

# **ENGINEERING THE POLYAMIDE SELECTIVE LAYER OF THIN FILM COMPOSITE MEMBRANES FOR OSMOTIC POWER GENERATION**

**by Ralph Rolly Gonzales**

Thesis submitted in fulfilment of the requirements for  
the degree of

**Doctor of Philosophy**

under the supervision of **Professor Ho Kyong Shon** and  
**Dr. Sherub Phuntsho**

University of Technology Sydney  
Faculty of Engineering and Information Technology

January 2021



## Certificate of Original Authorship

I, *Ralph Rolly Gonzales*, declare that this thesis, is submitted in fulfilment of the requirements for the award of *Doctor of Philosophy*, in the *Faculty of Engineering and IT* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

Signature:      Production Note:  
                         Signature removed prior to publication.

Date: 29 January 2021



I dedicate this thesis and my PhD degree to my family,

**Rolito, Ruby, Ruelle Ela, and Raphael Lorenz,**

for the love and the faith;

and to my precious nephews, my favourite persons in the world,

**Kaelan Raphael and Kristoff Reese,**

may you never grow tired of learning.

My success is nothing without you.

At the end of this journey, this is not just my PhD, this OUR PhD.



## ACKNOWLEDGEMENTS

---

My PhD would not be possible without several people and institutions, to whom I shall express my gratitude through these acknowledgements.

First of all, this PhD thesis would not come into fruition without the support, guidance, and mentorship of my supervisors, Professor Ho Kyong Shon and Dr. Sherub Phuntsho. During my PhD, I have lost focus and determination many times, but the constant drive, passion, and management of Prof. Shon have kept me going. The fortnightly groups meetings and occasional personal meetings have proved effective in keeping my progress in check, and have helped me to constantly perform beyond expectations. I would also like to thank Prof. Shon for the scholarship provision during my entire PhD candidature, and for the opportunity to involve in a number of collaborative projects and a research experience in Kobe, Japan. Thank you also, Dr. Phuntsho, for allowing me to be part of the organising committee of 2020 MSA ECR Membrane Symposium; the experience taught me a lot and inspired me to be more involved in my professional network and research community.

Aside from my supervisors, I have been fortunate to have been guided and constantly cheered on by other people in our NanoMemPro research group who, despite not being my supervisors, have proved to be great help in completing my PhD work. Thank you, Dr. Leonard Tijing, Dr. Myoung Jun Park, Dr. Jungeun Kim, Dr. Donghan Seo, and Dr. Laura Chekli. Special thanks to Dr. Tijing for being instrumental in me doing my PhD in UTS under Prof. Shon – if we had not met in CESE in 2015, I would have done my PhD in an entirely different group, university, or country.

My research on development of PRO membranes was made possible through a grant from the Qatar National Research Fund, under its National Priorities Research

Program, and through our collaborators at Texas A&M University at Qatar (Professor Ahmed Abdel-Wahab) and Conoco-Phillips (Dr. Samer Adham).

It is comforting to know that I am not in this journey alone, I feel quite lucky that our research group had been among the largest one in the school, that I constantly did not feel alone. I would like to thank the whole NanoMemPro research group, for the shared times in and out of the laboratory. It is quite difficult to list everyone down in this acknowledgement, but I would like to particularly thank the 4SeaBrothers and the offspring dining club, for all the good food, good conversations, and good company shared: Dr. David Inhyuk Kim, Dr. Federico Volpin, Dr. Syed Muztuza Ali, Dr. Van Huy Tran, Dr. Pema Dorji, Dr. Minwei Yao, Dr. Nawshad Akther, Dr. Jiawei Ren, and Dr. Ugyen Dorji.

I also would like to acknowledge the help in the laboratory by Dr. Md Abu Hassan Johir, Dr. Nirenkumar Pathak, and Dr. Sungil Lim, as well as the administrative support of Ms. Van Le, Ms. Maya Tanaka, Ms. Trish Dimasi, Mr. Alex Chen, Ms. Minnie Wan, and Mr. Samuel Ho. Doing my PhD had taken its toll on my health, and I also wish to thank the UTS Health Service, specifically Dr. Leonie Matthews, Dr. Melissa Noetel for guiding me in taking care of my physical, emotional, and mental health.

The last chapter of my thesis was wholly done at Kobe University, Japan, wherein I conducted my overseas research collaboration program. This would not have been possible without the support of Professor Hideto Matsuyama and the Center on Membrane and Film Technology.

I always look back at the rigorous research training I received from the Environmental Processes and Materials Laboratory (now situated in Yonsei University; previously the Environmental Energy Research Laboratory at Daegu

University), headed by Professor Sang-Hyoun Kim, which provided the foundation of academic research career and the opportunities which led me to where I am now.

I am very grateful to my cousin and her family, Kimberly Miana, Christian Miana, and their children Cataleya and Cornelius, for providing me a home and for making sure that I did not encounter any problems during my stay in Sydney. Through them, I also found other families in Sydney, the Gutierrez and the Paras families, with whom I have celebrated milestones and personal victories.

Many people say that friends are family you choose. I would then like to thank my chosen family. Living in another country is tough, but it always gets better knowing you are not alone. Thank you to my Filipino friends in Australia: Dr. Joshua Tapas, Dr. Yami Bautista, Mara Gonzales, Dr. Nina Versoza, Dr. William Infante, Kami Navarro, Dr. Jeff Hora, Dianne Relajo, Justelle Tuiza, Faith Santos, Patrick Santos, Sarah Genelsa, Elmer Austria, Ross Anne Yumol, Nikki Natividad, Vhon Garcia, Anthon Repollo, Billy Uy, Mia Pavia, Mika Sioson, Dr. Bobby Katigbak, and Dr. Stephanie Chua, among others. Thank you also to my Korean circle at UTS – Dr. Seongchul Ryu, Weonjung Sohn, Dr. Yonghyun Shin, Dr. Youngkwon Choi, and Yunju Jo – for adopting me as a part of your group, despite not being Korean. Thank you as well to my Engineering PhD friend circle, for the random dinners and fun times, Dr. Alex Phuong, Dr. Kireesan Sornalingam, Dr. Sara Farahmandian, and Dr. Hannah Sun. During my stay in Sydney, I have found myself living in several shared houses, and I have been lucky to have met housemates, who despite not being graduate students in Sydney or staying for a short time due to working holiday visa conditions, have shown me kindness and generosity: Yoongi Shim, Yunje Jung, Dongil Shin, Hongseon Lee, and Junsik Lim. Lastly, thank you to all my friends in the Philippines and Korea,

who have made time to meet me during my short trips to these countries during my PhD candidature.

I was only supposed to stay in Japan for a few months, but ended up staying longer due to CoViD-19. I was able to get by through a few people who make my stay here more bearable, despite being alone in a foreign country. I am fortunate to have Filipino friends, whom I have known for over ten years, here in Japan, Dr. Mellissa Alcantara, Dr. Alvin Acebedo, and Dr. Lubai Punzalan-Enriquez. I also gained a few friends in my current research group: Titik Istirokhatun, Kyoko Miyake, Dr. Lei Zhang, Dr. Kecheng Guan, Dr. Yuqing Lin, Yuki Kawabata, Kai Ushio, Takafumi Ueda, and Wataru Kushida. Outside the university, I met these people and gained great friends: Isao Ohara, Fuminori Nagae, Andy Limas, Kenichi Kawahira, and Yoshio Yoshimura.

Last but not the least, I offer my eternal gratitude and love to my family for their overwhelming support during my entire PhD. They are mainly the reason why I constantly thrived and continued, despite numerous setbacks and issues. I did not give up primarily because I did not want to disappoint them, but I ultimately persevered because I felt empowered by their constant care and love. Thank you, Papa, Mama, Ela, Lorenz, and babies, and I love you!

**Ralph Rolly Gonzales**



## LIST OF PUBLICATIONS RELATED TO THESIS DURING CANDIDATURE

---

1. **Gonzales, R.R.**, Park, M.J., Bae, T.-H., Yang, Y., Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2019. 'Melamine-based covalent organic framework-incorporated thin film nanocomposite membranes for enhanced osmotic power generation', *Desalination*, vol. 459, pp. 10-19. **(Chapter 4)**
2. **Gonzales, R.R.**, Yang, Y., Park, M.J., Bae, T.-H., Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2020. 'Enhanced water permeability and osmotic power generation with sulfonate functionalised porous polymer-incorporated thin film nanocomposite membranes', *Desalination*, vol. 496, pp. 114756-114765. **(Chapter 5)**
3. **Gonzales, R.R.**, Abdel-Wahab, A., Adham, S., Phuntsho, S., Suwaileh, W., Hilal, N. & Shon, H.K. 2020. Salinity gradient energy generation via pressure retarded osmosis: A review', *Desalination*, vol. 500, pp. 114841-114852. **(Chapter 2)**
4. **Gonzales, R.R.**, Abdel-Wahab, A., Phuntsho, S., Matsuyama, H. & Shon, H.K. 2020. 'Aliphatic polyketone-based thin film composite membrane with mussel-inspired polydopamine interlayer for high performance osmotic power generation'. **(Chapter 7)**
5. **Gonzales, R.R.**, Abdel-Wahab, A., Matsuyama, H., Phuntsho, S. & Shon, H.K. 2020. 'Control of the antagonistic effects of chlorine oxidative degradation on pressure retarded osmosis thin film composite membrane surface'. **(Chapter 6)**

**PhD Candidate Credit Statement:** Conceptualisation; Methodology; Formal analysis; Investigation; Data curation; Writing of original draft; Review and editing; Visualisation

## LISTS OF OTHER PUBLICATIONS DURING CANDIDATURE

---

1. **Gonzales, R.R.**, Park, M.J., Tijing, L., Han, D.S., Phuntsho, S. & Shon, H.K. 2018, 'Modification of support layer for thin film composite forward osmosis membranes via layer-by-layer polyelectrolyte deposition', *Membranes*, vol. 8, no.3, pp. 70-84.
2. Park, M.J., **Gonzales, R.R.**, Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2018. 'Hydrophilic polyvinyl alcohol coating on hydrophobic electrospun nanofiber membrane for high performance thin film composite forward osmosis membrane', *Desalination*, vol. 426, pp. 50-59.
3. Volpin, F., **Gonzales, R.R.**, Lim, S., Pathak, N., Phuntsho, S. & Shon, H.K. 2018. 'GreenPRO: A novel fertiliser-driven osmotic power generation process for fertigation', *Desalination*, vol. 447, pp. 158-166.
4. Park, M.J., Lim, S., **Gonzales, R.R.**, Phuntsho, S., Han, D.S., Abdel-Wahab, A., Adham, S. & Shon, H.K. 2019. 'Thin-film composite hollow fiber membrane incorporated with graphene oxide in polyethersulfone support layer for enhanced osmotic power density', *Desalination*, vol. 464, pp. 63-75.
5. Kim, D.I., **Gonzales, R.R.**, Dorji, P., Gwak, G., Phuntsho, S., Hong, S. & Shon, H.K. 2020. 'Efficient recovery of nitrate from municipal wastewater via MCDI using anion-exchange polymer coated electrode embedded with nitrate selective resin', *Desalination*, vol. 484, pp. 11425-11433.
6. Park, M.J., Wang, C., Seo, D.H., **Gonzales, R.R.**, Matsuyama, H. & Shon, H.K. 2021. 'Inkjet-printed single walled carbon nanotube as an interlayer for high performance thin film composite nanofiltration membrane', *Journal of Membrane Science*, in press.

7. **Gonzales, R.R.**, Phuntsho, S., Matsuyama, H. & Shon, H.K. 2021. 'Facile development of comprehensively fouling-resistant and self-cleaning reduced aliphatic polyketone-based thin film composite forward osmosis membranes for treatment of oily wastewater'.
8. Zhang, L., **Gonzales R.R.**, Shon, H.K., & Matsuyama, H. 2021. 'In situ engineering of an ultrathin polyampholyte layer on polyketone-based thin film composite forward osmosis membrane for comprehensive anti-fouling performance'.

## CONFERENCE PRESENTATIONS DURING CANDIDATURE

---

1. **Gonzales, R.R.**, Park, M.J., Bae, T.-H., Yang, Y., Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2018. 'Melamine-based covalent organic framework-incorporated thin film nanocomposite membranes for enhanced osmotic power generation', *The 11th Conference of the Aseanian Membrane Society*, Queensland, Australia, 3-6 July 2018.
2. **Gonzales, R.R.**, Yang, Y., Park, M.J., Bae, T.-H., Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2019. 'Enhanced water permeability and osmotic power generation with sulfonate functionalised porous polymer-incorporated thin film nanocomposite membranes', *The 12th Conference of the Aseanian Membrane Society*, Jeju Island, South Korea, 2-5 July 2019.
3. **Gonzales, R.R.**, Abdel-Wahab, A., Phuntsho, S. & Shon, H.K. 2020. 'Control of antagonistic chemical modification effects of chlorine and ionic liquids on thin film composite membranes for enhanced osmotic power generation', *The 12th International Conference on Membranes & Membrane Processes*, London, United Kingdom (online), 7-11 December 2020.

## LIST OF ABBREVIATIONS

---

<b>AEMA</b>	2-aminoethyl methacrylate hydrochloride
<b>APTMS</b>	3-aminopropyltrimethoxysilane
<b>APS</b>	Ammonium persulfate
<b>ANOVA</b>	Analysis of variables
<b>AFM</b>	Atomic force microscopy
<b>AL-DS</b>	Active layer facing the draw solution (also known as, PRO mode)
<b>AL-FS</b>	Active layer facing the feed solution (also known as, FO mode)
<b>ATR</b>	Attenuated total reflectance
<b>BattMix</b>	Battery mixing
<b>BTDA</b>	3,3',4,4'-benzophenone tetracarboxylic dianhydride
<b>BET</b>	Brunauer-Emmett-Teller theory
<b>CapMix</b>	Capacitive mixing
<b>CNT</b>	Carbon nanotube
<b>CQD</b>	Carbon quantum dots
<b>CA</b>	Cellulose acetate
<b>CTA</b>	Cellulose triacetate
<b>CCD</b>	Central composite design
<b>COF</b>	Covalent organic frameworks
<b>CP</b>	Concentration polarisation
<b>DI water</b>	Deionised water
<b>DCE</b>	1,2-dichloroethane
<b>DCM</b>	Dichloromethane
<b><i>p</i>-DCX</b>	$\alpha$ - $\alpha'$ -dichloro- <i>p</i> -xylene
<b>DMF</b>	N,N-dimethylformamide
<b>DMSO</b>	Dimethylsulfoxide
<b>DS</b>	Draw solution (i.e., solution of higher solute concentration)
<b>ERD</b>	Energy recovery device
<b>EDTA</b>	Ethylenediaminetetraacetic acid
<b>ECP</b>	External concentration polarisation
<b>FE-SEM</b>	Field emission scanning electron microscopy
<b>FO</b>	Forward osmosis
<b>FS</b>	Feed solution (i.e., solution of lower solute concentration)
<b>FTIR</b>	Fourier transform infrared spectroscopy
<b>GMVP</b>	Global MVP project
<b>GA</b>	Glutaraldehyde
<b>GO</b>	Graphene oxide
<b>HNT</b>	Halloysite nanotube
<b>HTI</b>	Hydration Technologies, Inc.
<b>HPI</b>	Hydroxypolyimide
<b>HPG</b>	Hyperbranched polyglycerol
<b>ICP</b>	Internal concentration polarisation

<b>IP</b>	Interfacial polymerisation
<b>LbL</b>	Layer-by-layer
<b>LIS</b>	Liquid-phase ion stripping
<b>LPRO</b>	Low-pressure reverse osmosis
<b>MPD</b>	<i>m</i> -phenylenediamine
<b>MBR</b>	Membrane bioreactor
<b>MD</b>	Membrane distillation
<b>MPC</b>	2-methacryloxyloxyethylphosphorylcholine
<b>MDI</b>	Methylene diamine
<b>MPDI</b>	Methylphenylene diamine
<b>MED</b>	Multi-effect distillation
<b>NF</b>	Nanofiltration
<b>NOM</b>	Natural organic matter
<b>NIPS</b>	Nonsolvent-induced phase separation
<b>OHE</b>	Osmotic heat engine
<b>PAO</b>	Pressure assisted osmosis
<b>PAA</b>	Poly(acrylic acid)
<b>PAN</b>	polyacrylonitrile
<b>PAH</b>	Poly(allylamine hydrochloride)
<b>PA</b>	Polyamide
<b>PAI</b>	Polyamide-imide
<b>PBI</b>	Polybenzoxazole-co-imide
<b>PDA</b>	Polydopamine
<b>PEi</b>	Polyetherimide
<b>PES</b>	Polyethersulfone
<b>PE</b>	Polyethylene
<b>PEG</b>	Polyethylene glycol
<b>PET</b>	Polyethylene terephthalate
<b>PEI</b>	Polyethylenimine
<b>POSS</b>	Polyhedral oligomeric silsesquioxane
<b>PI</b>	Polyimide
<b>PK</b>	Polyketone
<b>PSf</b>	Polysulfone
<b>PVA</b>	Polyvinyl alcohol
<b>PVP</b>	Polyvinylpyrrolidine
<b>POPs</b>	Porous organic polymers
<b>PP</b>	Porous polymer
<b>PRO</b>	Pressure retarded osmosis
<b>PWP</b>	Pure water permeability
<b>RED</b>	Reverse electrodialysis
<b>RO</b>	Reverse osmosis
<b>RSF</b>	Reverse salt flux
<b>RSM</b>	Response surface methodology
<b>SNW</b>	Schiff-based network
<b>SWRO</b>	Seawater reverse osmosis
<b>TA</b>	Terephthalaldehyde
<b>THF</b>	Tetrahydrofuran

<b>TEOS</b>	Tetraorthyl orthosilicate
<b>TFC</b>	Thin film composite
<b>TFN</b>	Thin film nanocomposite
<b>TIPS</b>	Thermal-induced phase separation
<b>TOC</b>	Total organic carbon
<b>TMP</b>	Transmembrane pressure
<b>TBP</b>	Tributylphosphate
<b>TMC</b>	Trimesoyl chloride
<b>UF</b>	Ultrafiltration
<b>XPS</b>	X-ray photoelectron spectroscopy

## LIST OF SYMBOLS

---

$a_s$	Activity coefficient
$A_m$	Area, membrane (m <sup>2</sup> )
$C_i$	Concentration at active layer interface
$C_{d,b}$	Concentration of bulk draw solution
$C_{f,b}$	Concentration of bulk feed solution
$C_{d,m}$	Concentration of draw solution at membrane active layer interface
$C_{f,m}$	Concentration of feed solution at support and active layer interface
$C_f$	Concentration of the feed solution during RO experiments
$C_p$	Concentration of the permeate solution during RO experiments
$\mu$	Chemical potential
$d_h$	Diameter, cross-flow cell hydraulic
$\Delta H_{mix}$	Enthalpy of mixing (J kg <sup>-1</sup> )
$\Delta S_{mix}$	Entropy of mixing (J K <sup>-1</sup> )
$G_B$	Gibbs free energy of brackish water (J mol <sup>-1</sup> )
$G_F$	Gibbs free energy of freshwater (J mol <sup>-1</sup> )
$\Delta G_{mix}$	Gibbs free energy of mixing freshwater and salt water
$G_S$	Gibbs free energy of salt water
$\Delta P$	Hydraulic pressure, applied; transmembrane pressure (bar)
$R$	Ideal gas constant (8.314 x 10 <sup>-2</sup> bar L K <sup>-1</sup> mol <sup>-1</sup> )
$L$	Length, channel
$k$	Mass transfer coefficient (m s <sup>-1</sup> )
$n$	Number of solute molecules (mol)
$\pi$	Osmotic pressure (bar)
$\pi_d$	Osmotic pressure, draw stream (bar)
$\pi_f$	Osmotic pressure, feed stream (bar)
$\Delta \pi$	Osmotic pressure difference (bar)
$\mu_p$	Pore diameter, mean
$V_{micro}$	Pore volume, microporous
$V_{total}$	Pore volume, total
$\varepsilon$	Porosity, membrane support
$W$	Power density, membrane
$W_{max}$	Power density, membrane, maximum
$P/P^o$	Pressure, relative
$\sigma$	Reflection coefficient
$\beta_{iji}$	Regression interactive coefficient
$\beta_i$	Regression linear coefficient
$\beta_{ii}$	Regression quadratic coefficient
$\beta_0$	Regression y-intercept
$Y$	Response, response surface methodology
$J_s$	Reverse salt flux (g m <sup>-2</sup> s <sup>-1</sup> )
$Re$	Reynolds number
$R_{ms}$	Ridge elevation, root mean square
$R_a$	Roughness, mean
$Sc$	Schmidt number
$Sh$	Sherwood number
$D_s$	Solute diffusion coefficient
$B$	Solute permeability constant (m s <sup>-1</sup> ; L m <sup>-2</sup> h <sup>-1</sup> )
$R$	Solute rejection

<b><i>K</i></b>	Solute resistivity, membrane support ( $\text{s m}^{-1}$ )
<b><i><math>\sigma_p</math></i></b>	Standard deviation, geometric
<b><i>S</i></b>	Structural parameter, m
<b><i>S<sub>BET</sub></i></b>	Surface area, BET theory
<b><i>S<sub>micro</sub></i></b>	Surface area, microporous
<b><i>T</i></b>	Temperature (K)
<b><i>t</i></b>	Thickness, membrane support (m)
<b><i><math>\tau</math></i></b>	Tortuosity, membrane support
<b><i>i</i></b>	Van't Hoff factor
<b><i><math>\bar{V}_s</math></i></b>	Volume, moral
<b><i>V<sub>w</sub></i></b>	Volume, solvent
<b><math>\Delta V</math></b>	Volume change
<b><i>J<sub>w</sub></i></b>	Water flux ( $\text{L m}^{-2} \text{h}^{-1}$ )
<b><i>A</i></b>	Water permeability constant ( $\text{m s}^{-1} \text{bar}^{-1}$ ; $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )

## LIST OF TABLES

Table 2.1 Flat-sheet PRO TFC membranes in literature .....	79
Table 2.2 Nanofibre-based PRO TFC membranes in literature .....	82
Table 2.3 Hollow fibre PRO TFC membranes in literature .....	89
Table 2.4 Commercial PRO membrane modules in literature .....	97
Table 3.1 PRO hollow fiber membrane substrate spinning conditions.....	128
Table 3.2 Membrane characterisation technique employed in this thesis .....	130
Table 4.1 Chemical composition of the TFC and SNW-1-incorporated TFN membrane surfaces .....	151
Table 4.2 Intrinsic transport properties of TFC and COF-incorporated TFN membranes .....	156
Table 5.1 The surface area and pore volume values of PP-SO <sub>3</sub> H .....	172
Table 5.2 Properties of the hollow fibre membrane substrate .....	174
Table 5.3 Chemical composition of the TFC and PP-SO <sub>3</sub> H-incorporated TFN membrane surfaces .....	177
Table 5.4 Intrinsic membrane transport parameters of the TFC (PP-0) and the PP-SO <sub>3</sub> H incorporated TFN (PP-0.001, P-0.002, and P-0.005) membranes .....	180
Table 6.1 Full factorial central composite face-centred experimental design for chlorine oxidative degradation of membranes.....	191
Table 7.1 Surface elemental analysis of the PDA intermediate layer using X-ray photoelectron spectrometry .....	214
Table 7.2 Average roughness (R <sub>ms</sub> ) of the membrane substrates characterized.....	219
Table 7.3 Atomic composition and the degree of cross-linking of the polyamide selective layer of the TFC membranes.....	221
Table 7.4 Intrinsic transport properties of the TFC membranes .....	224

Table 8.1 Intrinsic transport properties and osmotic performance of commercial flat-sheet PRO TFC membrane by Toray, compared with those developed in this thesis  
.....236

## LIST OF FIGURES

---

Figure 1.1 Graphical abstract of this thesis on engineering of polyamide selective layer of thin film composite membranes for osmotic power generation .....	46
Figure 2.1 Schematic diagrams of the operational conditions of reverse osmosis, forward osmosis, pressure assisted osmosis, and pressure retarded osmosis.....	52
Figure 2.2 Schematic diagram of a conventional FO system (Amini, Jahanshani & Rahimpour 2013).....	53
Figure 2.3 Schematic diagram of the conventional PRO process (Skilhagen, Dugstad & Aaberg 2008) .....	54
Figure 2.4 Ideal water flux ( $J_w$ ) and power density ( $W$ ) during PRO operation as a function of applied hydraulic pressure ( $\Delta P$ ). The conditions surrounding FO, PRO, and RO operation are also shown (Achilli, Cath & Childress 2009) .....	57
Figure 2.5 Concentration profile of the membrane during PRO operation as influenced by ECP and ICP. $C_{D,b}$ , $C_{D,m}$ , $C_{F,m}$ , and $C_{F,b}$ are the concentration of the bulk draw solution, concentration of the draw solution at the membrane active layer interface, concentration of the feed solution at the support and active layer interface, and concentration of the bulk feed solution, respectively .....	60
Figure 2.6 Scanning electron microscope images showing the morphology of the (a) membrane substrate top surface, (b) membrane cross section, (c) membrane substrate bottom surface, and (d) membrane polyamide active layer surface of a flat sheet TFC PRO membrane.....	75
Figure 2.7 Scanning electron microscope images showing the morphology of the (a) membrane substrate top surface, (b) membrane cross section, (c) membrane substrate bottom surface, and (d) membrane polyamide active layer surface of a hollow fibre TFC PRO membrane .....	84

Figure 2.8 Representations of the commercial membrane modules for PRO: (a) spiral-wound and (b) hollow fibre.....	94
Figure 2.9 Schematic of the integrated Mega-ton RO-PRO hybrid system (Kim, Jeong, et al. 2015; Tanioka, Kurihara & Sakai 2018).....	100
Figure 2.10 Schematic of the integrated GMVP RO-PRO hybrid system (Lee, Kim & Park 2018).....	101
Figure 2.11 Schematic of four proposed RO-PRO hybrid system configurations (Kim, Park, et al. 2013).....	102
Figure 2.12 Schematic of proposed combined water treatment, seawater desalination, and energy production RO-NF-PRO hybrid process (Touati et al. 2020).....	104
Figure 2.13 Schematic of the proposed integrated vacuum MD-PRO process (Lee et al. 2015).....	106
Figure 2.14 Schematic of the proposed integrated LIS-PRO hybrid system (Wang et al. 2020).....	107
Figure 2.15 The conceptual schematic of dual-stage PRO operation using two different feed streams (Altaee et al. 2014) .....	109
Figure 2.16 Four different proposed configurations of a dual-stage PRO system: (a) CDCF (continuous draw and feed); (b) DDDF (divided treatment of draw and feed); (c) CDDF (continuous draw and divided feed); and (d) DDCF (divided draw and continuous feed) (He, Wang & Shaheed 2015) .....	111
Figure 2.17 Proposed pool PRO system (Arias & De Las Heras 2020).....	112
Figure 2.18 Schematic of the proposed facultative RO-PRO system, which can do both (a) RO operation and (b) PRO operation, but not at the same time, as the system switches between the two operating modes (Blankert et al. 2020).....	113

Figure 2.19 The proposed fertiliser-driven PRO process, GreenPRO (Volpin et al. 2018) .....	114
Figure 2.20 The proposed integrated PRO and waterflooding process, for enhanced oil recovery (Janson et al. 2020).....	116
Figure 2.21 (L) Illustration of the combined PRO and geothermal heat plant system of SaltPower, showing how geothermal heat production and PRO could work together to provide both district heating and electricity; (R) Schematic diagram of how the geothermal plant acts as the heat exchanger in this system (Madsen et al. 2020) .	117
Figure 3.1 Hollow fibre spinning machine .....	127
Figure 3.2 Bench-scale PRO system used in membrane osmotic performance evaluation in this thesis .....	134
Figure 4.1 FE-SEM image of the synthesised SNW-1 covalent organic framework nanoparticles.....	146
Figure 4.2 Observed change in solution colour of benzene-1,3,5-tricarbonyl chloride and SNW-1 after 60 min, indicating a reaction between the two substances .....	147
Figure 4.3 FTIR spectra of (a) TFC polyamide and (b) product formed after the reaction of SNW-1 and benzene-1,3,5-tricarbonyl chloride.....	148
Figure 4.4 FTIR spectra of the TFC and SNW-1-incorporated TFN membranes.....	150
Figure 4.5 XPS spectra of the TFC and SNW-1-incorporated TFN membranes.....	151
Figure 4.6 Surface morphologies of the (a) TFC, (b) TFN-0.01, (c) TFN-0.02, (d) TFN-0.05, (e) TFN-0.01 PRO, (f) substrate top surface, (g) substrate cross section, and (h) substrate bottom surface membranes, respectively, taken through FE-SEM imaging; Contact angle measurements of each membrane were also included inset.....	152

Figure 4.7 Surface roughness of TFC and TFN membranes obtained by atomic force microscopy (AFM) analysis of (a) TFC, (b) TFN-0.01, (c) TFN-0.02, (d) TFN-0.05, and (e) TFN-0.1 PRO membranes.....	155
Figure 4.8 Water flux ( $J_w$ ) of the TFC and TFN PRO membranes in comparison with Toray TFC PRO membrane at 0 bar hydraulic pressure. (Feed solution: DI water; Draw solution: 1.0 M NaCl; Flow rate: 200 mL min <sup>-1</sup> ).....	157
Figure 4.9 Water flux ( $J_w$ ), reverse salt flux ( $J_s$ ), and power density of the membranes at various hydraulic pressures. (Feed solution: DI water; Draw solution: 1.0 M NaCl; Flow rate: 200 mL min <sup>-1</sup> ) .....	158
Figure 5.1 Self-polymerisation of p-DCX to synthesise PP .....	168
Figure 5.2 Functionalisation of PP with chlorosulfonic acid to synthesise PP-SO <sub>3</sub> H .....	168
Figure 5.3 FESEM images of PP-SO <sub>3</sub> H at two different magnifications .....	170
Figure 5.4 The FTIR spectrum of the synthesised PP-SO <sub>3</sub> H, after the sulfonate functionalisation of PP; Chemical structure of PP-SO <sub>3</sub> H is also shown inset .....	171
Figure 5.5 FTIR spectra of the TFC (PP-0) and TFN (PP-0.001, PP-0.002, and PP-0.005) PRO membranes .....	173
Figure 5.6 The shell (outer) side surface, cross section, and lumen (inner) side surface morphologies of the as-spun hollow fibre membrane substrates using FESEM imaging .....	175
Figure 5.7 The membrane cross section and selective layer morphologies for PP-0, PP-0.001, PP-0.002, and PP-0.005 PRO hollow fibre TFC and TFN membranes using FESEM imaging; Surface contact angle values of each membrane were included inset .....	178

Figure 5.8 The osmotic performance during PRO operation at varying applied hydraulic pressure values, expressed in (a) water flux ( $J_w$ ), (b) specific reverse salt flux ( $J_s/J_w$ ), and (c) power density, for PP-0, PP-0.001, PP-0.002, and PP-0.005. DI water and 1.0 M NaCl were the feed and draw, respectively, during PRO operation..... 185

Figure 6.1 Proposed mechanism of chlorine oxidative degradation and heat treatment on polyamide..... 194

Figure 6.2 Burst pressures of the PRO TFC membranes subjected to chlorine oxidative degradation; Three membranes sustained critical damage on the polyamide layer and were observed to burst after application of hydraulic pressure of 6 bar: membranes 3 (pH 13, 4000 ppm  $Cl_2 \cdot h$ , and 10 min heating time), 8 (pH 13, 1000 ppm  $Cl_2 \cdot h$ , and 10 min heating time), and 10 (pH 13, 2500 ppm  $Cl_2 \cdot h$ , and 5 min heating time)..... 195

Figure 6.3 Contour plots showing the influence of pH and free chlorine exposure on the water flux, specific reverse salt flux, and power density, at constant heating time of 5 min ..... 197

Figure 6.4 Contour plots showing the influence of pH and heating time on the water flux, specific reverse salt flux, and power density, at constant free chlorine exposure of 2500 ppm ..... 199

Figure 6.5 Contour plots showing the influence of free chlorine exposure and heating time on the water flux, specific reverse salt flux, and power density, at constant pH of 9 ..... 200

Figure 6.6 FTIR spectra of the pristine PRO TFC membrane and three chosen membranes with different severity of chlorine oxidative degradation conditions ..... 203

Figure 6.7 Sessile water contact angle measurements of the membrane samples subjected to chlorine oxidative degradation..... 204

Figure 6.8 Surface morphology of the pristine PRO TFC membrane and three chosen membranes with different severity of chlorine oxidative degradation conditions .....	205
Figure 7.1 FTIR spectra of the pristine polyketone and PDA-modified membrane substrates .....	213
Figure 7.2 Surface morphology of the (a) pristine polyketone and PDA-coated membrane substrates: (b) sPDA, (c) nPDA-pH8, (d) nPDA-pH9, and (e) nPDA-pH10; Average water contact angles are included inset .....	216
Figure 7.3 Pore size distribution and average pore size of the (a) pristine polyketone and PDA-coated membrane substrates: (b) sPDA, (c) nPDA-pH8, (d) nPDA-pH9, and (e) nPDA-pH10 .....	217
Figure 7.4 Surface roughness characterization of (a) pristine polyketone and PDA-coated membrane substrates: (b) sPDA, (c) nPDA-pH8, (d) nPDA-pH9, and (e) nPDA-pH10 .....	218
Figure 7.5 Cross-section FE-SEM images of the TFC membranes with the polyamide layer thickness: (a) plain TFC, (b) sPDA-TFC, (c) nPDA-pH8-TFC, (d) nPDA-pH9-TFC, and (e) nPDA-pH10-TFC .....	222
Figure 7.6 Polyamide selective layer surface FE-SEM images of the TFC membranes: (a) plain TFC, (b) sPDA-TFC, (c) nPDA-pH8-TFC, (d) nPDA-pH9-TFC, and (e) nPDA-pH10-TFC .....	223
Figure 7.7 Osmotic performance, in terms of water flux ( $J_w$ ), specific reverse salt flux ( $J_s/J_w$ ), and power density, of the TFC membranes during PRO operation at different applied hydraulic pressures using DI water as FS and 1.0 M NaCl as DS .....	226

# TABLE OF CONTENTS

---

1.	Introduction.....	38
1.1	Thesis .....	38
1.2	Background.....	39
1.3	Aims, objectives, and significance.....	42
1.3.1	Aims.....	42
1.3.2	Objectives .....	43
1.3.3	Significance of the study .....	43
1.4	Thesis structure.....	44
2	Literature review.....	47
2.1	Theory.....	47
2.1.1	Engineered osmosis .....	47
2.1.2	Power generation via pressure retarded osmosis.....	54
2.1.3	Reverse salt flux .....	57
2.1.4	Concentration polarisation .....	58
2.2	History and timeline of pressure retarded osmosis .....	62
2.3	Fouling, scaling, and mitigation .....	66
2.3.1	Fouling studies for PRO .....	66
2.3.2	Pre-treatment processes and fouling mitigation .....	68
2.3.3	Anti-fouling PRO membranes.....	71
2.4	Membrane development for pressure retarded osmosis .....	72
2.4.1	Flat sheet TFC PRO membranes .....	73
2.4.2	Hollow fibre TFC PRO membranes .....	83
2.4.3	Free-standing PRO membranes .....	92
2.5	Module and spacer development for pressure retarded osmosis .....	93
2.5.1	PRO module development.....	93
2.5.2	PRO spacer development.....	98
2.6	Integration of PRO with membrane pretreatment techniques.....	98
2.6.1	Reverse osmosis and pressure retarded osmosis hybrid.....	99
2.6.2	Forward osmosis and pressure retarded osmosis hybrid .....	104
2.6.3	Membrane distillation and pressure retarded osmosis hybrid.....	105
2.6.4	Liquid phase ion stripping - pressure retarded osmosis hybrid.....	106
2.7	Novel configurations and niche applications of pressure retarded osmosis.....	107
2.7.1	Closed-loop osmotic heat engine.....	107

2.7.2	Dual-stage PRO.....	109
2.7.3	Pool PRO.....	112
2.7.4	Facultative RO/PRO system.....	113
2.7.5	GreenPRO.....	114
2.7.6	PRO for enhanced oil recovery.....	115
2.7.7	Geothermal PRO.....	116
2.8	Technical challenges, feasibility, and future perspectives.....	118
2.8.1	Technical challenges and feasibility.....	118
2.8.2	Future perspective.....	120
3	General Methods.....	124
3.1	Introduction.....	124
3.2	TFC membrane preparation.....	124
3.2.1	TFC membrane substrate preparation.....	124
3.2.2	Interfacial polymerisation.....	128
3.3	Membrane characterisation.....	129
3.3.1	Field emission scanning electron microscopy.....	130
3.3.2	Attenuated total reflectance-Fourier transform infrared spectroscopy.....	130
3.3.3	X-ray photoelectron spectroscopy.....	131
3.3.4	Atomic force microscopy.....	131
3.3.5	Optical tensiometry.....	131
3.3.6	Capillary flow porometry and other membrane porosity characterisation.....	131
3.3.7	Mechanical strength determination via tensile testing.....	132
3.4	Membrane intrinsic transport property evaluation.....	132
3.5	Membrane performance evaluation.....	134
3.5.1	Experimental.....	134
3.6	Response surface methodology and statistical analysis.....	136
4	Melamine-based covalent organic framework-incorporated thin film nanocomposite membrane for enhanced osmotic power generation.....	138
4.1	Introduction.....	138
4.2	Materials and methods.....	144
4.2.1	Materials.....	144
4.2.2	Schiff-based synthesis of SNW-1.....	144
4.2.3	Interfacial polymerisation and SNW-1 incorporation.....	145
4.3	Results and Discussion.....	146
4.3.1	SNW-1 covalent organic framework material.....	146
4.3.2	Mode of incorporation of SNW-1.....	147

4.3.3	TFC and TFN membrane characterisation.....	149
4.3.4	Membrane intrinsic transport properties .....	155
4.3.5	PRO membrane performance .....	156
4.4	Conclusions.....	161
5	Enhanced water permeability and osmotic power generation with sulfonate-functionalised porous polymer-incorporated thin film nanocomposite membranes.....	163
5.1	Introduction .....	164
5.2	Experimental.....	167
5.2.1	Materials .....	167
5.2.2	Synthesis of PP .....	168
5.2.3	Sulfonate-functionalisation of PP.....	168
5.2.4	PP-SO <sub>3</sub> H characterisation.....	169
5.2.5	Interfacial polymerisation and PP-SO <sub>3</sub> H incorporation.....	169
5.3	Results and Discussion.....	170
5.3.1	PP-SO <sub>3</sub> H characterisation.....	170
5.3.2	Membrane characterisation .....	172
5.3.3	Membrane intrinsic transport parameters.....	179
5.3.4	Performance of membranes for PRO process.....	180
5.4	Conclusions.....	186
6	Control of antagonistic effects of chlorine oxidative degradation on pressure retarded osmosis thin film composite membrane surface .....	187
6.1	Introduction .....	188
6.2	Materials and Methods.....	190
6.2.1	Materials .....	190
6.2.2	Chlorine oxidative degradation.....	191
6.2.3	Optimisation of chlorine oxidation using response surface methodology.....	191
6.3	Results and Discussion.....	192
6.3.1	Mechanism of chlorine oxidative degradation of polyamide .....	192
6.3.2	Influence of chlorine oxidative degradation on TFC membrane stability .....	195
6.3.3	Optimisation of chlorine oxidative degradation conditions.....	197
6.3.4	Membrane characterisation .....	202
6.4	Conclusions.....	206
7	Aliphatic polyketone-based thin film composite membranes with mussel-inspired polydopamine interlayer for high performance osmotic power generation .....	207
7.1	Introduction .....	207
7.2	Experimental.....	211
7.2.1	Chemicals.....	211

7.2.2	Membrane preparation .....	211
7.3	Results and discussion .....	212
7.3.1	Polydopamine modification and formation of smooth and nanoparticle polydopamine interlayer .....	212
7.3.2	TFC membrane characterisation .....	219
7.3.3	Membrane intrinsic transport properties .....	224
7.3.4	Membrane osmotic performance and energy generation capability.....	225
7.4	Conclusions.....	228
8	Conclusions and recommendations .....	230
8.1	Conclusions.....	230
8.2	Comparison with commercial PRO membrane standard and comparison of techniques in this thesis .....	233
8.3	Recommendations .....	237
8.3.1	Development and optimisation of membrane substrate .....	237
8.3.2	Larger-scale membrane development .....	237
8.3.3	Extended studies on controlled polyamide degradation via chemical treatment 238	
8.3.4	Other methods of nanomaterial and functional material incorporation .....	239
8.3.5	Evaluation of membrane integrity under chlorine cleaning regime.....	239
8.3.6	Use of developed membranes for niche PRO applications .....	239

## ABSTRACT

---

Population increase and economic growth have played huge parts in the continuously increasing global energy consumption, which has led to the fossil fuel reserves decline and greenhouse gas emissions. Thus, there is a significant increase in interest in alternative renewable energy sources, among which is osmotic power or salinity gradient energy. Osmotic power is harnessed upon the mixing of water streams with different solute concentrations and osmotic pressures (typically, freshwater and saltwater). Pressure retarded osmosis (PRO) is a process which exploits the osmotic pressure difference between the water streams and allows water to pass through a selectively permeable membrane from the less concentrated stream to the pressurised more concentrated stream. While PRO presents itself as an environmentally benign energy-harnessing process, its wide-scale implementation and technological development are hindered by challenges, among which is the available of suitable and high-performance membranes. Thin film composite (TFC) membranes are conventionally utilised for PRO, due to their porous membrane substrate and dense thin film selective layer, which, together, can exhibit outstanding separation performance and withstand the application of hydraulic pressure during PRO operation. In this thesis, TFC membrane development for PRO was conducted by engineering specifically the polyamide thin film selective layer. Several techniques were conducted in this thesis, which include: (1) nanomaterial filler incorporation; (2) surface functionalisation via nanomaterial incorporation; (3) chemical treatment; and (4) substrate-and-selective-layer interface modification.

First, melamine-based covalent organic framework nanomaterial, Schiff base network-1 (SNW-1), was incorporated into the polyamide selective layer to develop a

thin film nanocomposite (TFN) PRO membrane. This material was chosen due to its size, porosity, and intrinsic hydrophilicity, and these properties could further enhance the performance of the TFC PRO membrane. SNW-1 deposition during interfacial polymerisation (IP) was first investigated, and it was observed that the secondary amine functional groups of SNW-1 react with the carbonyl groups of the acyl chloride IP precursor, effectively reducing the available reactive groups for the amine precursor; thus, SNW-1 was incorporated through the amine precursor, *m*-phenylenediamine (MPD). Upon incorporation, the porosity and intrinsic hydrophilicity of SNW-1 facilitated water transport across the membranes, while maintaining satisfactory salt rejection ability, resulting in enhanced water flux and power density. The best performing membrane with 0.02 wt% loading of SNW-1 exhibited an initial water flux of 42.5 L m<sup>-2</sup> h<sup>-1</sup> and a maximum power density of 12.1 W m<sup>-2</sup>.

The second study on functionalisation of the polyamide selective layer was achieved via the incorporation of a sulfonate-functionalised porous polymer, PP-SO<sub>3</sub>H. Following the successful development of SNW-1, another nano-sized porous material was chosen due to its size, porosity, hydrophilicity, and functionality. The sulfonate functional group of the material was hypothesised to provide better affinity with water molecules and resistance with solute particles. PP, a hydrophobic porous organic polymer synthesised via *Friedel-Crafts* alkylation of dichloro-*p*-xylene, was reacted with chlorosulfonic acid to produce the hydrophilic sulfonate-functionalised PP-SO<sub>3</sub>H. Not only did the presence of the highly hydrophilic functional group assist in the nanomaterial compatibility with the aqueous amine precursor during IP, it was also able to extend its functionality with the selective layer, enhancing the membrane water permeability, porosity, and osmotic energy harvesting capability. The best performing

membrane with 0.002 wt% loading of PP-SO<sub>3</sub>H exhibited an initial water flux of 46.3 L m<sup>-2</sup> h<sup>-1</sup> and a maximum power density of 14.6 W m<sup>-2</sup>.

TFC membranes are known to be highly susceptible to constant exposure to chemicals, such as chlorine, present in the water streams, which damage the membrane selective layer after continuous exposure. After TFC membrane modification via nanomaterial incorporation was performed for the first two technical chapters of this thesis, TFC membrane modification was then performed using chemical agents. Exploiting the chemical reactions of the polyamide with chemical agents and controlling the antagonistic effects were hypothesised to improve the water permeability performance of the TFC membranes. In the third study, the TFC membranes were placed in control oxidative degradation conditions using active chlorine in aqueous NaOCl solution. Chlorine and heat can thin out the dense selective layer, and when controlled and optimised, can tune the membrane surface properties and separation performance. Optimisation was performed in terms of chlorine exposure (a factor of both exposure time and chlorine dosage), solution pH, and subsequent heat treatment time. The resultant membranes exhibited various levels of polyamide degradation and increase in water permeability, at the expense of salt rejection performance. Response surface methodology (RSM) was performed to maximise the water permeability and power density and the antagonistic effects of the chlorine modification on the TFC membrane rejection capability was controlled. The RSM results showed that modification of the TFC membrane using 4000 ppm Cl<sub>2</sub>·h, pH 10.9, and 216 s (3.6 min) heating time would yield the highest water flux of 84.7 L m<sup>-2</sup> h<sup>-1</sup>, specific reverse solute flux of 1.8 g L<sup>-1</sup>, and power density of 4.7 W m<sup>-2</sup> at 5 bar. These results indicate the usability of chlorine modification for TFC PRO

membranes for specific and niche PRO applications, especially those which does not require a high hydraulic pressure and high membrane selectivity.

The relationship of the membrane substrate morphology and the formation of the polyamide selective layer during IP was lastly investigated. This study aimed to bring together both chemical modification and nanomaterial incorporation to enhance the PRO membrane performance. The membrane substrate-and-selective-layer interface was modified by the introduction of bio-inspired polydopamine (PDA) interlayer. Two types of PDA layer were prepared and compared in this study: (1) the conventional PDA layer formed from the self-polymerisation of dopamine, and (2) the PDA nanoparticle layer formation formed from ammonia-initiated dopamine polymerisation. The difference in the interlayer morphology revealed differences in the way the polyamide selective layer was formed during IP, leading to difference in osmotic performance, as well. While the smooth interlayer was known to be preferred due to the ability to form thinner and less dense polyamide, the nanoparticle interlayer exhibited the formation of a looser polyamide, similar to nanomaterial-incorporated TFN membranes, with the PDA nanoparticles providing enhanced hydrophilicity and additional channels for water molecule transport. The best performing membrane with nanoparticulate PDA layer formed at pH 9.0 exhibited an initial water flux of  $40.8 \text{ L m}^{-2} \text{ h}^{-1}$  and a maximum power density of  $17.1 \text{ W m}^{-2}$ .

The four studies presented in this thesis show how vital the engineering of the polyamide selective layer is in enhancing the separation performance and osmotic energy harvesting capability of TFC PRO membranes. These techniques prove not only facile and effective, these are also versatile and applicable for a variety of membrane substrates and even larger-scale membrane development.