Design, fabrication, and characterization of high-performance membranes for osmotic energy generation

Li, Ye

2017

Li, Y. (2017). Design, fabrication, and characterization of high-performance membranes for osmotic energy generation. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73259>

<https://doi.org/10.32657/10356/73259>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

DESIGN, FABRICATION, AND CHARACTERIZATION OF HIGH PERFORMANCE
MEMBRANES FOR OSMOTIC ENERGY GENERATION

**DESIGN, FABRICATION, AND CHARACTERIZATION
OF HIGH-PERFORMANCE MEMBRANES
FOR OSMOTIC ENERGY GENERATION**

LI YE
2017

LI YE

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2017

**DESIGN, FABRICATION, AND CHARACTERIZATION
OF HIGH-PERFORMANCE MEMBRANES
FOR OSMOTIC ENERGY GENERATION**

LI YE

LI YE

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirements for the degree of Doctor of Philosophy

2017

ACKNOWLEDGEMENTS

First of all, my deepest appreciation goes to my supervisor Prof. Wang Rong, for the countless and valuable guidance, advice and support. I am truly thankful for the continuous encouragement and trust she has offered in these four years. This thesis will never be possible without her help. It is also a great pleasure to thank Prof. Tang Chuyang, who provided precious comments and revision for my manuscript.

I would like to take this opportunity to thank the staff and students in Singapore Membrane Technology Center (SMTC) and staff from the Environmental lab in Civil and Environmental Engineering (CEE) department. The research life would be more difficult without their help and support. Special thanks to Dr. Qi Saren, Dr. Zhao Shanshan, Dr. Laurentia Setiawan, Dr. Wang Yining for the guidance and cooperation in research work and manuscripts. Sincere gratitude goes to Dr. Wei Jing, Dr. Wu Bing, Mr. Zhang Lizhi, Dr. Fang Wangxi, Dr. Liu Chang and Dr. Loh Chuheng for the academic and research advice.

I sincerely thank my qualification exam reviewer committee, Assistant Professor Chong Tzyy Haur, Associate Professor Dong Zhili, and Professor Liu Yu, for their kind advice and valuable comments.

I also thank the lab staff in SMTC and CEE environmental lab for their assistance and guidance in the lab facilities; I would like to thank the administration staff in NEWRI center and CEE department for the kind support provided.

My acknowledgment goes to the financial support of my Ph.D. scholarship provided by the National Research Foundation of Singapore under its National Research Foundation (NRF) Environmental and Water Technologies (EWT) Ph.D. Scholarship Programme.

Finally, I feel grateful for the support from my parents and friends. Their love and support encourage me to pursue my study and research.

LIST OF PUBLICATIONS

Journal papers:

Li, Y; Wang, R; Qi, S; Tang, C. (2015). "Structural stability and mass transfer properties of pressure retarded osmosis (PRO) membrane under high operating pressures." Journal of Membrane Science 488: 143-153.

Li, Y; Zhao, S; Setiawan, L; Zhang, L; Wang, R. (2017) "Integral hollow fiber membrane with chemical cross-linking for pressure retarded osmosis operated in the orientation of active layer facing feed solution. " Journal of Membrane Science 550: 163-172.

Li, Y; Qi, S; Wang, Yining; Setiawan, L; Wang, R. (2017). "Modification of thin film composite hollow fiber membranes for osmotic energy generation with low organic fouling tendency". Desalination, 424 (Supplement C), 131-139.

Wei, J; **Li, Y**; Setiawan, L; Wang, R. (2016). "Influence of macromolecular additive on reinforced flat-sheet thin film composite pressure-retarded osmosis membranes." Journal of Membrane Science 511: 54-64.

Qi, S; **Li, Y**; Wang, R; Tang, C.Y. (2016). "Towards improved separation performance using porous FO membranes: The critical roles of membrane separation properties and draw solution." Journal of Membrane Science 498: 67-74.

Conference presentation:

Li Y; Wang R, Qi S, Tang C. (2014) "Synthesis and characterization of high-performance thin film composite flat sheet membranes for pressure retarded osmosis." Advanced Membrane Technology VI: Water, Energy, and New Frontiers

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
LIST OF PUBLICATIONS	II
TABLE OF CONTENTS.....	III
ABSTRACT.....	VI
LIST OF TABLES	IX
LIST OF FIGURES	X
LIST OF SYMBOLS	XIV
CHAPTER 1 Introduction.....	1
1.1 Background	1
1.1.1 Osmotic energy generation	1
1.1.2 Pressure retarded osmotic processes	2
1.1.3 Fabrication of pressure retarded osmosis membranes	3
1.2 Objectives and Scope	4
1.3 Thesis outline	5
CHAPTER 2 Literature Review	8
2.1 Pressure retarded osmosis technology process	8
2.1.1 Theory of pressure retarded osmosis process	8
2.1.2 Challenges in PRO process	9
2.2 Preparation of PRO membranes.....	21
2.2.1 Thin film composite (TFC) membranes and integral cellulose triacetate (CTA) membranes	21
2.2.2 Membrane fabrication for stable high power generation	27
2.3 Summary	33
CHAPTER 3 Fabrication and characterization of high-performance flat-sheet TFC PRO membranes	35
3.1 Introduction.....	35
3.2 Experiments	37
3.2.1 Materials for experiments	37

3.2.2 Synthesis of TFC PRO flat sheet membranes.....	37
3.2.3 Characterization of substrates and TFC membranes	38
3.2.4 Intrinsic separation parameters of TFC-PRO membranes	39
3.2.5 PRO experiments	40
3.2.6 Membrane deformation and stability study	42
3.3 Results and discussion	43
3.3.1 Morphology and characteristics of the PEI flat sheet substrates	43
3.3.2 Intrinsic separation properties of TFC flat sheet membranes	46
3.3.3 PRO Performance of the TFC- PEI membranes	46
3.3.4 Stability of the TFC- PEI membrane in pressure cycle tests	49
3.4 Conclusions.....	54
CHAPTER 4 Fabrication and characterization of high-performance hollow fiber	
TFC PRO membranes	56
4.1 Introduction.....	56
4.2 Experiments	59
4.2.1 Materials and chemicals.....	59
4.2.2 Fabrication of Thin-film composite PEI membranes.....	59
4.2.3 Modification of TFC hollow fiber membranes	60
4.2.4 Characterization of PEI hollow fiber substrates	60
4.2.5 Characterization of TFC membranes	61
4.2.6 PRO experiments	62
4.3 Results and discussion	63
4.3.1 Characteristics of the hollow fiber substrates	63
4.3.2 Characteristics of TFC membranes.....	66
4.3.3 PRO performance of the TFC membranes.....	67
4.3.4 PRO fouling test.....	70
4.3.5 Summary of low-fouling PRO membranes in literature	75
4.4 Conclusions.....	76
CHAPTER 5 Fabrication and characterization of high-performance integral	
PRO membranes	77
5.1 Introduction.....	77
5.2 Experiments	80

5.2.1 Materials	80
5.2.2 Fabrication of PAI hollow fiber substrates	80
5.2.3 Fabrication of integral PRO hollow fiber membrane by chemical cross-linking.....	81
5.2.4 Hollow fiber membrane characterization and performance evaluation	81
5.3 Results and discussion	84
5.3.1 Fabrication of PRO membrane by PAH cross-linking modification	84
5.3.2 Fabrication of PRO membrane by PAH cross-linking followed by GA cross-linking.....	90
5.3.3 PRO performance using real wastewater RO retentate as feed	98
5.3.4 Comparison to other membranes reported in the literature	99
5.4 Conclusions.....	101
CHAPTER 6 Conclusions and Recommendations	103
6.1 Overall conclusions.....	103
6.2 Recommendations for future work	106
REFERENCES	108

ABSTRACT

Concerning the rapid increase in global energy consumption and severe environmental issues, sustainable energy is being increasingly investigated as an alternative to fossil fuels. Osmotic energy, as one form of sustainable energy, can be harnessed by pressure retarded osmosis (PRO) technology, and the semi-permeable membrane is employed as an essential element in the PRO process. However, it is challenging to achieve highly efficient PRO operations due to internal concentration polarization (ICP) effect, mechanical deformation and fouling issues regarding the PRO membranes. Developing membranes that could maintain continuous energy generation with various feed and draw streams is critical for the real-world PRO applications.

The objectives of this thesis are to design and fabricate novel PRO membranes with stable power output using various feed and draw solutions. Firstly, this thesis covers the study of substrate structure design and performance evaluation of a novel thin film composite (TFC) flat sheet PRO membrane with excellent mechanical stability under high hydraulic pressures. Subsequently, a TFC membrane in the configuration of hollow fiber with excellent performance was synthesized, which could be applied in a mild fouling environment and maintain the energy output after a low-fouling surface modification. Finally, a specially-designed integral membrane that could be operated in active layer facing feed (AL-FS) orientation under high pressure was fabricated and could produce stable energy generation in a severe fouling environment.

To begin with, TFC polyetherimide (PEI) flat sheet membranes were fabricated and characterized. Firstly, three substrates with various morphologies were developed, and subsequently, an interfacial polymerization method was conducted on top of the substrates to form a thin-film selective skin layer for solutes rejection. The membrane performance was evaluated in terms of water flux, power density and reverse solute flux, and these factors were found to vary with the substrate structure.

Among three as-prepared TFC membranes, TFC-PEI#2 membrane was chosen for subsequent stability tests due to its relatively high performance as well as satisfactory mechanical strength. The membrane intrinsic properties in terms of water and salt permeability altered with hydraulic pressure were studied for two ascending and descending pressure cycles. Both the intrinsic properties and PRO performance could reach similar values at each applied pressure within the two cycles, which indicated a reversible deformation within 0~17.2 bar. With a 300-min period of PRO test performed at 17.2 bar, a stable $12.8 \text{ W}\cdot\text{m}^{-2}$ power density was achieved.

In the second study, thin-film composite polyetherimide (TFC-PEI) hollow fiber membranes with excellent performance were synthesized by phase inversion and interfacial polymerization method. The resultant membranes consisted of small-dimension fibers which bestowed excellent mechanical properties to withstand high pressure without any supporting spacers. The membrane surface facing feed stream was modified by depositing polyelectrolytes to increase surface negative charge and hydrophilicity. The introduction of this method was then proven to be effective in reducing protein and poly-alginate fouling while maintaining mechanical properties and intrinsic separation properties of the membranes. The modified TFC-PEI-M membranes resulted in almost no flux reduction at 15 bar with alginate as feed foulants. It demonstrated that osmotic power generation of TFC membranes could be well maintained after polyelectrolytes-deposited low-fouling modification with a feed stream containing organic foulants.

Finally, a novel integral polyamide-imide (PAI) membrane was designed and fabricated in order to maintain performance using a feed stream consisting of a complex fouling system. Two PAI substrates with various morphologies were acquired by adjusting the internal coagulant solution during the spinning process. Subsequently, a surface cross-linking post-treatment using poly(allylamine hydrochloride) (PAH) was conducted to synthesize the selective layer. The PRO performances of the two resultant integral membranes were evaluated in the active layer-facing-feed (AL-FS) orientation. The membrane with a sponge-like substrate

could produce higher power output using deionized water (DI) as feed, and 1 M MgCl_2 as the draw stream compared to that with the other substrate structure and was selected for further optimization. The NaCl rejection of this membrane was then further improved by a secondary cross-linking procedure using glutaraldehyde (GA). The as-prepared integral membrane was characterized by a series of protocols to investigate the pore size and functional groups on the surface. Fouling tests were conducted with a real wastewater reverse osmosis (RO) retentate adopted as the feed. With 1 M NaCl as the draw stream, the membrane could produce a stable power density $4.3 \text{ W}\cdot\text{m}^{-2}$ at 12~13 bar hydraulic pressure. Although the AL-FS orientation has been recognized as the orientation with low fouling occurrence, the mechanical robustness of traditional TFC membranes is weak in this orientation and impossible to be operated under high pressures. Fabricating an integral membrane with promising performance and stability in AL-FS mode demonstrated great potential for this low-fouling strategy in PRO process.

The future work for the next stage includes four parts. Firstly, the effect of mono and divalent ions in the feed solution will be studied for the low-fouling modified thin film composite membrane. Secondly, the PRO performance of the integral membrane is recommended to be further improved by exploring different cross-linking chemicals and conditions. Thirdly, the stability tests of the integral cross-linking membranes and long-term fouling tests will be conducted to further study the viability in real-world applications. Fourthly, the substrates with low cost and suitable for chemical cross-linking will be investigated to explore the possible applications.

LIST OF TABLE

Table 2.1 PRO membrane performance from literature	26
Table 2.2 The fouling behaviors of PRO membranes in the literature	32
Table 3.1 Synthesis conditions for TFC-PEI membranes.....	38
Table 3.2 Characteristics of PEI membrane substrate	45
Table 3.3 Intrinsic separation properties of TFC PEI composite membranes with optimal polyamide layer.	46
Table 4.1 Properties of hollow fiber membrane substrates.....	66
Table 4.2 Intrinsic separation properties of TFC membranes.....	67
Table 4.3 Summary of the membranes in current work and other low-fouling PRO membranes in literature.....	75
Table 5.1 Dope composition and spinning conditions.....	80
Table 5.2 Characteristics of the PAI hollow fiber substrates.....	85
Table 5.3 Intrinsic properties of PAH cross-linked hollow fiber membranes	87
Table 5.4 Intrinsic properties of the ST#2–PAH/GA hollow fiber membrane....	94
Table 5.5 Properties and rejections of the neutral solutes a.....	95
Table 5.6 Comparison of water flux, specific salt flux and power density of various PRO membranes tested in AL–FS orientation.....	100
Table 5.7 Comparison of power density of PRO membranes tested in the AL–FS orientation using wastewater RO retentate as feed	100

LIST OF FIGURES

Figure 1.1 Three types of osmotic processes (ΔP is the hydraulic pressure difference, $\Delta \pi$ is the osmotic pressure difference).....	2
Figure 2.1 Illustrative diagram of concentration polarization in FO/PRO membrane; (a) in the orientation of active layer facing draw (AL-DS orientation); (b) in the orientation of active layer facing feed (AL-FS orientation).....	11
Figure 2.2 Feed spacer induced membrane deformation during PRO process; (a) images of spacers with different openings and membranes after the operation; (b) B/A parameter with applied pressure; (c) power density with applied pressure (She et al. 2013). Copyright 2013. Reproduced with permission from Elsevier Ltd.....	14
Figure 2.3 Schematic diagram of hollow fiber membrane deformation during PRO operation (Han et al. 2013) Copyright 2013. Reproduced with permission from American Chemical Society.	16
Figure 2.4 Fouling in PRO process with (a) only external fouling occurs in the orientation of AL-FS, and (b) both internal and external fouling occur in the orientation of AL-DS.	20
Figure 2.5 Performances of PRO membranes in the literature (Open symbols represent the flat sheet membranes and closed symbols represent the hollow fiber membranes).	27
Figure 2.6 Schematic diagram of fouling phenomenon: (a) the conventional TFC membrane and (b) the double polyamide skin TFC membrane in FO process (in AL-DS orientation) and PRO processes (Han et al. 2017). Copyright 2017. Reproduced with permission from Elsevier Ltd.	31
Figure 3.1 Schematic diagram of PRO set up.....	43
Figure 3.2 SEM images of PEI substrate: (a1) Cross section of S-PEI#1; (a2) Cross section of S-PEI#2; (a3) Cross section of S-PEI#3; (b1) Top surface of S-PEI#1; (b2) Top surface of S-PEI#2; (b3) Top surface of S-PEI#3.	44
Figure 3.3 AFM micrographs of the flat sheet membranes: (a) Surface of S-PEI#1; (b) Surface of S-PEI#2; (c) Surface of S-PEI#3.	45

Figure 3.4 PRO performance of TFC PEI flat sheet membranes at various applied pressures (a) Water flux; (b) Specific salt flux J_s/J_w ; (c) Power density. (Feed solution: 10 mM NaCl; Draw solution: 1 M NaCl solution).....	47
Figure 3.5 Power density of TFC-PEI#2 flat sheet membrane under different feed solution concentrations. (Draw solution: 1 M NaCl solution)	49
Figure 3.6 Schematic diagrams of (A) RO cell; (B) PRO cell; (a) No membrane deformation in RO cell; (b) An illustration of possible membrane deformation in PRO cell.	50
Figure 3.7 FESEM images of TFC-PEI#2 membrane (A) Surface at no compaction; (B) Surface at 17 bar compactions; (a) Cross-section at no compaction; (b) Cross-section at 17 bar compactions.	51
Figure 3.8 Water and salt permeabilities of the TFC-PEI#2 flat sheet membrane at various transmembrane pressures. Testing condition: 10 mM NaCl as feed solution, membrane coupons were compressed under various pressure at ambient temperature.	51
Figure 3.9 Pressure cycle tests of the TFC-PEI#2 membrane (a) Water flux; (b) Specific salt flux J_s/J_w ; (c) Power density. (Feed solution: 10 mM NaCl concentration; Draw solution: 1 M NaCl solution).....	53
Figure 3.10 Water flux and power density of TFC-PEI#2 flat sheet membrane under different pressures over 300 min. (Feed solution: 10 mM NaCl concentration; Draw solution: 1 M NaCl solution)	54
Figure 4.1 FESEM images of hollow fiber membrane substrate S-PEI showing (a-b) cross-section, (c) lumen surface, (d) shell surface, (e) shell surface at higher magnification, and (f) the outer surface after polyelectrolytes modification (membrane substrate (S-PEI-M))......	64

Figure 4.2 ATR-FTIR spectra for the S-PEI and the S-PEI-M. The analysis was performed from the shell surface of the membranes.	64
Figure 4.3 Zeta potential of the shell surfaces of the S-PEI and S-PEI-M membrane substrates. 0.01 M NaCl was adopted as the electrolyte solution.	65
Figure 4.4 FESEM images of TFC-PEI membrane showing (a) the plan view of polyamide surface and (b) the cross-section view.	67
Figure 4.5 PRO performance of the membrane TFC-PEI and TFC-PEI-M as a function of applied pressure. (a) Water flux, (b) specific solute flux, and (c) power density. Testing conditions: DI water and 1 M NaCl were utilized as feed and draw, correspondingly. The performance was obtained after the membranes were stabilized for 30 minutes at each pressure. Each error bar was calculated based on three replicates.	69
Figure 4.6 Effect of foulants on PRO membrane performance. 200 ppm alginate (a) or 200 ppm BSA (b) was present in the feed solution. Draw solution contained 1 M NaCl. The applied pressure was maintained at 15 bar.	71
Figure 4.7 Water flux of TFC-PEI and TFC-PEI-M membranes under applied pressure of 2 bar (a) 10 bar (b) and 15 bar (c), and their power density at 0 and 300 min of alginate fouling (d). The PRO experiments were conducted using NaCl draw stream (1.0 M) and DI water as the feed for baseline test while 200 ppm alginate was present in the feed for fouling test.	74

Figure 5.1 FESEM images of PAI supports: (a1 and b1) cross section of ST# 1 and ST#2; (a2 and b2) cross-section adjacent to the inner area of ST#1 and ST#2; (a3 and b3) inner area of ST#1 and ST#2; (a4 and b4) outer skin of ST# 1 and ST#2.	85
Figure 5.2 FESEM images of the inner surface morphologies (a1 and b1), outer surface morphologies (a2 and b2), and cross-section morphologies near the outer surface (a3 and b3) of the PAH cross-linked membranes ST#1–PAH (a series) and ST#2–PAH (b series)	86
Figure 5.3 PRO performance of the PAH cross-linked hollow membranes at various operating pressures: (a) PRO water flux J_w , (b) specific salt flux (J_s/J_w), (c) power density W . Testing conditions: DI water as the feed, and 1M $MgCl_2$ as the draw solution at ambient temperature.	90
Figure 5.4 Possible mechanism of chemical cross-linking reaction between PAI and PAH/GA.	92
Figure 5.5 ATR-FTIR spectra of the substrate and modified membranes.....	93
Figure 5.6 Surface zeta-potential of the substrate and modified membranes as a function of pH.....	94
Figure 5.7 Separation performances of the PAH and PAH/GA cross-linked hollow fiber membranes. Experiments were conducted at 2 bar using 500 ppm single salt solution.	96
Figure 5.8 PRO performance of the ST#2–PAH/GA membrane at various operating pressures: (a) water flux J_w , (b) specific salt flux J_s/J_w , (c) power density W . Testing conditions: DI water as the feed and 1 M NaCl as the draw at ambient temperature.....	97
Figure 5.9 The power density of the ST#2–PAH/GA membrane as a function of operation time. The PRO experiment was performed continuously using 1.0 M NaCl as the draw solution and DI water as the feed for baseline test while wastewater RO retentate as the feed for fouling test at ambient temperature at hydraulic pressure of 12~13 bar.	99

LIST OF SYMBOLS

Letters

A	water permeability of the membrane active layer, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$
A_m	effective membrane area, m^2
B	salt permeability of the membrane active layer, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1}$
A_p	water permeability at different applied pressure, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$
B_p	salt permeability at different applied pressure, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1}$
C_f, C_p	concentration of feed and permeate in RO, M
C_{fe}, C_d	concentration of feed and draw in FO or PRO process, M
$C_{f,bulk}, C_{d,bulk}$	concentration of bulk feed and draw solution, M
$C_{f,m}, C_{d,m}$	actual concentration on the feed and draw side of the membrane surface, M
D	diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
J	permeate water flux in RO process, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1}$
J_s	salt flux, $\text{mole} \cdot \text{m}^{-2} \text{ h}^{-1}$
J_w	water flux, $\text{L} \cdot \text{m}^{-2} \text{ h}^{-1}$
K	the solute resistivity for diffusion, $\text{s} \cdot \text{m}^{-1}$
ΔP	Applied pressure difference across the membrane, bar
P_i	pressure applied on the lumen surface, bar
R	universal gas constant, $\text{N} \cdot \text{m} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
R_s	salt rejection, %
R_p	salt rejection at different pressure, %
r_i	inner diameter of hollow fiber, μm
r_o	outer diameter of hollow fiber, μm
S	structure parameter, mm
Δt	predetermined time interval, h
V_f	volume of feed water, L
ΔV	volume change, L
W	power density, $\text{W} \cdot \text{m}^{-2}$

Greek letters

β	van't Hoff factor
ε	the porosity of the membrane
μ	the Poisson's ratio
π_d, π_f	the osmotic pressure of draw and feed streams, bar
$\Delta\pi$	the osmotic pressure difference across the membrane, bar
σ_s	surface stress, Pa
τ	tortuosity of the membrane

CHAPTER 1 Introduction

1.1 Background

1.1.1 Osmotic energy generation

With the continuous economic development and population growth, renewable energy resources have received increasing attention globally (Chung et al. 2012). Due to the limited fossil fuel resources and detrimental environmental effects, a lot of countries and regions have focused on the research of renewable energy (Kontorovich et al. 2014, Montoya et al. 2014). The proposed renewable energies include solar photovoltaic, wind power, hydropower, biomass and osmotic energy. However, uneven availability of energy sources and high installation costs are still preventing these forms of energy from being prevalent, and continuous research is imperative to discover robust technologies that could utilize these new energies.

Osmotic energy, one form of the renewable energy, can be produced when fresh water mixes with salt water through a semi-permeable membrane (Pattle 1954). The proposed water resources for generating osmotic energy include river water, wastewater, wastewater brine for the low salinity solution or feed stream; seawater, brine from seawater desalination plants for the high salinity solution or draw stream (Sim et al. 2013). It has been reported that the estimated capacity of energy from the merging of major rivers' outflow and seawater can reach 980 gigawatts (GW) globally (Logan et al. 2012). Osmotic energy can be harnessed by reverse electrodialysis (RED) (Post et al. 2008, Daniilidis et al. 2014), pressure retarded osmosis (PRO) technology (Loeb et al. 1976, Achilli et al. 2010, Helfer et al. 2014) and capacitive mixing (Hatzell et al. 2013, Rica et al. 2014). PRO has significant advantages over other technology concerning power output efficiency and costs (Yip et al. 2014).

1.1.2 Pressure retarded osmotic processes

Pressure retarded osmosis (PRO) belongs to the category of the osmotically driven process that occurs when different salinity streams are separated by a semi-permeable membrane. There are three types of osmotically driven processes: forward osmosis (FO), PRO, and reverse osmosis (RO), as illustrated in Figure 1.1. PRO and FO are similar processes in which water flows from fresh water stream to salty water stream driven by osmotic pressure difference across the membrane ($\Delta P < \Delta\pi$). The only difference is that no hydraulic pressure is applied in forward osmosis process ($\Delta P = 0$). The water flux in PRO process is smaller to that in FO process and water flux declines with the increase of the ΔP until reaching zero flux at $\Delta P = \Delta\pi$. Further increasing ΔP ($\Delta P > \Delta\pi$) leads to reverse osmosis process, in which the hydrostatic pressure is higher than the osmotic pressure and water molecules diffuse from the high salinity solution to pure water side.

Figure 1.1 Three types of osmotic processes (ΔP is the hydraulic pressure difference, $\Delta\pi$ is the osmotic pressure difference).

PRO technology utilizes the chemical potential difference between two streams of different salinity concentrations, in which water molecules are driven through the membrane from feed to draw stream while solutes are retained. The pressurized water flow is led through a turbine system to produce energy (Helfer et al. 2014). The efficiency of PRO process is dominated by a series of operational parameters

including feed and draw solution concentrations, hydraulic pressure difference, temperature, membrane performance and cross flow rate (Altaee et al. 2015).

1.1.3 Fabrication of pressure retarded osmosis membranes

Although the concept of PRO was initially conceived in 1976 (Loeb 1976, Loeb et al. 1976), its development has been hindered attributed to the absence of effective membranes (Loeb 1998, Loeb 2001, McCutcheon et al. 2006). Until now there are no commercially available membranes specially designed for PRO application. Reverse osmosis membranes were adopted for PRO process at the initial stage of this technology, however, the membranes produced low water flux owing to the dense substrates that could induce internal concentration polarization (ICP) resulting in low energy generation (Loeb 1976, Mehta 1982). Cellulose triacetate membranes that supplied by Hydration Technology Innovations (HTI) and designed for forward osmosis application have been widely adopted to study PRO process. Nonetheless, it was reported that both the power output and mechanical robustness of these membranes were not satisfactory (Achilli et al. 2009, She et al. 2012). In the recent years, some membranes with high performance have been fabricated in lab-scale for PRO process study (Yip et al. 2011, Chou et al. 2013, Han et al. 2013, Song et al. 2013, She et al. 2016). Generally, two substrate configurations (hollow fiber and flat sheet) have been employed in PRO membrane fabrication via non-solvent phase inversion or electro-spinning approach. Interfacial polymerization method has been adopted to synthesize the solute rejection layer, and the resultant thin film composite (TFC) membranes have been commonly applied for PRO process study owing to the excellent water/solute separation property. However, the application of PRO technology is still constrained by concentration polarization, mechanical deformation and membrane fouling, leading to the decline of power output and module lifetime. The detailed discussion of the challenges in PRO process and the development of membrane design will be presented in Chapter 2.

1.2 Objectives and Scope

The overall objectives of this thesis are to fabricate, characterize, and evaluate membranes with high and stable performance in PRO process, to tailor the structure and properties of membranes, and to adopt alternative approaches to PRO membrane fabrication and modification.

Specific objectives and tasks include:

- To fabricate a thin film composite (TFC) polyetherimide (PEI) PRO flat sheet membrane with high performance under high operating pressure and to:
 - Investigate the impact of PEI substrate morphology on the membrane performance in PRO process;
 - Fabricate a TFC flat sheet membrane specially designed for PRO process with high porosity, high robustness, and excellent water/solute separation property;
 - Evaluate stability of the as-prepared TFC PEI flat sheet membrane under high hydraulic pressures in PRO experiments.
- To fabricate a TFC PEI hollow fiber membrane with high performance using a feed stream containing organic foulants and to:
 - Fabricate a TFC hollow fiber membrane with high water permeability and high mechanical property;
 - Modify the porous substrate using a green and facile polyelectrolyte deposition method to maintain performance with a feed stream containing organic foulants;

- Investigate the changes of functional groups and charge of substrate surface before and after post-treatment;
 - Evaluate the performance stability of the modified TFC hollow fiber membrane with organic foulants present in the feed solution at different applied pressures.
- Fabricate an integral PRO membrane with stable performance in a severe fouling environment and to:
 - Demonstrate the effect of membrane substrate morphology on membrane performance;
 - Characterize the membrane surface chemistry and charge of the substrate surface before and after cross-linking post treatments;
 - Conduct PRO tests using DI water as feed and NaCl (1 M) as draw in the orientation of AL-FS at high hydraulic pressure;
 - Evaluate the stability of PRO performance of integral membranes using wastewater brine as the feed stream;

1.3 Thesis outline

This thesis comprises six chapters. Chapters 1, 2 and 6 include introduction, literature review, and conclusions, respectively. Chapters 3, 4, and 5 are the research work on the proposed topic. The main contents are briefly summarized below.

Background information regarding osmotic energy, pressure retarded osmosis technology and membranes is presented in Chapter 1. The outline, objectives, and scope are also included in this chapter as well.

Chapter 2 provides a brief literature of PRO technology. The first part focuses on the concepts, theories of pressure retarded osmosis process, as well as some major challenges of PRO technology. The recent development of lab-scale PRO membranes was reviewed in the second part, including the membrane materials, substrate structure, PRO performance, and the drawbacks.

In Chapter 3, flat sheet TFC membranes were fabricated using phase inversion and interfacial polymerization methods that could produce stable power density under high operating pressure. Three types of substrates with various morphologies were developed to investigate the effect of substrate structure towards membrane performance. The TFC PRO membranes were characterized using a series of protocols regarding FESEM, AFM images, and intrinsic separation properties. Stability tests were conducted to evaluate the PRO performance with two ascending and descending pressure cycles. The membrane performance was investigated with a 300-min testing.

Chapter 4 introduces the fabrication of a TFC hollow fiber membrane that could produce high performance using feed stream containing organic foulants. The fabrication method of the thin film composite membrane was dry-wet spinning followed by interfacial polymerization. Subsequently, the membrane surface facing feed solution was modified by polyelectrolyte deposition. The changes of functional groups and zeta potential of membrane surface were investigated. Fouling behaviors of the control and modified TFC hollow fiber membranes at various applied pressure were evaluated by 300-min tests using model organic foulants.

In Chapter 5, integral membranes that could maintain stable performance with a feed stream of severe fouling propensity were designed and evaluated. The novel integral polyamide-imide (PAI) membrane was fabricated by phase inversion and cross-linking reaction using polyallylamine hydrochloride (PAH) and glutaraldehyde (GA). Two types of PAI substrate with different structure were evaluated with regards to water permeability, burst pressure, and surface pore size. The PRO performance was assessed in the orientation of AL-FS using 1 M NaCl as

draw stream and deionized water as feed stream, followed by a real waste-water RO retentate as feed.

In Chapter 6, the important findings of this thesis are summarized. Recommendations and plans for the continuous research in the next stage are also proposed in the chapter: (1) The effect of mono and divalent ions in the feed solution will be studied for the low-fouling modified thin film composite membrane (2) the performances of the integral membranes will be further improved by exploring different cross-linking conditions and chemicals; (3) stability tests of the integral cross-linking membranes and long-term fouling tests will be conducted to further study the viability in real application; (4) substrates using low-cost materials that suitable for chemical cross-linking will be investigated to explore the possible applications.

CHAPTER 2 Literature Review

2.1 Pressure retarded osmosis technology process

Osmotic energy or salinity gradient energy can be harnessed from the mixing of low and high salinity streams (Pattle 1954). Pressure retarded osmosis, one of the osmotically driven processes, has been proposed to extract salinity gradient energy (Loeb et al. 1976, Loeb 2001, Achilli et al. 2009). In the PRO process, low salinity solution (feed solution) is circulated through one side of the membrane while high salinity stream (draw solution) is pressurized on the other side. The pressurized water can drive a hydro-turbine to generate energy (Loeb 1998, Loeb 2001). It is estimated that global potential of the salinity energy could reach 2 terawatts when mixing river water and seawater and up to 980 gigawatts could be harnessed (Logan et al. 2012).

2.1.1 Theory of pressure retarded osmosis process

The ideal water flux J_w can be calculated from the Eq. (2.1)

$$J_w = A \cdot (\Delta\pi - \Delta P) \quad (2.1)$$

Where A is the water permeability of membrane active layer ($\text{L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), ΔP is the hydraulic pressure (bar), and $\Delta\pi$ is the differential osmotic pressure (bar).

The PRO membrane performance is usually evaluated by the value of power density W ($\text{W} \cdot \text{m}^{-2}$), which is known as the energy generated per unit area of the membrane. According to Eq.(2.2), W equals to the ΔP (bar) across the membrane multiplied by the water flux J_w (Lee et al. 1981, Thorsen et al. 2009).

$$W = \Delta P \times J_w \quad (2.2)$$

Substitute Eq. (2.1) in Eq. (2.2):

$$W = A \cdot (\Delta\pi - \Delta P) \cdot \Delta P \quad (2.3)$$

Theoretically, the power density reaches the maximum value (W_{max}) when hydraulic pressure equals to half of the osmotic pressure difference.

$$W_{max} = A \cdot \frac{\Delta\pi^2}{4} \quad (2.4)$$

For the pair of river and seawater brine, the ideal hydraulic pressure is around 24.0~24.5 bar to achieve the highest power density (the osmotic pressure difference between river water and seawater brine is around 48~49 bar (Han et al. 2014)).

In PRO process, the solutes diffuse from the feed to draw stream in the reverse direction to water flux. This reverse salt flux, J_s , can be calculated from Eq. (2.5) (She et al. 2012):

$$\frac{J_s}{J_w} = \frac{B}{A\beta RT} \left(1 + \frac{A\Delta P}{J_w} \right) \quad (2.5)$$

where B and A are the salt permeability ($\text{L} \cdot \text{m}^{-2} \text{h}^{-1}$) and the water permeability ($\text{L} \cdot \text{m}^{-2} \text{h}^{-1} \text{bar}^{-1}$), respectively. β is the van't Hoff factor, R is the universal gas constant ($\text{N} \cdot \text{m} \cdot \text{mol}^{-1} \text{K}^{-1}$), and T is the absolute temperature (K). This equation only applies when the osmotic pressure is in a linear relationship with concentration. Lee J et al. compared the osmotic pressures calculated from van't Hoff equation and those obtained with the OLI software. They concluded the difference could be negligible when NaCl concentration is below 1.5 M (Lee et al. 2016).

2.1.2 Challenges in PRO process

There are several challenges for the development of PRO technology. As mentioned in Chapter 1, the progress of PRO technology has been held back for decades attributed to the absence of suitable membranes. The requirements of applicable PRO membranes are as follows: (1) thin and porous substrate reduce internal concentration polarization (ICP) effect (Lee et al. 1981, Achilli et al. 2009, Yip et al.

2010); (2) excellent mechanical properties that can endure high pressure in PRO process (She et al. 2012, Li et al. 2013). In addition, foulants in the feed stream could penetrate the membrane support layer resulting in the decline of water flux and power density. The pre-treatment of feed and draw solutions carried out in PRO process would cost a considerable amount of energy (Elimelech et al. 2011). Therefore, the development of fouling-resistant PRO membranes with superior performance, as well as mechanical strength, is important.

➤ **Concentration polarization**

Concentration polarization is a phenomenon that can significantly decrease the actual osmotic pressure difference, thus reducing the driving force (Lee et al. 1981). This could be explained by the accumulation or depletion of ions near membrane surface. The solutes are concentrated near the feed side while diluted near the permeate side of the membrane. Concentration polarization happens externally near the dense skin and internally in the porous support layer, which is referred as the external and internal concentration polarization (ECP and ICP), respectively. The illustration of concentration polarization effect is shown in Figure 2.1. $C_{d,bulk}$ and $C_{f,bulk}$ refer to the salt concentrations of the bulk draw and feed streams, correspondingly. $C_{f,m}$ and $C_{d,m}$ are the actual concentrations on the membrane active layer of the feed and draw side, respectively. $C_{d,m}$ is smaller than $C_{d,bulk}$ owing to the dilution effect of the inward water flux, resulting in dilutive ECP. $C_{f,m}$ is higher than $C_{f,bulk}$ because of the reverse diffused salt (salt flux), causing the concentrated ECP. Both dilutive and concentrative ECP can be mitigated by escalating water flow rate. Meanwhile, the solutes can penetrate and accumulate inside the porous substrate of the membrane. Thus, the salt concentration difference across the membrane active layer is lower than the bulk salinity gradient. This refers to the phenomenon of concentrative ICP. ICP effect is highly affected by substrate structure, salt and water flux (Gerstandt et al. 2008, Yip et al. 2011).

Figure 2.1 Illustrative diagram of concentration polarization in FO/PRO membrane; (a) in the orientation of active layer facing draw (AL-DS orientation); (b) in the orientation of active layer facing feed (AL-FS orientation).

Considering the ICP effect, the water flux J_w in PRO process can be calculated from Eq. (2.6), which was rearranged from Eq. (2.1).

$$J_w = A \cdot \left(\frac{\pi_d \left(1 - \frac{C_{fe}}{C_d} \exp(J_w K) \right)}{1 + \frac{B}{J_w} (\exp(J_w K) - 1)} - \Delta P \right) \quad (2.6)$$

where π_d is the osmotic pressure of draw stream (bar), C_{fe} and C_d are the concentration of the feed and draw water (M), respectively. The solute resistivity for diffusion K ($s \cdot m^{-1}$) can be estimated from Eq. (2.7):

$$K = \frac{S}{D} \quad (2.7)$$

where D refers to the solute diffusion coefficient in water ($m^2 \cdot s^{-1}$) and S is the structural parameter (m) that is decided by the thickness l , the tortuosity τ , the porosity ε of the substrate:

$$S = \frac{l\tau}{\varepsilon} \quad (2.8)$$

Yip et al, (Yip et al. 2011) reported a modified model combining the effect of both ICP and ECP:

$$J_w = A \cdot \left(\frac{\pi_d \exp\left(-\left(\frac{J_w}{K}\right)\right) - \pi_f \exp\left(\frac{J_w S}{D}\right)}{1 + \left(\frac{B}{J_w}\right) \exp\left(\frac{J_w S}{D}\right) - \exp\left(-\left(\frac{J_w}{K}\right)\right)} - \Delta P \right) \quad (2.9)$$

where J_w is the actual water flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) and π_f is the osmotic pressure of feed stream (bar). Therefore, the power density that includes the impact of both ICP and ECP can be calculated as follows:

$$W = A \cdot \left(\frac{\pi_d \exp\left(-\left(\frac{J_w}{K}\right)\right) - \pi_f \exp\left(\frac{J_w S}{D}\right)}{1 + \left(\frac{B}{J_w}\right) \exp\left(\frac{J_w S}{D}\right) - \exp\left(-\left(\frac{J_w}{K}\right)\right)} - \Delta P \right) \cdot \Delta P \quad (2.10)$$

From the Eq. (2.10), the power density is dominated by water permeability (A), salt permeability (B) and structure parameter (S). The value of A is preferred to be as great as possible and B and S to be as small as possible to reduce the ICP effect and achieve high power density. For FO membranes, the membrane supports are designed to be thin, hydrophilic and highly permeable to mitigate the ICP effect (Widjojo et al. 2011). However, without the optimization of the membrane materials and structures, these membranes possess weak mechanical strength that would lead to collapse during operation under high pressure in PRO process (Li et al. 2013). She et al. (She et al. 2012) reported that the reverse salt flux rose with the increase of the hydraulic pressure, resulting in the discrepancy between the experimental and theoretical water flux. To summarize, PRO membranes with desirable performance should possess an ideal combination of A , B , S and good mechanical properties.

➤ Mechanical deformation

It has been reported in some recent publications that membrane deformation would adversely affect the PRO performance (Xu et al. 2010, Kim et al. 2012, She et al. 2012). The situation of mechanical deformation depends on membrane configuration. Flat sheet membranes are typically supported by spacers that are placed in both feed and draw flow channels during PRO testing. The spacers are employed to enhance the mass transfer while maintaining the flow channel geometry (Da Costa et al. 1994, Koutsou et al. 2009, Fimbres-Weihs et al. 2010). Moreover, the spacers in feed side were designed to withstand the hydraulic pressure from draw channel and protect the membrane in a PRO system. However, the PRO membrane could undergo severe deformation due to the large spacing of feed spacer, resulting in power output decline (Xu et al. 2010, Kim et al. 2012, She et al. 2012). The membrane deformation was firstly reported in a study using a spiral wound module in PRO process (Xu et al. 2010). She et al. also observed reverse solute diffusion increased due to the membrane deformation, thus enhancing the internal concentration polarization leading to reduced energy generation (She et al. 2012). It was reported by another research work that severe deformation could significantly elevate the solute permeability (Kim et al. 2012). She et al. (She et al. 2013) further evaluated the relation between the design of feed spacers and the energy output in PRO process, concluding that the spacers of larger gaps resulted in more significant deformation at higher hydraulic pressure. As shown in Figure 2.2 (a), the deformation on the membrane surface was more obvious with feed spacers of larger openings used. Figure 2.2 (b) shows that the B/A value was small using the spacers of small openings. With the increase of B/A value, the reverse salt flux increased, resulting in low power generation, as indicated in Figure 2.2 (c).

Figure 2.2 Feed spacer induced membrane deformation during PRO process; (a) images of spacers with different openings and membranes after the operation; (b) B/A parameter with applied pressure; (c) power density with applied pressure (She et al. 2013). Copyright 2013. Reproduced with permission from Elsevier Ltd.

For the self-supported hollow fibers, the mechanical robustness could be critical to the whole process due to no supporting spacers in the module. Han et al. (Han et al. 2013) reported an interesting phenomenon when testing hollow fiber membranes in PRO process. The water flux decreased with the increase of hydraulic pressure. However, after reaching certain pressure, the water flux started to increase. This phenomenon was contrary to the theoretical prediction in which the water flux would decrease with the rise of applied pressure due to the decrease of driving force. The explanation could be the expansion of both the hollow fiber support and

polyamide layer due to the applied pressure, leading to an enlarged effective membrane area and reduced wall thickness. The deformation may be irreversible below the critical pressure as shown in Figure 2.3. Chou et al. (Chou et al. 2013) developed an equation to calculate the stretching stress σ_s at the lumen side of the hollow fiber based on Eq. (2.11):

$$\sigma_s = \left(\frac{\left(\frac{r_o}{r_i} \right)^2 + 1}{\left(\frac{r_o}{r_i} \right)^2 - 1} + \mu \right) \cdot P_i \quad (2.11)$$

where r_o and r_i are the outer and the inner diameter of the hollow fiber membrane, correspondingly. μ is the Poisson's ratio, and P_i is the internal pressure on the inner surface.

The expansion of hollow fibers under pressure was elastic at low pressure leading to a slow increment of the water permeability. Further increasing the pressure, the membrane deformation would be irreversible, and eventually membranes would collapse. Referring to the equation (2.11), increasing the value of r_o/r_i , e.g., reducing the inner diameter or increasing the thickness of the fiber, would enhance the membrane mechanical properties. A 200-h long-term study of hollow fiber membrane stability was conducted by Chen et al. (Chen et al. 2016). In this study, the creeping phenomenon of hollow fiber PRO membranes was observed at the hydraulic pressure exceeding the allowable operating pressure (critical pressure).

Figure 2.3 Schematic diagram of hollow fiber membrane deformation during PRO operation (Han et al. 2013) Copyright 2013. Reproduced with permission from American Chemical Society.

➤ Fouling issues

The proposed feed/draw streams, such as wastewater, seawater, and brine water, contain a lot of foulants. Wan et al. (Tian et al. 2015) adopted seawater brine as the draw solution and observed that the membrane fouling in the draw side was negligible owing to the dense selective layer preventing the diffusion of foulants and permeate water flux washing off the foulants attached on the selective layer. On the other hand, the foulants in the feed stream could deposit on the membrane surface or penetrate the pores of substrate, leading to a severe water flux decline.

The fouling behaviors of membranes in PRO process with feed streams containing organic model foulants (i.e., alginates, proteins, and humic materials), inorganic matter and bacteria have been intensely studied by researchers (She et al. 2013, Thelin et al. 2013, Yip et al. 2013, Bar-Zeev et al. 2015, Chen et al. 2015). Yip et al. (Yip et al. 2013) investigated the detrimental effect of organic fouling to water flux and demonstrated that osmotic backwash could effectively recover the membrane performance. She et al. reported that the aggregation of organic molecules on the membrane could be aggravated by the existence of divalent ion (e.g., Mg^{2+} and Ca^{2+}) in the feed and draw streams (She et al. 2013). Chen et al. (Chen et al. 2015) reported that the co-existence of gypsum and alginate in the feed stream led to a

more serious reduction of water flux compared to the sole presence of alginate or gypsum foulants at zero hydraulic pressure. However, this synergistic fouling was not observed under high applied pressure, which could be attributed to the enhanced reverse solute diffusion inhibiting the deposition of gypsum. The gypsum scaling caused by the precipitation of inorganic scalants in PRO process was studied by Zhang et al. (Zhang et al. 2014). It was observed that the scaling situation was dominated by draw solution concentration, hydraulic pressure, surface chemistry and morphology of membrane. The colloidal fouling phenomenon that induced by the existence of SiO₂ in the feed stream was investigated by Kim et al. (Kim et al. 2016), and it was observed that severe flux decline occurred with feed stream containing small size colloidal particles or poly-disperse suspension (including both small and large size particles). Bar-Zeev et al. (Bar-Zeev et al. 2015) found that biofouling would induce irreversible water flux decline while increasing the pressure loss across the feed channel due to the biofilm formation on the surface of the membrane and feed spacers.

Other than the feed and draw stream compositions, membrane material and morphology could also affect the fouling situation. Thelin et al. (Thelin et al. 2013) observed that organic fouling significantly reduced the power densities of both cellulose triacetate (CTA) and thin film composite (TFC) membranes. The CTA membranes exhibited less water flux decline compared with the TFC, which could be attributed to the higher hydrophilicity of the former.

In addition, hydrodynamic conditions could intensely affect the fouling situation in PRO process. It was observed that fouling became more critical with higher initial water flux (She et al. 2013, Chen et al. 2014), which was attributed to more foulants contacting the membrane surface in the same time period. Several studies on the osmotic driven process have shown that increasing cross-flow velocity could alleviate external fouling occurring within the dense selective skin in the orientation of AL-FS (Lee et al. 2010, Li et al. 2012, Boo et al. 2013, Hickenbottom et al. 2013). However, it was worth mentioning that increasing flow rate had negligible effects on mitigating internal fouling (Arkhangelsky et al. 2012).

Moreover, the feed spacer used in flat sheet membrane testing could reduce ECP and external fouling by increasing the mass transfer and shear rate. However, Wang et al. (Wang et al. 2010) observed that foulants tended to accumulate near the “hydrodynamic dead zone”, the area between the membrane surface and spacer filaments. A recent study associated with the propensity of foulant accumulation in the hydrodynamic dead zones developed owing to the occurrence of spacer via a novel method named optical coherence tomography (Gao et al. 2014). The fouling phenomenon for flat sheet membranes was more complicated than the hollow fibers due to the spacers used.

Different strategies have been addressed to mitigate or control the fouling in PRO process, such as pre-treatments of the feed or draw stream (Tian et al. 2015, Chen et al. 2016), membrane modification for low-fouling propensity (Li et al. 2014, Cai et al. 2016), and cleaning of the fouled membrane (Yip et al. 2013). Several pre-treatment methods were proposed to eliminate foulants and to improve osmotic energy generation, such as sand filtration, NF filtration (Abbasi-Garravand et al. 2016), UF filtration (Tian et al. 2015), antiscalant pre-treatment, and pH adjustment (Chen et al. 2016). Although pre-treatment of feed water could drastically diminish membrane fouling, the pre-treatment would add extra cost and introduce additional chemical by-products that would cause adverse environmental impact.

Various cleaning approaches, e.g., water flushing (Chen et al. 2016), osmotic backwash (Yip et al. 2013, Bar-Zeev et al. 2015), and chemical cleaning (Han et al. 2016), were proposed to remove the foulants from the fouled membranes and recover the water flux. Yip et al. proposed an osmotic backwash by switching the feed water and draw water in the system, and the water flux would diffuse in the opposite direction to the one that foulants depositing on the surface, leading to detachment of organic foulants and water flux recovery (Yip et al. 2013). Bar-Zeev (Bar-Zeev et al. 2015) adopted osmotic backwash with pressure aid on feed stream. However, this cleaning method was inefficient in removing biofilms in the membrane. Osmotic backwash was a unique membrane cleaning method applied in FO/PRO process and consume fewer chemicals or less energy than other methods.

However, chemical cleaning was still necessary for some severe and complex fouling situation, since osmotic backwash could only remove the fouling on the outmost surface of the membrane (Bar-Zeev et al. 2015).

Anti-fouling membranes were designed by modifying the bottom surface that faces the feed stream using grafting (Li et al. 2014, Cai et al. 2016, Zhang et al. 2016, Lieu Le et al. 2017) and coating (Zhao et al. 2016) methods. The detailed modification methods will be discussed in Section 2.2.2. Some double skin membranes have been proposed to be applied in FO/PRO process. A highly selective primary skin for rejecting solutes and a secondary skin on the bottom surface to prevent foulant penetration were developed (Fang et al. 2012, Qi et al. 2012, Han et al. 2017).

Membrane orientation could also severely affect the fouling. It was reported by different research groups that the fouling propensity in the orientation of active layer-facing feed solution (AL-FS) was lower compared to that in the other orientation active layer-facing draw solution (AL-DS) in osmotically driven membrane process. (Tang et al. 2010, Wang et al. 2010, Zhao et al. 2011, Zhang et al. 2012, Zou et al. 2013). As illustrated in Figure 2.4 (a), membrane fouling in the orientation of AL-FS occurs due to foulant deposition on the selective layer surface, which is referred to as external fouling. Figure 2.4 (b) exemplifies that both internal and external fouling occur in the orientation of AL-DS. While in this orientation, the fouling situation is more complex as the foulants of small size could penetrate the porous substrate while those of big size would deposit on the bottom surface of the substrate. Besides negligible crossflow within the porous substrate could enhance the internal foulant deposition in AL-DS orientation. And austere pore blockage of the support layer enhances the ICP in the orientation of AL-DS. It was reported that the external fouling in the orientation of AL-FS was easier to be removed by surface flushing (Lee et al. 2010, Mi et al. 2010, Valladares Linares et al. 2012, Mi et al. 2013), while the internal fouling in the orientation of AL-DS showed less effectiveness in cleaning (Arkhangelsky et al. 2012).

In FO process, membranes could be operated in two orientations (AL-FS and AL-DS orientation), while in PRO process, membranes are usually run in AL-DS orientation due to two reasons. First, the initial water flux in AL-DS is much higher than that in AL-FS orientation owing to less ICP effect (Gray et al. 2006, Tang et al. 2010, Wang et al. 2010). Second, membranes could undergo reduced mechanical stability in the orientation of AL-FS (She et al. 2012). However, the advantages of AL-DS orientation could be reduced when the feed water contains complex foulants. Despite the low fouling tendency in AL-FS orientation, thin film composite membranes could suffer from a severe deformation under this orientation, and the thin polyamide layer would even delaminate from the substrate under even low pressure (Bar-Zeev et al. 2015, She et al. 2017). In this case, integral membranes with better mechanical stability in the orientation of AL-FS under high pressures would be a better option. Kim et al. (Kim et al. 2016) demonstrated the mechanical stability of CTA membranes in the AL-FS orientation at high pressure with proper handling and optimized spacer design, and the fouling propensity in this orientation was lower than that in the opposite orientation.

Figure 2.4 Fouling in PRO process with (a) only external fouling occurs in the orientation of AL-FS, and (b) both internal and external fouling occur in the orientation of AL-DS.

➤ **Energy cost in real implementation**

Decreasing energy consumption is one of the critical challenges to make PRO more competitive compared to other energy generation technology. The actual energy generation from a PRO plant could be much lower than the calculated value (Straub et al. 2016). Most PRO studies were based on a lab-scale membrane setup using membrane coupons or small modules. However, large membrane modules would be utilized in realistic implementation, leading to significant energetic losses owing to practical constraints for continuous run. Besides, the additional energetic cost for pre-treatment, maintenance and backwashing are required (Straub et al. 2016). It was reported that although the potential of the pairing of the river water and seawater was remarkably promising, the energy density was low ($0.256 \text{ kW} \cdot \text{h}$ per cubic meter volume) (Lin et al. 2014). Draw solutions of higher solute concentrations, such as seawater retentate and dead sea water, were proposed to produce more net energy to cover energy lost.

2.2 Preparation of PRO membranes

2.2.1 Thin film composite (TFC) membranes and integral cellulose triacetate (CTA) membranes

Until now, no commercial PRO membranes are available. Several FO membranes have been adopted in PRO process due to the capability to produce high water flux. CTA-FO membranes supplied from Hydration Technology Innovations (HTI, Albany, OR) have been employed for PRO studies in many publications (Achilli et al. 2009, She et al. 2012, Kim et al. 2013). Achilli et al. (Achilli et al. 2009) reported a peak power density of $5.06 \text{ W} \cdot \text{m}^{-2}$ at 9.72 bar with deionized (DI) water as feed and $60 \text{ g} \cdot \text{L}^{-1}$ sodium chloride (NaCl) solution as the draw water. She et al. (She et al. 2012) observed that the CTA-FO membrane could produce the maximum power density of $4.5 \text{ W} \cdot \text{m}^{-2}$ by utilizing 10 mM and 1 M sodium chloride solution as feed and draw, correspondingly. Kim and Elimelech (Kim et al. 2013) achieved a peak power density of $4.7 \text{ W} \cdot \text{m}^{-2}$ using 0.5 and 2 M sodium chloride solution as feed and draw, respectively. Regrettably, the mechanical robustness of the HTI

CTA-FO and other FO membranes was not satisfactory as severe deformation was observed using FO membranes in PRO process (Li et al. 2013, She et al. 2013). The first PRO prototype plant named as Statkraft was established in Norway in 2009 using HTI CTA membranes. However, the plant was terminated in 2014 due to low energy production (Gerstandt et al. 2008, Chung et al. 2015). According to Statkraft's analyses, the minimum power density required to make PRO technology commercially viable was $5 \text{ W}\cdot\text{m}^{-2}$ for flat sheet membranes and $3 \text{ W}\cdot\text{m}^{-2}$ for hollow fiber membranes (Gerstandt et al. 2008, Thorsen et al. 2009, Skilhagen 2010). Membranes that could produce high power density and withstand high pressure need to be developed for PRO application.

So far thin film composite membranes fabricated and reported by several research groups have shown promising results (Chou et al. 2013, Han et al. 2013, Song et al. 2013). The TFC membranes have been developed via in-situ interfacial polymerization to form a dense polyamide solute rejection skin on a porous support layer. This approach has been utilized to synthesize RO membranes for decades (Cadotte et al. 1981) and could be used to fabricate salt selective and robust membranes for PRO process. As discussed in Section 2.1.2, to reduce the ICP effect, the substrates of PRO membranes must be thinner, more porous with less tortuosity compared to those of traditional RO membranes. Unfortunately, these substrates not only led to high water flux but also suffered from severe deformation under high pressures (as discussed in Section 2.1.2). The mechanical robustness of the porous substrates was of particular importance attributed to the stability of the polyamide active skin under high pressure.

Generally, PRO membranes could be fabricated in two configurations: flat sheet and hollow fiber. For flat sheet membranes, two types of substrates have been employed: asymmetric membrane substrates fabricated by non-solvent phase inversion method (Han et al. 2013, She et al. 2016) and nanofibers by electrospinning method (Song et al. 2013, Tian et al. 2015, Park et al. 2016). Both could be mechanically reinforced by woven or non-woven fabrics. For hollow fiber membranes, the substrates could be developed via dry-wet spinning method. For

both configurations, the polyamide selective skin has been formed on top of the substrate (e.g. top surface of flat sheet substrate and inner/outer surface of hollow fiber support layer).

For flat sheet configuration, asymmetric substrates could be prepared by the non-solvent induced phase inversion method. Generally, a sponge-like structure could provide higher robustness and minimize membrane deformation at high pressures in the PRO performance (Li et al. 2013). Chlorine post-treatment (Yip et al. 2011, Han et al. 2013), alcohol immersion (Li et al. 2013, Zhang et al. 2013), and solvent soaking (Cui et al. 2014) were adopted to post-treat membranes to improve the water permeability of the substrate.

On the other hand, electro-spun nanofibers have also been adopted as the support for TFC membrane fabrication by producing nanofibers on customized nonwoven fabrics in several studies (Song et al. 2013, Bui et al. 2014, Tian et al. 2015). According to the recent study, the porous, interconnected structures of nanofibers were ideal as substrates for TFC-FO membranes. Nonetheless, due to the large pore structures, the substrates had weak mechanical properties leading to creeping under high pressure. Several research groups have investigated different approaches to overcoming this problem. Papkov et al. have demonstrated a significant improvement in nanofiber strength by decreasing the diameter of the fiber (Papkov et al. 2013). However, this could lead to decreased mass transfer coefficient and elevated ICP effect. Bui et al. used a tiered nanofiber support, which consisted of finer fibers on the top and coarser fibers on the bottom to minimize membrane deformation without reducing the porosity (Bui et al. 2014). Song et al. added nano-SO₂ particles to nanofibers to increase the mechanical robustness while maintaining the water permeability (Song et al. 2013). Tian et al. reported a tiered structured PEI nanofibrous support using multi-walled carbon nanotubes (CNT) to reinforce the support and achieved a 17.3 W·m⁻² power density at 16.9 bar with DI water as feed and 1 M NaCl as a draw. The burst pressure of the CNT-incorporated membrane could reach up to 24 bar.

The polyamide selective skin could be synthesized by interfacial polymerization method using two basic monomers: m-phenylenediamine (MPD) and trimesoyl chloride (TMC). The water permeability of the polyamide skin could be improved by optimizing the condition of interfacial polymerization method (e.g. additive types, concentration of reaction monomer, and post treatment) (Han et al. 2013, Li et al. 2013, Cui et al. 2014). Li et al. (Li et al. 2013) blended an additive p-xylylenediamine into MPD solution leading to more free volume in the selective layer causing the increase in water permeability. Cui et al. (Cui et al. 2014) added sodium dodecyl sulfate (SDS) into MPD solution, resulting in a significant increase in the power density from $\sim 8 \text{ W}\cdot\text{m}^{-2}$ to $\sim 15 \text{ W}\cdot\text{m}^{-2}$ at the pressure of 22 bar using 1 M NaCl as the draw stream and pure water as the feed. NaOCl was also adopted to modify the polyamide selective layer to improve the water permeability, thereby increasing the power density (Yip et al. 2011, Han et al. 2013).

For Hollow fiber configuration, membranes had certain advantages compared to the flat sheet counterpart in terms of higher packing density, self-supporting property and no shadow effects (Peng et al. 2012, Han et al. 2015). Feed spacers were not required in hollow fiber membrane modules, which could eliminate the adverse interaction between membranes and spacers under high pressure (Sivertsen et al. 2012). The hollow fiber substrates could be prepared by non-phase inversion method using a spinning machine. The dope concentration, inner-coagulant, air gap etc. could be adjusted to obtain the optimized structure for PRO application (Han et al. 2014). The salt rejection skin was usually synthesized on the lumen surface of the hollow fibers by conducting interfacial polymerization method. The maximum power density produced by TFC hollow fiber membranes could reach above $20 \text{ W}\cdot\text{m}^{-2}$ using deionized (DI) water as feed and sodium chloride solution (1 M) as draw (Chou et al. 2013, Zhang et al. 2013).

On the other hand, several outer-selective hollow fiber membranes were fabricated with polyamide selective layers synthesized on the outer surface of the supports (Sun et al. 2013, Cheng et al. 2016, Le et al. 2016, Cheng et al. 2017). Compared to inner-selective membranes, outer-selective ones could provide more membrane

areas per fiber and encounter less pressure drop during PRO operation. However, the fabrication procedures would be much more complicated than the inner-selective membranes, and until now only one research group could produce this type of membrane (Sun et al. 2013, Cheng et al. 2016, Le et al. 2016, Cheng et al. 2017).

The membrane materials and PRO performance in the literature are presented in Table 2.1 and Figure 2.5. As shown in Table 2.1, the self-developed membranes reported in the literature were mostly TFC membranes due to the higher power density produced compared to the commercially available HTI CTA membranes. The highest power density reported was $24.3 \text{ W}\cdot\text{m}^{-2}$ produced by a TFC PES hollow fiber membrane in 2014 (Zhang et al. 2014). Studies on the development of membranes that could produce decent yet stable performance have been carried out since 2014 (She et al. 2016) (Tian et al. 2015) (Zhao et al. 2016). For instance, membranes with enhanced mechanical properties, low-fouling propensity have been developed, indicating the endeavors to resolve the concern for stable operation for real world application.

Table 2.1 PRO membrane performance from literature

S/N	Membrane	Material	Feed	Draw	Pressure (bar)	W (W·m ⁻²)	Ref.
1	TFC flat-sheet nanofiber with nonwoven fabric	Polyamide-polyethersulfone	DI water	1 M NaCl	12.5	9.5	(Park et al. 2016)
2	TFC flat-sheet with woven fabric	Polyamide-polysulfone	DI water	1 M NaCl	22	12.9	(Wei et al. 2016)
3	TFC flat-sheet with woven fabric	Polyamide-polysulfone	10 mM NaCl	1 M NaCl	18.4	7.1	(She et al. 2016)
4	TFC flat-sheet nanofiber with nonwoven fabric	Polyamide-polyetherimide	DI water	1 M NaCl	16.9	17.3	(Tian et al. 2015)
5	TFC flat-sheet	Polyamide-polyetherimide	10 mM NaCl	1 M NaCl	17.2	12.76	(Li et al. 2015)
6	TFC flat-sheet	Polyamide-polyimide	DI water	1 M NaCl	22	18.09	(Cui et al. 2014)
7	TFC flat-sheet nanofiber with non-woven fabric	Polyamide-polyacrylonitrile	DI water	0.5 M NaCl	10.34	8	(Bui et al. 2014)
8	TFC flat-sheet	Polyamide-P84 copolyimide	DI water	1 M NaCl	9	6	(Li et al. 2013)
9	TFC flat-sheet nanofiber with non-woven fabric	Polyamide-polyacrylonitrile	0.9 mM NaCl	1.06 M NaCl	15.2	15.2	(Song et al. 2013)
10	TFC flat-sheet	Polyamide-polyimide	DI water	1 M NaCl	15	12	(Han et al. 2013)
11	HTI flat-sheet	Cellulose acetate	10 mM NaCl	1 M NaCl	15 ^a	3.7 ^a	(She et al. 2012)
12	TFC hollow-fiber	Polyamide-polyethersulfone	DI water	1 M NaCl	22	10.05	(Cheng et al. 2017)
13	TFC hollow-fiber	Polyamide-polyetherimide	DI water	1 M NaCl	17	9.59	(Le et al. 2016)
14	TFC hollow-fiber	Polyamide-polyetherimide	DI water	1 M NaCl	15	19.2	(Chen et al. 2016)
15	Triple-layer Hollow-fiber	Outer layer: polybenzimidazole Middle layer: polyacrylonitrile/ polyvinylpyrrolidone Inner layer: polyacrylonitrile	10 mM NaCl	1 M NaCl	22	6.23	(Fu et al. 2015)
16	TFC hollow-fiber	Polyamide-polyethersulfone	DI water	1 M NaCl	20	24.3	(Zhang et al. 2014)
17	TFC hollow-fiber	Polyamide-polyimide	DI water	1 M NaCl	15	16.5	(Han et al. 2014)
18	TFC hollow-fiber	Polyamide-P84 copolyimide	DI water	1 M NaCl	21	12	(Rica et al. 2014)
19	TFC hollow-fiber	Polyamide-polyetherimide	1 mM NaCl	1 M NaCl	15.1	20.9	(Chou et al. 2013)
20	TFC hollow-fiber	Polyamide-polyethersulfone	40 mM NaCl	1 M NaCl	24	21	(Zhang et al. 2013)
21	TFC hollow-fiber	Polyamide-polyimide	Tap water	1 M NaCl	16	14	(Han et al. 2013)
22	TFC hollow-fiber	Polyamide-polyimide Outer layer: polybenzimidazole/ polyhedraloligomeric silsesquioxane	DI water	1 M NaCl	20	7.63	(Sun et al. 2013)
23	Dual-layer hollow- fiber	Inner layer: polyacrylonitrile/ polyvinylpyrrolidone	10 mM NaCl	1 M NaCl	7	2.47	(Fu et al. 2013)
24	TFC hollow-fiber	Polyamide-polyethersulfone	40 mM NaCl	1 M NaCl	9	10.6	Chou, Wang et al. 2012)

Note:

^a Read from the figures

Figure 2.5 Performances of PRO membranes in the literature (Open symbols represent the flat sheet membranes and closed symbols represent the hollow fiber membranes).

2.2.2 Membrane fabrication for stable high power generation

It is important to fabricate PRO membranes that could generate stable high power density. As mentioned previously in Section 2.1, internal concentration polarization effect could drastically reduce the driving force leading to reduced water flux. In addition, mechanical deformation could induce damage and possibly cause breakdown of the membrane modules resulting in disruption of the continuous operation. Moreover, foulants that widely exist in feed and draw streams could penetrate the support layer leading to water flux decline. To continuously produce high power output during the operation, the above issues must be considered when designing and fabricating PRO membranes.

The internal concentration polarization effect has been intensely studied for the past decades for forward osmosis membrane design (Wang et al. 2010, Wei et al. 2011,

Zhao et al. 2012). A series of new membranes have been designed for forward osmosis that focusing on reducing ICP with a combination of high water permeability, good solute selectivity, and minimal structural parameter. The thin film composite asymmetric membranes would be promising as the membrane support layers could be optimized to reduce S value by adopting a thin and highly porous structure. However, the difference between FO and PRO membranes is that PRO membranes are required to withstand the high operating pressure that applied to the draw side. A thin and porous substrate that applicable to FO process would be susceptible to damage and deform in PRO experiments.

To improve mechanical properties of PRO membranes, utilizing the polymeric material with high tensile modulus seems a promising approach. According to the summary table in Section 2.2.1, some membranes that could be operated under high pressures have been fabricated using highly robust polymers such as polyethersulfone (PES), polyetherimide (PEI) (Chou et al. 2013, Chen et al. 2016), polysulfone (PS) (She et al. 2016, Wei et al. 2016) and polyimide (PI) (Han et al. 2013, Cui et al. 2014). Additionally, a sponge-like structure was also preferred to dissipate stresses and to prevent structural collapse that often occurred to membranes with finger-like structures (macrovoid structures) under hydraulic pressure (Chou et al. 2013, Han et al. 2013). Severe deformation was observed by Li et al. during testing a TFC polyamide-imide (PAI) membrane with a finger-like structure under 14 bar hydraulic pressure, resulting in 47.4% reduced thickness and collapsed pores (Li et al. 2013). Han et al. developed a TFC polyimide membrane with a fully-sponge like support layer that could withstand 15 bar pressure and yield a power density of $12 \text{ W} \cdot \text{m}^{-2}$ even with a small membrane thickness ($\sim 50 \mu\text{m}$) (Han et al. 2013). Chou et al. adopted a fully-sponge like polyetherimide substrate to develop a TFC hollow fiber membrane that could produce $20.9 \text{ W} \cdot \text{m}^{-2}$ power density at 15 bar with DI water as feed and 1 NaCl as draw (Chou et al. 2013). As discussed in Section 2.1.2, decreasing the inner diameter of hollow fiber membrane could also enhance mechanical robustness. Chen et al. developed a PEI TFC hollow fiber membrane with a reduced inner diameter that could withstand hydraulic pressure up to 23.5 bar. The resultant membrane could generate stable power

density at 15 bar for over 200 hours (Chen et al. 2016). Incorporated with woven/non-woven fabric was also an alternative technique to enhance the mechanical robustness of flat sheet membranes (Song et al. 2013, Tian et al. 2015, She et al. 2016, Wei et al. 2016). She et al. (She et al. 2016) investigated three different fabrics by integrating them in polysulfone flat sheet membrane fabrication. In this study, the tricot fabric-reinforced membrane exhibited the best performance while the nonwoven fabric-reinforced membrane generated the lowest power density due to the increased structural parameter, suggesting the reinforce fabric should possess both high opening and robust mechanical property.

Although pretreatment could mitigate fouling, it would add extra energy and chemical consumptions as well as footprint. Fabricating membranes with low fouling propensity would be a viable tactic to reduce the affinity for membranes and foulants. As mentioned in Section 2.1.2, some membranes were grafted or coated with hydrophilic polymers to minimize foulants deposition on the surfaces or on the back side of the selective skin. The fouling studies of PRO membranes in the literature are shown in Table 2.2. Hydrophilic poly(ethylene glycol) (PEG) was widely employed to be grafted on membrane surface due to its low fouling property via hydrogen bonding (Asatekin et al. 2006, Hyun et al. 2006, Liu et al. 2007). Li et al. (Li et al. 2014) grafted a dendritic hyper-branched polyglycerol (HPG) on a polydopamine pre-treated polyether sulfone (PES) membrane. The HPG grafted membrane exhibited low-fouling propensity towards protein and bacterial adhesion with a high flux recovery after cleaning. Nonetheless, the HPG lacked strong repellent forces to ions and was vulnerable to scaling. Li et al. (O'Toole et al. 2016) further improved the antifouling performances of PRO membranes by grafting a new negatively-charged hyperbranched polyglycerol (CHPG) polymer on the surface facing the feed solution. By using concentrated wastewater as feed stream and 0.81 M sodium chloride as draw stream, the average power density of the CHPG TFC membrane could be maintained at $5.6 \text{ W} \cdot \text{m}^{-2}$ compared with $3.6 \text{ W} \cdot \text{m}^{-2}$ of the original membrane. However, PEG was vulnerable to oxidation and not sustainable for the long-term process (Herold et al. 1989, Harder et al. 1998, Ostuni et al. 2001). Zwitterion-based materials containing both positive and negative

functional groups have been considered for the preparation of the low fouling membranes due to the excellent anti-adhesion properties against protein and bacteria (Yu et al. 2014, Zheng et al. 2016). During the grafting process between zwitterion polymers and membranes, a stable hydration layer could be formed on the membrane via the electrostatic induced interaction rather than hydrogen bonding (Chang et al. 2006, Zhang et al. 2006, Chang et al. 2007). Cai et al. (Cai et al. 2016) modified the membrane surfaces by grafting zwitterionic copolymers on the outer surface of an inter-selective TFC hollow fiber membrane. The resulted membrane showed a water flux recovery up to 98% using a real wastewater retentate. Lieu et al. (Lieu Le et al. 2017) used a surface-adsorbed macro-initiator to conduct a cross-linking reaction with zwitterionic polymer on the lumen side of an outer-selective PRO membrane. Some other hydrophilic polymers have also been utilized as the antifouling agent to modify PRO membranes. Zhao et al. (Zhao et al. 2016) grafted 2-methacryloyloxyethyl-phosphorylcholine (MPC) onto the polydopamine (PDA) coated PES membrane and achieved high resistance to bacterial adhesion and protein adsorption. In another study from the same group, poly (vinyl alcohol) PVA was adopted to coat the membrane surface to increase hydrophilicity. PDA was coated on the surface of PES substrate prior to PVA coating to activate the substrate surface. The resultant membranes showed improved fouling resistance to alginate and the alginate-calcium complex compared to the pristine membranes (Zhang et al. 2016). Zhang et al. evaluated the effect of aminosilane in developing the low-fouling PRO membranes (Zhang et al. 2016). 3-aminopropyltrimethoxysilane (APTMS) was grafted on the lumen surface of membrane substrate for three reasons: (1) increasing the hydrophilicity of the substrate (2) minimizing pore clogging due to the small sizes (3) simple procedures to directly react with the polyetherimide substrate. By post-treatment with APTMS, the increase of surface hydrophilicity resulted in increased water permeability and reduced fouling tendency. APTMS was also proposed as a monomer to replace m-Phenylenediamine (MPD), which was a common monomer for thin film composite membrane selective layer fabrication via interfacial polymerization. The resulted APTMS synthesized TFC membranes had similar contact angle, water permeability, salt permeability to those APTMS-grafted selective layers. This alternative synthesizing receipt could be used for anti-fouling

TFC membrane fabrication. Except for surface modification, the double skin concept was applied in several studies of antifouling FO/PRO membrane fabrication (Fang et al. 2012, Qi et al. 2012, Su et al. 2012, Duong et al. 2014, Fang et al. 2015, Lim et al. 2017). The concept was initiated by Wang et al. to counteract the adverse effect of fouling in PRO mode for the osmotically-driven process (Wang et al. 2010). The double-skin membrane could be prepared by synthesizing a primary skin facing the draw solution to reject solutes, while a secondary skin could be formed on the porous support facing the feed streams to prevent foulants penetration. Han et al. (Han et al. 2017) designed a secondary polyamide skin on the porous substrate to counteract the foulants diffusion from wastewater feed water, as depicted in Figure 2.6. The advantage of the double-layer approach was to eliminate the internal fouling that was difficult to clean due to the substrate tortuosity. However, the techniques for developing a secondary layer were complicated, and there was a possibility that solutes could be trapped between two skins inducing severe ICP, leading to water flux decline (Tang et al. 2011).

Figure 2.6 Schematic diagram of fouling phenomenon: (a) the conventional TFC membrane and (b) the double polyamide skin TFC membrane in FO process (in AL-DS orientation) and PRO processes (Han et al. 2017). Copyright 2017. Reproduced with permission from Elsevier Ltd.

Table 2.2 The fouling behaviors of PRO membranes in the literature

S/N	Membrane	Modification method	FS	DS	Pre-treatment	Initial W ($W \cdot m^{-2}$)	Applied Pressure (bar)	Final W ($W \cdot m^{-2}$)	Reference
1	PES-double skin	Double polyamide skin	Wastewater brine	1 M NaCl	/	10.7	15	~9 after 720 min	(Han et al. 2017)
2	PEI-M-0.25/6	Zwitterions grafting	200 ppm BSA	1 M NaCl	/	/	12	15 @ 170 $L \cdot m^{-2}$	(Lieu Le et al. 2017)
3	TFC-PES	/	Wastewater brine	1 M NaCl	Adjust pH=5.5	17.2	20	10.8 ^a after 2 runs	(Chen et al. 2016)
4	TFC-PES	/	Wastewater brine	1 M NaCl	1.1 mM EDTA	15.9	20	10.0 ^a after 2 runs	(Chen et al. 2016)
5	TFC-PES	/	Wastewater brine	1 M NaCl	/	11.5	15	4.8 after 3 runs	(Zhao et al. 2016)
6	TFC-PES	/	Wastewater brine	0.81 M NaCl	/	8.3	15	3.6 after 4 runs	(O'Toole et al. 2016)
7	TFC-PES	/	Wastewater brine	1 M NaCl	/	17.1	20	5.7 after 2 runs	(Chen et al. 2016)
8	TFC-PES-PDA-CHPG	Charged hyperbranched PEG grafting	Wastewater brine	0.81 M NaCl	/	8.2	15	5.6 after 4 runs	(O'Toole et al. 2016)
9	TFC-PES-PDA-MPC	Zwitterions coating	Wastewater brine	1 M NaCl	/	11.3	15	7.2 after 3 runs	(Zhao et al. 2016)
10	TFC-PEI-APTMS	APTMS grafting	3 mM $CaCl_2$ 200 ppm humic acid	1 M NaCl	/	7 ^a	9	16 @ 60 min	(Zhang et al. 2016)
11	TFC-PES	/	Wastewater brine	SWBr	/	21.1	20	4.6 @ 30 min	(Tian et al. 2015)
12	TFC-PES	/	Wastewater brine	SWBr	UF pretreated	21.1	20	6.6 @ 30 min	(Tian et al. 2015)
13	TFC-PES	/	Wastewater brine	SWBr	NF pretreated	21.1	20	8.9 @ 30 min	(Tian et al. 2015)
14	HTI-CTA	/	1 mM $CaCl_2$ 200 ppm alginate	1.2 M NaCl	/	6.2	15	40.0 @ 300 min	(Kim et al. 2015)
15	TFC-PES	/	200 ppm alginate	1 M NaCl	/	11.2	18	55.1 @ 3000 min	(Chen et al. 2015)
16	HPG-PES	Hyperbranched PEG grafting	200 ppm BSA	0.6 M NaCl	/	6.7	12.5	10.0 @ 140 $L \cdot m^{-2}$	(Li et al. 2014)

Note:

a. read from the figures

2.3 Summary

PRO technology for salinity energy production has been intensely investigated over the past decades. Studies of ICP effect, mechanical deformation phenomenon, fouling behaviors etc. have been conducted to provide guidance for PRO membrane fabrication. Membranes with high performance, excellent mechanical properties have been developed due to the breakthrough in osmotic-driven process theory development and membrane fabrication technology.

Membranes reported in the literature could produce a high power density and withstand high hydraulic pressure using pure water as feed and high concentration of sodium chloride as draw. However, organic compounds and inorganic particles are ubiquitous in various water resources and could induce fouling on membrane surface or within the porous layer causing severe power output decline. Thus, fouling control is critical in PRO process, which could be done by pre-treatments of water solutions, membrane modification and regular cleaning of fouled membranes. Pre-treatments and cleaning could add extra cost to the process, thereby modification of membrane is more promising to be applied in this process than other approaches. Modifying the surface of membrane facing the feed stream by grafting or coating with hydrophilic chemicals could increase surface hydrophilicity and reduce the attachment of foulants. Changing the membrane orientation from active layer-facing draw stream to active layer-facing feed could also significantly reduce internal fouling. Nevertheless the TFC membranes could not be operated in AL-FS orientation under high pressure. Developing integral membranes with high mechanical stability in AL-FS orientation is imperative to mitigate fouling in a long-term operation.

Although the performances of PRO membranes seem promising, it should be pointed out that these data were acquired based on laboratory scale study. Therefore, further study is imperative to upscale it in a real pilot plant. In addition, most feed and draw solutions reported in the published journals were synthesized salt solution (with only sodium chloride molecules) instead of real water sources and brine. In addition, the power densities calculated in the publication were only based on

membrane performance without calculating the loss in pipes and turbines. Long-term prototype plant tests are required in the future to evaluate the PRO process efficiency.

Generally, PRO technology is still under development, where a further study in large scale is required to convince industry to integrate this technology with desalination or other processes. Driven by the huge commercial values and environmental benefit, more efforts will be put in the optimizations of PRO system and membrane fabrication process.

CHAPTER 3 Fabrication and characterization of high-performance flat-sheet TFC PRO membranes

This chapter has been published as Ye Li, Rong Wang, Saren Qi, Chuyang Tang (2015) *Structural stability and mass transfer properties of pressure retarded osmosis (PRO) membrane under high operating pressures*. Journal of Membrane Science, 488:143-153. Permission has been granted by the licensed content publisher “Elsevier” to use the published content as a chapter in this thesis.

3.1 Introduction

As described in Chapter 2, the major hinder back of PRO technology is the absence of commercially available PRO membranes. The power density threshold is higher than $5 \text{ W}\cdot\text{m}^{-2}$ for flat sheet membrane and $3 \text{ W}\cdot\text{m}^{-2}$ for hollow fibers to make membranes commercially viable (Skilhagen et al. 2008, Thorsen et al. 2009). Reverse osmosis (RO) membranes were designed to be highly robust and the dense substrates could induce ICP effect, leading to extremely low water flux in the osmotically-driven process (Lee et al. 1981). The CTA and TFC membranes supplied by Hydration Technologies Inc (HTI) were designed with a porous substrate for mitigating ICP effect (Wei et al. 2011, Wang et al. 2012, Tiraferri et al. 2013). Nonetheless, these FO membranes lacked the mechanical toughness mandatory to endure the high hydrostatic pressures in PRO experiments (Xu et al. 2010, Kim et al. 2012, She et al. 2012). Membrane deformation was commonly observed in PRO process and could result in severe salt leakage and significantly decreases the power density (She et al. 2013) as well as accelerates membrane fouling and scaling (She et al. 2013, Zhang et al. 2014). Therefore, the balance between membrane permeability and mechanical strength needs to be evaluated.

Adjusting membrane substrate structure and porosity is one of the approaches to investigating the relationship between structure and performance. A high porosity usually leads to an increment in water permeability and reduction in mechanical

robustness, and vice versa. While in PRO process, producing a high power output requires a high water flux at high hydraulic pressure. Therefore, it is difficult to reach a balance between mechanical robustness and high water permeability. For substrate, sponge-like structure usually has smaller porosity compared to finger-like structure and (Han et al. 2013)

Thin film composite (TFC) membranes have been widely used in osmotically driven membrane process owing to their high water permeability and solute selectivity (Arena et al. 2011, Bui et al. 2011). TFC membranes could be synthesized by conducting interfacial polymerization on the porous membrane substrate, which has been adopted as a common method to produce RO membranes (Cadotte et al. 1981). Undeniably, flat sheet PRO membranes experience severe deformation under high hydraulic pressure attributed to the large opening of the spacers (Xu et al. 2010, She et al. 2013). Therefore, more attention is demanded to further investigate the mechanical changes of flat sheet membranes under pressure. Principles and strategies for improving membrane performance should be evaluated. The fabricating conditions for PRO membranes need to be studied, with due consideration of the compromise between membrane mass transfer properties and mechanical robustness. In this chapter, high-performance TFC PRO flat sheet membranes with various pore structure were fabricated via non-solvent induced phase inversion followed by an interfacial polymerization method. The resultant membranes possessed a high water permeability with a low salt permeability. A series of characterization protocols were conducted by FESEM imaging and tensile modulus measuring to investigate the association between membrane morphology and PRO performance. The stability tests were systematically conducted for a long period. This chapter aims to conduct a detailed study of PRO membrane fabricating method and the fundamental study of the relationship between membrane micro and meso structure with membrane performance.

3.2 Experiments

3.2.1 Materials for experiments

Polyetherimide (PEI, Ultem[®], GE Plastics), ethanol (> 99.5%, Merck) and N-Methyl-2-pyrrolidone (NMP, >99.5%, Merck) were applied as the polymer, additive and solvent to prepare the PEI substrate. Trimesoyl chloride with 99.0% purity and m-Phenylenediamine (MPD) with >99.0% purity from Sigma-Aldrich were employed to synthesize the polyamide selective layer by conducting interfacial polymerization. N-hexane (> 99.0%) ordered from Merck was applied as the solvent for the TMC monomer. Sodium dodecyl sulfate (SDS, Scientific Apparatus Supplier) was used as an additive in MPD solution. Sodium chloride (NaCl, Merck) was the solute employed to prepare feed and draw solutions. Isopropyl alcohol (IPA, $\geq 99.8\%$, Merck) was adopted as the wetting solvent in porosity tests. The deionized water was provided by a Milli-Q system (18.2 M Ω ·cm, Milli-pore Singapore Pte Ltd).

3.2.2 Synthesis of TFC PRO flat sheet membranes

The detailed procedures of preparing TFC membranes were similar to our previous study (Wei et al. 2011). Briefly, the PEI resins were stored at 50 ± 2 °C in a vacuum oven for more than 3 days to remove moisture before preparing the dope. Three dope solutions were prepared using NMP as solvent and the composition of each solution is present in Table 3.1. The substrates were customized under the same circumstances by dispersing each solution onto a clean and dry glass plate with a casting knife of 200 μ m gap, then the glass plate with the dope solution on top was immersed in a water tank for phase inversion. The as-prepared three types of membrane substrates were denoted as S-PEI#1, S-PEI#2 and S-PEI#3. The polyamide solute rejecting skin was then developed on the top of the support via interfacial polymerization using MPD and TMC as two basic monomers. The concentration of each monomer is also listed in Table 3.1. Briefly, the MPD solution was poured on the top surface of the substrate and rested for 20 minutes. Then the excess solution was removed by nitrogen gas purging gun until no water

drop was visible. The TMC-n-hexane solution was poured on the surface and reacted for 2 minutes. The resultant TFC membranes were named as TFC-PEI#X (X indicates the number of the substrate) and stored in DI water before further usage.

Table 3.1 Synthesis conditions for TFC-PEI membranes

Membrane	Casting solution composition for membrane substrate			Rejection layer via interfacial polymerization		
	PEI (%)	Ethanol (%)	NMP (%)	MPD (%) in water	SDS (%) in water	TMC (%) in n-hexane
TFC-PEI#1	12	13	75			
TFC-PEI#2	14.5	13	72.5	1	0.1	0.1
TFC-PEI#3	17	13	70			

3.2.3 Characterization of substrates and TFC membranes

Membrane surface and cross section structure were observed using a Zeiss EVO 50 Scanning Electron Microscope (SEM) supplied from Carl Zeiss Pte Ltd. Membrane samples were prepared using liquid nitrogen before freeze drying. A thin film of platinum was coated on the surface of the samples prior to SEM observation. The roughness of TFC membrane surface was tested by a Park XE-100 Atomic Force Microscopy (AFM) in non-contact mode.

Tensile modulus of membrane substrate was obtained using a Zwick 0.5 kN Universal Testing Machine to denote the mechanical robustness. The flat sheet sample with known size was clamped at both ends and pulled in tension at a constant elongation velocity of 50 mm/min with an initial gauge length of 25 mm. Membrane porosity was evaluated by measuring the dry and wet masses of the membrane sample according to the gravimetric method using isopropyl alcohol (IPA) as the wetting solvent (Wang et al. 2010).

3.2.4 Intrinsic separation parameters of TFC-PRO membranes

The intrinsic separation parameters of TFC PRO membranes were tested using a cross-flow filtration setup similar to Tang et al. (Tang et al. 2010). The water permeability A was evaluated by pumping DI water on the active skin side with at 10 bar pressure. The A value was calculated according to:

$$A = \frac{J}{\Delta P} \quad (3.1)$$

where ΔP is the trans-membrane pressure and J is the permeate water flux. The water permeability of the substrate was tested similarly except that the applied pressure is 1 bar.

The NaCl rejection R_s and salt permeability B were determined at 10 bar and 10 mM NaCl solution was adopted as feed solution. Rejection R_s was calculated based on the conductivity of the feed and permeate streams:

$$R_s = \frac{(C_f - C_p)}{C_f} \quad (3.2)$$

where C_f and C_p are the salt concentrations of feed and permeate, correspondingly. The salt permeability was calculated by Eq.(3.3):

$$B = \left(\frac{I}{R_s} - I \right) \cdot J \quad (3.3)$$

A series of water permeability (A_p) and salt permeability (B_p) values under various pressures (ranging from 2~17 bar) were also determined using a PRO setup (discussed in 3.2.6 section).

The membrane structure parameter (S) was calculated using Eqs. (3.4) and (3.5). The water flux (J_w) was obtained from the FO experiments in both orientations and

the A and B values were attained from the RO experiments (Tang et al. 2010, Wei et al. 2011). AL-DS refers to the orientation of the active layer of the membrane facing draw solution and AL-FS refers to that of the active layer facing feed solution.

$$S = \frac{D}{J_w} \ln \left(\frac{\pi_d - \left(\frac{J_w}{A} \right) + \left(\frac{B}{A} \right)}{\pi_f + \left(\frac{B}{A} \right)} \right) \quad (\text{AL-DS orientation}) \quad (3.4)$$

and

$$S = \frac{D}{J_w} \ln \left(\frac{\pi_d + \left(\frac{B}{A} \right)}{\pi_f + \left(\frac{J_w}{A} \right) + \left(\frac{B}{A} \right)} \right) \quad (\text{AL-FS orientation}) \quad (3.5)$$

3.2.5 PRO experiments

The PRO setup employed in this study was similar to the one reported in our previous studies (Chou et al. 2013, She et al. 2013). The detailed diagram for PRO performance evaluation was present in Figure 3.1. PRO tests were conducted at a predetermined pressure (ranging from 3 to 20.7 bar) that applied to the draw side. At each pressure, the PRO test was continued for 30 min to reach a stable water flux. The water flux was determined by measuring the weight change of dosing deionized water with time. The water flux J_w was calculated using Eq. (3.6)

$$J_w = \frac{\Delta V}{A_m \Delta t} \quad (3.6)$$

where ΔV is the volume change of dosing water in the time period of Δt , A_m is the effective membrane area. The solute flux was calculated based on the measurements of the conductivity of the feed stream. The salt concentration of the feed solution

can be determined by using a calibration curve. The salt flux J_s was calculated using Eq. (3.7):

$$J_s = \frac{\Delta(C_{fe} V_f)}{A_m \Delta t} \quad (3.7)$$

where C_{fe} and V_f are the salt concentration and the volume of the feed solution, correspondingly.

The testing condition for evaluating PRO performance was similar to (She et al. 2013) and set as follows:

- Draw solution: 1 M NaCl solution; feed solution: 10 mM NaCl solution;
- Membrane orientation: AL-DS orientation;
- Cell flow channel dimension: 85mm length $\times$ 40 mm width
- Temperature: 23 ± 1 °C for both feed and draw solution;
- Crossflow: the cross-flow velocity employed was $0.17 \text{ m}\cdot\text{s}^{-1}$ for the draw solution while a flow velocity of $0.08 \text{ m}\cdot\text{s}^{-1}$ was used for the feed stream.
- Spacer: One piece of net-type spacer with a thickness around 1.55 mm and an opening ratio around 0.55, provided from GE Power&Water (GE Osmonics, SEPA), was used in the draw solution side. Six pieces of RO permeate carriers with a thickness around 0.25 mm and an opening ratio around 0.35, that was from Dow FilmTec RO module (BW30-4040), were used as feed spacer for better support.

The power density was calculated by multiplying water flux and the effective trans-membrane pressure:

$$W = J_w \Delta P \quad (3.8)$$

3.2.6 Membrane deformation and stability study

Pressure cycle experiments were conducted to study the membrane deformation in PRO process. The setup and flow diagram are the same as in the Section 3.2.5. One pressure cycle refers to the applied pressure inside increasing from zero bar to the peak pressure (theoretically, the power density of the membrane at this pressure is the highest) and then return to zero bar. Two pressure cycles were continuously applied to the membrane active layer to observe the change of water flux, power density and specific salt flux (J_s/J_w). Water permeability (A_p) and solute permeability (B_p) value at different pressures were measured using the PRO setup to detect the deformation of the membrane. It is noted that the A_p and B_p value here are different with the ones measured using the RO setup, where the membranes were supported using a porous flat stainless steel to minimize the deformation. Therefore, the water permeability and solute permeability under in RO experiments cannot reflect the deforming situation in the PRO process (Kim et al. 2012, She et al. 2012, She et al. 2013). In this study, the PRO cell was modified to an RO test cell. 10 mM NaCl was introduced to the draw solution channel of the PRO cell, and the applied pressure at the draw solution flow channel was increased to a predetermined value. The membrane was supported by spacers used in PRO testing cell and the intrinsic properties obtained in this modified RO testing could directly indicate the membrane deformation situation under PRO testing when the applied pressure in this modified RO setup was equal to the hydraulic pressure on the draw solution side in the PRO tests. The permeate flow in the feed side was collected in a certain time interval, and the A_p value was calculated using Eq. (3.1). The B_p value and R_p were calculated using Eqs. (3.2) and (3.3), respectively. The detailed procedure can be found elsewhere (She et al. 2013).

The stability of membrane performance was evaluated over ten hours under the PRO condition. The water flux and power density were recorded along the process.

Figure 3.1 Schematic diagram of PRO set up

3.3. Results and discussion

3.3.1 Morphology and characteristics of the PEI flat sheet substrates

Three types of substrates were fabricated by the phase inversion method according to the recipes listed in Table 3.1. The FESEM images of the resultant PEI flat sheet substrates are shown in Figure 3.2. From the cross-section of each substrate, it can be seen that two distinct layers were formed (Figures 3.2 (A), (B) and (C)). A sponge-like structure occurred in the top section while the bottom part contains relatively large finger-like pores. The ratio of sponge-like structure to the finger-like macrovoid structure follows the order of S-PEI#3 > S-PEI#2 > S-PEI#1 corresponding to the increase of polymer concentration in the polymer dope solution, as listed in Table 3.1. It seems that a more concentrative polymer solution tended to form a sponge-like structure due to delayed demixing of the dope solution (Setiawan et al. 2012). It is well recognized that the finger-like macrovoid structure

is favorable for FO process due to reduced ICP (Qin et al. 2010, Yip et al. 2010, Setiawan et al. 2011, Shi et al. 2011). However, such a structure is vulnerable in the PRO process because the structure may encounter heterogeneous compaction and uneven deformation under high pressure (Widjojo et al. 2011, Li et al. 2013, Zhang et al. 2013). In contrast, the sponge-like structure is more suitable for PRO process for the advantages of strong mechanical strength to minimize the deformation under high hydraulic pressures (Thorsen et al. 2009, Huang et al. 2013, Zhang et al. 2013), but it has the constraint of high mass transfer resistance. Comparing the three substrates, the S-PEI#2 possesses a medium portion of the sponge-like structure. In addition, it was observed that the pore size on the top surface of the substrates reduced with increasing the polymer solution, as shown in Figures 3.2 (a), (b) and (c). From the AFM micrographs of the three substrates shown in Figure 3.3, it can be seen that the roughness (R_a) of the substrate surface increased with an increase in the polymer concentration. The R_a of S-PEI#1 was around 63.8 nm, while the R_a of S-PEI#2 and S-PEI#3 was 100.6 nm and 156.7 nm, respectively.

Figure 3.2 SEM images of PEI substrate: (a1) Cross section of S-PEI#1; (a2) Cross section of S-PEI#2; (a3) Cross section of S-PEI#3; (b1) Top surface of S-PEI#1; (b2) Top surface of S-PEI#2; (b3) Top surface of S-PEI#3.

Figure 3.3 AFM micrographs of the flat sheet membranes: (a) Surface of S-PEI#1; (b) Surface of S-PEI#2; (c) Surface of S-PEI#3.

The properties of PEI flat sheet membrane substrates are shown in Table 3.2 in terms of water permeability, thickness, porosity and mechanical strength. With an increase in PEI concentration, the water permeability and porosity reduced while the mechanical strength was increased. These trends are in consistent with their corresponding cross-section structure and surface pore size, shown in Figure 3.2. Obviously, the sponge-like structure is able to well distribute the stress in the membrane, which contributes to the better mechanical property (Chou et al. 2013). However, the high concentration of PEI also leads to a thicker membrane sacrificing the water permeability and porosity. It seems that S-PEI-2# membrane is a balanced case, possessing a relatively high pure water flux ($483 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$), good porosity (73%) and reasonably high Young's modulus (150 MPa).

Table 3.2 Characteristics of PEI membrane substrate				
Membrane	Water Permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Thickness (μm)	Porosity (%)	Young's Modulus (Mpa)
S-PEI#1	1668 ± 75	68.5	83.1 ± 2.1	107 ± 6
S-PEI#2	483 ± 38	76.2	73.5 ± 9.0	150 ± 6
S-PEI#3	240 ± 6.1	82.5	63.7 ± 5.2	201 ± 12

3.3.2 Intrinsic separation properties of TFC flat sheet membranes

The intrinsic separation properties of TFC flat sheet membranes evaluated using an RO setup are summarized in Table 3.3. The water permeability of TFC-PEI#1 membrane is as high as $2.28 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ with the low salt permeability of $0.67 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ while the water permeability of TFC-PEI#2 and TFC-PEI#3 membranes is 2.09 and $1.65 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, respectively. This trend is in line with the pure water permeability of the substrate. Since the selective layers of the three TFC membranes were fabricated using the same interfacial polymerization condition, it suggests that the water permeability of the TFC membrane is highly affected by the substrate structure. The solute permeability for all the TFC membranes is relatively small. The structure parameters (S) of S-PEI#1 and S-PEI#2 membranes are similar or even smaller compared with the commercial HTI membrane, which is around $590 \sim 1400 \mu\text{m}$ (She et al. 2012, Li et al. 2013, Zhang et al. 2013). The lower S value benefits the PRO process to achieve high water flux and high power density.

Table 3.3 Intrinsic separation properties of TFC PEI composite membranes with optimal polyamide layer.

Membrane	Water permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Salt permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Structural parameter (mm)	Rejection (%)
TFC-PEI#1	2.28 ± 0.2	0.67 ± 0.04	0.510	97.14 ± 0.1
TFC-PEI#2	2.09 ± 0.3	0.87 ± 0.08	0.554	96.13 ± 1.1
TFC-PEI#3	1.65 ± 0.5	0.75 ± 0.09	0.687	94.60 ± 0.6

3.3.3 PRO Performance of the TFC- PEI membranes

The TFC-PEI membranes were tested in the active layer facing draw solution configuration using 1.0 M NaCl as the draw solution and 10 mM NaCl as the feed solution, and the results are shown in Figure 3.4. The draw solution used was to simulate the seawater brine with similar osmotic pressure, while the feed solution was to simulate river water. A wide range of pressure of $3.4 \sim 20.7 \text{ bar}$ ($50 \sim 300$

psi) was applied to the draw solution side to examine the PRO performance of three TFC membranes.

Figure 3.4 PRO performance of TFC PEI flat sheet membranes at various applied pressures (a) Water flux; (b) Specific salt flux J_s/J_w ; (c) Power density. (Feed solution: 10 mM NaCl; Draw solution: 1 M NaCl solution)

It can be seen from Figure 3.4(a) that the water flux decreases with increasing the applied pressure due to the decrease of the driving force across the membrane. On the other hand, reverse salt diffusion was widely observed in osmotically driven membrane processes. The specific salt flux, defined by the ratio of salt flux to water flux (J_s/J_w), was normally used as an indicator. The salt permeation to the feed side through the membrane results in an elevation of salt concentration in the feed water and thus a decrease of the driving force. As depicted in Figure 3.4 (b), the three membranes show a slow salt increase in the low-pressure range. However, with the increase of applied pressure over 17 bar, the J_s/J_w value for TFC-PEI#1 rises much higher than the TFC-PEI#2 and TFC-PEI#3 membranes, which suggests the deformation of TFC-PEI#1 membrane due to its lower mechanical properties (see Table 3.2).

The power density is an important parameter in PRO process. Theoretically, the peak power density for a pair of 10 mM NaCl and 1 M NaCl solutions should be achieved at around 24 bar. However, the experimental data in Figure 3.4 (c) shows that the power density decreases after reaching 17.2 bar, which is believed to be attributed to the concentrative ICP in the porous substrate, caused by the significant reverse salt diffusion to the feed water (see Figure 3.4 (b)). The highest power density achieved by the TFC-PEI#1 at 17.2 bar is $16.7 \text{ W}\cdot\text{m}^{-2}$, followed by the second highest power density of $12.8 \text{ W}\cdot\text{m}^{-2}$ obtained by the TFC-PEI#2 at the same pressure. Due to the low mechanical property of the TFC-PEI#1, the TFC-PEI#2 membrane was selected for further study.

Figure 3.5 shows the effect of different salt concentrations in the feed solution on the power density of TFC-PEI#2 PRO membrane. The feed solution used was DI water, synthetic river water (10 mM NaCl), waste water RO retentate (40 mM NaCl) and concentrated waste water RO retentate (80mM NaCl), respectively. A 1 M NaCl solution was used as draw solution to simulate the seawater retentate. It can be seen from the figure that with increasing salt concentration in the feed solution, the power density presents a declining trend. For instance, when the salt concentration increased from DI water to 80 mM NaCl, the peak power density

decreased from 14.6 to 8.8 $\text{W}\cdot\text{m}^{-2}$. This phenomenon is not unexpected because of enhanced ICP that lowered down the driving force across the membrane.

Figure 3.5 Power density of TFC-PEI#2 flat sheet membrane under different feed solution concentrations. (Draw solution: 1 M NaCl solution)

3.3.4 Stability of the TFC- PEI membrane in pressure cycle tests

3.3.4.1 Change of membrane structure under pressure

In PRO process, a high pressure applied on the draw solution side may affect membrane integrity, leading to membrane deformation such as enlarged membrane surface area, reduced membrane thickness, and even membrane collapse. In other words, the polyamide selective layer and membrane substrate may experience reversible or irreversible or both reversible and irreversible changes (Han et al. 2013).

A series of water permeability (A_p) and salt permeability (B_p) values under different pressures were measured using a PRO setup to examine structure under pressure. The schematic diagram of PRO cell is presented in Figure 3.6 along with a typical RO cell for comparison. It can be seen that due to the strong support by a flat porous stainless-steel support, the membrane tested in the RO cell is able to maintain its original shape, and assumed no deformation occurred. In contrast, the

membrane mounted in the PRO cell was supported by two woven spacers to enhance mass transport while against the high pressure from the draw solution side. Hence, the membrane tends to be deformed under pressure, as illustrated in Figure 3.6 (b). Therefore, the A and B values obtained using the RO cell cannot accurately reflect the membrane separation property in the PRO process (She et al. 2013). The A_p and B_p values as well as the rejections of the membranes obtained from the measurement in the PRO cell would be better indicators to present the membrane separation property at different pressures, which is believed to be associated with the structure of the top polyamide selective layer of the membrane.

Figure 3.6 Schematic diagrams of (A) RO cell; (B) PRO cell; (a) No membrane deformation in RO cell; (b) An illustration of possible membrane deformation in PRO cell.

Figures 3.7 (A) and (B) show the morphologies of the polyamide layer without pressure impaction and after testing under 17 bar, respectively. No obvious change can be observed on the top surface. However, from Figure 3.8 we can see that both A_p and B_p increased with raising the applied pressure. It seems that the membrane active layer has subjected to a certain degree of deformation. Interestingly, as the applied pressure reduced, the A_p and B_p can return to the previous values. When the second cycle was performed, all the data points show considerable consistency with the first cycle. It indicates that, within the operating pressure range of 17.2 bar, the top polyamide layer experienced most likely an elastic deformation, which is reversible.

Figures. 3.7 (a) and (b) depict the cross sections of the membrane substrate without and with 17.2 bar pressure impaction, respectively. Different from the top polyamide layer, the porous substrate has been compacted with ~3.5% deduction in the membrane thickness. Obviously, the change in the substrate is permanent, which is irreversible.

Figure 3.7 FESEM images of TFC-PEI#2 membrane (A) Surface at no compaction; (B) Surface at 17 bar compactions; (a) Cross-section at no compaction; (b) Cross-section at 17 bar compactions.

Figure 3.8 Water and salt permeabilities of the TFC-PEI#2 flat sheet membrane at various transmembrane pressures. Testing condition: 10 mM NaCl as feed solution, membrane coupons were compressed under various pressure at ambient temperature.

3.3.4.2 Impact of membrane structure change on the PRO performance

During the PRO pressure cycle tests, a series of pressure (i.e., from 0 to 17.2 bar) were applied on the draw solution side. Each testing point was lasted for 30 minutes to obtain a stable water flux. After reaching the peak pressure, the pressure was decreased stepwise back to zero. Two pressure cycles were completed to examine the water flux, specific salt flux and power density variations. The results are shown in Figure 3.9. It is observed that the data obtained in the upward and downward measurements in each cycle are closed to each other. By comparing the first cycle with the second cycle, the water flux, specific salt flux, and power density show excellent reproducibility. The water flux, specific salt flux, and power density returned to the original values after two cycles of tests. Referring to Figure 3.8 which shows the A_p and B_p as a function of applied pressure, it is further confirmed that the deformation of the membrane selective layer is reversible under given testing conditions within 0~17 bar. The impact of the irreversible change in the substrate on the PRO performance seems to be negligible in the given testing condition.

This stability of PRO membrane was also tested under high pressure for the first time. Figure 3.10 presents the water flux and power density of TFC-PEI#2 membrane under 6.9 bar and 17.2 bar, respectively, for over ten hours. The membrane could maintain almost unchanged water flux and power density of $12.8 \text{ W}\cdot\text{m}^{-2}$ at 17.2 bar over the long testing time, again, confirming that the membrane possesses superior structural stability. This result suggests that the membrane has great potential to be used in practical application in the future.

Figure 3.9 Pressure cycle tests of the TFC-PEI#2 membrane (a) Water flux; (b) Specific salt flux J_s/J_w ; (c) Power density. (Feed solution: 10 mM NaCl concentration; Draw solution: 1 M NaCl solution)

Figure 3.10 Water flux and power density of TFC-PEI#2 flat sheet membrane under different pressures over 300 min. (Feed solution: 10 mM NaCl concentration; Draw solution: 1 M NaCl solution)

3.4. Conclusions

Flat sheet PRO membranes with three types of substrate structures have been fabricated via phase inversion and interfacial polymerization methods. Membrane characterization was performed to study the relationship between membrane structure and PRO performance. The structural stability was evaluated systematically through pressure cycle experiments and stability performance tests. The following conclusions can be drawn from the current study:

- (1) By varying the polymer concentration of membrane dope solution, the best of the three prepared membrane substrates was identified concerning the high water permeability and good mechanical strength, which possessed a high

water permeability of $483 \text{ L}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a high tensile modulus of 150 Mpa.

- (2) The polyamide layer was synthesized on the surface of flat sheet substrate. The resultant TFC-PEI#2 membrane could achieve a stable power density of $12.8 \text{ W}\cdot\text{m}^{-2}$ at 17.2 bar, using 1M NaCl solution as draw and 10 mM NaCl solution as feed, respectively.
- (3) Water permeability (A_p) and salt permeability (B_p) under different pressures were measured using a PRO setup. A_p and B_p are better indicators than the conventional A and B for examining the variation of PRO membrane structure under pressure. Within current operating pressure range of 17.2 bar, the top polyamide layer of TFC-PEI#2 membrane mainly experienced a reversible deformation.
- (4) The structural stability of TFC-PEI#2 membrane was evaluated systematically through two pressure cycle tests. The water flux, specific salt flux and power density obtained in the upward and downward measurements in each cycle were approximately at the same value. The first cycle and the second cycle also showed excellent reproducibility.
- (5) The stability of PRO membrane was also tested under high pressure for the first time. The membrane could maintain almost unchanged water flux and power density of $12.8 \text{ W}\cdot\text{m}^{-2}$ at 17.2 bar over the 300-min testing time, suggesting the membrane's great potential to be used in practical application in the future.

CHAPTER 4 Fabrication and characterization of high-performance hollow fiber TFC PRO membranes

This chapter has been published as Ye Li, Saren Qi, Yining Wang, Setiawan Laurentia, Rong Wang (2017). *Modification of thin film composite hollow fiber membranes for osmotic energy generation with low organic fouling tendency. Desalination*, 424 (Supplement C), 131-139. Permission has been granted by the licensed content publisher “Elsevier” to use the published content as a chapter in this thesis.

4.1 Introduction

Membrane is one of the crucial elements in the PRO process, and according to the discussion in Chapter 2, there are two types of PRO membrane designs distinguished in terms of configurations: the flat sheet and the hollow fiber (Song et al. 2013, Cui et al. 2014, Han et al. 2014, Han et al. 2014, Rica et al. 2014, Curcio et al. 2015, Tian et al. 2015, Chen et al. 2016). As discussed in Chapter 3, flat sheet membranes could suffer from severe deformation due to the supporting spacers used. Compared with that of the other configuration, the self-supported hollow fiber membranes produces higher power density due to its higher packing density in each membrane module (Gerstandt et al. 2008, Nijmeijer et al. 2010, Skilhagen 2010). Some recent developed membranes could produce the maximum power density of above $15 \text{ W} \cdot \text{m}^{-2}$ using deionized (DI) water as feed and synthesized seawater RO brine as draw stream (Cui et al. 2014, Han et al. 2014, Zhang et al. 2014, Curcio et al. 2015, Tian et al. 2015, Chen et al. 2016).

PRO membranes are usually run in the orientation of active layer facing draw solution (AL-DS). Compared with its counterpart, the orientation of active layer facing feed solution (AL-FS), higher power density could be observed in AL-DS orientation due to the higher water flux due to less severe ICP effect. However, membrane fouling significantly reduces the power density in AL-DS orientation with feed water contains foulants (She et al. 2013, Chen et al. 2015). These foulants

can penetrate the porous support skin of membrane, causing significant reduction of the power density (She et al. 2013, Li et al. 2014). Different strategies have been investigated to reduce and control membrane fouling such as pretreatment of feed solution (Tian et al. 2015, Chen et al. 2016), chemical cleaning of fouled membrane (Li et al. 2017), and membrane surface modification with added anti-fouling properties (Li et al. 2014, Cai et al. 2016). Among these strategies, surface modification via molecular design has the advantage of relatively low cost and easy scale-up (Logan et al. 2012). However, for flat sheet membranes, fouling situation could be severely affected by the supporting spacers placed in the feed channel due to the foulants could be trapped between the spacer filaments and membrane surface (Bar-Zeev et al. 2015). Thus, modifying the flat sheet membrane surface is not sufficient in fouling control.

On the other hand, self-supporting hollow fiber membranes could be modified by grafting or coating methods for antifouling purpose (Li et al. 2014, Cai et al. 2016, O'Toole et al. 2016, Zhang et al. 2016, Zhang et al. 2016, Zhao et al. 2016, Lieu Le et al. 2017). Hydrophilic chemicals, such as hyper-branched polyglycerol (HPG), zwitterionic copolymers, poly (vinyl alcohol) (PVA), 3-aminopropyltrimethoxysilane (APTMS) was applied to reduce fouling tendency of PRO membranes. However, some modification induces high salt leakage (Zhang et al. 2016), some chemical synthesis procedures are too complicated to be applied for large scales (Li et al. 2014, Cai et al. 2016, O'Toole et al. 2016) and some preparation procedures could produce environmentally unfriendly matter (Zhao et al. 2016). Except for surface modification, the double skin concept was applied in several studies of antifouling FO/PRO membrane fabrication (Fang et al. 2012, Qi et al. 2012, Su et al. 2012, Duong et al. 2014, Fang et al. 2015, Lim et al. 2017). The double-skin membrane was prepared by phase inversion and a primary skin facing the draw solution to reject solutes, while a secondary skin formed on the porous support facing the feed streams to prevent foulants penetration. Han et al. (Han et al. 2017) developed a second polyamide layer on the porous substrate to counteract the diffusion of foulants from wastewater feed water. However, the techniques for developing a secondary layer is complicated and solutes could be

trapped between two skins and could induce severe ICP and cause water flux decline.

Polyelectrolyte deposition has been adopted to develop a selective layer for nanofiltration and reverse osmosis membranes (Ouyang et al. 2008, Rajabzadeh et al. 2014) and to coat membrane surface for controlling organic and bio-fouling (Ma et al. 2015, Sanyal et al. 2016). In the polyelectrolyte deposition process, cationic and anionic polyelectrolytes are deposited on the membrane surface in an alternate sequence via electrostatic adsorption and form a nano-film on top of the substrate (Decher 1997, Bertrand et al. 2000). This method has the advantage of simple preparation procedures, environmentally friendly process and flexibility in changing surface properties such as wettability and zeta potential (Hammond 1999, Egueh et al. 2010). However, limited studies have been conducted to modify PRO membranes using the polyelectrolyte deposition method. Unlike pressure-driven membranes and forward osmosis membranes, where polyelectrolytes are usually deposited on the substrate to serve as the active skin layer itself or coating the active layer to control fouling, the polyelectrolytes coated on the bottom surface of a PRO membrane will play a different role. It is expected that this polyelectrolyte layer on the membrane bottom surface has potential to mitigate fouling during PRO operation through reduced pore blocking. In addition, well controlled thickness/density of polyelectrolyte layer on the bottom surface may induce minimal adverse effect on the intrinsic properties and mechanical strength, which is important for maintaining the high performance of the PRO membrane.

In this study, the anti-fouling property of a PRO membrane was improved via polyelectrolytes deposition with two oppositely charged polyelectrolytes - poly-(allylamine hydrochloride) and poly acrylic acid. In specific, polyelectrolytes were deposited on the outer surface of a hollow fiber thin film composite (TFC) PRO membrane, which could potentially increase the charge density and hydrophilicity of the bottom surface for better retaining the organic foulants in feed water. The resultant membranes were characterized, and the anti-fouling behaviors were evaluated with model foulants.

4.2 Experiments

4.2.1 Materials and chemicals

Commercially available polymer, polyetherimide (PEI, Ultem 1000, General Electric Plastics) was utilized as polymeric material and N-Methyl-2-pyrrolidone (NMP; >99.5% Merck) was adopted as the solvent in fabrication of the hollow fiber substrate. Trimesoyl chloride (TMC; >99% Sigma-Aldrich) and m-Phenylenediamine (MPD; $\geq 99\%$ Sigma-Aldrich) were employed for the formation of active layer. Sodium hydroxide (NaOH; Merck), poly-(allylamine hydrochloride) (PAH; Molecular weight (Mw) $\sim 120,000$, Sigma-Aldrich) and poly acrylic acid (PAA; Mw $\sim 250,000$, Sigma-Aldrich) were adopted as modification chemicals. Dextran ((C₆H₁₀O₅)_n, Mw 6,000 to 500,000 Dalton (Da), Sigma-Aldrich) was used in measurement of molecular weight cut-off (MWCO) of the substrates. Sodium chloride (NaCl; Merck) was adopted in the draw stream preparations. Bovine serum albumin (BSA; Sigma-Aldrich, Mw $\sim 66,000$ Da) and sodium alginate (Sigma-Aldrich) were used as the model protein foulant and model polysaccharide foulant, respectively. The deionized (DI) water was provided by a Milli-Q integral water purification system.

4.2.2 Fabrication of Thin-film composite PEI membranes

The substrate of hollow fiber membrane was fabricated using non-solvent induced phase separation method, and the detailed spinning method can be refer to our previous work (Chou et al. 2013, Chen et al. 2016). Based on the dimension measurement using microscope (Keyence VHX 500F Digital Microscope), the average wall thickness of the substrates was $\sim 106\ \mu\text{m}$ with an inner and outer diameter of $398\ \mu\text{m}$ and $611\ \mu\text{m}$, respectively. Prior to the formation of selective layer, fifteen fibers were placed in a module of 20 cm effective length and $\frac{1}{2}$ inch diameter and were sealed with epoxy. A polyamide solute rejection skin was synthesized on the lumen surface of the hollow fiber by conducting interfacial polymerization with the two monomers: MPD and TMC (Chou et al. 2013, Li et al. 2015). Briefly, 1.0 wt.% MPD solution was in contact with the lumen side of the

substrate for 30 min to thoroughly wet the surface. Subsequently, n-hexane was used to rinse the lumen side to remove the excess MPD. After that, 0.1% (wt/v) TMC in n-hexane was adopted to react with the remaining MPD to form an ultrathin skin. The unreacted chemical residues inside the membrane module was rinsed thoroughly with pure water.

4.2.3 Modification of TFC hollow fiber membranes

The shell surface modification was conducted by exposing the shell surface of the as-prepared TFC membrane or hollow fiber substrate to the chemicals. The membrane was firstly soaked in a $0.04 \text{ g}\cdot\text{L}^{-1}$ NaOH solution for 60 min in order to introduce negative charged group on the membrane substrate (Stephans et al. 2000). Subsequently followed by soaking in pure water for 5 min to rinse the remaining alkaline solution off membrane surface. Then, the cationic PAH solution ($1 \text{ g}\cdot\text{L}^{-1}$) was adopted to soak the membrane for 60 min and subsequently DI water was to rinse off the remaining chemicals for 5 min. The same procedure was repeated for anionic PAA solution ($1 \text{ g}\cdot\text{L}^{-1}$). After the modification with the polyelectrolytes, the membrane was stored in a tank filled with pure water prior to use. The membrane substrates before and after polyelectrolytes deposition were named S-PEI and S-PEI-M, while the TFC membranes before and after the modification were named TFC-PEI and TFC-PEI-M, respectively.

4.2.4. Characterization of PEI hollow fiber substrates

The morphology of the substrates was characterized via a field emission scanning electron microscopy (FESEM, Joel JSM 7600F). The membrane cross section was prepared by fracturing after it was frozen in liquid nitrogen. The surface of membrane samples was coated with a thin platinum layer ($\sim 5 \text{ nm}$) prior to FESEM imaging.

The pure water permeability (PWP) and MWCO of the substrates were measured with a reverse osmosis (RO) cross-flow system at pressure of 1 bar. The water

permeate was collected at the shell side with constant pressure applied on the lumen side. The PWP of the membrane substrate was calculated using Eq. (4.1):

$$PWP = \frac{\Delta V}{A_m \Delta t \Delta P} \quad (4.1)$$

where A_m is the effective area of the lumen surface, which was calculated by multiplying the fiber number and inner surface area of one fiber. ΔV is the volume of the permeate collected during the time period of Δt , and ΔP is the trans-membrane pressure. For the measurement of MWCO, a 2 g·L⁻¹ dextran solution (Mw ranging from 6,000 to 500,000 Da) was prepared as feed. Both permeate and feed were collected and examined using a Laboratories-GPC 50 plus system (Chou et al. 2010, Chen et al. 2016).

The surface charge (zeta potential) of the outer surface of the substrate was determined using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) with a 0.01 M sodium chloride electrolyte solution. The chemistry of the shell surface of the substrate was analyzed using attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR). ATR-FTIR spectra were collected over a range of 650-4000 cm⁻¹ with the resolution of 4.0 cm⁻¹. The spectra analysis was conducted with FTIR software (IR Solution, Shimadzu). The dynamic contact angle was obtained based on the Wilhelmy method using a tensiometer (DCAT11 Dataphysics). The average value was obtained by repeating three runs with different fibers. The tensile modulus of the support was measured via a Zwick 0.5 kN universal testing machine. Samples were stretched by tensile force at a constant rate of 50 mm·min⁻¹.

4.2.5 Characterization of TFC membranes

The membrane water permeability (A) and salt permeability coefficients (B) were determined using a RO cross-flow system. Pure water was pumped through the inner surface of the fibers with applied pressure of 2 bar. The A value was calculated using Eq. (3.1). The NaCl rejection R_s was measured at an applied

pressure of 2 bar with a 10 mM NaCl feed stream. The B value was determined from Eq. (3.3).

The structural parameter (S) was calculated with the aid of forward osmosis (FO) experiments using Eq.(3.4) (She et al. 2012, Chou et al. 2013). FO tests were performed using 1.0 M NaCl draw stream and pure water as the feed in the orientation of AL-DS. The crossflow velocities were $1.32 \text{ m}\cdot\text{s}^{-1}$ and $0.24 \text{ m}\cdot\text{s}^{-1}$ for the lumen side the shell side, respectively.

4.2.6 PRO experiments

The PRO testing system employed in this study was similar to that reported in previous studies (Chou et al. 2013, Chen et al. 2016). In brief, the membrane was orientated with the active layer facing draw stream for all the PRO tests. The effective area of a single membrane module was 47 cm^2 . The hydraulic pressure ranged from 2 to 20 bar was applied on the lumen surface (draw solution side) of the hollow fibers using a high-pressure pump. The crossflow velocity were the same as the FO tests ($1.32 \text{ m}\cdot\text{s}^{-1}$ for the lumen side and $0.24 \text{ m}\cdot\text{s}^{-1}$ for the shell side). All the runs were conducted at $23 \pm 1^\circ\text{C}$. During the test, the feed water volume (10 L) was maintained by dosing DI water. The NaCl concentration of the draw stream was kept constant by continuously dosing a concentrated stock solution. The water flux J_w was determined based on the change of the weight of the dosing water. The feed conductivity was recorded for the determination of solute flux J_s using Eq.(3.7). The power density W can be determined by multiplying the trans-membrane pressure (ΔP) and the water flux (J_w) in Eq. (3.8):

For measuring the power density of a fresh membrane, 1M NaCl draw stream and DI feed water were applied. The flux calculation was usually based on ~30 min flux performance. PRO fouling experiments were conducted with foulants added to the feed water, i.e., 200 ppm sodium alginate or 200 ppm BSA, and each run last for ~300 min. The baseline test was also performed using pure water as feed. The draw was NaCl stream (1 M) for all the experiments.

4.3. Results and discussion

4.3.1 Characteristics of the hollow fiber substrates

The morphology of the PEI hollow fiber supports is present in Figure 4.1. The sponge-like dense structure of the membrane cross-section can be observed in Figure 4.1(a-b). It should be successfully suppressed in this study. The dense structure is believed to provide robust mechanical property and minimize the deformation under high pressure (Thorsen et al. 2009, Huang et al. 2013, Zhang et al. 2013). The pores on the inner surface could not be observed (Figure 4.1(c)), likely due to the much denser structure close to/at the inner surface. In contrast, micropores are visible and they evenly spread over the outer surface (Figure 4.1(d)), with the surface pore size of about tens of nanometers as indicated in the magnified image (Figure 4.1(e)). Interestingly, after polyelectrolyte modification, these pores seemed to be covered by a dense layer, although some pores are still exposed of a much smaller quantity (Figure 4.1(f)), indicating the successful deposition of polyelectrolytes.

The ATR-FTIR results for the pristine (S-PEI) and modified (S-PEI-M) substrates are shown in Figure 4.2. The typical imide bands are at 1778 cm^{-1} and 1719 cm^{-1} , corresponding to the asymmetric C–O stretching of the pristine PEI substrates. The absorption band at 1353 cm^{-1} was appointed to the bond stretching vibration of C–N–C in phthalimide rings. After the modification, amine bands were detected at around 3380 cm^{-1} and 2919 cm^{-1} , assigned to the -NH^2 and -NH_3^+ groups, correspondingly. These amine bands confirmed the effective deposition of PAH on the surface of the PEI fiber. The zeta potential results of the two substrates (outer surface) at pH range of 3.5 – 9 are presented in Figure 4.3. The zeta potential of the S-PEI-M surface was observed to be more negatively charged at $\text{pH} > 4$. The zeta potential at pH 6 was about -30 mV and -60 mV for the S-PEI and S-PEI-M, respectively. The more negative charge on the S-PEI-M surface could be attributed to the negatively charged PAA (Gu et al. 2014). Again, the results reveal the successful modification of membrane shell surface by the polyelectrolytes.

Figure 4.1 FESEM images of hollow fiber membrane substrate S-PEI showing (a-b) cross-section, (c) lumen surface, (d) shell surface, (e) shell surface at higher magnification, and (f) the outer surface after polyelectrolytes modification (membrane substrate (S-PEI-M)).

Figure 4.2 ATR-FTIR spectra for the S-PEI and the S-PEI-M. The analysis was performed from the shell surface of the membranes.

Figure 4.3 Zeta potential of the shell surfaces of the S-PEI and S-PEI-M membrane substrates. 0.01 M NaCl was adopted as the electrolyte solution.

The other properties of the membrane supports are summarized in Table 4.1. Tensile modulus can indicate the membrane pressure endurance in the PRO experiments. The tensile modulus of substrate S-PEI was as high as 252 MPa, which is constant with that of the PEI substrates reported previously (Chou et al. 2013, Chen et al. 2016). The surface modification almost did not affect the mechanical property, as S-PEI-M substrate had a tensile modulus of ~246 MPa. The surface contact angle after the modification was reduced to ~ 58° from 75°, which can be explained by the hydrophilic property of the deposited polyelectrolytes. According to literature (Tiraferri et al. 2012, She et al. 2013, Zuo et al. 2013), the more hydrophilic surface is favorable for reducing membrane fouling. The PWP of the S-PEI-M substrate was approximately 134 L·m⁻²·h⁻¹·bar⁻¹, which was 13% lower than the pristine S-PEI substrate (155 L·m⁻²·h⁻¹·bar⁻¹). This result is consistent with the MWCO results. The S-PEI-M had smaller MWCO of 147 kDa, as compared to that of S-PEI substrate (168 kDa). The decrease in PWP and MWCO were consistent with the FESEM images (Figure 4.1(e-f)) where the narrowed pore size/decreased surface porosity was observed as a result of polyelectrolytes deposition. Another water permeability test was conducted with pressure applied to the outer surface of the membrane. The results show that the

PWP-O of S-PEI-M was slightly higher than that of the S-PEI, when the permeate flowed from the shell to the lumen side of the membrane.

Table 4.1 Properties of hollow fiber membrane substrates.

Membrane	Tensile modulus (MPa)	Contact angle (°)	Zeta potential @ pH 6 ^a	PWP (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	MWCO (kDa)
S-PEI	252 ± 17	74.7 ± 4.3	~ -30	154.7 ± 29.0	168 ± 48
S-PEI-M	246 ± 6	58.2 ± 3.9	~ -60	134.4 ± 10.0	147 ± 37

Note:

a. Measured at the shell side of the membrane.

4.3.2 Characteristics of TFC membranes

Figure 4.4 presents the FESEM images of the selective skin of the TFC-PEI membrane. A typical ridge and valley pattern of a polyamide layer was presented, indicating the effective development of the polyamide skin on the lumen side of the hollow fiber supports (Han et al. 2013, Chen et al. 2016, Wang et al. 2016). The membrane intrinsic properties are listed in Table 4.2. The pristine membrane TFC-PEI and modified membrane TFC-PEI-M had similar water permeability ($\sim 2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) and salt permeability ($\sim 0.1 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), revealing that the shell surface modification with polyelectrolytes had minimal impact on the intrinsic properties of the selective layer, which is beneficial for the modified PRO membranes to achieve a high water flux. The structural parameter (*S* value) of the S-PEI-M substrate ($\sim 620 \text{ } \mu\text{m}$) was smaller than that of the pristine S-PEI substrate ($\sim 750 \text{ } \mu\text{m}$), which could be attributed to the increase of hydrophilicity after modification (Liu et al. 2016, Zhang et al. 2016).

Figure 4.4 FESEM images of TFC-PEI membrane showing (a) the plan view of polyamide surface and (b) the cross-section view.

Table 4.2 Intrinsic separation properties of TFC membranes.

Membrane	Water permeability, A ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Salt permeability, B ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Rejection (%)	Structural parameter, S (μm)
TFC-PEI	1.96 ± 0.16	0.13 ± 0.02	96.8 ± 0.2	750 ± 16
TFC-PEI-M	2.00 ± 0.28	0.10 ± 0.03	97.5 ± 1.2	620 ± 23

4.3.3 PRO performance of the TFC membranes

The performance of the TFC membranes TFC-PEI and TFC-PEI-M at different applied pressures (2-20 bar) are present in Figure 4.5. Overall, the water flux decreased with the rise of hydraulic pressure (2-15) bar for both membranes (Figure 4.5(a)), due to the increased retard effect by hydraulic pressure. However, increased water fluxes were observed when the applied pressure was further raised from 15 to 20 bar for both membranes. It is generally expected that there is a critical pressure for a typical polymeric hollow fiber membrane, beyond which the membrane suffers from the irreversible deformation, accompanied by the increased water permeability and solute permeability (Han et al. 2013, Chen et al. 2016). In our case, the critical pressure for both membranes lied at around 15 bar. Compared with the control membrane TFC-PEI, the TFC-PEI-M exhibited slightly higher water flux, which can be elucidated by its smaller structural parameter (Table 4.1). This difference becomes more obvious at lower hydraulic pressure, as the corresponding

higher water fluxes induced more significant internal concentration polarization effect, thereby the more important role of S value at higher flux. In the aspect of specific solute flux J_s/J_w results (Figure 4.5(b)), both membranes showed similar performance and trend. Only minimal increase in J_s/J_w can be observed with increasing pressure when the applied pressure was equal to or less than 15 bar (i.e., $0.05 \text{ mol}\cdot\text{L}^{-1}$ at 2 bar to $0.15 \text{ mol}\cdot\text{L}^{-1}$ at 15 bar). This phenomenon has also been observed in other studies (She et al. 2012, Chou et al. 2013, Han et al. 2014), and it could be due to the combined effect of slightly increased J_s as a result of reversible deformation and the decreased J_w at higher pressure (She et al. 2012, Chou et al. 2013, Li et al. 2015). The J_s/J_w increased markedly to above $0.3 \text{ mol}\cdot\text{L}^{-1}$ at pressure of 20 bar, which was consistent with the increased water flux at this pressure (Figure 4.5(a)), indicating the irreversible deformation of selective layer. Figure 4.5(c) indicates that the power density increased with increasing pressure. The TFC-PEI-M membrane exhibited slightly higher power density than that of the control membrane as a result of the higher water flux. By considering the unwanted permanent deformation of membrane at 20 bar, the maximum power density attained by the TFC-PEI-M membrane was $\sim 16.2 \text{ W}\cdot\text{m}^{-2}$ at 15 bar.

Figure 4.5 PRO performance of the membrane TFC-PEI and TFC-PEI-M as a function of applied pressure. (a) Water flux, (b) specific solute flux, and (c) power density. Testing conditions: DI water and 1 M NaCl were utilized as feed and draw, correspondingly. The performance was obtained after the membranes were stabilized for 30 minutes at each pressure. Each error bar was calculated based on three replicates.

4.3.4 PRO fouling test

4.3.4.1 The effect of foulant type on PRO performance

The effect of organic foulant containing feed water on the membrane performance is presented in Figure 4.6. It is observed that the baseline fluxes (no foulant addition) for both membranes TFC-PEI and TFC-PEI-M are similar and stable during the 300-min test. When foulant alginate was added to the feed water (Figure 4.6(a)), obvious flux decline of ~17 % occurred for TFC-PEI membrane, and the power density dropped to $13.5 \text{ W}\cdot\text{m}^{-2}$ from $16.2 \text{ W}\cdot\text{m}^{-2}$. In contrast, almost no flux drop occurred for TFC-PEI-M membrane, which proved the anti-fouling effect of the modified membrane in reducing alginate fouling during PRO. Similarly, this effect was also demonstrated from the BSA fouling results (Figure 4.6(b)). Despite flux decline for both membranes, the modified membrane TFC-PEI-M suffered less severe flux drop (16 %) than TFC-PEI (41 %). The corresponding power density at the end of 300-min test was $13.8 \text{ W}\cdot\text{m}^{-2}$ and $9.7 \text{ W}\cdot\text{m}^{-2}$ for membrane TFC-PEI-M and TFC-PEI, respectively. Therefore, the TFC-PEI-M with deposited polyelectrolytes showed better PRO performance in the presence of alginate or BSA in feed water. The enhanced anti-fouling effect could be attributed to the more negatively charged and more hydrophilic modified back surface in addition to the narrowed pore size (as discussed in Section 4.3.1), leading to fewer foulants entering into/adsorbed to the support layer. It is worth pointing that the decline of the water flux triggered by BSA was more severe than that of the alginate. One of the reasons could be due to the more negatively charged alginate at neutral pH range. According to prior studies (Wang et al. 2011, Wang et al. 2011), the zeta potential of alginate and BSA at pH 6 is -66 mV and -13 mV, respectively. Since the membrane back surface was negatively charged (Figure 4.3), the electrostatic repulsion between the surface of the membrane and the more negatively charged alginate was stronger. In addition, alginate is more hydrophilic (Subhi et al. 2012) and has larger hydrodynamic diameter than BSA (i.e., the measured hydrodynamic diameter of alginate was $343.6 \pm 33.3 \text{ nm}$ and that of BSA was $10.0 \pm 0.3 \text{ nm}$ (measured using Nano Zetasizer, NanoZS, Malvern, UK), the trend of which was consistent with previously reported study (Liang et al. 2014)). These factors may

lead to the less adsorption of alginate on the membrane surface and/or in the porous substrate.

Figure 4.6 Effect of foulants on PRO membrane performance. 200 ppm alginate (a) or 200 ppm BSA (b) was present in the feed solution. Draw solution contained 1 M NaCl. The applied pressure was maintained at 15 bar.

4.3.4.2 The effect of applied pressure on PRO performance

The membrane performance under different applied hydraulic pressures (2, 10 and 15 bar) was studied with feed water containing 200 ppm alginate. The results of water flux are shown in Figure 4.7(a-c). As expected, increasing applied pressure led to the decline in water flux. The initial flux (at 0 min) for TFC-PEI-M membrane at 2 bar, 10 bar and 15 bar was 52, 44 and 38 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. A similar tendency was observed for TFC-PEI membrane as well. The presence of the alginate did not lead to flux drop at the beginning of the test, as compared with the baseline fluxes. The flux decline of TFC-PEI-M membrane after 300 min fouling was about 10%, 7% and 0% at the pressure of 2, 10 and 15 bar. The results are consistent with prior studies (Wang et al. , Wang et al. 2011, She et al. 2013, She et al. 2016) that lower initial flux induced less membrane fouling. The lower initial flux generally induces less hydrodynamic drag force on the foulant molecules and less concentration polarization of foulants on/within membrane support layer, leading to less foulant adsorption and more sustainable water flux. Similarly, the pristine TFC-PEI membrane also suffered slightly less flux drop with lower initial water flux operation. However, the overall flux drop was more significant compared with that of TFC-PEI-M. The corresponding power density results are presented in Figure 4.7(d). Consistently, the modified membrane TFC-PEI-M showed higher power density than pristine membrane TFC-PEI after 300-min alginate fouling over the tested pressures. The TFC-PEI-M still gained much higher power density at higher applied pressure despite the presence of foulants in the feed water (16.2 $\text{W}\cdot\text{m}^{-2}$ at 15 bar vs. 11.6 $\text{W}\cdot\text{m}^{-2}$ at 10 bar), owing to the sustainable water flux performance.

Figure 4.7 Water flux of TFC-PEI and TFC-PEI-M membranes under applied pressure of 2 bar (a) 10 bar (b) and 15 bar (c), and their power density at 0 and 300 min of alginate fouling (d). The PRO experiments were conducted using NaCl draw stream (1.0 M) and DI water as the feed for baseline test while 200 ppm alginate was present in the feed for fouling test.

4.3.5 Summary of low-fouling PRO membranes in literature

The power density of the membranes developed in this study is summarized with the other documented PRO membranes as listed in Table 4.3. In general, the TFC-PEI-M membrane in current work exhibited relatively high and stable power density compared with the membranes reported in recent literature in the presence of model organic foulants in the feed. The advantage of TFC-PEI-M is particularly obvious when the alginate was used as foulant, as almost no flux decline was observed and the power density could be maintained at $16.2 \text{ W}\cdot\text{m}^{-2}$ during the 300-min run. In addition, the membrane modification method employed in this study had negligible effects on the intrinsic properties of the membranes (i.e., not sacrificing the water permeability), and it is simple with high scalability compared with the grafting methods for making low-fouling membranes (Li et al. 2014, Cai et al. 2016, Li et al. 2016).

Table 4.3 Summary of the membranes in current work and other low-fouling PRO membranes in literature.

Membrane	Foulants in FS	NaCl DS (M)	Initial W ($\text{W}\cdot\text{m}^{-2}$)	Applied Pressure (bar)	% decrease in W	Ref.
TFC-PEI-M	200 ppm alginate	1	16.2	15	~ 0 @ 300 min	Current work
TFC-PEI-M	200 ppm BSA	1	16.2	15	~ 16 @ 300 min	Current work
PEI-M-0.25/6	200 ppm BSA	1	/	12	15 @ $170 \text{ L}\cdot\text{m}^{-2}$	(Lieu Le et al. 2017)
TFC-PEI-APTMS	3 mM CaCl_2 200 ppm humic acid	1	7 ^a	9	16 @ 60 min	(Zhang et al. 2016)
TFC-PES	200 ppm alginate	1	11.2	18	55.1 @ 3000 min	(Chen et al. 2015)
HPG-PES	200 ppm BSA	0.6	6.7	12.5	10.0 @ $140 \text{ L}\cdot\text{m}^{-2}$	(Li et al. 2014)
HTI-CTA	1 mM CaCl_2 200 ppm alginate	1.2	6.2	15	40.0 @ 300 min	(Kim et al. 2015)

Note:

^a read from the figures.

4.4. Conclusions

The membrane modification via polyelectrolytes deposition has been demonstrated as an effective method for imparting anti-fouling property to PRO membranes. This method has advantages of facile fabrication, environmental friendly, and ability to maintain membrane performance. The detailed conclusions are as follows:

- (1) The modified membrane after polyelectrolytes deposition showed slightly better PRO performance than that of the control membrane, attributing to the well-maintained intrinsic properties, and the reduced structural parameter as a result of increased hydrophilicity.
- (2) The modified membrane could better maintain performance during the PRO experiments with the foulant containing feed solutions, with better sustainable flux and higher power density achieved at increased pressure.
- (3) The in-house fabricated PRO membranes (with or without surface modification) had better fouling resistance towards alginate compared with BSA, presumably due to the higher charge density, higher hydrophilicity and larger hydrodynamic diameter of the alginate.

CHAPTER 5 Fabrication and characterization of high-performance integral PRO membranes

This chapter has been published as Ye Li, Shanshan Zhao, Laurentia Setiawan, Lizhi Zhang, Rong Wang (2017) *Integral hollow fiber membrane with chemical cross-linking for pressure retarded osmosis operated in the orientation of active layer facing feed solution..* **Journal of Membrane Science**, 550, 163-172.. Permission has been granted by the licensed content publisher “Elsevier” to use the published content as a chapter in this thesis.

5.1 Introduction

Over the past five years, several high-performance thin-film composite (TFC) PRO membranes have been designed with more desirable structure and permeability properties (Han et al. 2014, Han et al. 2014, Chen et al. 2016, Wei et al. 2016). In Chapter 3 and 4, thin film composite flat sheet and hollow fiber membranes were developed to be operated in PRO process. Most recently, PRO research is focused on the energy harvesting using reverse osmosis (RO) retentate from municipal wastewater treatment plants and seawater RO brine as a pair of feed water and draw solution, respectively. This process can convert the two wastes into useful energy with minimized disposal and adverse environmental impacts (Achilli et al. 2009, Han et al. 2015). Nonetheless, fouling is one of the main challenges as the porous support of the membrane is normally placed to face the feed water and is susceptible to fouling. In particular, the feed water from municipal wastewater process normally contains high amounts of organic, inorganic foulants and microbial species (Chen et al. 2015, Tian et al. 2015, Chen et al. 2016). The foulants can easily penetrate into the porous substrate and get stuck beneath the dense selective layer where the cross-flow induced hydrodynamic shear force is inefficient for the removal of the trapped foulants, resulting in a severe reduction of water flux (She et al. 2013, She et al. 2016). Many efforts have been made to alleviate fouling in the PRO process including the surface modification on the substrate (Li et al. 2014, Cai et al. 2016, Zhang et al. 2016), the fabrication of

double-skinned membrane (Han et al. 2017) and the employment of pretreatment process (Abbasi-Garravand et al. 2016, Chen et al. 2016). Nevertheless, these approaches only illustrated improved PRO performance at lab scale, and their applicability in large-scale PRO needs to be further evaluated. For instance, the modification methods for fabricating antifouling membranes are usually complicated with strict reaction conditions and difficult for scaling up; some solvents involved are environmental unfriendly (Li et al. 2014, Han et al. 2017). In addition, the increased energy and chemical consumptions, as well as high operating expenses caused by the pretreatment processes, are also a big concern (Logan et al. 2012).

Since the membrane fouling occurring within the substrate is the major barrier for sustainable power generation in PRO operation, changing the membrane orientation from active layer facing draw solution (AL-DS) to its counterpart, the orientation of active layer facing feed solution (AL-FS), may benefit the production of consistent power density due to its low membrane fouling potential (She et al. 2013, She et al. 2013, Tian et al. 2015). Besides, the fouling layer formed on the top of the selective layer is acknowledged as more reversible and easily removed by flushing (Lee et al. 2010, Mi et al. 2010, Valladares Linares et al. 2012, Mi et al. 2013). Kim's study also shows that for high fouling feed water, it is more economically feasible to operate PRO in the orientation of AL-FS rather than the AL-DS owing to alleviated membrane fouling that reduces the energy and expenses required for pretreatment and cleaning (Kim et al. 2016).

It was noted that most of the present PRO membranes reported in the literature are thin film composite (TFC) membranes, which show good mechanical stability in PRO operation in the AL-DS orientation (She et al. 2012, She et al. 2013). However, when the hydraulic pressure is applied to the porous substrate, the thin film polyamide selective layer tended to be damaged or even detached from surface even under low pressure (Bar-Zeev et al. 2015). The flat-sheet integral CTA membrane could withstand the high hydraulic pressure in the AL-FS orientation because of the fine mesh spacers used in the feed channel, but CTA membrane

usually suffers poor chemical and biological stability as compared to other membrane materials (Wang et al. 2016). Also, in some ways the performance of flat-sheet membranes depends on spacers used in the feed channel (She et al. 2013). The possible adverse effects induced by spacers used should be considered in real applications (Kim et al. 2012, Hickenbottom et al. 2016). In contrast, the hollow fiber membranes with self-support structures would be a promising alternative since no spacer is needed (Minier-Matar et al. 2016, Zhao et al. 2017). Thus, it is imperative to develop mechanically robust hollow fiber membrane with desirable transports properties for PRO operation in the orientation of AL-FS.

The objective of this study is to develop an integral PRO hollow fiber membrane suitable for running in the orientation of AL-FS under high pressure for osmotic energy harvesting. Polyamide-imide (PAI) was chosen as the polymeric substrate material, not only because it has excellent mechanical property and chemical stability which makes it a good candidate for mechanically robust PRO membrane, but also because it can be easily modified for diverse applications through functionalization of imide groups (Robertson et al. 2004, Kosuri et al. 2008). The integral PAI PRO hollow fiber membranes were developed using the phase inversion method, followed by a facile and scalable cross-linking post-treatment method using environmentally friendly solvents. The structures and properties of the newly developed membranes were characterized thoroughly using a wide range of standard protocols. The PRO performance of the membranes in terms of water flux, specific salt flux and power density in the AL-FS orientation using a real wastewater RO retentate as the feed were subsequently evaluated. This study is believed to be the first attempt to fabricate integral PAI hollow fiber membranes with facile post-treatment for PRO application in the AL-FS orientation. It is expected to provide new perspectives for fouling control so that the feed pretreatment and other measures associated with fouling can be eliminated for a sustainable PRO operation.

5.2 Experiments

5.2.1 Materials

Torlon® 4000T-MV (Polyamide-imide PAI, Solvay Advanced Polymers) and *N*-Methyl-2-pyrrolidone (NMP, >99.5%, Merck Millipore) were adopted for developing the hollow fiber support. Poly (allylamine hydrochloride) (PAH, Molecular Weight 450,000 g mol⁻¹) and glutaraldehyde (GA, 50 wt.% in H₂O) (Sigma-Aldrich) were adopted as cross-linking agents. Dextran with various molecular weights (M_w) (6000–500,000 Da) provided by Sigma-Aldrich was adopted to characterize the molecular weight cut-off (MWCO) of membrane substrates. Sodium chloride (NaCl), sodium sulfate (Na₂SO₄), magnesium sulfate (MgSO₄) and magnesium chloride (MgCl₂) were purchased from Merck Millipore and used for testing salt rejections of membranes. Chemicals were analytical grade and employed as received. Deionized (DI) water was provided by the Milli-Q® water purification system (Merck Millipore).

5.2.2 Fabrication of PAI hollow fiber substrates

Hollow fiber substrates were produced using a dry/jet wet phase inversion spinning technique. The detailed fabrication methods were reported elsewhere (Setiawan et al. 2011, Setiawan et al. 2012). Briefly, polyamide-imide powder and additives were dissolved in an NMP solution after removing moisture in the PAI at 50 °C over one day. The dope was continuously stirred at 60 °C for three days until the solution becomes homogeneous. The spinning conditions were listed in Table 5.1. Two different substrates, fabricated by controlling the bore fluid compositions, were denoted as ST#1 and ST#2.

Table 5.1 Dope composition and spinning conditions

Substrate code	ST#1	ST#2
Dope composition (PAI/PEG200/H ₂ O/NMP) (wt. %)	22/22.5/0.1/53.4	
Dope flow rate (mL/min)	2.4	
Bore fluid composition NMP/H ₂ O (vol. %)	90/10	50/50
Bore fluid flow rate (mL/min)	1.2	
Air gap (cm)	0.5	

Take up speed (m/min)	18.8
Ambient temperature (°C)	23 ± 1
Coagulation bath temperature (°C)	23 ± 1
Room humidity (%)	75-80
Dimension of spinneret (mm)	ID/OD = 0.5/1.0

5.2.3 Fabrication of integral PRO hollow fiber membrane by chemical cross-linking

The chemical cross-linking post-treatment was performed via soaking the substrates into a 0.06 mol·L⁻¹ PAH solution (a blend of 2-propanol and water: 50/50 vol. %, pH adjusted to 10) at a temperature of 70 °C for one hour followed by thoroughly rinsing using DI water to remove the unreacted chemicals. The resultant PAH cross-linked membranes were denoted as ST#X-PAH (X represents substrate number). To further improve membrane performance, the ST#X-PAH membrane was further cross-linked using 0.5wt. % GA solution for 30 minutes and the resultant membranes were denoted as ST#X-PAH/GA.

5.2.4 Hollow fiber membrane characterization and performance evaluation

5.2.4.1 Membrane morphology observation and surface chemistry analysis

The fibers before and after post-treatment were characterized using field emission scanning electron microscope (FESEM JSM-7200F, JEOL, Japan). Information about surface functional groups of the membranes before and after the modification was obtained by using via attenuated total reflection-fourier transforms infrared spectroscopy (ATR-FTIR) (IR-Prestige-21, Shimadzu, Japan). The surface chemistry of the membranes was performed within the range from 650 to 4000 cm⁻¹. The surface zeta potentials of the fibers were tested using an electrokinetic analyzer (SurPASSTM, Anton Paar GmbH, Austria) using a 10 mM NaCl background electrolyte solution in the pH range of 3~9. Automatic titration was conducted with 0.05 M HCl and 0.1 M NaOH solutions to adjust the pH. The surface charge results were obtained using Helmholtz-Smoluchowski equation (Saren et al. 2011,

Setiawan et al. 2011). The mechanical properties of the membranes were evaluated via tensile modulus and burst pressure. A Zwick 0.5 kN testing machine was adopted to determine the tensile modulus. The specific testing method of burst pressure was similar to our previous study (Chen et al. 2016).

5.2.4.2 Measurements of the intrinsic separation properties of PAI hollow fiber substrates

To test membrane separation performance, each hollow fiber module was made using fifteen hollow fibers in a Teflon tubing in 22 cm effective length. The pure water permeability (PWP) and MWCO of PAI substrates were tested on a cross-flow filtration system at 1 bar. For the PWP test, membrane modules were pressured for one hour with Milli-Q water circulated through the outer surface of fibers at a $0.11 \text{ m} \cdot \text{s}^{-1}$ cross-flow velocity prior to permeate sample collection. The PWP can be determined using Eq. (4.1).

A $2 \text{ g} \cdot \text{L}^{-1}$ mixed dextran solution (Mw ranges from 6,000 to 500,000 Da) was adopted as feed to test the MWCO of the substrates. The dextran concentrations were analyzed by gel permeation chromatography (GPC) (PL-GPC 50 plus system). The detailed method was described previously (Chen et al. 2016).

5.2.4.3 Measurement of intrinsic separation properties of cross-linking modified membranes

The properties of the modified membranes were determined using the above-mentioned filtration system at 2 bar. The water permeability coefficient (A value) of the cross-linked membrane was measured with deionized water as the feed stream, and the rejections to different inorganic salts were determined using 500 mg L^{-1} NaCl, MgCl_2 , Na_2SO_4 and MgSO_4 single salt as feed, respectively. The solute rejections were determined by the conductivity difference in feed solution and permeate. The MWCO of the cross-linking modified membranes were estimated

using a series of neutral solutes, including glycerol, ribose, and glucose. A total organic carbon analyzer was used to examine their concentrations (TOC-VCSH, Shimadzu, Japan). All these feed solutions were pumped through the outer skin of the membranes with a $0.18 \text{ m}\cdot\text{s}^{-1}$ cross-flow velocity.

5.2.4.4 PRO performance evaluation

The PRO performances of membranes after post treatment were evaluated via a PRO system which has been reported in our previous studies (Chou et al. 2013, Chen et al. 2016). The AL-FS orientation was chosen for all PRO tests throughout our study, and the solute rejection skin is on the shell side of the membranes. A 1.0 M magnesium chloride or sodium chloride was employed as the draw stream and driven through the lumen surface of the fibers at different pressures ranging from 0 to 18 bar. The solute concentration in the draw stream was reserved constant by continuously dosing a highly-concentrated salt solution. A variable-speed peristaltic pump was used to drive the feed streams through the shell side of the fibers, and its volume was also kept constant by dosing feed water during the experiments. The flow rates of the feed and draw streams were $1 \text{ L}\cdot\text{min}^{-1}$ and $0.15 \text{ L}\cdot\text{min}^{-1}$, correspondingly. The temperature was $23 \pm 1^\circ\text{C}$. The performance was tested in triplicate with fresh hollow fiber modules, and the average value was presented.

The water flux (J_w) through the selective layer of the membrane was calculated by the Eq. (3.6). The salt flux (J_s) in the feed water was given by Eq.(3.7). The power density (W) was obtained from Eq. (3.8).

To evaluate the low fouling properties of the integral membrane in the AL-FS orientation, a wastewater reverse osmosis retentate from a local municipal wastewater treatment plant was applied as the feed, while NaCl was adopted as the solute for draw stream (1.0 M). Prior to fouling experiments, baseline test was conducted using deionized water as feed at 12-13 bar for 300 minutes. After that,

the feed solution was changed to the wastewater RO retentate, and the experiment was conducted continually at 12-13 bar for 300 minutes.

5.3. Results and discussion

5.3.1 Fabrication of PRO membrane by PAH cross-linking modification

5.3.1.1 Characteristics of PAI hollow fiber substrate

The resultant supports were characterized using FE-SEM, and the images are shown in Figure 5.1. For the two substrates ST#1 and ST#2, the dope composition and spinning conditions were kept the same except for the bore fluid composition used. By adjusting the bore fluid solution, the lumen side surface and cross-section pore structures of the two substrates are rather different. It is observed from Figure 5.1 (a1 and b1) that the finger-like structure was developed beneath the inner surface of ST#1, while the ST#2 presented a sponge-like framework with several macrovoids in the middle. The finger-like structure is probably better for mitigating the internal concentration polarization (ICP) effect and increasing water permeability, while the sponge-like structure is believed to provide better mechanical stability (Chou et al. 2012, Chou et al. 2013). As shown in Figure 5.1 (a2 and b2), the more dense sponge-like pore structure beneath the inner surface of the ST#2 membrane makes it possible to better withstand the high pressure as compared to the ST#1 membrane. From the surface images Figure 5.1 (a3, b3, and a4, b4), abundant pores are observed on the inner surface of both substrates, while almost no pore is observed on the shell surface, indicating the more dense skins formed on the outer surface of the fibers.

The properties of the two polyamide-imide substrates are listed in Table 5.2. The hollow fiber substrates are designed to possess relatively smaller dimensions (inner diameter/outer diameter, ID/OD, around 0.4/0.7 mm/mm), which are favorable to membrane mechanical properties (Chou et al. 2013). The ST#1 membrane has slightly higher PWP than the ST#2 membrane, probably ascribing to the finger-like structure and very large pores on the inner surface. The MWCO values of both

substrates tested from the shell side are relatively small, which is favorable for the subsequent chemical post-treatment to further decrease the pore size and form the solute rejection layer on the outer surface. The two PAI substrates possess high rigidity with a tensile modulus of 215–244 MPa, which are comparable with our previous polyetherimide (PEI) hollow fiber membranes (Chou et al. 2013, Chen et al. 2016). In comparison with the ST#1 membrane, the tensile modulus of the ST#2 membrane is slightly higher due to its more uniform distribution of the tension in the sponge-like structure (Chou et al. 2013). The two substrates have similar burst pressures of up to 22 bar.

Figure 5.1 FESEM images of PAI supports: (a1 and b1) cross section of ST# 1 and ST#2; (a2 and b2) cross-section adjacent to the inner area of ST#1 and ST#2; (a3 and b3) inner area of ST#1 and ST#2; (a4 and b4) outer skin of ST# 1 and ST#2.

Table 5.2 Characteristics of the PAI hollow fiber substrates

Substrate	Dimensions (μm)			PWP (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Porosity (%)	MWCO (kDa) ^a	Tensile modulus (MPa)	Burst pressur e (bar)
	ID (μm)	OD (μm)	Thickness (μm)					
ST# 1	401 ± 6	666 ± 6	132 ± 5	106 ± 10	66 ± 5	6	215 ± 4	21 ± 2
ST# 2	432 ± 6	675 ± 11	121 ± 3	91 ± 8	53 ± 3	19	244 ± 6	22 ± 2

^a Dextran filtration was performed from the shell of the fiber.

5.3.1.2 Characteristics of PAH cross-linked hollow fiber membranes

Figure 5.2 shows the surface and cross-section morphologies of the PAH cross-linking modified hollow fiber membranes ST#1–PAH and ST#2–PAH. Compared with the original substrates, the pore structures of the membrane surface do not change much after modification as shown in Figure 5.2 (a1, b1 and a2, b2). There is no skin layer formed on the inner surface after modification, but small nodules are observed on both inner and outer surfaces. After the PAH cross-linking, suggesting the success of cross-linking reaction. Similar findings were reported in the recent publication, where the reaction between P84 polyimide membrane and polyethyleneimine was investigated (Gao et al. 2016). During the PAH cross-linking reaction, PAH molecules may be able to diffuse into the hollow fiber substrates from both lumen and shell sides. The PAH molecules could gradually anchor onto pore wall and seal the pore, leading to the decrease of the outer surface pore size and the increase in filtration resistance (Zhao et al. 2015). As shown in Figure 5.2(a3) and (b3), the cross-section near the outer surface of the modified membranes presents a dense selective layer supported by a porous sublayer.

Figure 5.2 FESEM images of the inner surface morphologies (a1 and b1), outer surface morphologies (a2 and b2), and cross-section morphologies near the outer

surface (a3 and b3) of the PAH cross-linked membranes ST#1–PAH (a series) and ST#2–PAH (b series)

The intrinsic properties of the ST#1–PAH and ST#2–PAH are summarized in Table 5.3. The permeation properties such as water permeability (A) and salt rejections were evaluated in RO mode at 2 bar, while the structure parameters (S values) were estimated using water flux tested in forward osmosis (FO) mode. The water permeability value of the ST#1–PAH and ST#2–PAH membranes are 1.98 and 1.14 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, respectively. The possible reason for the lower A value of the ST#2–PAH membrane is that its sponge-like structure and smaller inner surface pores increase mass transfer resistance as compared to the finger-like structure and very large inner surface pores of the ST#1–PAH membrane (Li et al. 2015). The rejections to 500 ppm NaCl and MgCl_2 of these two membranes are similar, around 70% and 92%, respectively. After the PAH cross-linking, an NF-like selective layer was formed on the outer surface of hollow fiber membrane. Since the MgCl_2 rejections of the membranes are relatively high, MgCl_2 was selected as draw solution to evaluate the PRO performances of the membranes in the AL–FS orientation, which will be discussed in the following section. As listed in Table 5.3, the tensile modulus of the fibers is not affected much by the cross-linking reaction.

Table 5.3 Intrinsic properties of PAH cross-linked hollow fiber membranes

Membranes	Water permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	NaCl rejection ^a (%)	MgCl_2 rejection ^a (%)	Structural parameter ^b (μm)	Tensile modulus (Mpa)
ST# 1-PAH	1.98 ± 0.3	71.8 ± 3.7	92.2 ± 2.9	621	207 ± 1
ST# 2-PAH	1.14 ± 0.2	69.3 ± 5.2	93.0 ± 0.7	437	243 ± 5

^a Salt rejections were tested using 500 ppm NaCl and MgCl_2 as feed at 2 bar, respectively.

^b The membrane structure parameter was calculated based on the methods reported in our previous publications (She et al. 2012, Chou et al. 2013). The water flux (J_w) was obtained from the FO experiments in both orientations using 1 M NaCl and DI water as draw and feed, respectively.

5.3.1.3 PRO performance of PAH cross-linked hollow fiber membrane

The PRO performances of the newly developed membranes were evaluated in the AL–FS orientation using 1.0 M MgCl_2 as the draw solution and DI water as the feed. Various hydraulic pressures were applied in the draw solution side, and the experiment results for water flux, specific salt flux and power density of the membranes are presented in Figure 5.3. It is shown in Figure 5.3 (a) that the water flux of the ST#1–PAH and ST#2–PAH membranes tested in the AL–FS orientation at a pressure of 0.4 bar are 20.5 and 26.9 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. In PRO, the water flux is governed by the permeation properties (water permeability coefficient A and salt permeability coefficient B) and structural parameter S of the membrane as well as the operation conditions. While the water permeability of the ST#2–PAH membrane is lower than that of the ST#1–PAH membrane, the smaller S value of the ST#2–PAH membrane is useful in mitigating the dilutive ICP effect, leading to a higher water flux than the ST#1–PAH membrane (Kim et al. 2016). As shown in Figure 5.3 (a), with the pressure increase from 0 to 18 bar, the PRO water flux of both membranes decreases gradually due to the decrease of osmotic driving force. The specific salt flux (J_s/J_w) is an important indicator in the osmotically driven membrane processes for revealing the reverse salt diffusion. Minimizing the reverse salt diffusion could reduce ICP effect and mitigate membrane fouling (Fane et al. 2015). As shown in Figure 5.3 (b), the J_s/J_w of the ST#2–PAH membrane shows relatively stable over the entire operating pressure, while the J_s/J_w of the ST#1–PAH membrane increases obviously with the increase in applied pressure. This suggests the ST#1–PAH membrane suffers severe salt leakage or deformation under high pressures. Figure 5.3(c) reveals that the ST#2–PAH membrane produces a peak power density around 6.5 $\text{W}\cdot\text{m}^{-2}$ at 15 bar while the ST#1–PAH membrane produces a peak power density around 3.3 $\text{W}\cdot\text{m}^{-2}$ at 10 bar. As observed from FESEM characterization, the sponge-like structure and smaller inner surface pores of the support makes the ST#2–PAH membrane a good candidate for PRO application. From the above discussion, the ST#2–PAH membrane has better mechanical stability under high-pressure operation and higher power density output, and thus it is chosen for further study.

Figure 5.3 PRO performance of the PAH cross-linked hollow membranes at various operating pressures: (a) PRO water flux J_w , (b) specific salt flux (J_s/J_w), (c) power density W . Testing conditions: DI water as the feed, and 1M MgCl_2 as the draw solution at ambient temperature.

5.3.2 Fabrication of PRO membrane by PAH cross-linking followed by GA cross-linking

In real PRO application, seawater or seawater desalination brine is usually used as the draw solution, in which NaCl is the main solute. Therefore, the selectivity to NaCl of PAH cross-linked membrane needs to be further improved for its potential application in PRO process. To improve the NaCl rejection, GA was adopted to conduct the second step of cross-linking on the ST#2-PAH membrane and the resultant membrane is denoted as ST#2-PAH/GA.

5.3.2.1 Characterizations of PAH/GA cross-linked hollow fiber membrane

The surface and cross-section morphologies of the ST#2-PAH/GA membrane were not changed compared to the ST#2-PAH membrane, and thus the relevant FESEM images are not shown here.

The possible cross-linking reactions between PAI substrate and PAH/GA are illustrated in Figure 5.4 and verified by the ATR-FTIR measurements as shown in

Figure 5.5. The imide rings in PAI were opened, and the amine groups from PAH were covalently bonded onto the PAI. After that, the free amine groups in PAH can be further covalently bonded with aldehyde groups from GA. As shown in Figure 5.5, a few characteristic bands for imide groups including 1778 and 1719 cm^{-1} (symmetric and asymmetric C=O stretching, respectively, imide I), 1379 cm^{-1} (C-N-C stretching, imide II), 1109 and 725 cm^{-1} (imide ring) are observed for the PAI hollow fiber substrate (Ba et al. 2009, Zhang et al. 2011). It can be seen clearly that the imide peaks became weakened after the cross-linking reaction with PAH due to the formation of a covalent bond between amine groups and imide rings (Setiawan et al. 2014).

Figure 5.4 Possible mechanism of chemical cross-linking reaction between PAI and PAH/GA.

Figure 5.5 ATR-FTIR spectra of the substrate and modified membranes.

The surface charge properties of the substrate and modified membranes were investigated using streaming potential measurement at pH 4~9 and the results are shown in Figure 5.6. It can be seen that the PAI hollow fiber substrate is negatively charged throughout the entire testing pH range. After PAH cross-linking, the membrane surface becomes positively charged at pH below the isoelectric point of 8.6 due to the protonation of amine groups imparted by the grafting of PAH. However, further introducing of GA consumes partial amine groups on PAH cross-linked membrane, lowering the surface positive charge. The isoelectric point of GA cross-linked membrane is around 4.9.

Figure 5.6 Surface zeta-potential of the substrate and modified membranes as a function of pH.

5.3.2.2 Intrinsic properties of PAH/GA cross-lined hollow fiber membrane

The intrinsic permeation properties of the ST#2–PAH/GA membrane including water permeability, salt permeability, and NaCl rejection are summarized in Table 5.4. It is observed that the water permeability of the membrane decreases to $0.66 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ while the NaCl rejection increases to 80.1 % after the GA modification. The reaction between GA and amine functional groups fixed on the membrane after the PAH cross-linking would be able to further seal the membrane pores, leading to an increase in filtration resistance and a decrease in pore size of rejection layer.

Table 5.4 Intrinsic properties of the ST#2–PAH/GA hollow fiber membrane

Membrane	Water permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Salt permeability ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	NaCl rejection ^a (%)
ST#2–PAH/GA	0.66 ± 0.09	0.32 ± 0.03	80.1 ± 2.2

^a Salt rejections were tested using 500 ppm NaCl as feed

The rejections to the neutral solutes with different molecular weights were measured to estimate the MWCO of the modified membranes. Table 5.5 lists the properties of these neutral solutes, and their rejections by the PAH cross-linked, and PAH/GA cross-linked membranes. The MWCO of the membranes can be determined by plotting the rejections against solute molecular weights. The MWCO of the ST#2-PAH and ST#2-PAH/GA membranes are 143 Da and 127 Da, respectively. This indicates that the selective layer is further tightened after the GA cross-linking.

Table 5.5 Properties and rejections of the neutral solutes ^a

Solute	Molecular weight (Da)	Stocks radius (nm)	ST#2-PAH rejection ^a (%)	ST#2-PAH/GA Rejection ^a (%)
Glycerol	92	0.26	59.0	80.8
Ribose	150	0.31	94.5	96.4
Glucose	180	0.35	96.8	97.4

^a The solute rejection was tested using 200ppm feed solutions at 2 bar.

The rejections of the modified membranes against different inorganic salts were determined by performing the filtration test with 500 ppm NaCl, MgCl₂, Na₂SO₄, and MgSO₄ single salt as feed, respectively. It is observed in Figure 5.7 that the PAH cross-linked membrane shows 68% rejection to NaCl and more than 93% rejections against MgCl₂, Na₂SO₄, and MgSO₄, suggesting the size exclusion plays a significant role in this case (Liu et al. 2015). After GA cross-linking, the NaCl rejection increases to 80.1% while the MgCl₂ rejection slightly decreases to 87.4%, which may be due to the change of surface charge property as shown in Figure 5.6.

Figure 5.7 Separation performances of the PAH and PAH/GA cross-linked hollow fiber membranes. Experiments were conducted at 2 bar using 500 ppm single salt solution.

5.3.2.3 PRO performance of the ST#2-PAH/GA membrane

The PRO performance of the ST#2-PAH/GA membrane was investigated in the AL-FS orientation using 1.0 M NaCl and DI water as draw and feed, respectively. The experiment results for water flux, specific salt flux and power density of the membrane are presented in Figure 5.8. The water flux J_w declines gradually with increase in the operating pressure. The specific salt flux J_s/J_w keeps constant at lower trans-membrane pressure (< 12 bar) and slowly increases with the increase of operating pressure from 12 to 16 bar. It produces a peak power density around $5.1 \text{ W} \cdot \text{m}^{-2}$ at 16 bar. This result demonstrates the potential of the PAH/GA cross-linked hollow fiber membrane for the PRO application under the AL-FS orientation. Then, the newly developed PRO membrane with high durability was examined using a real wastewater RO retentate as feed, which will be discussed in the following section.

Figure 5.8 PRO performance of the ST#2-PAH/GA membrane at various operating pressures: (a) water flux J_w , (b) specific salt flux J_s/J_w , (c) power density W . Testing conditions: DI water as the feed and 1 M NaCl as the draw at ambient temperature.

5.3.3 PRO performance using real wastewater RO retentate as feed

The wastewater RO retentate, containing various inorganic and organic foulants, is from a local municipal wastewater RO plant in Singapore. By using the wastewater RO retentate as the feed and 1 M NaCl as the draw solution, the fouling behaviors of the PAH/GA cross-linked membranes were evaluated in the AL–FS orientation in PRO process. Before conducting the fouling test, DI water was used as a feed for benchmarking. As illustrated in Figure 5.9, the average power density of the ST#2–PAH/GA membrane is $4.8 \text{ W}\cdot\text{m}^{-2}$ using DI water as the feed for 300 min continuously operation at a hydraulic pressure of 12~13 bar. After changing the feed to wastewater RO retentate, the power density slightly decreases and maintains constant at around $4.3 \text{ W}\cdot\text{m}^{-2}$. The slight decrease of the power density might be due to the increase in osmotic pressure in the feed solution (the conductivity of wastewater RO retentate is around $2.4 \text{ mS}\cdot\text{cm}^{-1}$) as compared to the benchmark. The power density of the newly developed membrane keeps constant during the entire experiment, indicating its advantages of lower membrane fouling operated in the AL–FS orientation. The results reveal that the novel PAH/GA cross-linked hollow fiber membrane is promising for fouling control in osmotic power generation process. After further cross-linked using GA solution, the resulted membrane has a negative charge when pH above 4 (Figure 5.6), which may also contribute to its antifouling properties due to most organic foulants are negatively charged. Since TFC membranes can only be applicable under the AL-DS orientation (In AL-FS orientation, the thin film selective layer would be deteriorated or even detached from surface even under low pressure (Bar-Zeev et al. 2015)), this cross-linking method provides an alternative approach to fabricate robust membranes to run in the AL-FS orientation in PRO process to resist fouling and maintain stable performance.

Figure 5.9 The power density of the ST#2–PAH/GA membrane as a function of operation time. The PRO experiment was performed continuously using 1.0 M NaCl as the draw solution and DI water as the feed for baseline test while wastewater RO retentate as the feed for fouling test at ambient temperature at hydraulic pressure of 12~13 bar.

5.3.4 Comparison to other membranes reported in the literature

The intrinsic PRO performances tested in the AL – FS orientation of the novel integral hollow fiber membranes together with the membranes reported in literature are summarized in Table 5.6, while their fouling performances using the real wastewater retentate as feed were compared in Table 5.7. It can be seen that the cross-linking modified integral hollow fiber membranes developed in the current study present better performance as compared to those reported integral CTA membranes. A peak power density of $5.1 \text{ W} \cdot \text{m}^{-2}$ can be achieved using deionized water as feed and sodium chloride (1.0 M) as draw streams in the AL – FS orientation as listed in Table 5.6. When using the real wastewater retentate as feed, the newly developed integral membrane showed a very stable performance with a

power density of $4.3 \text{ W}\cdot\text{m}^{-2}$ for 300 min operation at 13 bar, which is higher than that of the CTA membrane.

The results demonstrate the great potential of PAH/GA cross-linked hollow fiber membrane for PRO application. Further investigation is required to improve the performance of PAI-PAH/GA membranes, including optimizing the membrane structure to decrease S value and increase water permeability, and further enhancing the mechanical strength of the membranes to withstand higher pressures and thus produce a higher power density.

Table 5.6 Comparison of water flux, specific salt flux and power density of various PRO membranes tested in AL-FS orientation

Membrane	Feed solution	Draw solution	J_w @ 0 bar ($\text{L}\cdot\text{m}^{-2}\text{h}^{-1}$)	Peak Power density ($\text{W}\cdot\text{m}^{-2}$)	J_s/J_w @ peak power density ($\text{mol}\cdot\text{L}^{-1}$)	Collapse pressure (bar)	Orientation	Reference
ST#2-PAH	DI water	1 M MgCl_2	27.0	6.5	0.09	>18	AL-FS	Current work
ST#2-PAH/GA	DI water	1 M NaCl	20.0	5.1	0.16	>16	AL-FS	Current work
HTI-CTA	DI water	0.5 M NaCl	7.8 ^a	0.8 ^a	/	>15	AL-FS	(Kim et al. 2016)
HTI-CTA	DI water	1 M NaCl	10.1 ^a	2.3 ^a	/	>15	AL-FS	(Kim et al. 2016)

^a Readings from figures

Table 5.7 Comparison of power density of PRO membranes tested in the AL-FS orientation using wastewater RO retentate as feed

Membrane	DS	Feed	Initial W ($\text{W}\cdot\text{m}^{-2}$)	Final W ($\text{W}\cdot\text{m}^{-2}$)	Applied Pressure (bar)	Orientation	Reference
ST#2-PAH/GA	1 M NaCl	Wastewater retentate	4.3	4.3 @ 300 mins	13	AL-FS	Current work
HTI-CTA	1 M NaCl	Wastewater retentate	2.8 ^a	2.8 ^a @ 240 mins	10	AL-FS	(She et al. 2017)

^a Readings from figures

5.4 Conclusions

In this study, a novel integral hollow fiber membrane with robust mechanical strength was fabricated by employing facile cross-linking method for PRO application in the AL–FS orientation. The structure and properties of the newly developed membrane have been characterized thoroughly using a series of characterization protocols, and the membrane performance in PRO operation was subsequently investigated. The feasibility of PRO operation in the AL–FS orientation for sustainable power generation was also assessed using a real wastewater RO retentate as feed. The major findings of the work are summarized as follows:

- (1) Two hollow fiber substrates with different pore structures were fabricated to investigate the proper structure of the integral membrane that could be operated in the AL–FS orientation. The sponge-like structure with a selective layer on the outer surface and smaller inner surface pore was more suitable for PRO operation in the AL–FS orientation. The ST#2–PAH membrane could withstand the high pressure applied on the lumen side and produces a peak power density of $6.5 \text{ W}\cdot\text{m}^{-2}$ at 15 bar using DI water as the feed and 1.0 M MgCl_2 as the draw solution under the AL–FS orientation.
- (2) The PAH/GA cross-linked membrane showed high rejections against each of 500 ppm inorganic salt MgCl_2 , Na_2SO_4 and MgSO_4 under 2 bar. It presented an MWCO of 127 Da and 80% rejection to 500 ppm NaCl. It could produce a peak power density of $5.1 \text{ W}\cdot\text{m}^{-2}$ at 16 bar using DI water and 1 M NaCl as the feed and draw solution, respectively, under the AL–FS orientation.
- (3) By using a real wastewater RO retentate as the feed solution, the integral ST#2–PAH/GA membrane exhibited superior antifouling performance while the power density maintained constant at around $4.3 \text{ W}\cdot\text{m}^{-2}$ at 12~13 bar using 1 M NaCl as the draw solution (equivalent to seawater brine) during the entire experiment of 300 minutes.

These results demonstrate the advantages of the AL–FS orientation for alleviating membrane fouling in osmotic power generation process and indicate the great potential of the mechanically robust PAH/GA cross-linked hollow fiber membrane for osmotic energy harvesting.

CHAPTER 6 Conclusions and Recommendations

6.1 Overall conclusions

This thesis presents the development and challenges of PRO technology, and the membranes utilized for this application. Designing and fabricating membranes with high mechanical robustness, minimized structural parameter while maintaining power density with the feed stream containing various foulants are the main focus of this thesis. A series of novel PRO membranes were prepared with substrates and selective layers optimized to produce continuous performance over a long-time period.

A TFC flat sheet membrane (Chapter 3), a TFC hollow fiber membrane (Chapter 4), and an integral membrane (Chapter 5) were developed to produce stable performance using various feed and draw streams at high hydraulic pressures. The morphology of the TFC flat sheet membrane was optimized to enhance the mechanical property with reduced structure parameter. The PRO performances of the as-prepared membranes under high applied pressure were tested to demonstrate the mechanical stability of the membrane. On the other hand, surface modification by polyelectrolyte deposition was proposed to improve the anti-fouling property of a TFC hollow fiber membrane. The resultant membrane could produce stable performance with alginate present in the feed stream under the pressure of 15 bar. Subsequently, an integral membrane was developed using phase inversion and chemical cross-linking method to generate stable power output using wastewater brine as the feed and 1 M NaCl as the draw. The important findings and conclusions are summarized as follows:

In chapter 3:

- (1) A novel thin-film composite flat sheet PRO membrane with optimized substrate structure was fabricated via phase inversion and interfacial polymerization methods. By varying the polymer concentration of membrane dope solution, an

optimized membrane substrate was identified, which possessed high water permeability of $483 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and high porosity of 73.5%.

- (2) In PRO tests, TFC-PEI#2 membrane could achieve a stable power density of $12.8 \text{ W} \cdot \text{m}^{-2}$ at 17.2 bar in AL-DS orientation, using 1 M NaCl solution and 10 mM NaCl solution as draw and feed, respectively.
- (3) Water permeability (A_p) and salt permeability (B_p) under different pressures were measured using a PRO setup. A_p and B_p were better indicators than conventional A and B for examining the variation of PRO membrane structure under pressure. Within current operating pressure range of 17.2 bar, the top polyamide layer of TFC-PEI#2 membrane mainly experienced a reversible deformation.
- (4) The structural stability of TFC-PEI#2 membrane was systematically evaluated through two pressure cycle tests. The water flux, specific salt flux and power density obtained in the upward and downward measurements in each cycle were close to each other. The first cycle and the second cycle also showed excellent reproducibility.

The stability of PRO membrane was also tested under high pressure. The membrane could maintain almost unchanged water flux and power density of $12.8 \text{ W} \cdot \text{m}^{-2}$ at 17.2 bar over the 300-min testing time, suggesting the membrane's great potential to be used in a practical application in the future.

In chapter 4:

- (5) The modified membrane after polyelectrolytes deposition showed slightly better PRO performance than that of the control membrane, attributing to the well-maintained intrinsic properties, and the reduced structural parameter as a result of increased hydrophilicity.

- (6) The modified membrane could better maintain performance during the PRO experiments with the foulant containing feed solutions, with better sustainable flux and higher power density achieved at increased pressure.
- (7) The in-house fabricated PRO membranes (with or without surface modification) had better fouling resistance towards alginate compared with BSA, presumably due to the higher charge density, higher hydrophilicity and larger hydrodynamic diameter of the alginate.

In chapter 5:

- (8) A novel integral hollow fiber membrane with robust mechanical strength was fabricated by the cross-linking method and could be operated in PRO process in the AL-FS orientation under high pressure. Two types of PAI substrates were fabricated and cross-linked using PAH solution to synthesize integral PRO membranes.
- (9) The sponge-like structure could better withstand high pressure and the resulted membranes could produce stable water flux under high pressure applied from the porous substrate side. The ST#2-PAH membrane produced the highest power density $6.45 \text{ W} \cdot \text{m}^{-2}$ at 15 bar using DI water and 1 M MgCl_2 as feed and draw, respectively.
- (10) The PAH/GA cross-linked PAI membrane showed high rejections against each of 500 ppm inorganic salt MgCl_2 , Na_2SO_4 and MgSO_4 under 2 bar. It presented an MWCO of 127 Da and 80% rejection to 500 ppm NaCl. It could produce a peak power density of $5.1 \text{ W} \cdot \text{m}^{-2}$ at 16 bar using DI water and 1 M NaCl as the feed and draw solution, respectively, under AL-FS orientation.
- (11) By using a real wastewater RO retentate as the feed solution, the integral PAH/GA-PAI membrane exhibited superior antifouling performance where the power density maintained constant at around $4.3 \text{ W} \cdot \text{m}^{-2}$ at 12~13 bar using 1 M

NaCl as the draw solution (equivalent to seawater brine) during the entire experiment.

(12) These results demonstrate the advantages of AL-FS orientation for alleviating membrane fouling in osmotic power generation process and indicate the great potential of the mechanical robust PAH/GA cross-linked hollow fiber membrane for osmotic energy harvesting.

6.2 Recommendations for future work

The proposed future research topics include: (1) The effect of mono and divalent ions in the feed solution will be studied for the low-fouling modified thin film composite membrane (2) the performances of the integral membranes will be further improved by exploring different cross-linking conditions and chemicals; (3) stability tests of the integral cross-linking membranes and long-term fouling tests will be conducted to further study the viability in real application; (4) substrates using low-cost materials that suitable for chemical cross-linking will be investigated to explore the possible applications. All approaches will be briefly introduced here;

To study the effect of mono and divalent ions in the feed solution for the low-fouling modified thin film composite membranes to further investigate the anti-fouling properties. Since in real application, some inorganic solutes are present in the feed water, it is important to study the combination effect of both inorganic and organic foulants.

To further increase the performances of the integral membranes, increasing the solute rejection of the selective layer is important. Different approaches can be adopted to seal the defects of the outer surface such as increasing cross-linking temperature, cross-link agent concentration and reaction time. However, these approaches could also deteriorate the membrane mechanical stability due to the presence of alkaline solution. Another approach is synthesizing the selective layer on the lumen surface. The lumen side of the hollow fiber is well protected from breakage and defects from mishandling the fibers, which could be more suitable for

forming the active layer. The substrate with dense lumen surface could be designed by adjusting the dope composition and inner coagulant solution. Additionally, tuning the fabrication condition of the substrate can further improve water permeability and minimizing the structural parameter, thereby increasing the water flux of the integral membrane.

The integral membrane stability and long-term fouling performance, which are critical in real application and commercialization, still need to be investigated. Therefore, the stability tests include the changes of intrinsic properties and power density under different pressure, and the critical turning point will be conducted to provide a better understanding of the integral membrane operated in AL-FS orientation. The long-term fouling test should also be conducted to confirm the anti-fouling properties.

It shall be necessary to scale up the current work from lab-scale to pilot-scale. The scale-up process of integral PRO membrane includes two major challenges: the fabrication of large quantities of membrane substrates with cross-linking post-treatment and the assemblage of large scale membrane modules. The cost of polymeric material used is extremely important to achieve profits economically. Therefore, a low-cost polymeric material is required to replace the expensive PAI material. PEI/PAI blend dope solution is proposed to develop the integral membranes. On the other hand, the resulted membrane substrate will be immersed in cross-linking chemical solutions and then be assembled in a membrane module.

REFERENCES

- Abbasi-Garravand, E., C. N. Mulligan, C. B. Laflamme and G. Clairet (2016). "Role of two different pretreatment methods in osmotic power (salinity gradient energy) generation." Renewable Energy **96**: 98-119.
- Achilli, A., T. Y. Cath and A. E. Childress (2009). "Power generation with pressure retarded osmosis: An experimental and theoretical investigation." Journal of Membrane Science **343**(1-2): 42-52.
- Achilli, A. and A. E. Childress (2010). "Pressure retarded osmosis: From the vision of Sidney Loeb to the first prototype installation - Review." Desalination **261**(3): 205-211.
- Altaee, A. and A. Sharif (2015). "Pressure retarded osmosis: Advancement in the process applications for power generation and desalination." Desalination **356**: 31-46.
- Arena, J. T., B. McCloskey, B. D. Freeman and J. R. McCutcheon (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 **375**(1-2): 55-62.
- Arkhangelsky, E., F. Wicaksana, S. Chou, A. A. Al-Rabiah, S. M. Al-Zahrani and R. Wang (2012). "Effects of scaling and cleaning on the performance of forward osmosis hollow fiber membranes." Journal of Membrane Science **415–416**: 101-108.
- Asatekin, A., A. Menniti, S. Kang, M. Elimelech, E. Morgenroth and A. M. Mayes (2006). "Antifouling nanofiltration membranes for membrane bioreactors from self-assembling graft copolymers." Journal of Membrane Science **285**(1–2): 81-89.
- Ba, C., J. Langer and J. Economy (2009). "Chemical modification of P84 copolyimide membranes by polyethylenimine for nanofiltration." Journal of Membrane Science **327**(1–2): 49-58.
- Bar-Zeev, E., F. Perreault, A. P. Straub and M. Elimelech (2015). "Impaired Performance of Pressure-Retarded Osmosis due to Irreversible Biofouling." Environmental Science and Technology **49**(21): 13050-13058.
- Bertrand, P., A. Jonas, A. Laschewsky and R. Legras (2000). "Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: Suitable materials, structure and properties." Macromolecular Rapid Communications **21**(7): 319-348.

Boo, C., M. Elimelech and S. Hong (2013). "Fouling control in a forward osmosis process integrating seawater desalination and wastewater reclamation." Journal of Membrane Science **444**: 148-156.

Bui, N. N., M. L. Lind, E. M. V. Hoek and J. R. McCutcheon (2011). "Electrospun nanofiber supported thin film composite membranes for engineered osmosis." Journal of Membrane Science **385-386**(1): 10-19.

Bui, N. N. and J. R. McCutcheon (2014). "Nanofiber supported thin-film composite membrane for pressure-retarded osmosis." Environmental Science and Technology **48**(7): 4129-4136.

Cadotte, J. E. and R. J. Petersen (1981). THIN-FILM COMPOSITE REVERSE-OSMOSIS MEMBRANES: ORIGIN, DEVELOPMENT, AND RECENT ADVANCES. ACS Symposium Series.

Cai, T., X. Li, C. Wan and T. S. Chung (2016). "Zwitterionic polymers grafted poly(ether sulfone) hollow fiber membranes and their antifouling behaviors for osmotic power generation." Journal of Membrane Science **497**: 142-152.

Chang, Y., S. Chen, Q. Yu, Z. Zhang, M. Bernards and S. Jiang (2007). "Development of Biocompatible Interpenetrating Polymer Networks Containing a Sulfobetaine-Based Polymer and a Segmented Polyurethane for Protein Resistance." Biomacromolecules **8**(1): 122-127.

Chang, Y., S. Chen, Z. Zhang and S. Jiang (2006). "Highly Protein-Resistant Coatings from Well-Defined Diblock Copolymers Containing Sulfobetaines." Langmuir **22**(5): 2222-2226.

Chen, S. C., G. L. Amy and T. S. Chung (2016). "Membrane fouling and anti-fouling strategies using RO retentate from a municipal water recycling plant as the feed for osmotic power generation." Water Research **88**: 144-155.

Chen, S. C., X. Z. Fu and T. S. Chung (2014). "Fouling behaviors of polybenzimidazole (PBI)-polyhedral oligomeric silsesquioxane (POSS)/polyacrylonitrile (PAN) hollow fiber membranes for engineering osmosis processes." Desalination **335**(1): 17-26.

Chen, S. C., C. F. Wan and T. S. Chung (2015). "Enhanced fouling by inorganic and organic foulants on pressure retarded osmosis (PRO) hollow fiber membranes under high pressures." Journal of Membrane Science **479**: 190-203.

Chen, Y., L. Setiawan, S. Chou, X. Hu and R. Wang (2016). "Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane." Journal of Membrane Science **503**: 90-100.

Cheng, Z. L., X. Li, Y. Feng, C. F. Wan and T. S. Chung (2017). "Tuning water content in polymer dopes to boost the performance of outer-selective thin-film composite (TFC) hollow fiber membranes for osmotic power generation." Journal of Membrane Science **524**: 97-107.

Cheng, Z. L., X. Li, Y. D. Liu and T. S. Chung (2016). "Robust outer-selective thin-film composite polyethersulfone hollow fiber membranes with low reverse salt flux for renewable salinity-gradient energy generation." Journal of Membrane Science **506**: 119-129.

Chou, S., L. Shi, R. Wang, C. Y. Tang, C. Qiu and A. G. Fane (2010). "Characteristics and potential applications of a novel forward osmosis hollow fiber membrane." Desalination **261**(3): 365-372.

Chou, S., R. Wang and A. G. Fane (2013). "Robust and High performance hollow fiber membranes for energy harvesting from salinity gradients by pressure retarded osmosis." Journal of Membrane Science **448**(0): 44-54.

Chou, S., R. Wang, L. Shi, Q. She, C. Tang and A. G. Fane (2012). "Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density." Journal of Membrane Science **389**: 25-33.

Chung, T.-S., X. Li, R. C. Ong, Q. Ge, H. Wang and G. Han (2012). "Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications." Current Opinion in Chemical Engineering **1**(3): 246-257.

Chung, T. S., L. Luo, C. F. Wan, Y. Cui and G. Amy (2015). "What is next for forward osmosis (FO) and pressure retarded osmosis (PRO)." Separation and Purification Technology **156**: 856-860.

Cui, Y., X. Y. Liu and T. S. Chung (2014). "Enhanced osmotic energy generation from salinity gradients by modifying thin film composite membranes." Chemical Engineering Journal **242**: 195-203.

Curcio, E., G. D. Profio, E. Fontananova and E. Drioli (2015). Membrane technologies for seawater desalination and brackish water treatment. Advances in Membrane Technologies for Water Treatment: Materials, Processes and Applications: 411-441.

Da Costa, A. R., A. G. Fane and D. E. Wiley (1994). "Spacer characterization and pressure drop modelling in spacer-filled channels for ultrafiltration." Journal of Membrane Science **87**(1-2): 79-98.

Daniilidis, A., D. A. Vermaas, R. Herber and K. Nijmeijer (2014). "Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis." Renewable Energy **64**: 123-131.

Decher, G. (1997). "Fuzzy nanoassemblies: Toward layered polymeric multicomposites." Science **277**(5330): 1232-1237.

Duong, P. H. H., T. S. Chung, S. Wei and L. Irish (2014). "Highly permeable double-skinned forward osmosis membranes for anti-fouling in the emulsified oil-water separation process." Environmental Science and Technology **48**(8): 4537-4545.

Egueh, A. N. D., B. Lakard, P. Fievet, S. Lakard and C. Buron (2010). "Charge properties of membranes modified by multilayer polyelectrolyte adsorption." Journal of Colloid and Interface Science **344**(1): 221-227.

Elimelech, M. and W. A. Phillip (2011). "The future of seawater desalination: Energy, technology, and the environment." Science **333**(6043): 712-717.

Fane, A. G., R. Wang and M. X. Hu (2015). "Synthetic membranes for water purification: Status and future." Angewandte Chemie - International Edition **54**(11): 3368-3386.

Fang, W., C. Liu, L. Shi and R. Wang (2015). "Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers for enhanced organic fouling resistance." Journal of Membrane Science **492**: 147-155.

Fang, W., R. Wang, S. Chou, L. Setiawan and A. G. Fane (2012). "Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers to enhance membrane properties of anti-scaling and anti-internal concentration polarization." Journal of Membrane Science **394-395**: 140-150.

Fimbres-Weihs, G. A. and D. E. Wiley (2010). "Review of 3D CFD modeling of flow and mass transfer in narrow spacer-filled channels in membrane modules." Chemical Engineering and Processing: Process Intensification **49**(7): 759-781.

Fu, F. J., S. Zhang and T. S. Chung (2015). "Sandwich-structured hollow fiber membranes for osmotic power generation." Desalination **376**: 73-81.

Fu, F. J., S. Zhang, S. P. Sun, K. Y. Wang and T. S. Chung (2013). "POSS-containing delamination-free dual-layer hollow fiber membranes for forward osmosis and osmotic power generation." Journal of Membrane Science **443**: 144-155.

Gao, J., S.-P. Sun, W.-P. Zhu and T.-S. Chung (2016). "Green modification of outer selective P84 nanofiltration (NF) hollow fiber membranes for cadmium removal." Journal of Membrane Science **499**: 361-369.

Gao, Y., S. Haavisto, W. Li, C. Y. Tang, J. Salmela and A. G. Fane (2014). "Novel Approach To Characterizing the Growth of a Fouling Layer during Membrane Filtration via Optical Coherence Tomography." Environmental Science & Technology **48**(24): 14273-14281.

Gerstandt, K., K. V. Peinemann, S. E. Skilhagen, T. Thorsen and T. Holt (2008). "Membrane processes in energy supply for an osmotic power plant." Desalination **224**(1-3): 64-70.

Gray, G. T., J. R. McCutcheon and M. Elimelech (2006). "Internal concentration polarization in forward osmosis: role of membrane orientation." Desalination **197**(1): 1-8.

Gu, M., J. Lee, Y. Kim, J. S. Kim, B. Y. Jang, K. T. Lee and B. S. Kim (2014). "Inhibiting the shuttle effect in lithium-sulfur batteries using a layer-by-layer assembled ion-permeable separator." RSC Advances **4**(87): 46940-46946.

Hammond, P. T. (1999). "Recent explorations in electrostatic multilayer thin film assembly." Current Opinion in Colloid and Interface Science **4**(6): 430-442.

Han, G., Z. L. Cheng and T. S. Chung (2017). "Thin-film composite (TFC) hollow fiber membrane with double-polyamide active layers for internal concentration polarization and fouling mitigation in osmotic processes." Journal of Membrane Science **523**: 497-504.

Han, G. and T. S. Chung (2014). High performance thin-film composite pressure retarded osmosis (PRO) hollow fiber membranes for renewable osmotic energy generation. 24th Annual Meeting of the North American Membrane Society, NAMS 2014.

Han, G. and T. S. Chung (2014). "Robust and high performance pressure retarded osmosis hollow fiber membranes for osmotic power generation." AIChE Journal **60**(3): 1107-1119.

Han, G., P. Wang and T. S. Chung (2013). "Highly robust thin-film composite pressure retarded osmosis (PRO) hollow fiber membranes with high power densities for renewable salinity-gradient energy generation." Environmental Science and Technology **47**(14): 8070-8077.

- Han, G., S. Zhang, X. Li and T. S. Chung (2013). "High performance thin film composite pressure retarded osmosis (PRO) membranes for renewable salinity-gradient energy generation." Journal of Membrane Science **440**: 108-121.
- Han, G., S. Zhang, X. Li and T. S. Chung (2015). "Progress in pressure retarded osmosis (PRO) membranes for osmotic power generation." Progress in Polymer Science **51**: 1-27.
- Han, G., J. Zhou, C. Wan, T. Yang and T. S. Chung (2016). "Investigations of inorganic and organic fouling behaviors, antifouling and cleaning strategies for pressure retarded osmosis (PRO) membrane using seawater desalination brine and wastewater." Water Research **103**: 264-275.
- Han, G., J. Zuo, C. Wan and T. S. Chung (2015). "Hybrid pressure retarded osmosis-membrane distillation (PRO-MD) process for osmotic power and clean water generation." Environmental Science: Water Research and Technology **1**(4): 507-515.
- Harder, P., M. Grunze, R. Dahint, G. M. Whitesides and P. E. Laibinis (1998). "Molecular Conformation in Oligo(ethylene glycol)-Terminated Self-Assembled Monolayers on Gold and Silver Surfaces Determines Their Ability To Resist Protein Adsorption." The Journal of Physical Chemistry B **102**(2): 426-436.
- Hatzell, K. B., M. Beidaghi, J. W. Campos, C. R. Dennison, E. C. Kumbur and Y. Gogotsi (2013). "A high performance pseudocapacitive suspension electrode for the electrochemical flow capacitor." Electrochimica Acta **111**: 888-897.
- Helfer, F., C. Lemckert and Y. G. Anissimov (2014). "Osmotic power with Pressure Retarded Osmosis: Theory, performance and trends - A review." Journal of Membrane Science **453**: 337-358.
- Herold, D. A., K. Keil and D. E. Bruns (1989). "Oxidation of polyethylene glycols by alcohol dehydrogenase." Biochemical Pharmacology **38**(1): 73-76.
- Hickenbottom, K. L., N. T. Hancock, N. R. Hutchings, E. W. Appleton, E. G. Beaudry, P. Xu and T. Y. Cath (2013). "Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations." Desalination **312**: 60-66.
- Hickenbottom, K. L., J. Vanneste, M. Elimelech and T. Y. Cath (2016). "Assessing the current state of commercially available membranes and spacers for energy production with pressure retarded osmosis." Desalination **389**: 108-118.
- Huang, L., N.-N. Bui, M. T. Meyering, T. J. Hamlin and J. R. McCutcheon (2013). "Novel hydrophilic nylon 6,6 microfiltration membrane supported thin film

composite membranes for engineered osmosis." Journal of Membrane Science **437**(0): 141-149.

Hyun, J., H. Jang, K. Kim, K. Na and T. Tak (2006). "Restriction of biofouling in membrane filtration using a brush-like polymer containing oligoethylene glycol side chains." Journal of Membrane Science **282**(1–2): 52-59.

Kim, D. I., J. Kim and S. Hong (2016). "Changing membrane orientation in pressure retarded osmosis for sustainable power generation with low fouling." Desalination **389**: 197-206.

Kim, J., B. Kim, D. Inhyuk Kim and S. Hong (2015). "Evaluation of apparent membrane performance parameters in pressure retarded osmosis processes under varying draw pressures and with draw solutions containing organics." Journal of Membrane Science **493**: 636-644.

Kim, J., M. J. Park, M. Park, H. K. Shon, S. H. Kim and J. H. Kim (2016). "Influence of colloidal fouling on pressure retarded osmosis." Desalination **389**: 207-214.

Kim, Y. C. and M. Elimelech (2012). "Adverse impact of feed channel spacers on the performance of pressure retarded osmosis." Environmental Science and Technology **46**(8): 4673-4681.

Kim, Y. C. and M. Elimelech (2013). "Potential of osmotic power generation by pressure retarded osmosis using seawater as feed solution: Analysis and experiments." Journal of Membrane Science **429**: 330-337.

Kontorovich, A. E., M. I. Epov and L. V. Eder (2014). "Long-term and medium-term scenarios and factors in world energy perspectives for the 21st century." Russian Geology and Geophysics **55**(5): 534-543.

Kosuri, M. R. and W. J. Koros (2008). "Defect-free asymmetric hollow fiber membranes from Torlon®, a polyamide-imide polymer, for high-pressure CO₂ separations." Journal of Membrane Science **320**(1-2): 65-72.

Koutsou, C. P., S. G. Yiantsios and A. J. Karabelas (2009). "A numerical and experimental study of mass transfer in spacer-filled channels: Effects of spacer geometrical characteristics and Schmidt number." Journal of Membrane Science **326**(1): 234-251.

Le, N. L., N. M. S. Bettahalli, S. P. Nunes and T. S. Chung (2016). "Outer-selective thin film composite (TFC) hollow fiber membranes for osmotic power generation." Journal of Membrane Science **505**: 157-166.

- Lee, J. and S. Kim (2016). "Predicting power density of pressure retarded osmosis (PRO) membranes using a new characterization method based on a single PRO test." Desalination **389**: 224-234.
- Lee, K. L., R. W. Baker and H. K. Lonsdale (1981). "Membranes for power generation by pressure-retarded osmosis." Journal of Membrane Science **8**(2): 141-171.
- Lee, S., C. Boo, M. Elimelech and S. Hong (2010). "Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO)." Journal of Membrane Science **365**(1-2): 34-39.
- Lee, S. S., S. W. Han, H. Jeong, J. Song, H. Y. Chung and W. Yu (2010). "Quality of Life of Long-term Survivors after a Subtotal or a Total Gastrectomy for Gastric Cancer." J Korean Gastric Cancer Assoc **10**(1): 34-39.
- Li, X., T. Cai, G. L. Amy and T. S. Chung (2017). "Cleaning strategies and membrane flux recovery on anti-fouling membranes for pressure retarded osmosis." Journal of Membrane Science **522**: 116-123.
- Li, X., T. Cai, C. Chen and T. S. Chung (2016). "Negatively charged hyperbranched polyglycerol grafted membranes for osmotic power generation from municipal wastewater." Water Research **89**: 50-58.
- Li, X., T. Cai and T. S. Chung (2014). "Anti-Fouling behavior of hyperbranched polyglycerol-grafted poly(ether sulfone) hollow fiber membranes for osmotic power generation." Environmental Science and Technology **48**(16): 9898-9907.
- Li, X. and T. S. Chung (2013). "Effects of free volume in thin-film composite membranes on osmotic power generation." AIChE Journal **59**(12): 4749-4761.
- Li, X., S. Zhang, F. Fu and T.-S. Chung (2013). "Deformation and reinforcement of thin-film composite (TFC) polyamide-imide (PAI) membranes for osmotic power generation." Journal of Membrane Science **434**(0): 204-217.
- Li, X., S. Zhang, F. Fu and T. S. Chung (2013). "Deformation and reinforcement of thin-film composite (TFC) polyamide-imide (PAI) membranes for osmotic power generation." Journal of Membrane Science **434**: 204-217.
- Li, Y., R. Wang, S. Qi and C. Tang (2015). "Structural stability and mass transfer properties of pressure retarded osmosis (PRO) membrane under high operating pressures." Journal of Membrane Science **488**: 143-153.

- Li, Z.-Y., V. Yangali-Quintanilla, R. Valladares-Linares, Q. Li, T. Zhan and G. Amy (2012). "Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis." Water Research **46**(1): 195-204.
- Liang, S., G. Qi, K. Xiao, J. Sun, E. P. Giannelis, X. Huang and M. Elimelech (2014). "Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with surface-tailored nanoparticles: Implications for organic fouling in membrane bioreactors." Journal of Membrane Science **463**: 94-101.
- Lieu Le, N., M. Quilitzsch, H. Cheng, P. Y. Hong, M. Ulbricht, S. P. Nunes and T. S. Chung (2017). "Hollow fiber membrane lumen modified by polyzwitterionic grafting." Journal of Membrane Science **522**: 1-11.
- Lim, S., M. J. Park, S. Phuntsho, L. D. Tijning, G. M. Nisola, W. G. Shim, W. J. Chung and H. K. Shon (2017). "Dual-layered nanocomposite substrate membrane based on polysulfone/graphene oxide for mitigating internal concentration polarization in forward osmosis." Polymer (United Kingdom) **110**: 36-48.
- Lin, S., A. P. Straub and M. Elimelech (2014). "Thermodynamic limits of extractable energy by pressure retarded osmosis." Energy and Environmental Science **7**(8): 2706-2714.
- Liu, C., L. Shi and R. Wang (2015). "Crosslinked layer-by-layer polyelectrolyte nanofiltration hollow fiber membrane for low-pressure water softening with the presence of SO₄²⁻ in feed water." Journal of Membrane Science **486**: 169-176.
- Liu, F., C.-H. Du, B.-K. Zhu and Y.-Y. Xu (2007). "Surface immobilization of polymer brushes onto porous poly(vinylidene fluoride) membrane by electron beam to improve the hydrophilicity and fouling resistance." Polymer **48**(10): 2910-2918.
- Liu, X., S. L. Ong and H. Y. Ng (2016). "Fabrication of mesh-embedded double-skinned substrate membrane and enhancement of its surface hydrophilicity to improve anti-fouling performance of resultant thin-film composite forward osmosis membrane." Journal of Membrane Science **511**: 40-53.
- Loeb, S. (1976). "Production of energy from concentrated brines by pressure retarded osmosis. I. Preliminary technical and economic correlations." J.MEMBR.SCI. **1**(1): 49-63.
- Loeb, S. (1998). "Energy production at the Dead Sea by pressure-retarded osmosis: Challenge or chimera?" Desalination **120**(3): 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 **141**(1): 85-91.

Loeb, S., F. Van Hessen and D. Shahaf (1976). "Production of energy from concentrated brines by pressure retarded osmosis. II. Experimental results and projected energy costs." Journal of Membrane Science **1**(3): 249-269.

Logan, B. E. and M. Elimelech (2012). "Membrane-based processes for sustainable power generation using water." Nature **488**(7411): 313-319.

Ma, W., M. S. Rahaman and H. Therien-Aubin (2015). Controlling biofouling of reverse osmosis membranes through surface modification via grafting patterned polymer brushes. Proceedings, Annual Conference - Canadian Society for Civil Engineering.

McCutcheon, J. R. and M. Elimelech (2006). "Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis." Journal of Membrane Science **284**(1-2): 237-247.

Mehta, G. D. (1982). "Further results on the performance of present-day osmotic membranes in various osmotic regions." Journal of Membrane Science **10**(1): 3-19.

Mi, B. and M. Elimelech (2010). "Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents." Journal of Membrane Science **348**(1-2): 337-345.

Mi, B. and M. Elimelech (2013). "Silica scaling and scaling reversibility in forward osmosis." Desalination **312**: 75-81.

Minier-Matar, J., A. Santos, A. Hussain, A. Janson, R. Wang, A. G. Fane and S. Adham (2016). "Application of Hollow Fiber Forward Osmosis Membranes for Produced and Process Water Volume Reduction: An Osmotic Concentration Process." Environmental Science and Technology **50**(11): 6044-6052.

Montoya, F. G., M. J. Aguilera and F. Manzano-Agugliaro (2014). "Renewable energy production in Spain: A review." Renewable and Sustainable Energy Reviews **33**: 509-531.

Nijmeijer, K. and S. Metz (2010). Chapter 5 Salinity Gradient Energy. Sustainability Science and Engineering. **2**: 95-139.

- O'Toole, G., L. Jones, C. Coutinho, C. Hayes, M. Napoles and A. Achilli (2016). "River-to-sea pressure retarded osmosis: Resource utilization in a full-scale facility." Desalination **389**: 39-51.
- Ostuni, E., R. G. Chapman, R. E. Holmlin, S. Takayama and G. M. Whitesides (2001). "A Survey of Structure–Property Relationships of Surfaces that Resist the Adsorption of Protein." Langmuir **17**(18): 5605-5620.
- Ouyang, L., R. Malaisamy and M. L. Bruening (2008). "Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations." Journal of Membrane Science **310**(1): 76-84.
- Papkov, D., Y. Zou, M. N. Andalib, A. Goponenko, S. Z. D. Cheng and Y. A. Dzenis (2013). "Simultaneously Strong and Tough Ultrafine Continuous Nanofibers." ACS Nano **7**(4): 3324-3331.
- Park, C. H., H. Bae, S. J. Kwak, M. S. Jang, J. H. Lee and J. Lee (2016). "Interconnection of electrospun nanofibers via a post co-solvent treatment and its open pore size effect on pressure-retarded osmosis performance." Macromolecular Research **24**(4): 314-322.
- Pattle, R. E. (1954). "Production of Electric Power by mixing Fresh and Salt Water in the Hydroelectric Pile." Nature **174**(4431): 660-660.
- Peng, N., N. Widjojo, P. Sukitpaneemit, M. M. Teoh, G. G. Lipscomb, T.-S. Chung and J.-Y. Lai (2012). "Evolution of polymeric hollow fibers as sustainable technologies: Past, present, and future." Progress in Polymer Science **37**(10): 1401-1424.
- Post, J. W., H. V. M. Hamelers and C. J. N. Buisman (2008). "Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system." Environmental Science and Technology **42**(15): 5785-5790.
- Qi, S., C. Q. Qiu, Y. Zhao and C. Y. Tang (2012). "Double-skinned forward osmosis membranes based on layer-by-layer assembly—FO performance and fouling behavior." Journal of Membrane Science **405–406**: 20-29.
- Qin, J. J., S. Chen, M. H. Oo, K. A. Kekre, E. R. Cornelissen and C. J. Ruiken (2010). "Experimental studies and modeling on concentration polarization in forward osmosis." Water Science and Technology **61**(11): 2897-2904.
- Rajabzadeh, S., C. Liu, L. Shi and R. Wang (2014). "Preparation of low-pressure water softening hollow fiber membranes by polyelectrolyte deposition with two bilayers." Desalination **344**: 64-70.

Rica, R. A., R. Ziano, D. Salerno, F. Mantegazza, R. van Roij and D. Brogioli (2014). "Capacitive mixing for harvesting the free energy of solutions at different concentrations." Entropy **15**(4): 1388-1407.

Robertson, G. P., M. D. Guiver, M. Yoshikawa and S. Brownstein (2004). "Structural determination of Torlon® 4000T polyamide-imide by NMR spectroscopy." Polymer **45**(4): 1111-1117.

Sanyal, O., Z. Liu, J. Yu, B. M. Meharg, J. S. Hong, W. Liao and I. Lee (2016). "Designing fouling-resistant clay-embedded polyelectrolyte multilayer membranes for wastewater effluent treatment." Journal of Membrane Science **512**: 21-28.

Saren, Q., C. Q. Qiu and C. Y. Tang (2011). "Synthesis and Characterization of Novel Forward Osmosis Membranes based on Layer-by-Layer Assembly." Environmental Science & Technology **45**(12): 5201-5208.

Setiawan, L., L. Shi and R. Wang (2014). "Dual layer composite nanofiltration hollow fiber membranes for low-pressure water softening." Polymer **55**(6): 1367-1374.

Setiawan, L., R. Wang, K. Li and A. G. Fane (2011). "Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer." Journal of Membrane Science **369**(1-2): 196-205.

Setiawan, L., R. Wang, K. Li and A. G. Fane (2012). "Fabrication and characterization of forward osmosis hollow fiber membranes with antifouling NF-like selective layer." Journal of Membrane Science **394-395**: 80-88.

Setiawan, L., R. Wang, L. Shi, K. Li and A. G. Fane (2012). "Novel dual-layer hollow fiber membranes applied for forward osmosis process." Journal of Membrane Science **421-422**(0): 238-246.

She, Q., D. Hou, J. Liu, K. H. Tan and C. Y. Tang (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 **445**(0): 170-182.

She, Q., X. Jin and C. Y. Tang (2012). "Osmotic power production from salinity gradient resource by pressure retarded osmosis: Effects of operating conditions and reverse solute diffusion." Journal of Membrane Science **401-402**: 262-273.

She, Q., R. Wang, A. G. Fane and C. Y. Tang (2016). "Membrane fouling in osmotically driven membrane processes: A review." Journal of Membrane Science **499**: 201-233.

- She, Q., J. Wei, N. Ma, V. Sim, A. G. Fane, R. Wang and C. Y. Tang (2016). "Fabrication and characterization of fabric-reinforced pressure retarded osmosis membranes for osmotic power harvesting." Journal of Membrane Science **504**: 75-88.
- She, Q., Y. K. W. Wong, S. Zhao and C. Y. Tang (2013). "Organic fouling in pressure retarded osmosis: Experiments, mechanisms and implications." Journal of Membrane Science **428**: 181-189.
- She, Q., L. Zhang, R. Wang, W. B. Krantz and A. G. Fane (2017). "Pressure-retarded osmosis with wastewater concentrate feed: Fouling process considerations." Journal of Membrane Science **542**: 233-244.
- Shi, L., S. R. Chou, R. Wang, W. X. Fang, C. Y. Tang and A. G. Fane (2011). "Effect of substrate structure on the performance of thin-film composite forward osmosis hollow fiber membranes." Journal of Membrane Science **382**(1-2): 116-123.
- Sim, V. S. T., Q. She, T. H. Chong, C. Y. Tang, A. G. Fane and W. B. Krantz (2013). "Strategic co-location in a hybrid process involving desalination and pressure retarded osmosis (PRO)." Membranes **3**(3): 98-125.
- Sivertsen, E., T. Holt, W. Thelin and G. Brekke (2012). "Modelling mass transport in hollow fibre membranes used for pressure retarded osmosis." Journal of Membrane Science **417-418**: 69-79.
- Skilhagen, S. E. (2010). "Osmotic power - A new, renewable energy source." Desalination and Water Treatment **15**(1-3): 271-278.
- Skilhagen, S. E., J. E. Dugstad and R. J. Aaberg (2008). "Osmotic power — power production based on the osmotic pressure difference between waters with varying salt gradients." Desalination **220**(1-3): 476-482.
- Song, X., Z. Liu and D. D. Sun (2013). "Energy recovery from concentrated seawater brine by thin-film nanofiber composite pressure retarded osmosis membranes with high power density." Energy and Environmental Science **6**(4): 1199-1210.
- Stephans, L. E., A. Myles and R. R. Thomas (2000). "Kinetics of Alkaline Hydrolysis of a Polyimide Surface." Langmuir **16**(10): 4706-4710.
- Straub, A. P., A. Deshmukh and M. Elimelech (2016). "Pressure-retarded osmosis for power generation from salinity gradients: Is it viable?" Energy and Environmental Science **9**(1): 31-48.

Su, J., T. S. Chung, B. J. Helmer and J. S. de Wit (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 **396**: 92-100.

Subhi, N., A. R. D. Verliefde, V. Chen and P. Le-Clech (2012). "Assessment of physicochemical interactions in hollow fibre ultrafiltration membrane by contact angle analysis." Journal of Membrane Science **403**: 32-40.

Sun, S. P. and T. S. Chung (2013). "Outer-selective pressure-retarded osmosis hollow fiber membranes from vacuum-assisted interfacial polymerization for osmotic power generation." Environmental Science and Technology **47**(22): 13167-13174.

Tang, C. Y., Q. She, W. C. L. Lay, R. Wang and A. G. Fane (2010). "Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration." Journal of Membrane Science **354**(1-2): 123-133.

Tang, C. Y., Q. She, W. C. L. Lay, R. Wang, R. Field and A. G. Fane (2011). "Modeling double-skinned FO membranes." Desalination **283**: 178-186.

Thelin, W. R., E. Sivertsen, T. Holt and G. Brekke (2013). "Natural organic matter fouling in pressure retarded osmosis." Journal of Membrane Science **438**: 46-56.

Thorsen, T. and T. Holt (2009). "The potential for power production from salinity gradients by pressure retarded osmosis." Journal of Membrane Science **335**(1-2): 103-110.

Thorsen, T. and T. Holt (2009). "The potential for power production from salinity gradients by pressure retarded osmosis." Journal of Membrane Science **335**(1-2): 103-110.

Tian, M., R. Wang, K. Goh, Y. Liao and A. G. Fane (2015). "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**: 151-160.

Tiraferri, A., Y. Kang, E. P. Giannelis and M. Elimelech (2012). "Superhydrophilic Thin-Film Composite Forward Osmosis Membranes for Organic Fouling Control: Fouling Behavior and Antifouling Mechanisms." Environmental Science & Technology **46**(20): 11135-11144.

Tiraferri, A., N. Y. Yip, A. P. Straub, S. Romero-Vargas Castrillon and M. Elimelech (2013). "A method for the simultaneous determination of transport and

structural parameters of forward osmosis membranes." Journal of Membrane Science **444**: 523-538.

Valladares Linares, R., V. Yangali-Quintanilla, Z. Li and G. Amy (2012). "NOM and TEP fouling of a forward osmosis (FO) membrane: Foulant identification and cleaning." Journal of Membrane Science **421–422**: 217-224.

Wang, K. Y., R. C. Ong and T.-S. Chung (2010). "Double-Skinned Forward Osmosis Membranes for Reducing Internal Concentration Polarization within the Porous Sublayer." Industrial & Engineering Chemistry Research **49**(10): 4824-4831.

Wang, Y.-N., X. Li and R. Wang "Silica scaling and scaling control in pressure retarded osmosis processes." Journal of Membrane Science.

Wang, Y.-N., J. Wei, Q. She, F. Pacheco and C. Y. Tang (2012). "Microscopic Characterization of FO/PRO Membranes – A Comparative Study of CLSM, TEM and SEM." Environmental Science & Technology **46**(18): 9995-10003.

Wang, Y., F. Wicaksana, C. Y. Tang and A. G. Fane (2010). "Direct Microscopic Observation of Forward Osmosis Membrane Fouling." Environmental Science & Technology **44**(18): 7102-7109.

Wang, Y. N., E. Järvelä, J. Wei, M. Zhang, H. Kyllönen, R. Wang and C. Y. Tang (2016). "Gypsum scaling and membrane integrity of osmotically driven membranes: The effect of membrane materials and operating conditions." Desalination **377**: 1-10.

Wang, Y. N. and C. Y. Tang (2011). "Fouling of nanofiltration, reverse osmosis and ultrafiltration membranes by protein mixtures: The role of inter-foulant-species interaction." Environmental Science & Technology **45**(15): 6373 - 6379.

Wang, Y. N. and C. Y. Tang (2011). "Nanofiltration membrane fouling by oppositely charged macromolecules: Investigation on flux behavior, foulant mass deposition, and solute rejection." Environmental Science and Technology **45**(20): 8941-8947.

Wang, Y. N. and C. Y. Tang (2011). "Protein fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes-The role of hydrodynamic conditions, solution chemistry, and membrane properties." Journal of Membrane Science **376**(1-2): 275-282.

Wang, Y. N., F. Wicaksana, C. Y. Tang and A. G. Fane (2010). "Direct microscopic observation of forward osmosis membrane fouling." Environmental Science and Technology **44**(18): 7102-7109.

Wei, J., Y. Li, L. Setiawan and R. Wang (2016). "Influence of macromolecular additive on reinforced flat-sheet thin film composite pressure-retarded osmosis membranes." Journal of Membrane Science **511**: 54-64.

Wei, J., C. Qiu, C. Y. Tang, R. Wang and A. G. Fane (2011). "Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes." Journal of Membrane Science **372**(1): 292-302.

Widjojo, N., T.-S. Chung, M. Weber, C. Maletzko and V. Warzelhan (2011). "The role of sulphonated polymer and macrovoid-free structure in the support layer for thin-film composite (TFC) forward osmosis (FO) membranes." Journal of Membrane Science **383**(1-2): 214-223.

Xu, Y., X. Peng, C. Y. Tang, Q. S. Fu and S. Nie (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 **348**(1-2): 298-309.

Xu, Y., X. Peng, C. Y. Tang, Q. S. Fu and S. Nie (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 **348**(1-2): 298-309.

Yip, N. Y. and M. Elimelech (2013). "Influence of natural organic matter fouling and osmotic backwash on pressure retarded osmosis energy production from natural salinity gradients." Environmental Science and Technology **47**(21): 12607-12616.

Yip, N. Y. and M. Elimelech (2014). "Comparison of energy efficiency and power density in pressure retarded osmosis and reverse electrodialysis." Environmental Science and Technology **48**(18): 11002-11012.

Yip, N. Y., A. Tiraferri, W. A. Phillip, J. D. Schiffman and M. Elimelech (2010). "High Performance Thin-Film Composite Forward Osmosis Membrane." Environmental Science & Technology **44**(10): 3812-3818.

Yip, N. Y., A. Tiraferri, W. A. Phillip, J. D. Schiffman, L. A. Hoover, Y. C. Kim and M. Elimelech (2011). "Thin-film composite pressure retarded osmosis membranes for sustainable power generation from salinity gradients." Environmental Science and Technology **45**(10): 4360-4369.

Yu, H.-Y., Y. Kang, Y. Liu and B. Mi (2014). "Grafting polyzwitterions onto polyamide by click chemistry and nucleophilic substitution on nitrogen: A novel approach to enhance membrane fouling resistance." Journal of Membrane Science **449**: 50-57.

Zhang, J., W. L. C. Loong, S. Chou, C. Tang, R. Wang and A. G. Fane (2012). "Membrane biofouling and scaling in forward osmosis membrane bioreactor." Journal of Membrane Science **403–404**: 8-14.

Zhang, L., Q. She, R. Wang, S. Wongchitphimon, Y. Chen and A. G. Fane (2016). "Unique roles of aminosilane in developing anti-fouling thin film composite (TFC) membranes for pressure retarded osmosis (PRO)." Desalination **389**: 119-128.

Zhang, M., D. Hou, Q. She and C. Y. Tang (2014). "Gypsum scaling in pressure retarded osmosis: Experiments, mechanisms and implications." Water Research **48**(1): 387-395.

Zhang, S. and T. S. Chung (2013). "Minimizing the instant and accumulative effects of salt permeability to sustain ultrahigh osmotic power density." Environmental Science and Technology **47**(17): 10085-10092.

Zhang, S., F. Fu and T. S. Chung (2013). "Substrate modifications and alcohol treatment on thin film composite membranes for osmotic power." Chemical Engineering Science **87**: 40-50.

Zhang, S., P. Sukitpaneenit and T. S. Chung (2014). "Design of robust hollow fiber membranes with high power density for osmotic energy production." Chemical Engineering Journal **241**: 457-465.

Zhang, S., Y. Zhang and T. S. Chung (2016). "Facile Preparation of Antifouling Hollow Fiber Membranes for Sustainable Osmotic Power Generation." ACS Sustainable Chemistry and Engineering **4**(3): 1154-1160.

Zhang, Y., R. Wang, S. Yi, L. Setiawan, X. Hu and A. G. Fane (2011). "Novel chemical surface modification to enhance hydrophobicity of polyamide-imide (PAI) hollow fiber membranes." Journal of Membrane Science **380**(1-2): 241-250.

Zhang, Z., S. Chen and S. Jiang (2006). "Dual-Functional Biomimetic Materials: Nonfouling Poly(carboxybetaine) with Active Functional Groups for Protein Immobilization." Biomacromolecules **7**(12): 3311-3315.

Zhao, D., G. Qiu, X. Li, C. Wan, K. Lu and T. S. Chung (2016). "Zwitterions coated hollow fiber membranes with enhanced antifouling properties for osmotic power generation from municipal wastewater." Water Research **104**: 389-396.

Zhao, S., J. Minier-Matar, S. Chou, R. Wang, A. G. Fane and S. Adham (2017). "Gas field produced/process water treatment using forward osmosis hollow fiber membrane: Membrane fouling and chemical cleaning." Desalination **402**: 143-151.

Zhao, S., Y. Yao, C. Ba, W. Zheng, J. Economy and P. Wang (2015). "Enhancing the performance of polyethylenimine modified nanofiltration membrane by coating a layer of sulfonated poly(ether ether ketone) for removing sulfamerazine." Journal of Membrane Science **492**: 620-629.

Zhao, S., L. Zou and D. Mulcahy (2011). "Effects of membrane orientation on process performance in forward osmosis applications." Journal of Membrane Science **382**(1-2): 308-315.

Zhao, S., L. Zou, C. Y. Tang and D. Mulcahy (2012). "Recent developments in forward osmosis: Opportunities and challenges." Journal of Membrane Science **396**: 1-21.

Zheng, S., Q. Yang and B. Mi (2016). "Novel antifouling surface with improved hemocompatibility by immobilization of polyzwitterions onto silicon via click chemistry." Applied Surface Science **363**: 619-626.

Zou, S., Y.-N. Wang, F. Wicaksana, T. Aung, P. C. Y. Wong, A. G. Fane and C. Y. Tang (2013). "Direct microscopic observation of forward osmosis membrane fouling by microalgae: Critical flux and the role of operational conditions." Journal of Membrane Science **436**: 174-185.

Zuo, G. and R. Wang (2013). "Novel membrane surface modification to enhance anti-oil fouling property for membrane distillation application." Journal of Membrane Science **447**: 26-35.