, J_v , was calculated by dividing the volumetric flux by the effective membrane area as follows:

$$J_v = \frac{\Delta m}{\Delta t \times A_{eff}} \quad 3-5$$

where A_{eff} is the effective membrane area and Δm is the volume of water permeated from the feed to the draw solution over a time Δt during FO tests.

The solute flux J_s was measured by calculating the change of the salt accumulation in the feed solution based on conductivity measurements:(Li *et al.* 2013b)

$$J_s = \frac{V_2 \times C_2 - V_1 \times C_1}{A_{eff} \times (t_1 - t_2)} \quad 3-6$$

where V_2 and V_1 are the volume of feed solution at time t_2 and t_1 , respectively; C_1 and C_2 are salt concentration of feed solution at time t_2 and t_1 .

The substrate structure parameter, S is defined as the product of the thickness, l , and tortuosity, τ , over porosity, ε :

$$S = \frac{\tau \times l}{\varepsilon} \quad 3-7$$

The S value was determined by fitting the A , B values obtained from RO test and J_v from FO test into Equation 3-8 and 3-9:

$$AL - FS : J_v = \frac{D}{s} \times \ln \left[\frac{A\pi_d + B}{A\pi_f + J_v + B} \right] \quad 3-8$$

$$AL - DS : J_v = \frac{D}{s} \times \ln \left[\frac{A\pi_d - J_v + B}{A\pi_f + B} \right] \quad 3-9$$

where D is the salt diffusion coefficient dependent on temperature and concentration ($1.61 \times 10^{-9} \text{ m}^2/\text{s}$ was used for NaCl in this paper), π_d and π_f are the osmotic pressures of the DS and FS respectively.

Figure 3-2 Schematic of customized FO system

3.3 Results and discussion

3.3.1 Structure of nanofiber substrates

In this current study, two nanofiber substrates, S1 and S2, were prepared. The morphologies of these two substrates are shown in **Figure 3-3** (a)–(c) for S1 and **Figure 3-3** (d)–(f) for S2. It can be seen that both substrates had a fiber network with fiber diameters ranging from 300 to 400 nm. The fiber diameter of substrate S1 is slightly thinner than that of S2, leading to a smaller mean pore size as compared with the S2. It was also observed that the fibers were melted together in the S2, which resulted in its relatively low porosity, as confirmed by the porosity measurement. Both S1 and S2 had high porosities of $67 \pm 2\%$ and $57 \pm 8\%$, respectively, shown in **Table 3-1**.

Figure 3-3 FE-SEM images of electrospun PVDF nanofibrous substrates. (a) top view of substrate S1 at 5,000X; (b) top view of S1 enlarged at 20,000X; (c) cross-sectional view of S1 at 10,000X; (d) top view of S2 at 5,000X; (e) top view of S2 enlarged at 20,000X; (f) cross-sectional view of S2 at 10,000X. (All scale bars in picture represent 1µm)

The mechanical properties of nanofiber substrates are also shown in **Table 3-1**. The tensile strength and elongation at break of the S2 substrate is slightly higher than that of S1. This is probably caused by the fibers fusing (**Figure 3-3** (e)) with each other in the S2 during the heat pressing step of the in fabrication process. It has reported that heat treatment can improve the mechanical properties of nanofiber mats (Gopal *et al.* 2006; Na *et al.* 2008).

Table 3-1 Properties of PVDF nanofibrous supports

Sample code	S1-PVDF	S2-PVDF
Contact angle (°)	137.8 ± 2.1	135.8 ± 2.4
Mean pore size (μm)	0.32 ± 0.07	0.40 ± 0.02
Max pore size (μm)	0.50 ± 0.10	0.59 ± 0.04
Thickness (μm)	63.8 ± 9.6	67.2 ± 8.3
Porosity (%)	67 ± 2	57 ± 8
Flux (L/m ² h)	1267	1938
Tensile Strength (Mpa)	11.1 ± 1.2 ^(a)	11.9 ± 1.9 ^(a)
	13.7 ± 2.3 ^(b)	20.4 ± 2.4 ^(b)
Elongation at break δ (%)	37.1 ± 12.0 ^(a)	40.2 ± 4.9 ^(a)
	52.4 ± 4.5 ^(b)	88.2 ± 6.7 ^(b)
S value(μm) ^(c)	812	325

(a) Axial direction;

(b) Peripheral direction;

(c) Average structure parameter, *s*, was obtained by fitting the experimental results into Equation 3-8 in section 3.2.5.

3.3.2 Interfacial polymerization on nanofiber substrates

Interfacial polymerization on traditional supports made by the phase inversion method has been well studied (Ghosh and Hoek 2009; Tiraferri *et al.* 2011; Wei *et al.* 2011b). However, since the nanofiber substrate exhibits a unique structure that is different from conventional asymmetric substrates, the optimized formula for the monomer concentrations needs to be identified in order to make good FO membranes. The interfacial polymerization reaction schemes of polyamide synthesis based on TMC and MPD is shown in **Figure 3-4**.

Figure 3-4 Interfacial polymerization reaction scheme of polyamide based on TMC and MPD. (The x in polymer chain represents the crosslinked part of the resulting polymer, y represents the linear part. $x+y=1$. If $x=1$, the resulting polyamide is fully crosslinked, if $y=1$, the resulting polyamide is fully linear)

Figure 3-5 illustrates the influence of MPD concentration (TMC fixed at 0.15 wt%) on the intrinsic properties of the membranes. It was found that the water permeability slightly decreased from 2.7 L/m² h·bar to 1.34 L/m² h·bar while the salt rejection increased from 52.3% to 92.1% when the MPD concentration was increased from 1.0 to 5.0 wt%. The separation properties of the ultrathin polyamide film synthesised via interfacial polymerization were greatly affected by the polymerization conditions including the monomer concentration and the reactant ratio (Roh *et al.* 2006). When the MPD/TMC ratio increased, cross-linked units were more likely to be produced, resulting in a lower portion of linear structures with hydrophilic pendant –COOH groups in the polyamide layer. Commonly, the monomer concentration of MPD is 2 wt% and TMC is 0.1 wt% with a reactant ratio of 20 for the conventional phase inversion based support layer. Since the nanofiber support surface possesses an open structure with large interconnected pores and

high roughness, further optimization of the monomer concentration and monomer molar ratio is needed.

Figure 3-5 Intrinsic properties of the nanofibrous TFC membranes fabricated with varied MPD concentrations and fixed TMC concentration (0.15 wt%). (RO testing conditions: 1000 ppm NaCl as feed solution at 5 bar applied pressure and 23 °C.).

Figure 3-6 shows the influence of varied TMC concentration on membrane water permeability and NaCl rejection, where the MPD concentration was fixed at 5.0 wt%. Increasing TMC concentration from 0.15 to 0.5 wt% resulted in a slight decrease of NaCl salt rejection. Based on the separation result, 5 wt% of MPD and 0.15 wt% of TMC were chosen as the most appropriate monomer concentrations for preparing nanofiber support.

Figure 3-6 Intrinsic properties of TFC membranes fabricated with varied TMC concentrations and fixed MPD concentration (5 wt%). (RO testing conditions: 1000 ppm NaCl as feed solution at 5 bar applied pressure and 23 °C)

The above results are consistent with those obtained from the conventional TFC membranes with an asymmetric support (Roh *et al.* 2006; Wei *et al.* 2011b), in which a higher MPD/TMC ratio normally tends to promote a denser polyamide layer, resulting in a decrease in water permeability and an increase in salt rejection; while a lower MPD/TMC ratio tends to result in a reduced degree of crosslinking of the polyamide rejection layer, which is responsible for the higher water permeability and lower salt rejection.

3.3.3 Characteristics of nanofiber-based TFC Membranes

Figure 3-7 shows the FE-SEM images of the surface morphologies of the nanofiber-based TFC membranes. A typical “ridge and valley” structure was observed, indicating the formation of a polyamide layer on the nanofiber substrate. Comparing with other nanofiber-based FO membranes (**Table 3-2**) (Bui *et al.* 2011; Song *et al.* 2011; Kaur *et al.* 2012), the TFC-1# exhibits reasonable water

permeability of $1.21 \text{ L/m}^2\text{h}\cdot\text{bar}$ and a high NaCl rejection of 93.6% at 5 bar pressure. However, the TFC-2# shows different separation properties with water permeability of $3.15 \text{ L/m}^2\text{h}\cdot\text{bar}$ and NaCl rejection of 84.4% at the same applied pressure.

Figure 3-7 FE-SEM images of electrospun nanofiber based TFC membrane. (a) top view of TFC-1# at 20,000X; (b) cross sectional view of TFC-1# at 10,000X; (c) top view of TFC-2# at 20,000X; (d) cross sectional view of TFC-2# at 10,000X. (All scale bars in picture represent $1\mu\text{m}$)

Since the preparation procedures for the polyamide layer were the same, the variations could be mainly attributed to the differences between the two substrates, which affect the formation of the polyamide layer. Referring to the section 3.3.1 which shows that the substrate S1 has thinner fibers, smaller pore sizes and higher roughness than the substrate S2, it may be concluded that a polyamide layer with better selectivity can be fabricated more easily on the substrate with smaller pores and thinner fibers.

To understand this result, one has to have look closely at the substrate structure and gain insight into the interfacial polymerization reaction that occurs on the

substrate. According to the conceptual model proposed by Ghosh *et al.* (Ghosh and Hoek 2009), at the start of the IP process, polyamide formation is nucleated above pore openings, followed by the vertical growth and lateral film growth to connect the initial nuclei. The nuclei reached a higher molecular weight than the laterally spreading base layer, which gives rise to the ridge-valley morphology of polyamide RO membranes.

In current work, the nanofiber substrates were first immersed in a solution of MPD for a fixed time and the excess MPD solution on the substrate surface was removed using a rubber roller, forming a thin MPD film on the substrate surface. Since the substrate is hydrophobic in nature, a convex meniscus of the MPD solution formed in the pores. Given the smaller pore sizes and thinner fiber diameter of the substrate S1 as compared to the substrate S2, the degree of the convex on the surface of the substrate S1 was higher in addition to its original higher surface roughness, as shown in **Figure 3-8**. It is believed that the nucleation and growth proceed much more readily on a rougher nanofiber surface, shown schematically in **Figure 3-8**, leading to a thin polyamide layer with a denser structure. As a result, the membrane using the S1 substrate exhibits a higher salt rejection but lower permeation than the counterpart S2 membrane.

Table 3-2 Separation properties of PVDF nanofiber based TFC membranes

Sample	Water permeability, A		NaCl Permeability, B		NaCl Rejection, R_s	B/A value (kPa)	Ref.
	L/m ² h·bar	m/(kPa·s)	L/m ² h	m/s			
TFC-1#	1.21	3.36×10^{-9}	0.33	9.17×10^{-8}	93.6% @ 5 atm	27.3	present work
TFC-2#	3.15	8.76×10^{-9}	2.33	6.48×10^{-7}	84.4% @ 5 atm	74.0	present work
1# NC-FO	1.7 ± 0.10	$4.73 \times 10^{-9(a)}$	1.1 ^(b)	$3.06 \times 10^{-7(b)}$	$97 \pm 1.0\%$ @ 24 atm	64.7	(Song <i>et al.</i> 2011)
2# NC-FO	1.65 ± 0.14	$4.59 \times 10^{-9(a)}$	1.1 ^(b)	$3.06 \times 10^{-7(b)}$	$97 \pm 1.2\%$ @ 24 atm	66.7	(Song <i>et al.</i> 2011)
Approach B	~0.13	-	-	-	67% @ 4.76 atm	-	(Kaur <i>et al.</i> 2012)
PSf	~0.58 ^(a)	1.59×10^{-9}	~0.17 ^(a)	4.79×10^{-8}	-	-	(Bui <i>et al.</i> 2011)

^(a) Unit was transferred based on the data in references.

^(b) Calculated based on the data reported in references.

- Means not reported in reference.

Figure 3-8 Schematic of polyamide layers formed on different supports.

The AFM images in **Figure 3-9** allow for comparison of nanofiber supports before and after interfacial polymerization. In most cases, a thin polyamide selective layer was formed via interfacial polymerization on a very smooth surface of a porous substrate with pore sizes ranging from 10 nm to 150 nm (Roh *et al.* 2006; Singh *et al.* 2006; Wang *et al.* 2010a; Chou *et al.* 2012), and the surface would become rougher after polyamide attachment. In this current work, the surface pore size of the nanofiber support ranged from 320 to 590 nm (as shown in **Table 3-1**), which is much bigger than in commonly used supports. It is interesting to see that the surface became much smoother after the interfacial polymerization.

Figure 3-9 AFM images of the two electrospun nanofiber substrates (S1 and S2) and nanofiber based TFC membrane (TFC-1# and TFC-2#). (R_a values of the sample are calculated based on three different positions of the samples)

The polyamide layer can be analyzed by XPS measurement. Typical XPS spectra and functional element concentrations are presented in **Figure 3-10** and **Table 3-3**, respectively. Before interfacial polymerization, the pure PVDF nanofiber support contains only the elements C and F. After interfacial polymerization, the XPS spectra show that O, N and C elements exist in the TFC-1# and TFC-2# surfaces, which confirms the formation of polyamide on the surface of the nanofiber support. According to prior studies (Tang *et al.* 2007; Akin and Temelli 2011), the element ratio of O/N can indicate the extent of polyamide crosslinking. The chemical formula of fully cross-linked polyamide is $[C_{15}H_{10}O_3N_3]$ in which the O/N ratio is 1; while for the fully linear structure of $[C_{15}H_{10}O_4N_2]$ the O/N ratio is 2, as shown in **Figure 3-4**. Referring to **Table 3-3**, it can be seen that the O/N ratios of TFC-1# and TFC-2# are 1.70 and 1.94 respectively. Thus the cross-linking degree of each membrane can be calculated as follows (Akin and Temelli 2011):

$$\%crosslinking = \frac{x}{x+y} \times 100\% \quad 3-10$$

where x and y represent the crosslinked and linear portions respectively. The total theoretical O/N ratio is expressed as (Tang *et al.* 2007):

$$\frac{O}{N} = \frac{3x + 4y}{2x + 2y} \quad 3-11$$

Figure 3-10 XPS survey spectra of PVDF nanofibrous substrate and TFC-1# and TFC-2# membranes

Table 3-3 Element concentration from XPS analysis

		XPS surface element analysis ^(a)			
		O (%)	N (%)	C (%)	O/N ratio
	TFC-1#	17.3	10.2	72.5	1.70
	TFC-2#	18.6	9.6	71.8	1.94
Theoretical values	Fully cross-linked	12.5	12.5	75	1
	Fully linear	19.1	9.5	71.4	2

^(a) Elemental compositions were computed based on O (1s), N (1s) and C (1s) peaks, which are centred around 532, 399 and 284 eV, respectively. The theoretical elemental compositions were computed based on **Figure 3-4**.

Based on the XPS tests, the cross-linking degree of TFC-1# and TFC-2# is 22.2% and 4.08% respectively. A higher crosslinking degree creates a more dense polyamide structure, which is responsible for the higher selectivity of TFC-1#. The carboxylic acid terminal site in the linear parts is likely to be responsible for the high permeability and flux demonstrated by TFC-2#.

3.3.4 FO performance of nanofiber-based TFC membranes

Theoretically (Lee *et al.* 1981; Wang *et al.* 2010a), water flux, J_v , in both AL-DS and AL-FW orientations can be evaluated using equation (3-12) and (3-13), respectively, when ICP is taken into account:

$$\text{AL-DS: } J_v = k_m \times \ln \left[\frac{A\pi_d - J_v + B}{A\pi_f + B} \right] \quad 3-12$$

$$\text{AL-FW: } J_v = k_m \times \ln \left[\frac{A\pi_d + B}{A\pi_f + J_v + B} \right] \quad 3-13$$

where A is the water permeability coefficient, and B is the NaCl salt permeability coefficient. π_d and π_f are the osmotic pressures of the draw solution and feed water, respectively. k_m is the mass transfer coefficient, which is associated with the structure parameter, S by equation (3-14):

$$S = \frac{D}{k_m} \quad 3-14$$

where D is the salt diffusion coefficient, assumed to be $1.61 \times 10^{-9} \text{ m}^2/\text{s}$ for NaCl. The ideal substrate for FO membrane should have a low structure parameter, which is the indicator for the substrate performance in a FO process. S is defined by the tortuosity, τ , thickness, l , and porosity, ε , of the porous structure, as shown in the equation below.

$$S = \frac{\tau \times l}{\varepsilon} \quad 3-15$$

The calculated structure parameters S for the TFC-1# and TFC-2# membrane were 8.12×10^{-4} m and 3.25×10^{-4} m, respectively, corresponding to their highly porous and open substrate structures. The S value of TFC-2# membrane is among the best in the literature. The structure parameter is used as an indicator to predict the ICP in an FO process. The smaller the S value of the membrane, the less ICP it would encounter.

The performances of nanofiber-based TFC-1# and TFC-2# membranes under the AL-DS and AL-FW orientations are shown in **Figure 3-11** and **Figure 3-12** respectively. It was observed that the water flux increased with increasing NaCl concentration, *i.e.*, the osmotic pressure. For the AL-FW orientation, TFC-1# has a water flux of 11.6 L/m²h and TFC-2# shows a water flux of 28.0 L/m²h when 1.0 M NaCl was used as the draw solution at 23 °C. In the AL-DS orientation, TFC-2# yields a water flux of 47.6 L/m²h and TFC-1# shows 30.4 L/m²h when using 1.0 M NaCl as the draw solution. Due to salt accumulation in the support layer drastically reducing the effective osmotic pressure across the selective layer, the water flux in the AL-FW orientation is much smaller than AL-DS orientation. This effect is already well-recognized. Meanwhile, the reverse salt flux over water flux, J_s/J_v , is as low as 0.21 g/L for TFC-1#, but is slightly higher (0.45 g/L) for TFC-2#. Referring to other lab-scaled nanofiber or conventional phase inversion based flat-sheet FO membranes listed in **Table 3-4** (Yip *et al.* 2010; Bui *et al.* 2011; Song *et al.* 2011; Tiraferri *et al.* 2011; Wei *et al.* 2011b; Han *et al.* 2012; Bui and McCutcheon 2013), both TFC-1# and TFC-2# membranes show reasonably good performance in both orientations.

Figure 3-11 Experimental results of water flux (solid symbols) and salt flux (open symbols) as a function of DS concentration for TFC-1# membrane. (AL-FW: circle symbol; AL-DS: square symbol; FW: DI water; temperature: 23 °C)

Figure 3-12 Experimental results of water flux (solid symbols) and salt flux (open symbols) as a function of DS concentration for TFC-2# membrane. (AL-FW: circle symbol; AL-DS: square symbol; FW: DI water; temperature: 23 °C)

Table 3-4 FO performances of various flat-sheet TFC membranes

		Sample	Water Flux (L/m ² h)	Salt Flux (g/m ² h)	Js/Jv (g/L)	FW	DS	Ref.
Nanofiber based FO membranes	AL-FW	TFC-1#	11.6	3.5	0.30	DI Water	1.0 M NaCl	present work
		TFC-2#	28.0	12.9	0.46	DI Water	1.0 M NaCl	present work
		Fig.5	46	-	-	DI Water	1.0 M NaCl	(Song <i>et al.</i> 2011)
		PAN	29 ± 4	8.7 ± 3	0.29	DI Water	1.5 M NaCl	(Bui and McCutcheon 2013)
	AL-DS	TFC-1#	30.4	6.4	0.21	DI Water	1.0 M NaCl	present work
		TFC-2#	47.6	21.6	0.45	DI Water	1.0 M NaCl	present work
		Fig.5	50	-	-	DI Water	1.0 M NaCl	(Song <i>et al.</i> 2011)
		PSf -flat sheet	24	8.63	0.37	DI Water	1.5 M NaCl	(Bui <i>et al.</i> 2011)
		PAN	52 ± 7	3.5 ± 1.5	0.06	DI water	1.5 M NaCl	(Bui and McCutcheon 2013)
Phase inversion based FO membranes	AF-FW	flat sheet	20.5 ± 3.8	-	-	DI Water	1.0 M NaCl	(Tiraferri <i>et al.</i> 2011)
		flat sheet	12.0	4.9	0.41	10 mM NaCl	0.5 M NaCl	(Wei <i>et al.</i> 2011b)
		TFC-FO-50	35	7	0.2	DI Water	2.0 M NaCl	(Han <i>et al.</i> 2012)
		TFC-FO	18.16 ± 0.96	-	-	DI Water	1.5 M NaCl	(Yip <i>et al.</i> 2010)
	AL-DS	flat sheet	20.5	5.9	0.29	10 mM NaCl	0.5 M NaCl	(Wei <i>et al.</i> 2011b)
		TFC-FO-50	50	9	0.18	DI Water	2.0 M NaCl	(Han <i>et al.</i> 2012)

- Means not reported in reference

3.4 Conclusions

In this work, polyamide thin films were successfully prepared on two PVDF nanofiber substrates with different surface pore sizes ranging from 320 to 590 nm. A more dense polyamide selective layer was formed on the S1 substrates which had smaller pore sizes (mean pore size of $0.32 \pm 0.07 \mu\text{m}$ and maximum pore size of $0.50 \pm 0.10 \mu\text{m}$), resulting in water permeability of $1.21 \text{ L/m}^2\text{h}\cdot\text{bar}$ and NaCl salt rejection of 93.6% at 5 bar pressure; while the TFC-2# membrane prepared on the substrates S2 with mean pore size of $0.40 \pm 0.02 \mu\text{m}$ demonstrated a water permeability of $3.15 \text{ L/m}^2\text{h}\cdot\text{bar}$ and an NaCl salt rejection of 84.4% under the same 5 bar pressure. By comparing the two cases, it was found that it is easier to form a thin polyamide selective layer with a higher crosslinking density on an ENM substrate with smaller pore sizes.

The two membranes showed a comparable performance in the FO process because of their superior porous and interconnected open structure resulting in reduced internal concentration polarization. The S value of the resultant membrane is as low as 0.315 mm, which is better than most FO membranes reported in the literature. As a result, a water flux of $30.4 \text{ L/m}^2\text{h}$ can be attained when using 1.0 M NaCl as the draw solution and DI water as the feed water in the AL-DS orientation. The electro-spun nanofiber membranes show good potential as substrates for making membranes applied for osmotic processes.

CHAPTER 4.

Synthesis and characterization of TFN FO membranes with nanofibrous support incorporated with silica

4.1 Introduction

In Chapter 3, it was shown that nanofiber supported TFC FO membranes offer advantages in mitigating severe ICP during the FO process, thanks to the unique structure of the nanofibrous substrate - interconnected pores and high porosity. Nevertheless, the nanofibrous substrate experiences porosity reduction during a necessary post-treatment (heat-press treatment (Liao *et al.* 2013b) and solvent vapor treatment (Huang *et al.* 2013b)). The post-treatment aims to bond the individual nanofibers together for retaining a reasonably high mechanical strength. In addition, the nanofibrous support layer may also suffer porosity loss during membrane filtration arising from the compaction between individual nanofibers, especially when high pressure is applied.

The emerging nanocomposite strategy that incorporates nanomaterials into the membrane matrix has shown great potential to improve the properties of FO membranes via the reduction in substrate structure parameter (Yin and Deng 2015). Nanomaterials such as zeolite, multi-walled nanotubes, and titanium dioxide have been demonstrated for enhancing FO water flux successfully via nanoparticle incorporation in phase-inversion generated substrates (Emadzadeh *et al.* 2013; Ma *et al.* 2013; Wang *et al.* 2013; Emadzadeh *et al.* 2014a; Emadzadeh *et al.* 2014b). On the other hand, the incorporation of inorganic nanoparticles into the nanofibers

is a possible way to mitigate nanofiber multilayer compaction under pressure. It has been reported that a polyethersulfone (PES) nanofibrous microfiltration (MF) membrane with zirconia embedded could resist compaction and prevent disintegration during MF filtration. The water permeability and selectivity were also greatly improved (Homaeigohar and Elbahri 2012). This advantage has not been demonstrated in nanofibrous FO membranes yet in the existing literature.

Here we proposed to design a polyetherimide (PEI) nanofibrous substrate for a FO membrane incorporating silica nanoparticles. PEI material was chosen in this study as it is a versatile polymer with a wide range of applications due to its excellent thermal, mechanical and solvent resistances and high hydrophilicity. Silica nanoparticles were chosen as the nanofibrous substrate filler due to their high thermal and chemical stability, neutral pH, non-toxicity, commercial viability and well characterized properties (Yin and Deng 2015). The objectives of this study were to minimize the porosity loss of the PEI nanofibrous substrate and demonstrate the improved FO performance as a result of the successful incorporation of silica nanoparticles. Specifically, the effect of different silica nanoparticle loadings on the FO membrane properties was evaluated. To the best knowledge of the author, this is the first study on nanofibrous FO membrane fabrication incorporating silica nanoparticles into the nanofibrous substrate in order to improve FO membrane performance.

4.2 Experiments

4.2.1 Materials and chemicals

Unless otherwise specified, all chemicals were used as received without further purification. Polyetherimide (PEI, Ultem 1000, General Electric Plastics) was used for membrane support preparation as it has outstanding thermal and mechanical properties (Chou *et al.* 2013) and high hydrophilicity. Silica nanoparticles in spherical shape with a particle size range of 5–15 nm (Sigma-Aldrich) were used as the substrate filler. N, N-dimethylformamide (DMF, >99.5%) and N-Methyl-2-

pyrrolidone (NMP, > 99.5%, Merck Chemicals.) were the solvents used for preparing PEI dope solutions. M-Phenylenediamine (MPD, $\geq 99\%$, Sigma-Aldrich) and trimesoyl chloride (TMC, > 99%, Sigma-Aldrich) were used to synthesize the polyamide rejection layer by interfacial polymerization. A commercial asymmetric cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations (HTI, Albany, US) was used for comparison with the in-house FO membranes fabricated for this study, and was named CTA-W in the study. Poly (ethylene terephthalate) (PET, Grade 3256, Ahlstrom) nonwoven mesh was used as a backing layer. Other chemicals and materials have been described in section 3.2.1.

4.2.2 Preparation of nanofibrous substrates

PEI polymer powder (~16 wt%) was dissolved in the NMP/DMF mixed solvent by stirring at 80 °C. The silica nanoparticles were added to the dope solution and stirred until homogeneously dispersed. A trace amount of LiCl was also added to regulate the solution conductivity. This viscous solution was delivered using a syringe pump and electrospun using an electrospinning apparatus as described in Chapter 3. The polymeric solutions were electrospun onto the PET backing layer under a potential field of 30 kV to form nanofibrous mats. The flow rate of the polymer solution delivered to the electrospinning tip was 15 $\mu\text{L}/\text{min}$, and the tip-to-collector distance was 12 cm. Electrospinning were conducted in an atmosphere with a relative humidity of 50% and a temperature of at 20 ± 2 °C. The electrospun nanofibrous mats were removed from the collector drum and kept in a fume hood overnight, then stored at 80 °C in an oven for at least 2 h to remove residual solvent. The mats were then subjected to a heat-press treatment at 160 °C for 1 h, and then at 190 °C for 10 min to obtain the nanofibrous substrates. The resulting nanofibrous substrates were named as #Control (without silica), #1S, #2S and #3S, corresponding to silica nanoparticle loading of 0%, 0.16%, 0.8% and 1.6% (**Table 4-1**).

Table 4-1 Dope composition of membrane substrates before electrospinning

Substrate ID	SiO ₂ (wt %)	PEI (wt %)	NMP (wt %)	DMF (wt %)	PEI:NMP:DMF ^a
#Control	0	16.0	58.8	25.2	16:58.8:25.2
#1S	0.16	16.0	58.7	25.2	
#2S	0.8	15.9	58.3	25.0	
#3S	1.6	15.7	57.9	24.8	

Notes:

a. The weight ratio of PEI, NMP and DMF was maintained constant for all the membrane substrates fabricated in this study.

4.2.3 Preparation of polyamide selective layer

An ultrathin polyamide separation layer was formed on the as-prepared nanofibrous substrate via interfacial polymerization between MPD and TMC monomers (Wei *et al.* 2011a). Briefly, the nanofibrous substrate was first pre-wetted thoroughly with IPA for 10 min, followed by washing with DI water. The substrate was then soaked in an MPD solution (3 wt% in water) for 5 min. Excess MPD solution was removed with a rubber roller. A TMC solution (0.15 wt% in n-hexane) was gently poured onto the substrate surface to react with the residual MPD for 1 min. The resulting FO membrane was cured in a water bath for 2 min at 90 °C and then washed with tap water. The resulting membranes were stored in DI water for further use.

4.2.4 Morphology and structure characterization

The characterization of the nanofibrous support layer has been described in Chapter 3. In brief, membrane thickness was measured using a micrometer. A porometer was used to measure the pore diameter. The average porosity (ϵ) of the substrate was determined using a gravimetric method via measuring the mass of a wetting agent contained in the pores.

The morphology of the synthesized nanofibrous substrates and the FO membranes was characterized using a field emission scanning electron microscopy (FESEM). Energy dispersive X-ray spectroscopy (EDX) mode was then used to verify and

semi-quantify the incorporation of silica into the PEI nanofibrous substrate. Other characterization methods for the analysis of surface roughness and mechanical strength have been described in section 3.2.4.

4.2.5 Intrinsic separation properties characterization

The intrinsic separation properties of the FO membranes were evaluated in a crossflow RO filtration setup (*i.e.*, pressurized mode) with detail shown in section 3.2.5. In brief, the FO membrane was compacted using DI water at an applied pressure of 51.7 kPa for 4 h prior to flux measurement. The feed water was then changed to 2 mM or 10 mM NaCl solution to determine the NaCl rejection at the same applied pressure. The membrane intrinsic water permeability coefficient (A), salt permeability coefficient (B) and salt rejection (R) were determined according to equations 3-2, 3-3 and 3-4 in section 3.2.5.

4.2.6 FO performance evaluation

A lab-scale crossflow FO system was used to measure the osmotic water flux and reverse salt flux. The detailed procedure can be found in section 3.2.5. The FO membrane cell (CF042-FO cell, Sterlitech) has an active membrane area of 42 cm². Diamond-patterned spacers were placed on both the feed water (FW) and draw solution (DS) channels. The FW and DS were circulated using gear pumps at a crossflow velocity of ~9 cm/s in both channels. The temperature was maintained at 23 ± 2 °C during the FO experiments.

4.3 Results and discussion

4.3.1 Characterization of silica-filled PEI nanofibrous substrates

EDX mapping results for silicon and carbon are presented in Figure 4-1. The silicon (Si) is shown as the green signals in Figure 4-1(a-c). The signals are uniformly

distributed in the images, indicating that the silica has been incorporated successfully into the PEI nanofibers. Figure 4-1(d) plots the silicon-carbon molar ratio (Si/C) based on the EDX results. The substrate #S1 (0.16% silica in dope) had the lowest Si/C ratio of ~ 0.005 and the #3S (1.6% silica in dope) had the highest ratio of ~ 0.015 . These results semi-quantitatively confirm the trend that increased silica nanoparticle loading in the polymer dope results in higher silica content in the nanofibrous substrate.

The surface morphologies of the four membrane substrates are shown in **Figure 4-2**. No significant difference could be observed among the nanofibers of the four substrates, #control, #1S, #2S and #3S. The four substrates had a similar average nanofiber diameter of $\sim 0.25\ \mu\text{m}$, indicating that the incorporation of silica nanoparticles did not change the morphology of the nanofibers. The 2D roughness along an individual nanofiber was analyzed using AFM in tapping mode (**Figure 4-3**). The root mean square roughness (R_q) of the nanofibers was within 38 nm to 45 nm for all the four substrates, indicating relatively smooth surfaces (Liao *et al.* 2013a) and no large silica aggregates on the nanofiber surface.

(a)

(b)

(c)

(d)

Figure 4-1 EDX images showing the silicon and carbon element in the nanofibrous substrates (a) #1S, (b) #2S, and (c) #3S; and (d) the silicon carbon molar ratio in these substrates.

Figure 4-2 Surface morphologies of the membrane substrates (a) #Control, (b) #1S, (c) #2S and (d) #3S. The insets show a higher magnification.

Figure 4-3 AFM topography images of the nanofibrous substrates (a) #Control; (b) #1S; (c) #2S and (d) #3S, and (e) the root mean square roughness along the individual nanofiber (red line) for the four substrates. The error bars were based on analysis of at least 6 nanofibers.

Figure 4-4 FESEM micrographs showing the cross-sections of the membrane substrates (a) #Control, (b) #1S, (c) #2S and (d) #3S.

The properties of the nanofibrous substrates are presented in **Table 4-2**. Despite the similar nanofiber thickness of the four substrates, it is interesting to notice that the mean pore size (diameter, d) of the four substrates followed this trend: $d_{Control} < d_{S1} < d_{S2} < d_{S3}$. In general, for a nanofibrous mat obtained after electrospinning, the mean pore size is proportional to the fiber diameter (Li *et al.* 2006; Qin and Wang 2006). Their difference in pore size (measured using a porometer) was probably due to the significant pore size variation along the substrate thickness direction (z direction). **Figure 4-4** shows the FESEM micrographs of substrate cross-sections. The pore size (or gap) between the fibers in the z direction appeared to be larger for the silica loaded substrates, especially for #3S. This observation agrees well with the different loop numbers used during electrospinning. In order to fabricate substrates with similar thickness, the loop number was 6 for #S3 and 9 for other substrates (*i.e.*, the spinning time for #3S was shorter). Increasing silica nanoparticle loading tended to improve the nanofibers' capability maintaining its pore structure; the reason was presumably due to that the silica based nanofiber mats were more capable of resisting thermal compaction during the heat-press treatment, resulting in less

thickness/pore size reduction along the z-direction. A similar observation has been reported for nanofibrous MF membranes incorporating zeolite, which exhibited better resistance to hydraulic pressure under MF operation (Homaieghar and Elbahri 2012). Consistent with the pore size, the porosity also markedly increased with the silica nanoparticle loading. The control substrate had the lowest porosity of ~60%, while the substrate with 1.6% silica loading had the highest porosity of ~83%.

The structure parameters of the four membranes are also listed in **Table 4-2**. Compared to the substrate #Control, the silica embedded substrates had smaller S values. This agrees well with the trend of substrate porosity, as they are inversely related ($S \sim 1/\epsilon$). The substrate with the highest silica content (#S3) had an S value of 174 μm , which is significantly smaller than that of the commercial CTA membrane (~1150 μm) (Wei *et al.* 2011b). In addition to the increased porosity, other contributions might be from the additional interface water channels generated by hydrophilic silica nanoparticles (improved hydrophilicity) (Jadav and Singh 2009; Hu *et al.* 2013).

The substrate mechanical property is presented in terms of tensile modulus. Adding silica nanoparticles till 0.8% (#1S and #2S) had negligible influence in substrate tensile modulus. Further increase of silica loading to 1.6% (#3S) resulted in a ~40% tensile modulus drop, probably due to the more porous structure of #3S.

Table 4-2 Characterization of the nanofibrous substrates

Membrane substrate	Nanofiber diameter ^a (μm)	Tensile modulus (Mpa)	Substrate thickness, l (μm)	Pore size, d (μm) ^b		Porosity, ε (%)	Structure parameter, S (μm) ^c
				Mean	Maximum		
#Control	0.246 ± 0.047	295 ± 24	76.8 ± 3.0	0.55 ± 0.03	0.82 ± 0.11	60 ± 6	523 ± 23
#1S	0.236 ± 0.044	265 ± 4	81.9 ± 5.0	0.74 ± 0.09	1.18 ± 0.12	72 ± 12	420 ± 40
#2S	0.248 ± 0.057	287 ± 18	79.7 ± 4.7	0.87 ± 0.05	1.45 ± 0.12	77 ± 3	402 ± 46
#3S	0.249 ± 0.038	173 ± 15	93.7 ± 8.0	1.28 ± 0.05	2.24 ± 0.26	83 ± 2	174 ± 36

Notes:

a. measured using the image analysis software MediaCybernetics, Inc. (Wang *et al.* 2010b). About 15 nanofibers were measured to get the average value and standard deviation for substrate sample.

b. pore size measured using porometer

c. calculated using Equations 3-8 in Chapter 3.

4.3.2 Characterization of the silica-filled TFN FO membrane

The FESEM images of the polyamide active surfaces are shown in **Figure 4-5**. The typical ridge and valley morphology of polyamide surface can be observed for all four FO membranes, TFC#C, TFN#1, TFN#2 and TFN#3, indicating the successful formation of the rejection layer.

The membrane separation properties including water permeability (A), NaCl rejection (R) and NaCl permeability (B) are tabulated in **Table 4-3** for the in-house fabricated FO membranes and the commercial CTA-W membrane. The water permeability of the in-house fabricated FO membranes ranged from 2.20 to 2.99 L/m²h·bar, an order of magnitude higher than the water permeability of the CTA-W membrane. Although the same interfacial polymerization formula and procedure were applied for all four membranes, the silica loaded TFN membranes seemed to have higher water permeability, possibly due to the more porous substrates that lead to lower overall hydraulic resistance (Pendergast *et al.* 2010). On the other hand, other studies reported that the hydrophilic silica particles may help increase the water transport rate within the PSf support layer for RO membranes (Pendergast *et al.* 2010; Yin and Deng 2015). The B/A ratio showed almost no difference (12-13 kPa) for the three silica filled membranes; but they are smaller than that of the control membrane TFC#C and the CTA-W membrane, indicating less salt leakage during FO processes for these TFN membranes.

Figure 4-5 The FESEM micrographs showing the polyamide active surfaces of (a) TFC#C, (b) TFN#1, (c) TFN#2 and (d) TFN#3

Table 4-3 Intrinsic separation properties of FO membranes.

FO Membrane	Water Permeability, A		NaCl Permeability, B		B/A (kPa)	NaCl rejection (%)
	L/m ² h·bar	10 ⁻¹² m/(Pa·s)	L/m ² h	10 ⁻⁷ m/s		
TFC#C ^a	2.2 ± 0.27	6.1 ± 0.75	0.31±0.11	0.86 ± 0.30	14.1	78.2 ± 6.4
TFN#1 ^a	2.31 ± 0.24	6.4 ± 0.66	0.29±0.08	0.80 ± 0.02	12.5	78.2 ± 4.1
TFN#2 ^a	2.65 ± 0.23	7.4 ± 0.64	0.34±0.11	0.94 ± 0.31	12.8	75.9 ± 4.0
TFN#3 ^a	2.99 ± 0.11	8.3 ± 0.31	0.41±0.12	1.1 ± 0.33	13.3	74.2 ± 3.9
CTA-W ^b	0.34	0.94	0.11	0.31	32.3	54.3 ^c

Notes:

a. 2 mM NaCl solution was used as the feed; the salt rejection was measured at 51.7 kPa applied pressure (equilibrated at 51.7 kPa for 10 h).

b. The water permeability and salt permeability of CTA-W membrane was tested with 10 mM NaCl feed water and under applied pressure of 7 bar. The measured NaCl rejection was under 7 bar and 10 mM feed. A higher pressure was chosen due to the very low water permeability of CTA-W.

c. The NaCl rejection of CTA-W membrane was estimated using the A and B values based on 2 mM NaCl feed water and 51.7 kPa applied pressure, in order to be comparable with the TFN FO membranes.

4.3.3 FO performance of TFN membranes

The membrane FO performance is evaluated in this section. The FO water fluxes at 1 M NaCl DS are presented for both membrane orientations in **Figure 4-6**. Consistent with previous studies, higher water fluxes were observed in the AL-DS orientation compared to the AL-FW orientation, arising from the more severe dilutive ICP in AL-FW. The control membrane TFC#C (without silica incorporation) had a water flux of 18 L/m²h in the AL-FW configuration. In contrast, the silica loaded membranes showed significantly higher osmotic water fluxes. With 0.16% silica incorporation, the water flux increased by 20%. The TFN#3 with the highest silica loading (1.6%) exhibited water flux of 42 L/m²h in the AL-FW, corresponding to 133% increase compared with TFC#C. A similar increasing trend was also observed in the AL-DS orientation. The higher FO water fluxes of the silica incorporated membranes are likely attributable to the reduced structure parameter in addition to the slightly increased *A* value. The results indicate that the incorporation of silica nanoparticles into the FO nanofibrous substrate is an effective strategy to improve its FO water flux performance.

Figure 4-6 FO flux performance at 1 M NaCl draw solution in both AL-FW and AL-DS orientations. Error bars were based on 2-3 replicates.

On the other hand, low salt leakage is also important for a high performance FO membrane. The reverse solute flux (J_s) and the specific solute flux (J_s/J_v) results are shown in **Figure 4-7**. The three TFN FO membranes have low reverse solute flux ($< 5 \text{ g/m}^2\text{h}$), in contrast to the $8 \text{ g/m}^2\text{h}$ of the control TFC membrane. Similarly, the membrane TFN#1~3 had a J_s/J_v ratio $< 0.15 \text{ g/L}$ while TFC#C had a ratio twice as great. This is in good agreement with their B/A ratio (see Table 4-3). In general, a low J_s/J_v is preferred to reduce the salt accumulation in the FW and to minimize the draw solute regeneration cost (Qi *et al.* 2012). In this context, the silica embedded FO membranes are more advantageous. Compared with the FO performance of CTA-W membrane, our in-house fabricated TFN FO membranes had much higher water fluxes as well as lower J_s/J_v ratio, revealing a promising FO membrane design.

The osmotic water fluxes of TFN#3 as a function of DS concentration are illustrated in **Figure 4-8**. The DS concentrations were varied from 0.5 to 2.0 M, while the FW was the DI water. In both orientations, the water flux increased with DS concentration, but the increase of the flux rate at higher concentration declined owing to more severe ICP (Tang *et al.* 2010; Zou *et al.* 2013). The highest flux achieved at 2 M NaCl concentration was 89 and 49 $\text{L/m}^2\text{h}$ in the AL-DS and AL-FW orientations, respectively. The high flux performance together with its relatively low J_s/J_v ratio makes TFN#3 a good candidate for FO applications.

(a)

(b)

Figure 4-7 A comparison of (a) reversed solute flux, J_s and (b) specific solute flux, J_s/J_v during FO process with 1 M NaCl DS. DI water was used as the FW. Error bars were based on 2-3 replicates.

Figure 4-8 Effect of DS concentration on FO water flux for membrane TFN#3. 0.5-2.0 M NaCl solutions were used as DS. DI water was used as FW. Error bars were based on 2-3 replicates.

4.4 Conclusions

In this study, the incorporation of silica nanoparticles with different loading (ranging from 0.16 wt% to 1.6 wt%) to PEI nanofibrous substrates was evaluated, with the purpose of improving FO membrane performance. The results showed that the pore size and porosity of the FO membrane substrate increased with the addition of silica nanoparticles, as the embedded nanoparticles helped the nanofibrous substrate better resist compaction during the heat-press treatment. The resulting substrates also had decreased structure parameters. The highest silica loading led to a TFN membrane with the maximum substrate porosity (83%) and the smallest structure parameter ($\sim 174 \mu\text{m}$) in the current investigation, and this membrane also demonstrated the most promising osmotic water flux, i.e., ~ 49 and $89 \text{ L/m}^2\text{h}$ in the AL-FW and AL-DS orientations with 2 M NaCl DS against DI feed.

The current study suggests that hydrophilic nanoparticles may equip the nanofibrous support layer with high porosity without altering the nanofiber morphology. The future work will be focused on the further enhancement of both

mechanical properties and FO water flux, with the aim of fabricating osmotically driven membranes with enough robustness for pressure retarded osmosis (PRO) applications.

CHAPTER 5.

Synthesis and characterization of TFN FO membranes with nanofibrous substrate reinforced by functionalized carbon nanotubes

5.1 Introduction

As verified in chapter 4, the incorporation of silica nanoparticles improved nanofibrous support porosity and reduced the overall structure parameter. The optimized nanocomposite membrane exhibited an improved water flux and comparatively low salt flux during the FO performance evaluation. However, it is more difficult to find a nanoparticle incorporation that can increase both water flux and membrane mechanical strength, as this would allow the fabrication of a FO membrane with a very thin thickness that, in turn, can enhance membrane permeation.

In this study, another type of nanomaterial, tubular carbon nanotubes (CNTs), was successfully incorporated into PEI nanofibrous mats to develop good FO membranes with excellent mechanical properties. CNTs are well known for their high strength, as well as other benefits shared with the above-mentioned nanomaterials. Prior studies have reported that the successful incorporation of CNTs in microfiltration (MF) and ultrafiltration (UF) membranes not only increased water permeability, but also reduced the compaction effect during filtration (Wang *et al.* 2005; Qiu *et al.* 2009; Wu *et al.* 2010; Homaeigohar and Elbahri 2012). Hence, it is highly possible that incorporating CNTs into the nanofiber substrate of an FO membrane could increase both flux and mechanical strength. So far, the utilization

of CNTs as a filler for preparing FO membranes has not been reported in the literature.

In this research, we successfully fabricated a novel TFN FO membrane consisting of a PEI nanofibrous support reinforced by functionalized multi-walled carbon nanotubes (f-CNTs) and an ultrathin polyamide rejection layer to demonstrate their high FO performance and high mechanical strength. To the best of authors' knowledge, it was the first time a high performance FO membrane has been fabricated with f-CNTs as a nanofibrous support filler.

5.2 Experiments

5.2.1 Materials and chemicals

Multi-walled carbon nanotubes (MWCNTs) were obtained from CNano Technology Ltd (China). Concentrated hydrochloric acid (HCl, 37.0%) and nitric acid (HNO₃, 65.0%) (Merck Chemicals, Germany) were used to purify and functionalize the MWCNTs. For chemicals used for the synthesis of polyamide via interfacial polymerization, please refer to section 4.2.1. Please refer to section 3.2.1 for more information about other common chemicals used herein, such as NMP, DMF, IPA, NaCl, LiCl.

5.2.2 Nanofibrous substrate via electrospinning

The MWCNTs (f-CNTs) functionalized with carboxyl groups were obtained after purification and functionalization using the concentrated HCl and HNO₃. Briefly, 1.0 g of the purified MWCNTs was added to 200 mL of HNO₃ and refluxed at 150 °C for 6 h. The resulting dispersion was filtered, and the MWCNT residue was rinsed with 500 mL of deionized water, followed by 1 L of 0.5 M NaOH solution and twice with 500 mL of deionized water until a pH of ~6.0 was obtained. The final rinse was completed with 200 mL of ethanol. This series of rinsing aid in removing the excess acid on the MWCNTs, oxidation debris and small

carbonaceous materials generated during functionalization. The functionalized MWCNTs (f-CNTs) obtained were left to dry at 60 °C for overnight.

0.3% (w/w, based on polymer weight) f-CNTs) were dispersed in NMP/DMF solution by sonication for 1 h using an ultrasonic processor (VC 750, Sonics & Materials, Inc., US) (VC 750, Sonics & Materials, Inc., United States) (Goh *et al.* 2013). PEI was then dissolved in the well-dispersed solution by stirring at 80 °C for at least two days. A trace amount of LiCl was added to adjust the dope conductivity. The detailed dope formula and spinning parameters are summarized in **Table 5-1**. In brief, three FO membrane substrates were fabricated, and named PEI-0, CNT-PEI and CNT-PEI-L. The PEI-0 and CNT-PEI denote the control substrate (without CNTs) and the CNT-filled substrate, respectively. The CNT-PEI-L refers to the CNT-reinforced substrate with larger pores, which was prepared by varying dope composition and electrospinning conditions. The as-prepared substrates were subsequently post-treated by heat-pressing (Carver Inc, US) to bond the nanofiber layers.

Table 5-1 Electrospinning conditions for preparation of the three nanofibrous supports.

membrane/ substrate	Substrate fabrication								Rejection layer via IP	
	Substrate				dope solution				Electrospinning condition	
	PEI (wt%)	f-CNTs (wt%)	NMP (wt%)	DMF (wt%)	Flow rate (μ L/min)	Applied voltage (kV)	Working distance (cm)	Humidity (%)	MPD (wt%)	TMC (wt%)
TFC-0 / PEI-0	16	0	58.8	25.2	15	30	12	40	3	0.15
TFN-1 / CNT-PEI	16	0.048	58.8	25.2	15	30	12	40	3	0.15
TFN-2 / CNT-PEI-L	16	0.048	84	0	30	30	12	60	3	0.15

5.2.3 Synthesis of polyamide skin by interfacial polymerization

An ultrathin polyamide selective skin was formed on the composite f-CNT/PEI nanofiber supports via interfacial polymerization between MPD and TMC monomers as described in section 3.2.3 with some modification (Wei *et al.* 2011a). Briefly, after being pre-wetted by IPA and MiliQ water, the nanofibrous support was soaked in an MPD solution (3 wt% in DI water) for 5 min. The excess MPD solution on the substrate surface was removed using a rubber roller. A TMC solution (0.15 wt% in n-hexane) was gently poured onto the surface to react with residual MPD for 1 min to form a polyamide skin layer. The membrane was then cured in a water bath for 2 min at 90 °C. After that, the nanofiber-based TFC FO membrane was washed with tap water and stored in MiliQ water for further tests.

5.2.4 Membrane characterization

Characterization of CNTs and membrane morphology

Raman spectroscopy (Renishaw Raman spectrometer) was used to characterize the purified and functionalized MWCNTs. The analysis was carried out using a 514 nm laser performing at 10% of the nominal laser intensity and an integration time of 10s.

The surface morphologies and cross-sectional structure of the nanofibrous support and the TFC membrane were observed using a FE-SEM at an accelerating voltage of 5 kV. Please refer to section 3.2.4 for the equipment specification and sample preparation procedure. The diameter of the electrospun nanofibers was determined from the FE-SEM images using the Adobe Acrobat software.

The f-CNTs reinforced nanofibers were characterized by transmission electron microscopy (TEM, JEM 2010F, JEOL Asia Pte Ltd, Japan) at 200 kV. TEM samples were prepared by dropping ethanol-dispersed samples onto carbon coated copper mesh and evaporating the excess solvent.

Nanofibrous support structure characterization

The thickness, pore size, porosity and mechanical properties of the nanofibrous supports were characterized by following the standard protocols described in section 3.2.4.

Pure water permeability (PWP) measurement of nanofibrous support

The pure water permeability (PWP) of the FO substrates was measured with a dead-end crossflow filtration system. An FO substrate coupon of 6 cm² active area was placed in a membrane cell, and 2.5 L MilliQ water was circulated under an applied pressure of 7 kPa. The PWP of the nanofiber substrate was calculated using the equation below:

$$J = \frac{Q}{A_{eff} \times \Delta t} \quad 5-1$$

where Q is the permeate volume; A_{eff} is the effective area; ΔP is the transmembrane pressure; and t is the sampling time.

Intrinsic separation properties characterization

The intrinsic separation properties of FO membranes were evaluated with a cross-flow RO setup as described in section 3.2.5. A membrane coupon was placed in a cell with an active area of 42 cm², and was compacted at testing pressure with MiliQ feed water for 4 h prior to flux measurement. The membrane intrinsic water permeability coefficient (A), salt permeability coefficient (B) and salt rejection (R_s) were evaluated according to equations in section 3.2.5.

FO performance evaluation

The FO performance of the in-house fabricated TFC membrane and the commercial HTI membranes were evaluated with a lab-scale cross-flow FO system described in section 3.2.6. The detailed measurement of water flux (J_v) and reverse salt flux (J_s) were measured according to the methodology in section 3.2.5. A commercial FO cell (CF042-FO cell) was purchased from Sterlitech Corporation. Diamond-patterned spacers were placed on both sides of the membrane.

5.3 Results and discussion

5.3.1 Characterization of f-CNTs

In general, high performance nanocomposites require a homogeneous distribution of nanoparticles in the polymeric matrix and a strong interfacial interaction between nanoparticles and the polymeric matrix. **Figure 5-1** (a) shows the photo images of the MWCNTs (as received) and f-CNTs (after functionalization) in the PEI/NMP/DMF dope solution. The f-CNTs could be dispersed well in the solution while this phenomenon was not observed for the MWCNTs, presumably due to the polar-polar affinity and electrostatic repulsion of the $-\text{COOH}$ on f-CNTs (Lee *et al.* 2007; Bergin *et al.* 2009; Frolov *et al.* 2012; Goh *et al.* 2013). The Raman spectra of the MWCNTs and f-CNTs are presented in **Figure 5-1** (b). The D and G bands, assigned to the disordered and ordered lattices of graphite crystals, are displayed at Raman shifts of ~ 1350 and 1580 cm^{-1} , respectively (Goh *et al.* 2013). The similarity of the two spectra suggests that the graphitic structure of the MWCNTs was preserved after functionalization. The G to D bands intensity ratio (I_G/I_D , an empirical measure of purity) was 0.665 and 0.634 for the MWCNTs and f-CNTs, respectively. The decreased ratio after functionalization indicated more structural defects, due to the carboxylic acid functional groups ($-\text{COOH}$) generated on f-CNTs after chemical oxidation (Liu *et al.* 2007; Goh *et al.* 2013). The hydrophilic functional group ($-\text{COOH}$) on f-CNTs is believed to increase the sites along the nanotubes interacting with the PEI polymeric matrix (Liu *et al.* 2007).

Figure 5-1 Comparison of MWCNTs and functionalized MWCNTs (f-CNTs) via (a) dispersion stability in PEI/NMP/DMF dope solution; and (b) Raman spectra. (Photographs were taken 7 days after preparation).

5.3.2 Characterization of nanofibrous substrates

One control substrate (PEI-0) and two f-CNT filled substrates (CNT-PEI and CNT-PEI-L) were synthesized in this study. **Figure 5-2** (a) shows the photo images of PEI-0 (left) and CNT-PEI (right). Compared with the yellowish white PEI-0, the CNT-PEI substrate appears homogenous gray on the entire fibrous sheet, indicating the even distribution of f-CNTs at the macroscopic level. **Figure 5-2** (b-d) present the FE-SEM micrographs of the three substrates. No free CNTs could be observed on the nanofibers with CNTs incorporated (**Figure 5-2** (c) and (d)). The TEM image of the CNT-PEI (inset of **Figure 5-2** (c)) shows that the dark tubular structured CNT aligned well along the nanofiber axis, again revealing the successful CNTs incorporation in the polymeric fiber matrix (Ge *et al.* 2004). The CNT-PEI-L substrate consisting of thicker nanofibers shows bigger pores, which can be explained by the faster solvent evaporation as a result of purer solvents used and higher humidity during electrospinning (Salalha *et al.* 2004; Spitalsky *et al.* 2010).

Figure 5-2 Characterization of nanofibrous substrates. (a) Photo images of the PEI-0 (Left) and CNT-PEI (Right). FE-SEM micrographs of (b) PEI-0, (c) CNT-PEI (inset is TEM image) and (d) CNT-PEI-L.

The substrate properties are tabulated in **Table 5-2**. By comparing CNT-PEI and PEI-0, the substrate incorporating CNTs demonstrated a 53% increase in tensile modulus. The highly porous CNT-PEI-L also showed a 42% increase compared to PEI-0, although it is normally understood that substrates with larger pore sizes or porosities are less mechanically stable (Han *et al.* 2013b). The effectiveness of the f-CNTs in enhancing the mechanical strength of a nanofibrous substrate was successfully demonstrated. It is likely that f-CNTs with a high aspect ratio could transfer their superior mechanical properties to the nanofiber matrix.

Referring to the porosity data listed in **Table 5-2**, it is observed that despite the similar pore size possessed by CNT-PEI and PEI-0, the CNT-PEI substrate has a porosity of ~71%, which is much higher than that of PEI-0 (59%). This is consistent with our hypothesis that the substrate with a higher mechanical strength is better able to withstand the heat-press treatment, resulting in less compression and less

porosity loss. The CNT-PEI had a greater thickness (85 μm) as compared with the PEI-0 substrate (77 μm), which also indicated that the CNT-PEI substrate underwent less compression. Another factor contributing to the CNT-PEI's higher porosity was probably the nano-sized water channels provided by the CNT in the substrate (Amini *et al.* 2013). Clearly, the f-CNT incorporation into the polymeric fiber matrix could help preserve the substrate porosity during the heat-press treatment. The CNT-PEI-L had significantly larger pores (2-fold increase) and was the most porous of the three substrates, showing consistency with the FE-SEM micrographs.

Table 5-2 Properties of nanofibrous substrates PEI-0, CNT-PEI and CNT-PEI-L

Nanofiber substrate	Mechanical strength			Mean pore diameter (μm)	Average porosity (%)	Substrate thickness (μm)	Pure water permeability ($\text{L}/\text{m}^2 \text{h}$)	Structure parameter (μm) ⁽¹⁾
	Tensile Modulus (MPa)	Yield strength (MPa)	Elongation at break (%)					
PEI-0	294 $\pm$ 24	9.8 $\pm$ 0.8	34.8 $\pm$ 8.9	0.55 $\pm$ 0.03	59 $\pm$ 4	77 $\pm$ 3	517 $\pm$ 128	674 $\pm$ 86
CNT-PEI	449 $\pm$ 21	17.2 $\pm$ 1.7	18.9 $\pm$ 4.2	0.43 $\pm$ 0.01	70 $\pm$ 11	85 $\pm$ 2	1031 $\pm$ 284	468 $\pm$ 125
CNT-PEI-L	417 $\pm$ 31	15.0 $\pm$ 1.7	14.3 $\pm$ 3.8	1.51 $\pm$ 0.13	81 $\pm$ 3	96 $\pm$ 3	2045 $\pm$ 272	310 $\pm$ 82

Notes:

The reported results were based on 2-5 tests.

⁽¹⁾ S values were determined by fitting A , B values from RO tests and J_v from FO tests into Equations 3-12 and 3-13 in Chapter 3.

The pure water permeability of the three substrates followed the same trend as porosity: CNT-PEI-L > CNT-PEI > PEI-0. The S values of PEI-0, CNT-PEI and CNT-PEI-L were 674, 468 and 310 μm , respectively. This expected trend was in good agreement with the substrate porosity. The smaller S values of the f-CNT filled substrates are favorable in reducing the ICP in the FO process. The S values of the f-CNT reinforced nanofibrous substrates are much smaller compared to those of the commercial cellulose triacetate (CTA) FO membranes ($\sim$ 720 μm for CTA-HW and $\sim$ 1000 μm for CTA-W) from Hydration Technology Innovations (HTI, Albany, USA) (Wei *et al.* 2011b).

5.3.3 High FO performance of TFN membranes

Three FO membranes, TFC-0, TFN-1 and TFN-2, were prepared using the nanofibrous substrates PEI-0, CNT-PEI and CNT-PEI-L, respectively. As shown in **Figure 5-3** (a-c), the typical ridge-and-valley morphology of the polyamide active surfaces can be observed for all three membranes. From the cross-sectional images (**Figure 5-3** (d-f)), it can be clearly seen that a thin layer of a few hundred nm is on top of the nanofibrous substrate, indicating the successful formation of the polyamide rejection layer. **Figure 5-4** presents the water permeability (*A*) and salt permeability (*B*) results. The *A* values were ~ 2.2 - 2.5 L/m²h·bar and *B* values were within 0.6 to 0.75 L/m²h for the three membranes. The similar *A* and *B* values of the three FO membranes result in their comparable *B/A* of ~ 25 -30 kPa.

Figure 5-3 FE-SEM micrographs showing the active surfaces of (a) TFC-0, (b) TFN-1 and (c) TFN-2 and the cross-sections of (d) TFC-0, (e) TFN-1 and (f) TFN-2.

Figure 5-4 Pure water permeability and solute permeability of the three FO membranes. They were obtained from RO tests at applied pressure of 7 bar. DI water was used as feed for determining A value, while 10 mM NaCl was used for the calculation of B value.

The FO performance comparison of the three membranes can be found in **Figure 5-5**. The water flux was obtained with 1 M NaCl DS and DI FW. It can be observed in **Figure 5-5** (a) that the water flux in the AL-FW orientation was almost half of that in the AL-DS orientation for all the three membranes, which can be explained by the more severe ICP in the AL-FW orientation (Tang *et al.* 2010; Lutchmiah *et al.* 2014). In both membrane orientations, the TFN-1 had a higher water flux (~ 20-30% increase) compared to the control membrane TFC-0, revealing that less ICP is suffered by the f-CNT filled TFN-1. The higher FO performance of TFN-1 is consistent with its smaller S value, attributed mainly to its higher substrate porosity as a result of CNT incorporation. Therefore, it is suggested that the CNT incorporation into a nanofibrous substrate is an effective strategy in reducing ICP and increasing FO water flux. As expected, the TFN-2 membrane, possessing a support layer of large pores and much higher porosity, is able to achieve a significantly higher water flux, *i.e.*, 33 L/m²h and 61 L/m²h in the AL-FW and AL-DS orientation, respectively. This corresponds to increase of about 35% and 46% in the two orientations compared to the less porous TFN-1 membrane. In addition to the high porosity, the large interconnected pores of the TFN-2 substrate may also help mitigate the ICP further via decreased tortuosity (facilitating mass transfer).

The corresponding specific solute flux (J_s/J_v) results are presented in **Figure 5-5** (b). Previous studies show that a low J_s/J_v ratio is preferred to minimize the salt accumulation in the FW and to reduce the replenishment cost of draw solutes when DS regeneration is needed (Zou *et al.* 2013). The three membranes demonstrated a relatively low J_s/J_v ratio (<0.4 g/L), and slightly lower J_s/J_v in the AL-DS compared to AL-FW. The TFN-2 membrane has a remarkably low J_s/J_v of ~ 0.1 g/L, making it a good candidate for ODMPs.

Figure 5-5 Performance of the synthesized FO membranes (A) water flux and (B) specific solute flux (J_s/J_v). (Milli-Q water was used as the feed and 1 M NaCl solution were employed as the draw solution. Error bars were based on 2-3 replicate tests.)

The osmotic water fluxes as a function of DS concentration (0.5, 1.0, 1.5 and 2.0 M) in both orientations are shown in **Figure 5-6**. In both orientations, higher water fluxes are observed at increased DS concentration. The highest water flux was ~ 90 L/m²h achieved by TFN-2 in the AL-DS orientation with 2 M DS, revealing the potential of the CNT incorporated nanofibrous FO membranes for high flux FO applications. However, the rate of flux increase was slower at higher DS concentrations, due to increased dilutive ICP at higher concentration. On the other hand, by comparing the TFC-0 and TFN-2, the control membrane TFC-0 had a slower rate of flux increase (with DS concentration), presumably due to its greater S value resulting in the membrane suffering more ICP (Song *et al.* 2011). Again, the advantage of CNT incorporation is demonstrated. **Table 5-3** summarizes the FO performance of TFN-1 and TFN-2 (current study) and compares with documented

nanofibrous FO membranes reported in the literature (Bui *et al.* 2011; Bui and McCutcheon 2013; Huang *et al.* 2013a; Tian *et al.* 2013). Our TFN-2 membrane shows very promising FO water flux together with the low specific solute flux.

Figure 5-6 Effect of draw solution concentration on FO water flux in (a) AL-DS and (b) AL-FW orientations. DI water was used as the feed. Error bars were based on 2-3 replicate tests.

Table 5-3 Comparison of nanofibrous FO membranes

Membrane ID	A, (L/m ² h·bar)	B, (L/m ² h)	Water flux (L/m ² h) (AL-DS/AL-FW)	J _s /J _v (g/L) (AL-DS/AL-FW)	FW	DS	Ref.
TFN-1	2.3	0.6	45.3 / 22.4	0.09 / 0.40	DI	1.0 M	This work
TFN-2	2.6	0.7	61.3/ 32.8	0.07 /0.12	DI	1.0 M	This work
nylon 6,6	0.917	0.300	22 / 6	0.036 / 0.111	DI	1.5 M	(Huang <i>et al.</i> 2013a)
PAN*	2.036	1.572	52 / 29 ⁽¹⁾	0.06 / 0.29 ⁽¹⁾	DI	1.5 M	(Bui and McCutcheon 2013)
PVDF(1#)	1.21	0.33	30.4 / 11.6	0.21 / 0.30	DI	1.0 M	(Tian <i>et al.</i> 2013)
PVDF(2#)	3.15	2.33	47.6 / 28.0	0.45 / 0.46	DI	1.0 M	(Tian <i>et al.</i> 2013)
PSf	0.58 ⁽²⁾	0.17 ⁽²⁾	24 / -	0.37 / -	DI	1.5 M	(Bui <i>et al.</i> 2011)

Note:

⁽¹⁾ Read from the figures in reference (Bui and McCutcheon 2013).

⁽²⁾ Determined from FO water flux by the authors (Bui *et al.* 2011).

- No data were reported in the references.

5.4 Conclusions

In this research, we successfully fabricated a novel TFN FO membrane consisting of a PEI nanofibrous substrate reinforced by f-CNTs and an ultrathin polyamide rejection layer. The well dispersed f-CNTs inside the fiber matrix significantly improved the substrate properties, *i.e.*, higher porosity and enhanced mechanical strength. The porous structure was presumably better preserved under heat-press treatment due to the presence of f-CNTs (better compaction resistance). The incorporation of f-CNTs in the polymeric nanofibers increased the substrate porosity by 18%, reduced the S value by 30%, and significantly improved the substrate tensile modulus by 53%. The high mechanical strength provided by the embedded f-CNTs enabled us to further increase the substrate pore size and porosity to reduce ICP. This was demonstrated by our high performance TFN-2 FO membrane with an S value of 310 μm and a water flux of 61 $\text{L}/\text{m}^2\text{h}$ and 33 $\text{L}/\text{m}^2\text{h}$ with 1.0 M NaCl DS against DI water in the AL-DS and AL-FW orientations, respectively. This study demonstrates the great potential of using CNTs as a filler for nanofibrous FO membrane preparation for ICP control from 1) increasing substrate porosity and 2) further improving substrate structure by improving the mechanical properties of the material. The high mechanical strength provided by CNTs also paves the way for the fabrication of PRO membranes.

CHAPTER 6.

Synthesis and characterization of TFN PRO membranes with tiered nanofiber support reinforced by functionalized carbon nanotubes

6.1 Introduction

It has been verified in Chapter 3 that the nanofiber diameter (pore size) greatly influences the formation of interfacial polymerized polyamide layer. A defect-free polyamide layer is easily formed on a nanofibrous support with a smaller pore size. Papkov *et al.* has demonstrated improvement of 133 and 116 times in modulus and strength respectively in electrospun polymeric nanofibers by reducing the diameters of the fiber from 2.8 μm to ~ 100 nm (Papkov *et al.* 2013). Most of the nanofibrous TFC membranes reported in the literature have an average fiber diameter larger than 200 nm. It is thus reasonable to expect that a further reduction in the fiber diameter would improve the support mechanical properties dramatically.

However, reduction in the fiber diameter would increase the support mass transfer resistance due to reduced porosity, thus exacerbating the ICP problem. To overcome this problem, Bui *et al.* have utilized a tiered PAN nanofibrous support, which consists of finer fibers on the top (near the polyamide layer) and coarse fibers at the bottom of the support, to minimize membrane deformation while maintaining a comparatively small support resistance in the PRO process. The membrane can withstand an applied pressure of 11.5 bar and harvest a peak power density near 8.0 W/m^2 using 0.5 M NaCl against deionised water (Bui and McCutcheon 2014).

Alternatively, Song *et al.* added nano-SiO₂ particles to improve the PAN nanofibrous mats mechanical properties and maintain the support's porosity (Song *et al.* 2013). The membrane skin layer was further modified with chlorine to enhance its water permeability, and peak power density was enhanced from 10.7 W/m² to 15.2 W/m² using 1.06 M NaCl against 0.9 mM NaCl at 15.2 bar. Compared with spherical silica, CNTs are ideal to serve as a filler for PRO membrane development as incorporation of CNTs in the PEI nanofibrous support of a FO membrane improves both flux and mechanical strength.

Based on these rationales, a novel tiered PEI nanofibrous support was designed and fabricated for use in the PRO process in this research. To further improve the mechanical properties to withstand the high pressure in the PRO process without aggravating the ICP effect of the support, f-CNTs were incorporated into the nanofibers to obtain a pyramid f-CNTs/PEI composite nanofibrous support. It is proposed that the carbon nanotubes, as typical reinforcing agents with outstanding mechanical properties, can strengthen the PEI polymeric nanofibers successfully. Interfacial polymerization was then performed to synthesize a polyamide layer on the top of the support to act as the rejection layer. In this study, the influence of the f-CNTs on the properties of the nanofibrous support, in particular, its mechanical properties and the burst pressure during the PRO process were investigated. In addition, the PRO performance of this novel membrane was evaluated to provide an insight into the effectiveness of the design strategy in the PRO process.

6.2 Experiments

6.2.1 Materials and chemicals

More information about the multi-walled carbon nanotubes (MWCNTs) f-CNTs is described in section 5.2.1. PEI polymer specifications and monomers (*i.e.*, MPD TMC) used to synthesize polyamide layer are given in section 4.2.1. Non-woven support (Grade 3258) was purchased from Ahlstrom. Other chemicals have been described in sections 3.2.1, 4.2.1 and 5.2.1

6.2.2 Fabrication of tiered nanofibrous composite substrates

The MWCNTs were purified and functionalized with carboxyl groups. The detailed procedure of the MWCNT purification and functionalization were described in section 5.2.2.

0.3 wt% (based on polymer weight) of f-CNTs was dispersed in NMP/DMF solution for 1 h using an ultrasonic processor (VC 750, Sonics & Materials, Inc., United States). PEI polymer particles were then dissolved in the well-dispersed solution by stirring at 80 °C for at least two days. A trace amount of LiCl was added to adjust the dope conductivity. PEI nanofibrous substrates with thicker fibers (assigned as bottom thicker layer) and finer fibers (assigned as top finer layer) were fabricated by varying the dope solution and operating conditions. Three PEI nanofibrous supports, T1, T2 and T3, were fabricated in this work with the design details listed in **Table 6-1**. The as-prepared substrates were subsequently post-treated with a bench-top heat-press (Carver Inc, USA) to bond the nanofiber layers.

6.2.3 Polyamide selective skin by interfacial polymerization

The details of the synthesis of the polyamide selective skin have been described in section 5.2.3 in Chapter 5. Briefly, the nanofibrous support was soaked in an MPD solution (3.0 wt% in DI water) for 5 min after being pre-wetted by IPA and Milli-Q water. A rubber roller was then utilized to remove the excess MPD solution on the substrate surface. A TMC solution (0.15 wt% in n-hexane) was then gently poured onto the surface to react for 1 min. The membrane was then cured in a water bath for 2 min at 70 °C. After that, the nanofiber-based TFC PRO membrane was washed with tap water and stored in Milli-Q water for further tests. The membranes formed by performing interfacial polymerization on different nanofibrous supports were thus designated as IP-T1, IP-T2 and IP-T3.

Table 6-1 Summary of the characteristics of the three PEI nanofibrous supports.

Sample code	T1		T2		T3	
	Top	Bottom	Top	Bottom (with CNTs)	Top (with CNTs)	Bottom (with CNTs)
Polymer dope	12% PEI in NMP/DMF (6/4)	16% PEI in NMP/DMF (7/3)	12% PEI in NMP/DMF (6/4)	16% PEI (0.3% CNTs) in NMP/DMF (7/3)	12% PEI (0.3% CNTs) in NMP/DMF (6/4)	16% PEI (0.3% CNTs) in NMP/DMF (7/3)
Flow rate ($\mu\text{L}/\text{min}$)	5	15	5	15	5	15
Applied voltage (kV)	28 ± 2	24 ± 2	28 ± 2	24 ± 2	28 ± 2	24 ± 2
Working distance (cm)	12	12	12	12	12	12
Humidity	$50 \pm 2\%$	$50 \pm 2\%$	$50 \pm 2\%$	$50 \pm 2\%$	$50 \pm 2\%$	$50 \pm 2\%$

6.2.4 Membrane characterization

Characterization of the membranes morphology

The characterizations by FE-SEM and TEM have been described in sections 3.2.4 and 5.2.4, respectively.

Substrate structure characterization: pore size, porosity and mechanical

The nanofiber supports were characterized by following the standard protocols as described in section 3.2.4.

Intrinsic separation properties characterization

The intrinsic separation properties (A , B , and R_s) of IP-T1, IP-T2, and IP-T3 were evaluated by a cross-flow RO setup as described in section 3.2.5. The membrane was compacted at testing pressure with MilliQ feed water for 4 h prior to the flux measurement.

6.2.5 Pressure retarded osmosis tests

PRO experiment setup

The PRO performances of IP-T1, IP-T2, and IP-T3 were evaluated with a lab-scale cross-flow PRO system with its working schematic diagram shown in **Figure 6-1** (Chou *et al.* 2013). A peristaltic pump was used to circulate the feed water, FW, (5.0 L, MilliQ water) and a diaphragm pump was employed to circulate the DS (6 L, 1.0 M NaCl). A pressure relief valve after the membrane cell and a needle valve prior to the cell were used to adjust the hydrostatic pressure and the cross-flow rate. The flow rate of the DS and the FW were estimated by rotary flow meters, respectively. A commercial cross flow FO cell (CF042-FO) with maximum testing pressure up to 6894.8 kPa (~69 bar) purchased from Sterlitech was employed for the testing.

Diamond-patterned spacers were placed in between the DS channels and the RO permeate carriers in FW channels respectively. The extra heat produced by the high-pressure pump was removed by chilled water flowing in a coiled tube submerged in the draw solution tank in order to maintain a constant temperature. During the testing, feed water conductivity, DS conductivity, FW weight, and hydraulic pressure in draw solution side were collected via data logging. Flow rates of both flow channels and the pressure of the feed water were collected manually.

PRO performance evaluation

The temperatures of both FW and DS were maintained at 22 ± 2 °C. NaCl salt was used as the solute for DS (1.0 M) and MilliQ water for FW. A membrane coupon was placed in the FO cell in AL-DS orientation. Each PRO test was initially started with low applied pressure (1~2 bar) to stabilize the testing system before a hydraulic pressure was applied on the DS side. The pressure was gradually increased to predetermined values and continued for at least 20 min after a steady stage was reached before the data was collected. The flow rates for both the draw solution and the FW were maintained at ~0.4 L/min (corresponding to a linear velocity of $\sim 8 \text{ cm s}^{-1}$). The power density (W) can be obtained from the product of the water flux (J_v) and applied hydraulic pressure (ΔP) in the DS as given by the equation below:

$$W = J_v \times \Delta P \quad 6-1$$

The water flux (J_v) was determined by measuring the weight loss of the FW using a digital balance (Mettler Toledo ML 6002) connected to a personal computer (PC) and calculated by dividing the volumetric flux with the effective membrane area as given by:

$$J_v = \frac{\Delta V}{\Delta t \times A_{eff}} \quad 6-2$$

where A_{eff} is the effective membrane area and ΔV is the volume of water that permeates from the feed to the draw solution over a time Δt during the PRO tests.

The reverse salt flux (J_s) was calculated from the change of the salt accumulation in the feed solution based on conductivity measurements (Li *et al.* 2013b):

$$J_s = \frac{V_2 \times C_2 - V_1 \times C_1}{A_{eff} \times (t_1 - t_2)} \quad 6-3$$

where V_2 and V_1 are the volumes of the feed solutions at time t_2 and t_1 , respectively; C_1 and C_2 are the salt concentrations of the feed solutions at time t_2 and t_1 , respectively.

The substrate structure parameter, S , is defined as the product of the thickness, l , and tortuosity, τ , over porosity, ϵ , as shown in equation below:

$$S = \frac{\tau \times l}{\epsilon} \quad 6-4$$

The S value of the TFC membrane, was estimated from the experimental water flux and specific salt flux in PRO by following equation (Chou *et al.* 2013):

$$S = \frac{D}{J_v} \ln \left(\frac{C_d - (J_v + A \times \Delta P) / A \beta R T + J_s / J_v}{C_f + J_s / J_v} \right) \quad 6-5$$

where D is the salt diffusion coefficient dependent on temperature and concentration (1.61×10^{-9} m²/s was used in this paper); C_d and C_f are the salt concentrations of the DS and FW respectively; β represents the van't Hoff coefficient; R is the universal gas constant; and T is the absolute temperature.

Figure 6-1 Schematic diagram of the lab-scale setup for PRO.

6.3 Results and discussion

6.3.1 Characteristics of nanofibrous supports incorporated with f-CNTs

Interfacial polymerization was utilized to synthesize the polyamide layer using the same formulation on the as-prepared tiered nanofibrous supports T1, T2 and T3 to give TFC membranes IP-T1, IP-T2 and IP-T3, respectively. The FE-SEM image of the PEI nanofibrous support T3 with tiered structure is shown in **Figure 6-2**. It can be seen that the thickness of the top fine fiber layer is around 14.9 μm , and 51 μm for the bottom coarse fiber layer. The two layers were connected smoothly. The fiber diameter distributions are summarized in **Figure 6-3**. As shown in **Figures 6-3A** and **6-3B**, the average fiber diameter of the fine fiber layer decreases from 184.2 ± 50 nm for pristine PEI to 142.8 ± 40 nm for f-CNT incorporated PEI due to the slight enhancement of the conductivity of f-CNT blended PEI dope. The fiber diameter of the bottom layer, in contrast, is tailored to be larger in an attempt to mitigate the effect of ICP and reduce the mass transfer resistance of the support. As shown in **Figure 6-3C**, the PEI nanofibers in the bottom layer possesses a diameter

of 287.4 ± 78.2 nm. **Figure 6-3D** illustrates a 24.1% increase in the tensile modulus of the pristine PEI nanofibrous support when its diameter decreases from 305 ± 121 nm to 184 ± 50 nm.

Figure 6-2 PEI nanofibrous support T3 with tiered structure. Note that the sample was prepared with the non-woven support peeled off.

Figure 6-3 Nanofiber diameter distribution of the designed layers.(A) finer fiber layer without CNT (B) finer fiber layer with CNT; (C) coarse fiber layer with CNT; (D) Mechanical properties of pure PEI nanofibrous support with various diameter distribution.

The TEM micrograph (**Figure 6-4A**) confirms the successful incorporation of CNTs inside the PEI nanofibers while preserving the PEI nanofibrous structure. The as-received multi-walled CNTs have an average length of 10 μm and a diameter of 11 nm (Goh *et al.* 2013). After dispersion by a probe sonicator, the f-CNTs were shortened with some of the tips of the multi-walled CNTs opened. The enlarged TEM image in **Figure 6-4B** further confirms the hollow structure of the multi-walled CNT with an opened tip.

Figure 6-4 (A) TEM image proves the existence of functionalized multi-walled carbon nanotubes (f-CNTs) inside the PEI nanofiber; (B) enlarged TEM image confirms the dark tubular features have the typical structure of multi-walled carbon nanotubes.

To understand the effects resulting from the incorporation of f-CNTs in the PEI nanofibrous support, three different supports were developed with their detailed fabrication parameters given in **Table 6-1**. All three supports have a dual-layered structure with a fine fiber layer on the top and a coarse fiber layer at the bottom. The T1 support was made with PEI layers without f-CNTs, the bottom layer of the T2 support was reinforced with f-CNTs, and both the top and bottom layers of the T3 support were reinforced by f-CNTs.

It can be observed from **Table 6-2** that the mean pore sizes of T1, T2 and T3 are 0.406 μm , 0.346 μm and 0.310 μm , respectively. The same descending trend is also found for the maximum pore size. This may be due to the slight increase in the spinning solution conductivity of the f-CNTs incorporated dopes, resulting in a decrease in the fiber diameter (Ra *et al.* 2005; Mazinani *et al.* 2009; Naebe *et al.* 2010). Compared with the pristine PEI support T1, the f-CNT reinforced supports of T2 and T3 show higher rigidity (tensile modulus) and much higher stretch resistances (yield strength). The improved tensile mechanical properties are a direct indication of its predicted outstanding pressure resistance in PRO testing, which is discussed later. For the conventional phase inversion method, the mechanical strength of the fabricated support is normally inversely proportional to its porosity

(Han *et al.* 2013a; Zhang *et al.* 2013). However, by incorporating f-CNTs into each nanofiber, it is possible to achieve increased mechanical strength and improved porosity simultaneously as demonstrated by the T3 support, which shows a ~15% and ~25% improvement in tensile modulus and yield strength respectively, while improving the porosity of the support by 10%. Previous studies have suggested that in engineered osmotic processes, a slight increase in porosity parameter (say ~10%) would be capable of reducing the ICP and maximizing the effective osmotic driving force, resulting in a 47% increase in FO water flux (Tiraferri *et al.* 2011). Thus, the TFC membranes incorporating f-CNTs are expected to have a greater pressure resistance to withstand the PRO process and at the same time to mitigate the ICP effect through improved mechanical properties and higher substrate porosity.

Table 6-2 Properties of nanofibrous substrates T1, T2 and T3.

Nanofibrous substrate	Mechanical strength			Mean pore size (μm)	Maximum Pore size (μm)	Average porosity (%)	Thickness (μm)
	Tensile Modulus (MPa)	Yield strength (MPa)	Elongation at yield (%)				
T1	319 ± 17	8.1 ± 1.0	7.0 ± 2.0	0.406 ± 0.056	0.531 ± 0.063	62 ± 4	91.8 ± 4.8
T2	353 ± 31	9.2 ± 0.8	7.4 ± 1.0	0.346 ± 0.024	0.434 ± 0.027	67 ± 5	96.9 ± 3.9
T3	366 ± 25	10.5 ± 1.6	7.6 ± 2.0	0.310 ± 0.096	0.390 ± 0.012	68 ± 4	92.3 ± 6.4

6.3.2 Characteristics of nanofibrous TFN membranes

Figure 6-5 shows the representative FE-SEM images of a typical PEI nanofibrous PRO membrane with a tiered structure. The surface morphology of the nanofibrous membrane support T3 before interfacial polymerization is shown in **Figure 6-5A**. It illustrates that the support consists of nanofibers which are overlapped and bonded together to form a 3-D integrated network. The inset shows that the support has a contact angle of around 130° due to the high roughness of the overlapped nanofibrous structure.

Figure 6-5 (A) Surface morphology of the top fine fiber layer before interfacial polymerization with average contact angle of 130° (inset picture); (B) Surface morphology after interfacial polymerization with average contact angle of $66 \pm 7^\circ$ (inset picture); (C) FE-SEM image of nanofibrous TFC membrane cross-sections; (D) Enlarged image of nanofiber layer underneath the polyamide layer; (E) Enlarged images of top fine fiber layer (inset top, scale bar 100 nm) and bottom coarse fiber layer (inset bottom, scale bar 100 nm), and the interface between these two layers.

A typical “ridge and valley” structured polyamide layer is observed above the nanofibrous layer after the interfacial polymerization process as illustrated in **Figure 6-5B**. As a result, the water contact angle of IP-T3 is reduced to $66 \pm 7^\circ$ as depicted in the insert, which is similar to other polyamide membranes reported in the literature. The low magnification FE-SEM image of the cross-sectional view shown in **Figure 6-5C** confirms the good integration of the nanofibrous layer with the non-woven support. No delamination is observed at the interface. Similarly to the structure of other developed nanofibrous supports mentioned elsewhere, this support consists of a 3-D network of overlapped and bonded nanofibers integrated with interconnected pore structures on a non-woven backing layer. The enlarged FE-SEM image in **Figure 6-5D** presents the cross-sectional morphologies of the top polyamide layer and the underneath. The image further confirms the excellent integration of the nanofibers and the polyamide layer. The thickness of the polyamide layer is roughly 200~400 nm, which is double the diameter of the fine

top fibers. It is thus reasonable to speculate that only one layer of the fine fibers is embedded as the backbone of the polyamide layer. The red arrows in **Figure 6-5D** indicate the region where the nanofibers integrate directly into the polyamide layer. This kind of combination of nanofibers with the polyamide layer helps strengthen the polyamide layer (Bui and McCutcheon 2013). **Figure 6-5E** clearly confirms that a tiered PEI nanofibrous support was successfully developed. The nanofibers are well bonded with each other and no delamination is observed within the nanofiber support. The top fine fiber layer (insert top image) has an average fiber diameter of 142.8 ± 40 nm in comparison to a diameter of 287.4 ± 78.2 nm in the bottom coarse fiber layer (insert bottom image).

To demonstrate the remarkable improvements in the endurance pressures of tiered structure nanofibrous supports, a control was synthesized by performing interfacial polymerization on a support made up of only PEI coarse nanofibers (287.4 ± 78.2 nm) incorporating f-CNTs, for comparison with the tiered IP-T3 membrane. The control sample only exhibited a pressure endurance of 10 bars before bursting. The FE-SEM images of the polyamide layer of IP-T3 membrane, as shown in **Figure 6-6**, show no obvious difference before and after PRO testing at 24 bar, but the polyamide layer of the control membrane is observed to collapse, and the pores generated by the coarse nanofibers can be seen. This suggests the strength of the thin fiber layer can help to reinforce the surface polyamide layer (Yoon *et al.* 2006).

Figure 6-6 Images of polyamide selective layer before and after PRO testing. (The fine fiber is the surface of T3 and coarse fiber is a control sample made from coarse fibers).

6.3.3 Osmosis performance of TFN membranes

Intrinsic permeability and structure parameter evaluations

Cross-flow RO testing was then utilized to characterize the intrinsic permeability of the prepared TFC membranes. **Table 6-3** summarizes the intrinsic separation properties of the skin layer and the substrate structure parameters of the aforementioned tiered TFC membranes. The three TFC membranes show similar water permeability coefficients (A values) in the range of 2.6 to 3.0 L/m² h·bar and salt rejections above 95% using NaCl solution at 10 bar hydraulic pressure. The structure parameters of the IP-T1, IP-T2 and IP-T3 are 649, 560, and 474 μm, respectively. Compared with the commercial CTA membrane, all the newly developed TFC membranes showed around 10 times higher water permeability with similar salt rejection and lower structure parameters. The significantly higher water permeability and relatively low structure parameter of the developed nanofibrous TFC membranes may be attributable to the open and highly porous surface of the nanofibrous supports.

Table 6-3 Intrinsic separation prosperities of prepared membranes

Membrane type	Water permeability coefficient, A (L m ⁻² h ⁻¹ bar ⁻¹)	Salt permeability coefficient, B (L m ⁻² h ⁻¹)	Salt rejection ^a , R (%)	Structure parameter , S (μm)
IP-T1	2.95 ± 0.38	0.84 ± 0.28	97.2 ± 1.0	649 ± 4 ^b
IP-T2	3.04 ± 0.07	1.39 ± 0.48	95.8 ± 1.2	560 ± 62 ^b
IP-T3	2.6 ± 0.04	0.98 ± 0.29	96.1 ± 1.3	474 ± 38.7 ^b
HTI-W	0.27 ± 0.08	0.05 ± 0.03	97.8 ± 0.8	1000 ± 540 ^c

^a A volume of 10 mM NaCl as the feed solution in cross-flow RO testing mode under applied pressure of 10 bar.

^b Calculate based on the experimental water and specific salt flux from PRO testing.

^c Obtained from reference (Wei *et al.* 2011b).

Figure 6-7 PRO performance versus different hydraulic pressures for three membranes (A) water flux; (B) power density. The data in the figures simply illustrate the trend using one set of experimental results but the replicates have been done to ensure reproducibility. (Testing conditions: 1.0 M NaCl as draw solution and DI water as feed water, flow rate at 400 ml/min in the cell)

PRO test results

Figure 6-7 presents the PRO performance versus different hydraulic pressures for the TFN membranes. In general, the water flux decreases linearly as the effective driving force ($\Delta\pi - \Delta P$) decreases with increasing applied pressure (ΔP) at the draw solution side. At the same testing hydraulic pressure, the order of water flux of these TFC membranes follows: IP-T3 > IP-T2 > IP-T1. This could be attributed to the smaller support structure parameters (S) and higher mechanical stability when f-CNTs are incorporated. In addition, the TFC membranes with f-CNTs reinforced

tiered nanofiber supports show good pressure resistance up to 22 bar for IP-T2 and 24 bar for IP-T3. The peak power density harvested from the membrane IP-T3 can reach 17.3 W/m^2 at a hydraulic pressure of 16.9 bar when using 1.0 M NaCl as DS against DI water as FW.

An interesting phenomenon was observed; that the water flux suddenly increases when the hydraulic pressure reaches a certain value for IP-T2 and IP-T3, as shown in region II in **Figure 6-7A**. This phenomenon deviates from the theoretical “linear decline” trend. For easy reference, we define this certain value as an “inflection point”. The data in the figures simply illustrate the trend using one set of experimental results but replicates have been performed to ensure reproducibility. The same phenomenon has also been observed in hollow fiber membranes (Chou *et al.* 2013; Han *et al.* 2013a) although it was not reported for nanofibrous membranes fabricated via electrospinning. This might be because the previous studies on nanofibrous membranes usually conduct a pre-pressurized treatment of their membranes near the burst pressure before the PRO evaluations (Song *et al.* 2013; Bui and McCutcheon 2014).

A possible reason for this interesting trend might be the deformation of the connected nanofibrous support under pressure, which results in an enlarged surface area and reduced thickness of the polyamide layer. A possible mechanism sketched in **Figure 6-8A** is proposed to help illustrate this deformation of the nanofibrous support. The membrane deformation process can be divided into three stages: stage I, stage II, and stage III. With reference to **Figure 6-7**, the region before the inflection point where water flux is observed to decline linearly is defined as stage I. No drastic deformation is observed in this stage. When the hydraulic pressure reaches the inflection point, the nanofiber support starts to suffer minor deformation and this may result in an expansion of the polyamide layer. This is defined as stage II and the expansion of the polyamide layer accounts for an increase in the water flux of the membrane. When the hydraulic pressure increases beyond the stage II, some connecting parts on the nanofibers would be broken and this results in permanent damage to the nanofibrous support, which is defined as stage III (in

region III in **Figure 6-7A**). The membrane at this stage become highly unstable and may burst at anytime with an increase in hydraulic pressure. A 50%~60% increase in water flux under low pressure PRO testing after pre-pressurized treatment shown in **Figure 6-8B** serves as an evidence of the permanent deformation of the membrane under high pressure. Due to the complex deformation of the nanofibrous membrane structure under high pressure, the burst pressures and the inflection points of different membranes may vary and these remain largely unpredictable without experimental support. However, the firm belief is that the pressure endurance of the nanofibrous support is strongly correlated to its individual fiber mechanical strength, fiber diameter, and assembly configuration.

Figure 6-8 (A) Hypothetical deduction of the deformation of the nanofibrous support under PRO testing. (B) PRO water flux of the membranes before and after pressurization at 15 bar.

The PRO performance of the IP-T3 membrane with a pre-pressurization treatment at 15 bar shows a similar trend in **Figure 6-9**. After the pre-pressurization treatment, the membrane shows comparatively stable flux during cycle testing. The long term stability of the nanofibrous membrane IP-T3 was evaluated in this study with its results presented in **Figure 6-10**. The burst pressure of the membrane for the long

term evaluation is ~ 24 bar. At a pressure of ~ 22 bar, where the peak power density is achieved, the membrane is able to maintain a flux of 23.2 ± 0.4 L/m² h and power density of 15.0 ± 0.5 W/m² for the test period of 10 h. During the period of the testing time, the J_s/J_v (salt back diffusion flux/water flux) remains unchanged. When the pressure is increased to ~ 24 bar, permanent damage to the membrane is observed.

Figure 6-9 PRO performance versus different hydraulic pressures of IP-T3 after compaction at 15 bar under RO condition for 2~4 hour. (A) water flux, (B) power density. (Testing conditions: 1.0 M NaCl as draw solution and DI water as feed water, flow rate at 400 ml/min in the cell).

Figure 6-10 Long term PRO performance of nanofibrous TFC membrane IP-T3. (A) water flux and power density; (B) J_s/J_v (salt back diffusion flux/water flux) (Testing condition: 1.0 M NaCl as draw and MilliQ as feed, $23 \pm 2^\circ\text{C}$, and dosing every 0.5~1 hour to regulate the conductivity of DS and FW)

6.4 Conclusions

In this study, tiered structured PEI nanofibrous supports were successfully fabricated for PRO, consisting of a thin fiber layer (average diameter 142.8 ± 40 nm) on the top and a coarse fiber layer (average diameter 287.4 ± 78.2 nm) at the bottom with both layers reinforced using f-CNTs. By incorporating f-CNTs into both nanofibers layers, we were able to achieve simultaneous improvements to both the mechanical properties and the porosities of the supports. The comparative pore size of the supports decreased with the addition of f-CNTs. Furthermore, our newly developed membranes have shown water permeability coefficients up to 10 times higher with similar salt rejections when compared to a commercial HTI-CTA membrane. The thin finer fiber with well dispersed f-CNTs is found to increase mechanical stability of the polyamide layer at high hydraulic pressure in the PRO process. Our best membrane with both fine and coarse fiber layers reinforced with f-CNTs can withstand a trans-membrane pressure up to 24 bar and generate a peak power density as high as 17.3 W/m^2 at 16.9 bar when using synthetic seawater brine (1.0 M NaCl) draw solution against DI water. To achieve a more significant mechanical enhancement to the polyamide layer, we suggest reducing the nanofiber diameter down to 100 nm or less in order to further increase the endurance pressure of the membrane. Through this approach, an ideal PRO membrane suitable for industrial application may be realized.

CHAPTER 7.

Conclusions and recommendations

7.1 Overall conclusions

Electrospinning is a feasible and effective method for fabricating a wide range of structured nanofibrous substrates. The unique structure of nanofibrous substrates, including an interconnected pore structure (low tortuosity), high porosity of up to 80%, and easy incorporation of nanoparticles (*e.g.*, silica and carbon nanotubes) into individual nanofibers, makes them highly attractive for many applications, including ODMPs. This thesis presents the development of nanofiber supported polyamide TFC and TFN membranes for ODMPs including FO and PRO. A series of novel nanofiber-supported TFC membranes were prepared with tailored structures and surface properties for FO and PRO applications.

To date, most substrate materials used for FO membranes are hydrophilic which limits their application in some harsh environments with chemical wastes. Hydrophobic materials such as PVDF possess strong chemical resistance, which could extend its application in this area. Therefore, PVDF nanofiber supported MPD-TMC based polyamide TFC membranes have been fabricated for FO in Chapter 3. The effect of the surface structure of the PVDF ENMs on the formation of the polyamide selective layer was investigated. The preparation conditions of TFC polyamide layer on the intrinsic separation properties of the resultant FO membrane were also examined. Finally, we evaluated the FO performance of the prepared membranes in two orientations. In Chapter 4, SiO₂ nanoparticles were

successfully incorporated into PEI nanofibrous supports, where a polyamide selective layer was formed. Results showed that the porosity of the support of SiO₂/PEI TFN membranes was improved upon addition of SiO₂ leading to a higher water flux. To further enhance the membrane osmotic water flux without sacrificing its mechanical strength, f-CNTs were incorporated in PEI nanofibers and were proved to effectively increase both the mechanical strength and osmotic water flux in Chapter 5. Additionally, to further improve the mechanical properties of electrospun nanofiber supported polyamide TFC membranes and investigate the f-CNTs incorporation effect on membrane performance in PRO system, tiered structured nanofibrous supports reinforced with carbon nanotubes were designed, constructed and evaluated in Chapter 6. All the membranes were characterized by standard protocols in terms of structure and morphology, pore size and pore size distribution, mechanical properties, intrinsic permeability, FO/PRO performance, etc.

The major findings and conclusions are summarized as follows:

- 1) PVDF nanofiber supported polyamide TFC FO membranes desirable for harsh environments with chemical wastes have been successfully developed. A RO-like polyamide selective layer was formed through interfacial polymerization with NMP and TMC on two hydrophobic PVDF nanofibrous substrates with different surface pore sizes ranging from 320 to 590 nm.
- 2) By comparing the two cases, it was found that it is easier to form a thin polyamide selective layer with a higher crosslinking density on an ENM substrate with smaller pore sizes. A denser polyamide selective layer was formed on the substrates which had smaller pore sizes (mean pore size of $0.32 \pm 0.07 \mu\text{m}$ and maximum pore size of $0.50 \pm 0.10 \mu\text{m}$), resulting in water permeability of $1.21 \text{ L/m}^2\text{h}\cdot\text{bar}$ and NaCl salt rejection of 93.6% at 5 bar pressure; while the other membrane prepared on the substrates with a mean pore size of $0.40 \pm 0.02 \mu\text{m}$ presented water permeability of $3.15 \text{ L/m}^2\text{h}\cdot\text{bar}$ and NaCl salt rejection of 84.4% under the same 5 bar pressure.

- 3) The two membranes showed excellent performance in a FO process because of their superior porous and interconnected open structure resulting in reduced ICP. The S value of the resultant membrane is as low as 0.315 mm, which is better than most of the FO membranes reported in the literature. As a result, a water flux of 30.4 L/m²h can be attained when using 1.0 M NaCl draw solution against DI water in the AL-DS orientation.
- 4) In this study, the incorporation of silica nanoparticles with different loadings (ranging from 0.16 wt% to 1.6 wt%) in PEI nanofibrous substrates was evaluated, with the purpose of improving FO membrane performance. The results showed that the pore size and porosity of the FO membrane substrate were increased upon the addition of silica nanoparticles, as the embedded nanoparticles helped the nanofibrous substrate better resist compaction during the heat-press treatment.
- 5) The highest silica loading led to a TFN membrane with the maximum substrate porosity (83%) and the smallest structure parameter (~174 μ m) in the current investigation, and this membrane also demonstrated the most promising osmotic water flux, i.e., ~49 and 89 L/m²h in the AL-FW and AL-DS orientations with 2 M NaCl DS against DI feed.
- 6) It was demonstrated for the first time that both the osmotic flux and mechanical strength of the FO membranes can be greatly improved by incorporating the f-CNTs in the nanofibrous substrates. It is very likely that the superb mechanical property of the embedded f-CNTs helped to reduce the porosity loss during membrane synthesis (*i.e.*, heat-press treatment). The membrane mechanical strength improvement provides an additional degree of freedom for further increasing substrate porosity and/or decreasing the thickness (*i.e.*, reducing the S value) to mitigate the ICP.
- 7) It was found that substrate incorporating f-CNTs had a higher porosity of

71%, as compared to that of the control substrate (59%). This observation was consistent with our hypothesis that a substrate with a higher mechanical strength may suffer less compression and thus less porosity loss during the heat-press treatment.

- 8) With the f-CNTs as fillers, increasing the substrate porosity without decreasing the mechanical strength (instead, increasing the mechanical strength in the current study) can be readily achieved.
- 9) It was revealed that the incorporation of f-CNTs reduced the substrate structure parameter (*i.e.*, S value). In both membrane orientations, the PEI nanofiber supported polyamide TFC membrane incorporated with f-CNTs had a higher water flux (20-30% increase) compared to the control membrane without f-CNTs incorporation, revealing it suffered less ICP. Hence, it is suggested that the f-CNT incorporation into the nanofibrous substrate is an effective strategy in reducing ICP and increasing FO water flux.
- 10) Novel tiered structured PEI nanofibrous supports consisting of a thin fiber layer (average diameter 142.8 ± 40.0 nm) on the top and a coarse fiber layer (average diameter 287.4 ± 78.2 nm) at the bottom, both being reinforced with f-CNTs, were successfully designed and fabricated for PRO process.
- 11) Through incorporation of f-CNTs into both nanofibers layers, we are able to achieve simultaneous improvements in both mechanical properties and porosity of the supports. The pore size of the supports was comparatively decreased with the addition of f-CNTs.
- 12) Furthermore, our newly developed membranes have shown a water permeability coefficient up to 10 times higher at a similar salt rejection when compared to the commercial HTI-CTA membrane.

13) The fine fiber with well dispersed f-CNTs is found to increase mechanical stability of the polyamide layer at high hydraulic pressure in the PRO process. Our best membrane with both fine and coarse fiber layers reinforced with f-CNTs can withstand a trans-membrane pressure up to 24 bar and generate a peak power density as high as 17.3 W/m^2 at 16.9 bar when using synthetic seawater brine (1.0 M NaCl) draw solution against DI water.

7.2 Recommendations for future research

In past decades, significant progress has been made in the development of electrospun nanofiber based ODMPs membranes. However, there is still much room for improvement in the following research areas.

- 1) Investigation of the preparation of thin-film polyamide selective layers with RO-like selectivity on a variety of nanofibrous substrates is one of focuses of this thesis. Future work could extend to ODMPs membranes with NF-like selective layers.
- 2) The nanomaterials strategy was only employed in designing the nanofibrous substrates for ODMPs in this thesis, without touching on the incorporation of nanomaterials into the polyamide selective layer. Nanomaterials (*e.g.*, zeolite, carbon nanotube, Aquaporin) may be incorporated in the polyamide selective layer to enhance the water permeation without losing its selectivity.
- 3) One major challenge in membrane processes is membrane fouling when treating heavy duty wastewater. Fouling is associated with the membrane materials used. Generally, hydrophilic membranes are less prone to absorptive fouling than hydrophobic membranes, making them more suitable for wastewater treatments. Future research could focus on the development of self-cleaning FO membranes and new anti-fouling materials.

- 4) To achieve a more significant mechanical enhancement to the polyamide layer, we suggest reducing the nanofiber diameter down to 100 nm or less. Through this approach, an ideal PRO membrane suitable for industrial application may be realized.
- 5) The techniques used to fabricate membranes strongly influence membrane behaviour and efficiency. To facilitate the commercialization of electrospun membranes for water industries on a large scale, more research is needed with respect to electrospinning setup design, fiber morphology control, production efficacy, etc.

REFERENCES

Achilli, A., et al. (2009a). "Power generation with pressure retarded osmosis: An experimental and theoretical investigation." Journal of Membrane Science Vol. 343 No. (1-2)pp.: 42-52.

Achilli, A., et al. (2009b). "The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes." Desalination Vol. 239 No. (1-3)pp.: 10-21.

Akin, O. and F. Temelli (2011). "Probing the hydrophobicity of commercial reverse osmosis membranes produced by interfacial polymerization using contact angle, XPS, FTIR, FE-SEM and AFM." Desalination Vol. 278 No. (1-3)pp.: 387-396.

Alsvik, I. and M.-B. Hägg (2013). "Pressure Retarded Osmosis and Forward Osmosis Membranes: Materials and Methods." Polymers Vol. 5 No. (1)pp.: 303-327.

Amini, M., et al. (2013). "Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes." Journal of Membrane Science Vol. 435 No. pp.: 233-241.

Arena, J. T., et al. (2011). "Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis." Journal of Membrane Science Vol. 375 No. (1-2)pp.: 55-62.

Armaroli, N. and V. Balzani (2007). "The Future of Energy Supply: Challenges and Opportunities." Angewandte Chemie International Edition Vol. 46 No. (1-2)pp.: 52-66.

Baek, W. I., et al. (2012). "Mechanical property enhancement of non-bonding electrospun mats via adhesive." Polymer International Vol. 61 No. (5)pp.: 844-849.

Barakat, N. A. M., et al. (2009). "Spider-net within the N6, PVA and PU electrospun nanofiber mats using salt addition: Novel strategy in the electrospinning process." Polymer Vol. 50 No. (18)pp.: 4389-4396.

Bemporad, G. A. (1992). "The Use of Pressure-Retarded Osmosis for Increasing the Solar Pond Efficiency." Solar Energy Vol. 48 No. (6)pp.: 375-379.

Bergin, S. D., et al. (2009). "Multicomponent solubility parameters for single-walled carbon nanotube-solvent mixtures." ACS Nano Vol. 3 No. (8)pp.: 2340-2350.

Bhardwaj, N. and S. C. Kundu (2010). "Electrospinning: A fascinating fiber fabrication technique." Biotechnology Advances Vol. 28 No. (3)pp.: 325-347.

Bui, N. N., et al. (2011). "Electrospun nanofiber supported thin film composite membranes for engineered osmosis." Journal of Membrane Science Vol. 385 No. (1-2)pp.: 10-19.

Bui, N. N. and J. R. McCutcheon (2013). "Hydrophilic nanofibers as new supports for thin film composite membranes for engineered osmosis." Environmental Science & Technology Vol. 47 No. (3)pp.: 1761-1769.

Bui, N. N. and J. R. McCutcheon (2014). "Nanofiber supported thin-film composite membrane for pressure-retarded osmosis." Environmental Science & Technology Vol. 48 No. (7)pp.: 4129-4136.

Cartinella, J., et al. (2006). "Removal of natural steroid hormones from wastewater using membrane contactor processes." Environmental Science & Technology Vol. 40 No. (23)pp.: 7381-7386.

Cath, T. Y., et al. (2005). "Membrane contactor processes for wastewater reclamation in space." Journal of Membrane Science Vol. 257 No. (1-2)pp.: 111-119.

Cath, T. Y., et al. (2006). "Forward osmosis: Principles, applications, and recent developments." Journal of Membrane Science Vol. 281 No. (1-2)pp.: 70-87.

Chen, C., et al. (2013). "Morphology and performances of electrospun polyethylene glycol/poly (dl-lactide) phase change ultrafine fibers for thermal energy storage." Solar Energy Materials and Solar Cells Vol. 117 No. pp.: 372-381.

Choi, Y. J., et al. (2009). "Toward a combined system of forward osmosis and reverse osmosis for seawater desalination." Desalination Vol. 247 No. (1-3)pp.: 239-246.

Chou, S., et al. (2010). "Characteristics and potential applications of a novel forward osmosis hollow fiber membrane." Desalination Vol. 261 No. (3)pp.: 365-372.

Chou, S., et al. (2013). "Robust and High performance hollow fiber membranes for energy harvesting from salinity gradients by pressure retarded osmosis." Journal of Membrane Science Vol. 448 No. pp.: 44-54.

Chou, S., et al. (2012). "Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density." Journal of Membrane Science Vol. 389 No. (0)pp.: 25-33.

Coday, B. D., et al. (2014). "The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams." Desalination Vol. 333 No. (1)pp.: 23-35.

Cornelissen, E. R., et al. (2008). "Membrane fouling and process performance of forward osmosis membranes on activated sludge." Journal of Membrane Science Vol. 319 No. (1-2)pp.: 158-168.

Cui, Y., et al. (2014). "Enhanced osmotic energy generation from salinity gradients by modifying thin film composite membranes." Chemical Engineering Journal Vol. 242 No. pp.: 195-203.

Deitzel, J. M., et al. (2001). "The effect of processing variables on the morphology of electrospun nanofibers and textiles." Polymer Vol. 42 No. (1)pp.: 261-272.

Dumée, L., et al. (2013). "Fabrication of thin film composite poly(amide)-carbon-nanotube supported membranes for enhanced performance in osmotically driven desalination systems." Journal of Membrane Science Vol. 427 No. pp.: 422-430.

Elimelech, M. (2007). "Yale constructs forward osmosis desalination pilot plant." Membrane Technology Vol. 2007 No. (1)pp.: 7-8.

Emadzadeh, D., et al. (2013). "Synthesis of thin film nanocomposite forward osmosis membrane with enhancement in water flux without sacrificing salt rejection." Desalination Vol. 330 No. (0)pp.: 90-99.

Emadzadeh, D., et al. (2014a). "Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization." Journal of Membrane Science Vol. 449 No. pp.: 74-85.

Emadzadeh, D., et al. (2014b). "A novel thin film composite forward osmosis membrane prepared from PSf-TiO₂ nanocomposite substrate for water desalination." Chemical Engineering Journal Vol. 237 No. (0)pp.: 70-80.

Enomoto, H., et al. (2010). "A feasibility study of pressure-retarded osmosis power generation system based on measuring permeation volume using reverse osmosis membrane." Electrical Engineering in Japan Vol. 173 No. (2)pp.: 8-20.

Feng, C., et al. (2008). "Production of drinking water from saline water by air-gap membrane distillation using polyvinylidene fluoride nanofiber membrane." Journal of Membrane Science Vol. 311 No. (1-2)pp.: 1-6.

Fong, H., et al. (1999). "Beaded nanofibers formed during electrospinning." Polymer Vol. 40 No. (16)pp.: 4585-4592.

Fong, H. and D. H. Reneker (2000). Electrospinning and the formation of nanofibers. Cincinnati, Ohio, Hanser.

Frolov, A. I., et al. (2012). "Molecular mechanisms of salt effects on carbon nanotube dispersions in an organic solvent (N-methyl-2-pyrrolidone)." Chemical Science Vol. 3 No. (2)pp.: 541-548.

Garcia-Castello, E. M. and J. R. McCutcheon (2011). "Dewatering press liquor derived from orange production by forward osmosis." Journal of Membrane Science Vol. 372 No. (1-2)pp.: 97-101.

Ge, J. J., et al. (2004). "Assembly of well-aligned multiwalled carbon nanotubes in confined polyacrylonitrile environments: electrospun composite nanofiber sheets." Journal of the American Chemical Society Vol. 126 No. (48)pp.: 15754-15761.

Ge, Q., et al. (2012). "Polyelectrolyte-promoted forward osmosis-membrane distillation (FO-MD) hybrid process for dye wastewater treatment." Environmental Science & Technology Vol. 46 No. (11)pp.: 6236-6243.

Geise, G. M., et al. (2010). "Water Purification by Membranes: The Role of Polymer Science." Journal of Polymer Science Part B-Polymer Physics Vol. 48 No. (15)pp.: 1685-1718.

Gerstandt, K., et al. (2008). "Membrane processes in energy supply for an osmotic power plant." Desalination Vol. 224 No. (1-3)pp.: 64-70.

Ghosh, A. K. and E. M. V. Hoek (2009). "Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes." Journal of Membrane Science Vol. 336 No. (1-2)pp.: 140-148.

Gibson, P., et al. (2001). "Transport properties of porous membranes based on electrospun nanofibers." Colloids and Surfaces a-Physicochemical and Engineering Aspects Vol. 187 No. pp.: 469-481.

Goh, K., et al. (2013). "Fabrication of novel functionalized multi-walled carbon nanotube immobilized hollow fiber membranes for enhanced performance in forward osmosis process." Journal of Membrane Science Vol. 446 No. pp.: 244-254.

Gopal, R., et al. (2006). "Electrospun nanofibrous filtration membrane." Journal of Membrane Science Vol. 281 No. (1–2)pp.: 581-586.

Han, G. and T.-S. Chung (2014). "Robust and high performance pressure retarded osmosis hollow fiber membranes for osmotic power generation." AIChE Journal Vol. 60 No. (3)pp.: 1107-1119.

Han, G., et al. (2012). "Thin-film composite forward osmosis membranes with novel hydrophilic supports for desalination." Journal of Membrane Science Vol. 423–424 No. (0)pp.: 543-555.

Han, G., et al. (2013a). "Highly robust thin-film composite pressure retarded osmosis (PRO) hollow fiber membranes with high power densities for renewable salinity-gradient energy generation." Environmental Science & Technology Vol. 47 No. (14)pp.: 8070-8077.

Han, G., et al. (2013b). "High performance thin film composite pressure retarded osmosis (PRO) membranes for renewable salinity-gradient energy generation." Journal of Membrane Science Vol. 440 No. pp.: 108-121.

Hancock, N. T., et al. (2011). "Comprehensive bench- and pilot-scale investigation of trace organic compounds rejection by forward osmosis." Environmental Science & Technology Vol. 45 No. (19)pp.: 8483-8490.

He, J.-H., et al. (2005). "Critical length of straight jet in electrospinning." Polymer Vol. 46 No. (26)pp.: 12637-12640.

Hoehn H, H. (1985). Aromatic Polyamide Membranes. Materials Science of Synthetic Membranes. American Chemical Society. 269pp.: 81-98.

Holloway, R., et al. (2007). "Forward osmosis for concentration of anaerobic digester centrate." Water Research Vol. 41 No. (17)pp.: 4005-4014.

Homaeigohar, S. S. and M. Elbahri (2012). "Novel compaction resistant and ductile nanocomposite nanofibrous microfiltration membranes." Journal of colloid and interface science Vol. 372 No. (1)pp.: 6-15.

Hoover, L. A., et al. (2013). "Nanofibers in thin-film composite membrane support layers: Enabling expanded application of forward and pressure retarded osmosis." Desalination Vol. 308 No. (0)pp.: 73-81.

Hu, D., et al. (2013). "A high performance silica–fluoropolyamide nanofiltration membrane prepared by interfacial polymerization." Separation and Purification Technology Vol. 110 No. (0)pp.: 31-38.

Hu, J., et al. (2011). "One-step Electro-spinning/netting Technique for Controllably Preparing Polyurethane Nano-fiber/net." Macromolecular Rapid Communications Vol. 32 No. (21)pp.: 1729-1734.

Huang, L., et al. (2013a). "Novel hydrophilic nylon 6,6 microfiltration membrane supported thin film composite membranes for engineered osmosis." Journal of Membrane Science Vol. 437 No. pp.: 141-149.

Huang, L., et al. (2013b). "Increasing strength of electrospun nanofiber membranes for water filtration using solvent vapor." Journal of Membrane Science Vol. 436 No. pp.: 213-220.

Huang, Z.-M., et al. (2003). "A review on polymer nanofibers by electrospinning and their applications in nanocomposites." Composites Science and Technology Vol. 63 No. (15)pp.: 2223-2253.

Huebner, A. L. and H. N. Chu (1971). "Instability and breakup of charged liquid jets." Journal of Fluid Mechanics Vol. 49 No. (02)pp.: 361-372.

Isaacs, J. D. and W. R. Schmitt (1980). "Ocean energy: Form and Prospects." Science Vol. 207 No. pp.: 265-273.

Jadav, G. L. and P. S. Singh (2009). "Synthesis of novel silica-polyamide nanocomposite membrane with enhanced properties." Journal of Membrane Science Vol. 328 No. (1-2)pp.: 257-267.

Jellinek, H. H. G. and H. Masuda (1981). "OSMO-POWER - THEORY AND PERFORMANCE OF AN OSMO-POWER PILOT-PLANT." Ocean Engineering Vol. 8 No. (2)pp.: 103-128.

Jin, X., et al. (2012a). "Rejection of pharmaceuticals by forward osmosis membranes." Journal of Hazardous Materials Vol. 227-228 No. pp.: 55-61.

Jin, X., et al. (2012b). "Removal of boron and arsenic by forward osmosis membrane: Influence of membrane orientation and organic fouling." Journal of Membrane Science Vol. 389 No. (0)pp.: 182-187.

Karagiannis, I. C. and P. G. Soldatos (2008). "Water desalination cost literature: review and assessment." Desalination Vol. 223 No. (1-3)pp.: 448-456.

Kaur, S., et al. (2012). "Formation and characterization of polyamide composite electrospun nanofibrous membranes for salt separation." Journal of Applied Polymer Science Vol. 124 No. pp.: E205-E215.

Kim, E.-S., et al. (2009). "Preparation and characterization of polyamide thin-film composite (TFC) membranes on plasma-modified polyvinylidene fluoride (PVDF)." Journal of Membrane Science Vol. 344 No. (1-2)pp.: 71-81.

Kim, Y. and M. Elimelech (2012). "Adverse impact of feed channel spacers on the performance of pressure retarded osmosis." Environmental Science & Technology Vol. 46 No. (8)pp.: 4673-4681.

Lay, W. C. L., et al. (2011). "Study of integration of forward osmosis and biological process: Membrane performance under elevated salt environment." Desalination Vol. 283 No. pp.: 123-130.

Lee, J., et al. (2007). "Measurement of the dispersion stability of pristine and surface-modified multiwalled carbon nanotubes in various nonpolar and polar solvents." Measurement Science & Technology Vol. 18 No. (12)pp.: 3707-3712.

Lee, K. H., et al. (2003). "The change of bead morphology formed on electrospun polystyrene fibers." Polymer Vol. 44 No. (14)pp.: 4029-4034.

Lee, K. L., et al. (1981). "Membranes for power generation by pressure-retarded osmosis." Journal of Membrane Science Vol. 8 No. (2)pp.: 141-171.

Lee, R. (2011). "The Outlook for Population Growth." Science Vol. 333 No. (6042)pp.: 569-573.

Li, D., et al. (2006). "Characterization of nanofibrous membranes with capillary flow porometry." Journal of Membrane Science Vol. 286 No. (1-2)pp.: 104-114.

Li, X., et al. (2015a). "Nature gives the best solution for desalination: Aquaporin-based hollow fiber composite membrane with superior performance." Journal of Membrane Science Vol. 494 No. pp.: 68-77.

Li, X., et al. (2013a). "Effects of free volume in thin-film composite membranes on osmotic power generation." AIChE Journal Vol. 59 No. (12)pp.: 4749-4761.

Li, X., et al. (2013b). "Deformation and reinforcement of thin-film composite (TFC) polyamide-imide (PAI) membranes for osmotic power generation." Journal of Membrane Science Vol. 434 No. pp.: 204-217.

Li, Y., et al. (2015b). "Structural stability and mass transfer properties of pressure retarded osmosis (PRO) membrane under high operating pressures." Journal of Membrane Science Vol. 488 No. pp.: 143-153.

Li, Z.-Y., et al. (2012). "Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis." Water Research Vol. 46 No. (1)pp.: 195-204.

Liao, Y., et al. (2013a). "Engineering superhydrophobic surface on poly(vinylidene fluoride) nanofiber membranes for direct contact membrane distillation." Journal of Membrane Science Vol. 440 No. (0)pp.: 77-87.

Liao, Y., et al. (2013b). "Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation." Journal of Membrane Science Vol. 425 No. pp.: 30-39.

Lin, J., et al. (2012). "Mechanical robust and thermal tolerant nanofibrous membrane for nanoparticles removal from aqueous solution." Materials Letters Vol. 69 No. pp.: 82-85.

Lin, T., et al. (2004). "The charge effect of cationic surfactants on the elimination of fibre beads in the electrospinning of polystyrene." Nanotechnology Vol. 15 No. (9)pp.: 1375-1381.

Linares, R. a., et al. (2013). "Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance." Journal of Membrane Science Vol. 447 No. pp.: 50-56.

Liu, T., et al. (2007). "Preparation and characterization of carbon nanotube/polyetherimide nanocomposite films." Composites Science and Technology Vol. 67 No. (3-4)pp.: 406-412.

Lloyd, D. R. (1985). Membrane Materials Science. Materials Science of Synthetic Membranes. American Chemical Society. 269pp.: 1-21.

Lloyd, D. R. and T. B. Meluch (1985). Selection and Evaluation of Membrane Materials for Liquid Separations. Materials Science of Synthetic Membranes. American Chemical Society. 269pp.: 47-79.

Loeb, S. (1976). "Production of energy from concentrated brines by pressure-retarded osmosis : I. Preliminary technical and economic correlations." Journal of Membrane Science Vol. 1 No. pp.: 49-63.

Loeb, S. (1998). "Energy production at the Dead Sea by pressure-retarded osmosis: challenge or chimera?" Desalination Vol. 120 No. (3)pp.: 247-262.

Loeb, S. (2001). "One hundred and thirty benign and renewable megawatts from Great Salt Lake? The possibilities of hydroelectric power by pressure-retarded osmosis." Desalination Vol. 141 No. (1)pp.: 85-91.

Loeb, S. (2002). "Large-scale power production by pressure-retarded osmosis, using river water and sea water passing through spiral modules." Desalination Vol. 143 No. (2)pp.: 115-122.

Loeb, S. and G. D. Mehta (1979). "A two-coefficient water transport equation for pressure-retarded osmosis." Journal of Membrane Science Vol. 4 No. pp.: 351-362.

Loeb, S. and R. S. Norman (1975). "Osmotic power plants." Science Vol. 189 No. (4203)pp.: 654-655.

Loeb, S., et al. (1976). "Production of energy from concentrated brines by pressure-retarded osmosis : II. Experimental results and projected energy costs." Journal of Membrane Science Vol. 1 No. pp.: 249-269.

Loh, C., et al. (2015). Fabrication of Polymeric and Composite Membranes. Membrane Fabrication. CRC Press. pp.: 511-568.

Lutchmiah, K., et al. (2014). "Forward osmosis for application in wastewater treatment: a review." Water Research Vol. 58 No. pp.: 179-197.

Ma, N., et al. (2012). "Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis." Journal of Membrane Science Vol. 405-406 No. pp.: 149-157.

Ma, N., et al. (2013). "Nanocomposite substrates for controlling internal concentration polarization in forward osmosis membranes." Journal of Membrane Science Vol. 441 No. pp.: 54-62.

Ma, Z. W., et al. (2005). "Electrospun cellulose nanofiber as affinity membrane." Journal of Membrane Science Vol. 265 No. (1-2)pp.: 115-123.

Mazinani, S., et al. (2009). "Morphology, structure and properties of conductive PS/CNT nanocomposite electrospun mat." Polymer Vol. 50 No. (14)pp.: 3329-3342.

Mehta, G. D. and S. Loeb (1978). "Internal polarization in the porous substructure of a semipermeable membrane under pressure-retarded osmosis." Journal of Membrane Science Vol. 4 No. pp.: 261-265.

Mehta, G. D. L., S. (1979). "Performance of permasep B-9 and B-10 membranes in various osmotic regions and at high osmotic pressures." Journal of Membrane Science Vol. 4 No. pp.: 335-349.

Mulder, M. (1996). Basic principles of membrane technology. Springer Science & Business Media.

Na, H., et al. (2008). "Effect of hot-press on electrospun poly(vinylidene fluoride) membranes." Polymer Engineering and Science Vol. 48 No. (5)pp.: 934-940.

Naebe, M., et al. (2010). Carbon Nanotubes Reinforced Electrospun Polymer Nanofibres. Nanofibers. A. Kumar. Vienna, Austria, InTech. pp. 209-228.

Nijmeijer, K. and S. Metz (2010). Chapter 5 Salinity Gradient Energy. Sustainability Science and Engineering. C. E. Isabel and I. S. Andrea. Elsevier. Volume 2pp.: 95-139.

Norman, R. S. (1974). "Water salination: a source of energy." Science Vol. 186 No. (4161)pp.: 350-352.

Oki, T. and S. Kanae (2006). "Global Hydrological Cycles and World Water Resources." Science Vol. 313 No. (5790)pp.: 1068-1072.

Ong, R. C., et al. (2015). "Novel cellulose ester substrates for high performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes." Journal of Membrane Science Vol. 473 No. pp.: 63-71.

Papkov, D., et al. (2013). "Simultaneously strong and tough ultrafine continuous nanofibers." ACS nano Vol. 7 No. (4)pp.: 3324-3331.

Pattle, R. E. (1954). "production of electric power by mixing fresh and salt water in the hydroelectric pile." Nature Vol. 174 No. (4431)pp.: 660.

Pendergast, M. T. M., et al. (2010). "Using nanocomposite materials technology to understand and control reverse osmosis membrane compaction." Desalination Vol. 261 No. (3)pp.: 255-263.

Post, J. W., et al. (2007). "Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis." Journal of Membrane Science Vol. 288 No. (1-2)pp.: 218-230.

Qi, S., et al. (2011). "Synthesis and characterization of novel forward osmosis membranes based on layer-by-layer assembly." Environmental Science & Technology Vol. 45 No. (12)pp.: 5201-5208.

Qi, S., et al. (2012). "Double-skinned forward osmosis membranes based on layer-by-layer assembly—FO performance and fouling behavior." Journal of Membrane Science Vol. 405-406 No. pp.: 20-29.

Qin, X.-H. and S.-Y. Wang (2006). "Filtration properties of electrospinning nanofibers." Journal of Applied Polymer Science Vol. 102 No. (2)pp.: 1285-1290.

Qiu, C., et al. (2012). "High performance flat sheet forward osmosis membrane with an NF-like selective layer on a woven fabric embedded substrate." Desalination Vol. 287 No. pp.: 266-270.

Qiu, S., et al. (2009). "Preparation and properties of functionalized carbon nanotube/PSF blend ultrafiltration membranes." Journal of Membrane Science Vol. 342 No. (1-2)pp.: 165-172.

Ra, E. J., et al. (2005). "Anisotropic electrical conductivity of MWCNT/PAN nanofiber paper." Chemical Physics Letters Vol. 413 No. (1)pp.: 188-193.

Ramakrishna, S., et al. (2006). "Electrospun nanofibers: solving global issues." Materials Today Vol. 9 No. (3)pp.: 40-50.

Real, M. (1981). "Submarine hydro-electro-osmotic power plants for an efficient exploitation of salinity gradients." Energy Vol. 6 No. (3)pp.: 227-231.

Reneker, D. H. and I. Chun (1996). "Nanometre diameter fibres of polymer, produced by electrospinning." Nanotechnology Vol. 7 No. (3)pp.: 216-223.

Reneker, D. H. and H. Fong (2006). Polymeric Nanofibers: Introduction. Polymeric Nanofibers. American Chemical Society. 918pp.: 1-6.

Reneker, D. H., et al. (2002). "Nanofiber garlands of polycaprolactone by electrospinning." Polymer Vol. 43 No. (25)pp.: 6785-6794.

Reneker, D. H. and A. L. Yarin (2008). "Electrospinning jets and polymer nanofibers." Polymer Vol. 49 No. (10)pp.: 2387-2425.

Reneker, D. H., et al. (2000). "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning." Journal of Applied Physics Vol. 87 No. (9)pp.: 4531-4547.

Roh, I. J., et al. (2006). "Synthesis and characterization of interfacially polymerized polyamide thin films." Desalination Vol. 191 No. (1)pp.: 279-290.

Rutledge, G. C. and S. V. Fridrikh (2007). "Formation of fibers by electrospinning." Advanced Drug Delivery Reviews Vol. 59 No. (14)pp.: 1384-1391.

Ryu, Y. J., et al. (2003). "Transport properties of electrospun nylon 6 nonwoven mats." European Polymer Journal Vol. 39 No. (9)pp.: 1883-1889.

Sairam, M., et al. (2011). "Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis—Desalination using MgSO₄ draw solution." Desalination Vol. 273 No. (2-3)pp.: 299-307.

Salalha, W., et al. (2004). "Single-Walled Carbon Nanotubes Embedded in Oriented Polymeric Nanofibers by Electrospinning." Langmuir Vol. 20 No. (22)pp.: 9852-9855.

Saraf, A., et al. (2014). "Poly(vinyl) alcohol coating of the support layer of reverse osmosis membranes to enhance performance in forward osmosis." Desalination Vol. 333 No. (1)pp.: 1-9.

Setiawan, L., et al. (2011). "Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer." Journal of Membrane Science Vol. 369 No. (1-2)pp.: 196-205.

She, Q., et al. (2013). "Effect of feed spacer induced membrane deformation on the performance of pressure retarded osmosis (PRO): Implications for PRO process operation." Journal of Membrane Science Vol. 445 No. (0)pp.: 170-182.

Shin, Y. M., et al. (2001a). "Electrospinning: A whipping fluid jet generates submicron polymer fibers." Applied Physics Letters Vol. 78 No. (8)pp.: 1149-1151.

Shin, Y. M., et al. (2001b). "Experimental characterization of electrospinning: the electrically forced jet and instabilities." Polymer Vol. 42 No. (25)pp.: 09955-09967.

Sill, T. J. and H. A. von Recum (2008). "Electrospinning: applications in drug delivery and tissue engineering." Biomaterials Vol. 29 No. (13)pp.: 1989-2006.

Singh, P. S., et al. (2006). "Probing the structural variations of thin film composite RO membranes obtained by coating polyamide over polysulfone membranes of different pore dimensions." Journal of Membrane Science Vol. 278 No. (1-2)pp.: 19-25.

Skilhagen, S. E., et al. (2008). "Osmotic power -- power production based on the osmotic pressure difference between waters with varying salt gradients." Desalination Vol. 220 No. (1-3)pp.: 476-482.

Song, X., et al. (2011). "Nano gives the answer: breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate." Advanced Materials Vol. 23 No. (29)pp.: 3256-3260.

Song, X., et al. (2013). "Energy recovery from concentrated seawater brine by thin-film nanofiber composite pressure retarded osmosis membranes with high power density." Energy & Environmental Science Vol. 6 No. (4)pp.: 1199-1210.

Spitalsky, Z., et al. (2010). "Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties." Progress in Polymer Science Vol. 35 No. (3)pp.: 357-401.

Straub, A. P., et al. (2014). "Raising the Bar: Increased Hydraulic Pressure Allows Unprecedented High Power Densities in Pressure-Retarded Osmosis." Environmental Science & Technology Letters Vol. 1 No. (1)pp.: 55-59.

Su, J., et al. (2012). "Enhanced double-skinned FO membranes with inner dense layer for wastewater treatment and macromolecule recycle using Sucrose as draw solute." Journal of Membrane Science Vol. 396 No. pp.: 92-100.

Su, J., et al. (2010). "Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes." Journal of Membrane Science Vol. 355 No. (1-2)pp.: 36-44.

Subbiah, T., et al. (2005). "Electrospinning of nanofibers." Journal of Applied Polymer Science Vol. 96 No. (2)pp.: 557-569.

Sukitpaneevit, P. and T.-S. Chung (2012). "High performance thin-film composite forward osmosis hollow fiber membranes with macrovoid-free and highly porous structure for sustainable water production." Environmental Science & Technology Vol. 46 No. (13)pp.: 7358-7365.

Sun, B., et al. (2014). "Advances in three-dimensional nanofibrous macrostructures via electrospinning." Progress in Polymer Science Vol. 39 No. (5)pp.: 862-890.

Talwar, S., et al. (2010). "Electrospun Nanofibers with Associative Polymer-Surfactant Systems." Macromolecules Vol. 43 No. (18)pp.: 7650-7656.

Tan, C. H. and H. Y. Ng (2010). "A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system configuration." Desalination and Water Treatment Vol. 13 No. (1-3)pp.: 356-361.

Tang, C. Y., et al. (2007). "Probing the nano- and micro-scales of reverse osmosis membranes—A comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements." Journal of Membrane Science Vol. 287 No. (1)pp.: 146-156.

Tang, C. Y., et al. (2010). "Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration." Journal of Membrane Science Vol. 354 No. (1-2)pp.: 123-133.

Taylor, G. (1964). "Disintegration of Water Drops in an Electric Field." Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences Vol. 280 No. (1382)pp.: 383-397.

Taylor, G. (1969). "Electrically Driven Jets." Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences Vol. 313 No. (1515)pp.: 453-475.

Thorsen, T. and T. Holt (2009). "The potential for power production from salinity gradients by pressure retarded osmosis." Journal of Membrane Science Vol. 335 No. (1-2)pp.: 103-110.

Tian, M., et al. (2013). "Preparation of polyamide thin film composite forward osmosis membranes using electrospun polyvinylidene fluoride (PVDF) nanofibers as substrates." Separation and Purification Technology Vol. 118 No. pp.: 727-736.

Tiraferri, A., et al. (2012). "Highly hydrophilic thin-film composite forward osmosis membranes functionalized with surface-tailored nanoparticles." ACS Appl Mater Interfaces Vol. 4 No. (9)pp.: 5044-5053.

Tiraferri, A., et al. (2011). "Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure." Journal of Membrane Science Vol. 367 No. (1-2)pp.: 340-352.

Vandezande, P., et al. (2008). "Solvent resistant nanofiltration: separating on a molecular level." Chemical Society Reviews Vol. 37 No. (2)pp.: 365-405.

Vankelecom, I. F. J., et al. (2005). Nanofiltration. Principles and Applications. A. I. Schafer, A. G. Fane and T. D. White. Oxford, Elsevier. pp.: 33-65.

Vorosmarty, C. J., et al. (2010). "Global threats to human water security and river biodiversity." Nature Vol. 467 No. (7315)pp.: 555-561.

Wan, C. F. and T.-S. Chung (2015). "Osmotic power generation by pressure retarded osmosis using seawater brine as the draw solution and wastewater retentate as the feed." Journal of Membrane Science Vol. 479 No. pp.: 148-158.

Wang, H., et al. (2012). "Highly permeable and selective pore-spanning biomimetic membrane embedded with aquaporin Z." Small Vol. 8 No. (8)pp.: 1185-1190, 1125.

Wang, K. Y., et al. (2007). "Polybenzimidazole (PBI) nanofiltration hollow fiber membranes applied in forward osmosis process." Journal of Membrane Science Vol. 300 No. (1-2)pp.: 6-12.

Wang, R., et al. (2010a). "Characterization of novel forward osmosis hollow fiber membranes." Journal of Membrane Science Vol. 355 No. (1-2)pp.: 158-167.

Wang, X., et al. (2005). "High flux filtration medium based on nanofibrous substrate with hydrophilic nanocomposite coating." Environmental Science & Technology Vol. 39 No. (19)pp.: 7684-7691.

Wang, X., et al. (2011). "Large-scale fabrication of two-dimensional spider-web-like gelatin nano-nets via electro-netting." Colloids and Surfaces B: Biointerfaces Vol. 86 No. (2)pp.: 345-352.

Wang, X., et al. (2006). "High performance ultrafiltration composite membranes based on poly(vinyl alcohol) hydrogel coating on crosslinked nanofibrous poly(vinyl alcohol) scaffold." Journal of Membrane Science Vol. 278 No. (1-2)pp.: 261-268.

Wang, Y.-N., et al. (2010b). "Direct microscopic observation of forward osmosis membrane fouling." Environmental Science and Technology Vol. 44 No. (18)pp.: 7102-7109.

Wang, Y., et al. (2013). "Preparation of polyethersulfone/carbon nanotube substrate for high-performance forward osmosis membrane." Desalination Vol. 330 No. (0)pp.: 70-78.

Wei, J., et al. (2011a). "Influence of monomer concentrations on the performance of polyamide-based thin film composite forward osmosis membranes." Journal of Membrane Science Vol. 381 No. (1-2)pp.: 110-117.

Wei, J., et al. (2011b). "Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes." Journal of Membrane Science Vol. 372 No. (1-2)pp.: 292-302.

Wick, G. L. (1978). "Power from salinity gradients." Energy Vol. 3 No. (1)pp.: 95-100.

Wijmans, J. G. and R. W. Baker (2006). The Solution-Diffusion Model: A Unified Approach to Membrane Permeation. Materials Science of Membranes for Gas and Vapor Separation. John Wiley & Sons, Ltd. pp.: 159-189.

Wongchitphimon, S., et al. (2011). "Surface modification of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) hollow fiber membrane for membrane gas absorption." Journal of Membrane Science Vol. 381 No. (1-2)pp.: 183-191.

Wu, H., et al. (2010). "Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite." Journal of Membrane Science Vol. 362 No. (1-2)pp.: 374-383.

Xie, M., et al. (2012). "Rejection of pharmaceutically active compounds by forward osmosis: Role of solution pH and membrane orientation." Separation and Purification Technology Vol. 93 No. pp.: 107-114.

Xu, Y., et al. (2010). "Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis performance in a spiral wound module." Journal of Membrane Science Vol. 348 No. (1-2)pp.: 298-309.

Yang, S., et al. (2011). "Controllable fabrication of soap-bubble-like structured polyacrylic acid nano-nets via electro-netting." Nanoscale Vol. 3 No. (2)pp.: 564-568.

Yarin, A. L., et al. (2001). "Bending instability in electrospinning of nanofibers." Journal of Applied Physics Vol. 89 No. (5)pp.: 3018-3026.

Yin, J. and B. Deng (2015). "Polymer-matrix nanocomposite membranes for water treatment." Journal of Membrane Science Vol. 479 No. (0)pp.: 256-275.

Yip, N. Y., et al. (2010). "High Performance Thin-Film Composite Forward Osmosis Membrane." Environmental Science & Technology Vol. 44 No. (10)pp.: 3812-3818.

Yip, N. Y., et al. (2011). "Thin-Film Composite Pressure Retarded Osmosis Membranes for Sustainable Power Generation from Salinity Gradients." Environmental Science & Technology Vol. 45 No. (10)pp.: 4360-4369.

Yoon, K., et al. (2009). "High flux nanofiltration membranes based on interfacially polymerized polyamide barrier layer on polyacrylonitrile nanofibrous scaffolds." Journal of Membrane Science Vol. 326 No. (2)pp.: 484-492.

Yoon, K., et al. (2006). "High flux ultrafiltration membranes based on electrospun nanofibrous PAN scaffolds and chitosan coating." Polymer Vol. 47 No. (7)pp.: 2434-2441.

Yung, L., et al. (2010). "Fabrication of thin-film nanofibrous composite membranes by interfacial polymerization using ionic liquids as additives." Journal of Membrane Science Vol. 365 No. (1-2)pp.: 52-58.

Zhang, C. Q., et al. (2011a). "A novel two-nozzle electrospinning process for preparing microfiber reinforced pH-sensitive nano-membrane with enhanced mechanical property." European Polymer Journal Vol. 47 No. (12)pp.: 2228-2233.

Zhang, F., et al. (2011b). "Integrating forward osmosis into microbial fuel cells for wastewater treatment, water extraction and bioelectricity generation." Environmental Science & Technology Vol. 45 No. (15)pp.: 6690-6696.

Zhang, S. and T.-S. S. Chung (2013). "Minimizing the instant and accumulative effects of salt permeability to sustain ultrahigh osmotic power density." Environmental Science & Technology Vol. 47 No. (17)pp.: 10085-10092.

Zhang, S., et al. (2013). "Substrate modifications and alcohol treatment on thin film composite membranes for osmotic power." Chemical Engineering Science Vol. 87 No. pp.: 40-50.

Zhang, S., et al. (2010). "Well-constructed cellulose acetate membranes for forward osmosis: Minimized internal concentration polarization with an ultra-thin selective layer." Journal of Membrane Science Vol. 360 No. (1-2)pp.: 522-535.

Zhang, S., et al. (2014). "Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD)." Water Research Vol. 52 No. pp.: 112-121.

Zhao, S., et al. (2012). "Recent developments in forward osmosis: Opportunities and challenges." Journal of Membrane Science Vol. 396 No. pp.: 1-21.

Zhong, P., et al. (2013). "Development of thin-film composite forward osmosis hollow fiber membranes using direct sulfonated polyphenylenesulfone (sPPSU) as membrane substrates." Environmental Science & Technology Vol. 47 No. (13)pp.: 7430-7436.

Zong, X., et al. (2002). "Structure and process relationship of electrospun bioabsorbable nanofiber membranes." Polymer Vol. 43 No. (16)pp.: 4403-4412.

Zou, S., et al. (2013). "Direct microscopic observation of forward osmosis membrane fouling by microalgae: Critical flux and the role of operational conditions." Journal of Membrane Science Vol. 436 No. (0)pp.: 174-185.