Fabrication of novel nanocomposite membranes and 3D printed spacers for forward osmosis process

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FABRICATION OF NOVEL NANOCOMPOSITE MEMBRANES AND
3D PRINTED SPACERS FOR FORWARD OSMOSIS PROCESS**

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2016

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SPACERS FOR FORWARD OSMOSIS PROCESS

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Abstract

Forward osmosis (FO) is a novel osmotic-driven membrane process with lower energy consumption and many potential applications. However, the water flux of FO membranes was severely affected by concentration polarization (CP) of solutes on both the FO membrane surface and inside the FO membrane substrate. To address the CP issues in FO process, two strategies have been successfully developed. First, silica gel (SG)-based mixed matrix FO membranes have been systematically synthesized and characterized for the first time. The incorporation of SG particles into the polyacrylonitrile (PAN) support layer significantly enhanced water permeability of SG-based mixed matrix FO membranes. Water permeability of these membranes were improved after the embedment of SG particles with the range of 0.25 – 1.0 wt.% SG loading, possibly as a result of the both porous nature of SG particles and the enhanced membrane substrate porosity. However, further increasing in SG loading to 2.0 wt.%, a marginal reduction in both water permeability and salt rejection was observed, most likely due to the agglomeration of SG and hence reduce the mass transfer inside the membrane substrate. The optimal SG-based mixed matrix FO membrane with 1.0 wt.% SG loading had a significantly higher water permeability compared to the neat PAN membrane without embedment of any SG particles. This membrane can achieve the highest FO water fluxes of $> 100 \text{ L/m}^2 \text{ h}$ by using the 1 M MgCl_2 as the draw solution (DS) and DI water as the feed solution (FS).

Second, the effect of SG particles with different pore size on SG-based mixed matrix FO membranes was investigated. The objective of this study is to improve the mass transfer in the porous FO substrates and hence improving the internal concentration polarization (ICP) using the mixed matrix strategy. SG-based mixed matrix FO membranes with different pore size were

successfully fabricated via non-solvent includes phase inversion (NIPS) by adding silica gel particles with different pore size into the polyacrylonitrile dope solution. The thin salt rejection layer was synthesized using a layer-by-layer (LbL) self-assembly method on top of the SG-based mixed matrix FO substrate. The current study demonstrates the effect of different pore size of SG particle in mixed matrix FO substrate for improving the ICP in FO application for the first time.

Third, the use of environmental-friendly metal-organic frameworks (MOFs) as green template was proven to enhance porosity and interconnectivity of the water treatment membranes. In general, osmotic-driven membranes with high porosity can possibly be fabricated by removing MOFs template, such as low water stability or other nanoparticles, in polymeric matrix. It is important to note that greatly enhanced water permeability was observed, which might be ascribed to the increased mass transfer coefficient of the FO substrate layer, which can be considered as an ultrafiltration (UF) membrane.

Fourth, the use of metal-organic frameworks (MOFs) as removable filler was explored to prepare MOF-based porous matrix membranes (PMMs) for improving the mass transfer in the FO substrates and hence controlling the ICP. MOF-based porous matrix substrates (PMSs) with three different types of MOFs were prepared via phase inversion by adding MOF particles into the polyacrylonitrile (PAN) dope solution. The bond dissociation energy (BDE) between metal ions and organic linker of MOF particles played an important role for the selection of fillers of PMMs. For MOF particles with lower BDE ($< \sim 200$ kJ/mol), the corresponding MOF-based porous matrix FO membranes had higher membrane bulk porosity. This study shows the effect of different types of MOF particles in MOF-based porous matrix FO substrate for controlling the

ICP in FO application for the first time, which provides an additional dimension for ICP control in osmotic-driven membrane processes.

Finally, 3D printing is an emerging technology and has attracted massive attention in recent years. This part of thesis focuses on the recent developments on enhancing the spacer design with 3D printing technology. With the recent advancement of 3D printing technology, breakthroughs in fabricating novel FO feed spacers are expected in the near future. Improvement of 3D printing technologies in terms of resolution, materials and speed should assure the production of various 3D printed feed spacers with high efficiency and better performance.

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List of symbols

Symbol	Description
V_a	Volume of gas absorbed at standard temperature and pressure
V_m	Volume of gas absorbed at standard temperature and pressure to produce an apparent monolayer on the sample surface
P	Partial vapor pressure of adsorbed gas in equilibrium with the surface at 77.4K
P_0	Saturated pressure of absorbed gas
C	Dimensionless constant that is related to the enthalpy of adsorption of the adsorbed gas on the powder sample
ε	Membrane porosity
m_{dry}	Dry mass of membrane samples
m_{wet}	Wet mass of membrane samples
ρ_w	Density of water
ρ_m	Density of polymer
S	Structural parameter of the support layer
D	Solute diffusion coefficient
C_{draw}	Concentrations of draw solution
C_{feed}	Concentrations of feed solution
J_s	Solute flux
J_v	Water flux
β	van't Hoff coefficient
R_g	Universal gas constant
T	Absolute temperature
d_f	Diameter of the spacer filament
d_n	Diameter of the spherical node
θ	Mesh angle between spacer filaments
l_m	Mesh length between spacer filaments

ε	Voidage of spacer-filled channel
k	Mass transfer coefficient
$\Delta\pi_w$	Osmotic pressure on the membrane wall
L_p	Water permeability coefficient of membrane
ΔP_{TM}	Transmembrane pressure across the membrane
ΔP_{CH}	Pressure drop along the spacer-filled channel
V_{total}	Total volume of unit cell
V_{sp}	Total volume of spacer
h_{sp}	Overall thickness of spacer
S_{sp}	Surface area of spacer

List of abbreviations

Abbreviations	Description
AM	Additive Manufacturing
AL-DS	Active-layer-facing-draw-solution
AL-FS	Active-layer-facing-feed-solution
CA	Cellulose acetate
CFD	Computational Fluid Dynamics
CLIP	Continuous Liquid Interface Production
CTA	Cellulose triacetate
DLP	Digital Light Processing
DS	Draw solution
ECP	External concentration polarization
ED	Electrodialysis
EO	Engineered osmosis
ES	Electrospinning
FDM	Fused Deposition Modelling
FO	Forward osmosis
FS	Feed solution
GA	Glutaraldehyde
HTI	Hydration Technologies Innovations
ICP	Internal concentration polarization
IP	Interfacial polymerization
LbL	Layer-by-layer
xLbL	Crosslinked layer-by-layer
MF	Microfiltration
MMM	Mixed matrix membrane
MOF	Metal-organic framework
MPD	<i>m</i> -phenylenediamine
MWCNT	Multi-walled carbon nanotube
NF	Nanofiltration

PAH	Poly(allylamine hydrochloride)
PAN	Polyacrylonitrile
PES	Polyethersulfone
PI	Phase inversion
PMM	Porous matrix membrane
PSf	Polysulfone
PSS	Polystyrene sulfonate
PAO	Pressure-assisted osmosis
PRO	Pressure-retarded osmosis
RO	Reverse osmosis
SWM	Spiral wound modules
SG	Silica gel
SLA	Stereolithography Apparatus
SLS	Selective Laser Sintering
TFC	Thin film composite
TiO ₂	Titanium dioxide
TMC	Trimesoyl chloride
TMP	Transmembrane pressure
TNC	Thin-film nanofiber composite
TPP	Two Photon Polymerization
UF	Ultrafiltration

List of research output

(a) List of scientific papers

1. *The Potential to Enhance Membrane Module Design with 3D Printing Technology*

Lee, J.-Y.; Tan, W. S.; An, J.; Chua, C. K.; Tang, C. Y.; Fane, A.G.; Chong, T. H. *J. Membr. Sci.* **2016**, 499, 480.

2. *Mesoporous Silica Gel – Based Mixed Matrix Membranes for Improving Mass Transfer in Forward Osmosis: Effect of Pore Size of Silica Gel*

Lee, J.-Y.; Wang, Y.; Tang, C. Y.; Huo, F. *Sci. Rep.* **2015**, 5, 16808.

3. *Metal-Organic Framework – Based Porous Matrix Membranes for Improving Mass Transfer in Forward Osmosis Membranes*

Lee, J.-Y.; She, Q.; Huo, F.; Tang, C. Y. *J. Membr. Sci.* **2015**, 492, 392.

4. *Synthesis and Characterization of Silica Gel – Polyacrylonitrile Mixed Matrix Forward Osmosis Membranes Based on Layer-by-Layer Assembly*

Lee, J.-Y.; Qi, S.; Liu, X.; Li, Y.; Huo, F.; Tang, C. Y. *Sep. Purif. Technol.* **2013**, 124, 207.

5. *Fabrication of Porous Matrix Membrane (PMM) Using Metal-Organic Framework as Green Template for Water Treatment*

Lee, J.-Y.; Tang, C. Y.; Huo, F. *Sci. Rep.* **2013**, 4, 3740.

(b) List of scientific awards

1. *Green Talents 2014*

2. *Best Poster Award of Advanced Membrane Technology VI Conference*

3. *North American Membrane Society Student Fellowship Award 2015*

4. *European Membrane Society Best Paper Award 2015 & PhD Student Travel Award*

5. *Best Poster Award of Singapore International Water Week 2016*

Chapter 1

Introduction

1.1 Background

With the increasing world population, the demand for clean drinking water also increases exponentially (Elimelech and Phillip 2011). One of the most challenging global problems affecting many countries around the world is clean water shortage and thus growing concerns over the access to safe drinking water (Shannon, Bohn et al. 2008). To meet this challenge, membrane-based water treatment processes have become one of the most energy efficient and most reliable technologies for supplying water (Service 2006, Logan and Elimelech 2012). Compared to conventional thermal distillation processes, membrane-based water treatment processes have relatively lower energy consumption, improved cost effectiveness, and ensuring a more sustainable production of drinking water in the future (Van der Bruggen and Vandecasteele 2002, Shannon, Bohn et al. 2008). Hence, membrane-based water treatment processes have been employed in a wide range of applications such as oil/water separation (Chen and Xu 2013, Maphutha, Moothi et al. 2013, Shi, Zhang et al. 2013, Zhang, Zhang et al. 2013, Zhang, Shi et al. 2013) wastewater treatment (Greenlee, Lawler et al. 2009, Zhang, Zhang et al. 2009, Pérez-González, Urtiaga et al. 2012, Gao, de Jubera et al. 2013), water purification (Sekulić, ten Elshof et al. 2004, Liang, Cao et al. 2011, Han, Xu et al. 2013), seawater desalination (Kessler and Moody 1976, Lee, Arnot et al. 2011, Misdan, Lau et al. 2012, Gu, Lee et al. 2013), food processing (Álvarez, Riera et al. 2002, Matta, Moretti et al. 2004, Souza, Pagani et al. 2013), and valuable product recovery (Pink, Wong et al. 2008, Nair, Wong et al. 2009, Liang, Wang et al. 2010, Sereewatthanawut, Lim et al. 2010, So, Peeva et al. 2010, Liu, Li et al. 2011).

Among these membrane-based water treatment processes, forward osmosis (FO) is one of the most promising technologies that have attracted many attentions. In FO process, an osmotic pressure gradient is created across a semi-permeable FO membrane to drive the water from the low concentration feed solution (FS) to the high concentration draw solution (DS) (Cath, Childress et al. 2006, Chung, Li et al. 2012, Zhao, Zou et al. 2012). According to several excellent reviews about the FO membrane processes (Cath, Childress et al. 2006, Chung, Li et al. 2012, Zhao, Zou et al. 2012), the advantages of FO membrane processes are summarized as (1) low energy consumption, (2) high rejection of various kinds of contaminants, and (3) low propensity of membrane fouling. Therefore, FO can be potentially used in a range of industrial applications, such as valuable product concentration (Torreggiani and Bertolo 2004, Zou, Gu et al. 2011), food processing (Petrotos, Quantick et al. 1998, Torreggiani and Bertolo 2004), municipal and industrial wastewater reclamation (Holloway, Childress et al. 2007, Cornelissen, Harmsen et al. 2008, Achilli, Cath et al. 2009, Lay, Zhang et al. 2011), and seawater desalination (Kessler and Moody 1976, McCutcheon, McGinnis et al. 2005, McGinnis and Elimelech 2007).

1.2 Problems Statement

Despite FO technologies have many potential applications, there are still several critical challenges need to be addressed before FO processes could be used in industrial application. One of the most severe problems is the lack of high performance FO membranes and FO spacers with higher mass transfer to overcome internal concentration polarization inside FO support layer and external concentration polarization on the surface of FO membranes as shown in Fig 1-1.

Fig. 1-1 The schematic diagram of key challenges in FO process that are internal concentration polarization and external concentration polarization.

Up to present, the choices of commercial FO membranes are still very limited compared to the well-established commercial ultrafiltration (UF) membranes, nanofiltration (NF) membranes, and reverse osmosis (RO) membranes. These commercial available FO membranes are mainly manufactured by the Hydration Technologies Innovations (HTI) Company. In the earlier days, only HTI cellulose triacetate (CTA) FO membranes are commercial available in the market. Until very recently, new thin film composite (TFC) FO membranes are manufactured by HTI Company as well. For the CTA FO membranes, cellulose triacetate solution was casted onto the fabric to fabricate the FO membranes without the porous supporting layer. However, these CTA FO membranes can only be used in a narrow range of pH and could be easily degraded by bacteria or under harsh conditions. On the other hand, various kinds of methods have been tried

to fabricate FO membranes in universities or research institutes around the world. For example, thin film composite membrane is one of the most popular ways to fabricate FO membranes among all these methods (McCutcheon and Elimelech 2008, Wei, Liu et al. 2011, Wei, Qiu et al. 2011, Widjojo, Chung et al. 2011, Chou, Wang et al. 2012, Han, Chung et al. 2012, Jin, Shan et al. 2012, Li, Wang et al. 2012, Wang, Chung et al. 2012, Li, Zhang et al. 2013, Ma, Wei et al. 2013, Wei, Qiu et al. 2013). Briefly, TFC FO membranes are fabricated by two steps: (1) phase inversion (PI) of polymer solution to fabricate the porous substrate layer (Yang, Wang et al. 2009, Sairam, Sereewatthanawut et al. 2011) (2) interfacial polymerization (IP) between trimesoyl chloride (TMC) in oil phase and *m*-phenylenediamine (MPD) in the aqueous phase to synthesize the thin polyamide salt rejection layer (Wang, Shi et al. 2010, Yip, Tiraferri et al. 2010, Tiraferri, Yip et al. 2011, Wei, Liu et al. 2011, Wei, Qiu et al. 2011, Chou, Wang et al. 2012). Unfortunately, the polyamide layer is very fragile and could be easily attacked by the chlorine molecule and hence restricts the potential application of TFC FO membranes. On the other hand, layer-by-layer (LbL) FO membranes is another major class of FO membranes (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Qi, Li et al. 2012, Qi, Qiu et al. 2012, Duong, Zuo et al. 2013, Gu, Lee et al. 2013, Liu, Fang et al. 2013, Liu, Qi et al. 2013, Lee, Qi et al. 2014). The selective layer of LbL FO membranes are consisted of polycation electrolyte, such as poly(allylamine hydrochloride) (PAH), and polyanion electrolyte, such as polystyrene sulfonate (PSS). Compared to TFC FO membranes, these LbL FO membranes are NF-like FO membranes and hence lower salt rejection that depends on the number of bilayers.

Even though an ideal FO membrane (eg. high water permeation flux and 100% rejection), such as Aquaporin FO membranes can be fabricated, external concentration polarization is still

another critical challenging problem in FO process. The accumulation of solutes on the membrane surface will significantly decrease the effective osmotic pressure but the design of current FO feed spacer is still lack of appropriate attention. Therefore, fabrication of better FO membranes and feed spacers that can potentially reduce concentration polarization, either internal concentration polarization or external concentration polarization is worthwhile to further study for my PhD research.

1.3 Main Objectives

The overall objective of the current study is to investigate the fabrication of novel nanocomposite FO membranes (Part 1) and 3D printed FO feed spacers (Part 2) to address both internal concentration polarization and external concentration polarization in FO process. For the Part 1, the feasibilities of using porous materials-based mixed matrix membranes (MMMs) or porous matrix membranes (PMMs) were investigated and the objective is to improve the mass transfer and hence reducing internal concentration polarization in the supporting layer. For the Part 2, the possibility of fabricating FO feed spacer using 3D printing technology was examined and the objective is to increase mass transfer and hence reducing external concentration polarization on the membrane surface. More specific objectives are listed below:

(1) To explore the possibility of silica gel (SG)-based MMMs as FO substrates to improve mass transfer in the substrate layer and hence the FO water flux and to investigate the potential effect of different loadings of SG particle on the morphology, structure and FO performance in a systematical way. In addition, the other objective is to understand the effects of different pore

size of SG particle on the physiochemical properties, intrinsic separation properties, and FO performance of SG-based mixed matrix FO membranes in an orderly manner.

(2) To investigate the use of benign metal-organic frameworks (MOFs) as green template for the formation of macro-pores inside the FO substrate layer (i.e. an UF membrane) to enhance porosity and interconnectivity of the MOF-based PMMs. Next, these MOF-based PMMs were investigated in terms of intrinsic separation properties and FO performance in an orderly manner to improve the mass transfer coefficient in the FO support layer.

(3) To investigate the use of 3D printing technology as a tool for the fabrication of FO feed spacer to reduce external concentration polarization in a narrow spacer-filled channel. The author would like to continue this interesting study for his post-doctoral training and more experimental results will be reported in due course.

1.4 Overview of thesis

The outline of this thesis is consisted of nine chapters and two parts. Part 1 mainly focused on the fabrication and characterization of novel nanocomposite membranes, especially the SG-based mixed matrix membranes and MOF-based porous matrix membranes. On the other hand, Part 2 mainly focused on the potential of 3D printing to fabricate FO feed spacers. Chapter 2 presents the general introduction and literature review of different types of FO membranes. Chapter 3 explains the general methodology used in this PhD study, such as fabrication methods and

characterization methods of the FO membranes and FO spacers. The main contents of chapter 4-7 and 8 are summarized as following:

Chapter 4 and Chapter 5 show that the fabrication and characterization of SG-based mixed matrix membranes as FO supporting layer. The effect of SG loading, draw solution concentration, feed solution concentration, and membrane orientation on the FO performance was systematically studied (Chapter 4). Next, the effect of pore size of silica gel particles on SG-based mixed matrix FO membranes was also investigated (Chapter 5). The effect of pore size of silica gel particle on the intrinsic separation properties and FO performance were systematically investigated. The FO results revealed that the importance of loading and pore size of silica gel played an importance role on the overall FO performance.

Chapter 6 and Chapter 7 study the feasibility of MOF particles as green template to create macro-pores inside the MOF-based porous matrix membranes (PMMs) to improve the mass transfer coefficient. The porosity and interconnectivity of the MOF-based PMMs (i.e. UF membranes) were improved after removal of MOF particles by using water as mild etching solution (Chapter 6). Next, the potential of these MOF-based PMMs was explored to be used as the FO substrate due to their high membrane porosity and membrane pore interconnectivity (Chapter 7). The bond dissociation energy (BDE) between metal ions and organic linker of MOF particles played an important role for the selection of fillers of PMMs. For MOF particles with lower BDE ($< \sim 200$ kJ/mol), the corresponding MOF-based porous matrix FO membranes had higher membrane bulk porosity.

Chapter 8 investigates the design and fabrication of FO feed spacer with three different mesh length using 3D printing technology. The hypothesis is that the 3D printed feed spacers with smaller mesh length can give better mass transfer but also higher pressure drop along the spacer-filled feed channel. The preliminary results show that all the 3D printed FO feed spacers have smaller concentration polarization modulus compared to empty channel. However, further optimization, such as computational fluid dynamics (CFD) simulation are required to better understand the role of different parameters of 3D printed feed spacers to increase mass transfer in the narrow spacer-filled channel of FO process. Finally, Chapter 9 will give an overall conclusion of my PhD study and potential future work such as the design of 3D printed FO spacer with different geometry. The overview of my PhD thesis is summarized in the Fig. 1-2.

Fig. 1-2 The overview of my PhD thesis.

Part 1: Fabrication of Novel Nanocomposite Membranes

(a) Mixed Matrix Membrane

(a) [J.-Y. Lee et al. Sep. Purif. Technol. 2013, 124, 207;](#)

(b) [J.-Y. Lee et al. Sci. Rep. 2015, 5, 16808.](#)

(b) Porous Matrix Membrane

(a) [J.-Y. Lee et al. Sci. Rep. 2013, 4, 3740;](#)

(b) [J.-Y. Lee et al. J. Membr. Sci. 2015, 492, 392.](#)

Chapter 2

Literature review

2.1 Classification of membrane processes

Membrane processes can be generally classified into (1) pressure-driven membrane processes, (2) osmotic-driven membrane processes, and etc. based on the driving force of the membrane processes. For the pressure-driven membrane processes, an external pressure is applied at the feed solution to force the water passing through the semi-permeable RO membrane and leaves behind the contaminant as shown in Fig. 2-1 (c). For example, reverse osmosis membrane processes is one of the most prevalent pressure-driven membrane processes and have been used for a range of applications, such as seawater desalination (Elimelech and Phillip 2011), wastewater reclamation (Greenlee, Lawler et al. 2009), food processing (Cros, Ignot et al. 2004, Garcia-Castello, Mayor et al. 2011), and surface water treatment (Buonomenna 2013). However, the high energy requirement of pressure-driven membrane processes, such as RO membrane processes, and the polyamide linkage is susceptible to chlorine attack, scientist started to explore new alternative solution and osmotic-driven membrane processes have received much attention. Compared to the pressure-driven membrane processes, osmotic-driven membrane processes, such as forward osmosis membrane processes, is highly attractive due to the relatively lower amount of energy input and high rejection of solute and contaminants as shown in Fig. 2-1 (a). In summary, a plot of water flux against applied pressure plot can be used to explain the difference between pressure-driven membrane processes and osmotic-driven membrane processes as shown in Fig 2-1 (d). A detailed description of FO processes and recent advancement on the fabrication of FO membranes will be discussed on the following sections.

Fig. 2-1 General classification of osmotic-driven membrane processes and plot of water flux against applied pressure. (a) Forward Osmosis (FO); (b) Pressure retarded osmosis (PRO); and (c) Reverse osmosis (RO). Adapted from Refs. (Xu, Peng et al. 2010) with copyright permission.

2.2. Recent development on the fabrication of forward osmosis membrane

By using the osmotic pressure difference as the driving force between a low concentration FS and a high concentration DS to drive water through a semi-permeable membrane, FO membrane processes can possibly lower the energy consumption of current state-of-the-art technologies, such as RO and NF membrane processes by up to 30% (Cath, Childress et al. 2006, Zhao, Zou et al. 2012). Compared to these high pressure-driven RO and NF membrane processes, FO membrane processes has been summarized to have a series of advantages, mainly including (1) relatively lower hydraulic pressure and hence lower energy consumption and higher fouling resistance, (2) high rejection of a variety of contaminants and hence higher water quality could

be achieved, and (3) relatively lower operating cost because of the utilization of high osmotic pressure difference and hence the high water recovery (McCutcheon, McGinnis et al. 2005, Achilli, Cath et al. 2009, Lee, Boo et al. 2010) as shown in Fig. 2-2.

Fig. 2-2 The advantages of FO processes. Reproduced from Ref (Zhao, Zou et al. 2012) with copyright permission.

Based on the abovementioned advantages of FO membrane process, FO membrane process has been employed in a wide range of applications such as wastewater treatment (Cath, Adams et al. 2005, Cath, Gormly et al. 2005, Holloway, Childress et al. 2007, Cornelissen, Harmsen et al. 2008, Achilli, Cath et al. 2009, Cath, Hancock et al. 2010, Lay, Zhang et al. 2011, Xiao, Tang et al. 2011, Zhang, Ma et al. 2012), seawater desalination (Kessler and Moody 1976, McCutcheon, McGinnis et al. 2005, McGinnis and Elimelech 2007, Martinetti, Childress et al. 2009, Phuntsho,

Vigneswaran et al. 2012, Shaffer, Yip et al. 2012), food processing (Petrotos, Quantick et al. 1998, Petrotos, Quantick et al. 1999, Torreggiani and Bertolo 2004, Babu, Rastogi et al. 2006, Garcia-Castello, McCutcheon et al. 2009, Garcia-Castello and McCutcheon 2011), energy production (Achilli, Cath et al. 2009, Achilli and Childress 2010, Xu, Peng et al. 2010, Yip and Elimelech 2011, Hoover, Schiffman et al. 2013, Song, Liu et al. 2013) and valuable product concentration (Torreggiani and Bertolo 2004, Lutchmiah, Cornelissen et al. 2011, Zou, Gu et al. 2011, Lutchmiah, Lauber et al. 2014, Lutchmiah, Verliefde et al. 2014). A comprehensive description of recent developments on the fabrication of FO membranes mainly focused on CTA FO membranes, TFC FO membranes, and LbL FO membranes, will be discussed on the following sections.

2.2.1. Integral asymmetric membranes

2.2.1.1. Cellulosic membranes

In 1959, high salt rejection cellulose acetate film was firstly reported by Reid and co-worker (Reid and Breton 1959, Reid and Kupperts 1959). A few years later, a major breakthrough of preparing polymeric cellulosic RO membranes via phase inversion was prepared by Loeb and Sirirajan. Due to their high hydrophilicity, good mechanical strength, readily available starting material, and good chemical resistance of cellulose triacetate (CTA), it has been widely used to prepare CTA FO membranes via phase inversion method (McCutcheon and Elimelech 2008) on a woven or non-woven fabric. Both the structure and chemistry of the cellulosic membranes played an important role to achieve better FO performance (McCutcheon and Elimelech 2008, Su and Chung 2011). However, CTA is very susceptible to hydrolysis and bacteria attack and

hence the proper pH and temperature adjustment of both draw solution and feed solution is needed to prevent degradation of CTA FO membrane.

Fig. 2-3 Cross-sectional SEM images of cellulose acetate FO membranes from HTI. Reproduced from Ref (Zhao, Zou et al. 2012) with copyright permission.

Recently, both hollow-fibre and flat sheet of CTA FO membranes were developed by the research group of Chung (Su, Yang et al. 2010, Wang, Ong et al. 2010, Zhang, Wang et al. 2010, Ong, Chung et al. 2012). In general, the synthesis method of CTA FO membranes is quite simple: (a) dissolve CTA powder into a polar solvent such as acetone followed by phase inversion to generate the porous substrate and then heat water treatment to anneal the surface pore size (Zhang, Wang et al. 2010). In general, the FO membrane has two rejection skin layers, which may increase the water transport resistance but can significantly mitigate the adverse effect of ICP in the membrane porous support layer. In addition, same method was used by Sairam et al. to prepare flat sheet CTA FO membranes with different pore-forming agents such as organic acid and zinc chloride (Sairam, Sereewatthanawut et al. 2011). In their study, the cellulose was cast

onto nylon fabric followed by annealing the membranes at different temperature. They reported that the best FO performance was achieved by using the zinc chloride as pore-forming agent.

2.2.1.1. Polymeric membranes

In 2007, Wang et al. firstly reported that polybenzimidazole (PBI) NF membranes as a new kind of FO membranes (Wang, Chung et al. 2007) as shown in Fig. 2-4. PBI FO membranes have asymmetric structure with integral rejection layer and supporting layer and could be easily fabricated by using phase inversion method in a single step. PBI was selected as the polymer because of its excellent mechanical strength and chemical stability. In addition, asymmetric PBI FO membranes showed excellent rejection to the divalent ions, which could be attributed to the narrow pore size distribution.

Fig. 2-4 FESEM image of asymmetric PBI FO membranes. This figure was reproduced from Ref. (Wang, Chung et al. 2007) with copyright permission.

In 2009, Wang et al. showed that the asymmetric PBI FO membranes can be further chemically crosslinked by using *p*-xylene dichloride. (Wang, Yang et al. 2009) The crosslinking processes can further improve the salt rejection towards monovalent ions and smaller mean pore size. The amine group of the imidazole ring can react with the crosslinker and the proposed mechanism of the crosslinking process was shown in Fig. 2-5. The optimal PBI FO membranes with *p*-xylene dichloride modification gave the best FO water flux and enhanced salt selectivity. In addition, it is noteworthy that the longer crosslinking time could further improve salt rejection at the expense of the water permeability of the PBI FO membranes.

Fig. 2-5 Proposed mechanism between polybenzimidazole and *p*-xylene dichloride. This figure was reproduced from Ref. (Wang, Yang et al. 2009) with copyright permission.

2.2.2. Thin film composite (TFC) membranes

2.2.2.1. The substrate of thin film composite prepared by phase inversion

In general, TFC polyamide (PA) FO membranes were generally fabricated by phase inversion (PI) of the polymer dope solution followed by interfacial polymerization (IP) of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) for both hollow-fiber and flat-sheet FO membranes (Elimelech and Phillip 2011) as shown in Fig. 2-6.

Fig. 2-6 A schematic illustration of interfacial polymerization of *m*-phenylene-diamine (MPD) and trimesoyl chloride (TMC); B Cross-sectional TEM image of thin film composite (TFC) membranes and inset is the FESEM image of polyamide layer. Reproduced from Ref. (Elimelech and Phillip 2011) with copyright permission.

In 2010, TFC hollow fiber FO membrane was synthesized by Wang and et al. by using the TFC method (Chou, Shi et al. 2010, Wang, Shi et al. 2010, Shi, Chou et al. 2011). Either the inner surface or outer surface of the polyethersulfone (PES) hollow fiber substrate can undergo interfacial polymerization to form the polyamide rejection layer (Chou, Shi et al. 2010).

Excellent intrinsic separation properties of the FO hollow fiber membrane were observed while high water flux and low ratio of salt flux to water flux, which is better than all other commercial FO membranes, indicated that its potential application for seawater desalination (Chou, Shi et al. 2010, Shi, Chou et al. 2011). They highlighted that both the structure of porous substrate and the substrate surface structure played an important role in FO performance. Principally, spongy pore structure was less favorable than the straight finger-like pore structure due to enhanced ICP of the former and a substrate with <300 kDa MWCO was preferred to perform interfacial polymerization to form a rejection layer (Shi, Chou et al. 2011, Wei, Qiu et al. 2011). More recently, Wang and co-workers has successfully fabricated hollow fiber TFC-PRO membrane for power generation (Chou, Wang et al. 2012). This kind of TFC-PRO showed much higher mechanical strength and excellent intrinsic separation properties. As a result, the power density could be achieved as high as 10.6 W/m^2 using seawater brine as the draw solution and wastewater brine as the feed water. The TFC-PRO hollow fiber also showed good water permeability, low salt permeability, and small structural parameter. Due to its large diameter of the lumen, it can withstand transmembrane pressure as high as 9 bar, which suggested that this novel TFC-PRO hollow fiber membrane could be potentially used for PRO process to harvest salinity gradient energy. In summary, the ICP and water flux of FO membrane was mainly controlled by the membrane support layer while the salt rejection and reverse solute flux was regulated by the membrane rejection layer (Chou, Shi et al. 2010, Wang, Shi et al. 2010, Shi, Chou et al. 2011).

In 2010, Yip et al. also prepared the TFC flat sheet FO membrane by using interfacial polymerization of TMC and MPD on porous polysulfone (PSf) substrate and found that the

optimization of substrate support layer played an important role to reduce ICP (Yip, Tiraferri et al. 2010, Tiraferri, Yip et al. 2011). Both finger-like and sponge-like pore structure were produced by carefully controlling the composition of polymer solution and tailoring the casting process (Yip, Tiraferri et al. 2010). The relationship between the structure and performance of the TFC FO membranes were discussed and also compared with commercial HTI CTA FO membranes using pure water as feed water and NaCl as the draw water (Tiraferri, Yip et al. 2011). Other factors such as the height of casting blade, the composition of casting solution, the concentration of dope polymer, and the wetting of the fabric layer will also affect the FO performance (Tiraferri, Yip et al. 2011). In conclusion, the structural parameter (ie. tortuosity, thickness and porosity) and pore structure of the PSf supporting layer played an important role to give the high water flux by reducing the internal concentration polarization (Yip, Tiraferri et al. 2010, Tiraferri, Yip et al. 2011). Both the pore structure and hydrophilicity of substrate played key roles in reducing ICP and enhanced FO performance (Widjojo, Chung et al. 2011, Liu and Ng 2015, Liu, Ong et al. 2016).

2.2.2.2. The substrate of thin film composite prepared by electrospinning

In 2011, a new type of thin film nanofiber composite (TNC) FO membranes was synthesized by Song et al. via electrospinning followed by interfacial polymerization (ES-IP) (Song, Liu et al. 2011) as shown in Fig. 2-7. Due to its intrinsic properties of scaffold-like nanofiber support layers, such as interconnected pores formed by individual nanofiber, high porosity and low tortuosity, which can dramatically reduce both the internal concentration polarization and structural parameter. Therefore, the FO water flux of nanofiber support FO membrane was three

times higher than the TFC FO membranes prepared by the phase inversion followed by interfacial polymerization (PI-IP). More recently, this kind of TNC membrane has been fabricated and applied in PRO process for power generation (Song, Liu et al. 2013). The highest power density is about 21.3 W/m^2 by using seawater brine as the draw solution and river water as the feed solution. The highest transmembrane pressure (TMP) was about 15.2 bar and further increasing the pressure would result in breakage of the membrane.

Later, McCutcheon and co-workers also developed flat-sheet TNC-FO membranes using a similar method (Bui, Lind et al. 2011). They found that the compatibility between the rejection layer and nanofiber support is very crucial: poor adhesion between polyamide and polyethersulfone nanofiber support while stronger adhesion between polyamide and polysulfone nanofiber support. With high porosity and low tortuosity, the mass transfer coefficient was increased in the area of the rejection layer and hence decreased the structural parameter and internal concentration polarization. However, further optimization of the chemistry and fabrication method is needed to further improve the FO performance. Further, they also synthesized hydrophilic nanofiber support using two common hydrophilic polymers, polyacrylonitrile (PAN) and cellulose acetate (CA) (Bui and McCutcheon 2012). It is hypothesized that a robust blended nanofiber nonwoven can be tailored by low hydrolyzability of CA and high hydrophilicity of PAN for engineered osmosis (EO) application, such as forward osmosis and pressure retarded osmosis. In 2013, Elimelech and coworker also reported TNC-EO membranes by using the electrospun polyethylene terephthalate nanofiber to replace either the polyester non-woven fabric support or the polysulfone or polyethersulfone support layer (Hoover, Schiffman et al. 2013). In general, it is critical to resist the mechanical stress while without

compromising the structural changes to the support layer to minimize the internal concentration polarization. This work demonstrated that electrospun TNC-EO membranes with high resistance to mechanical stress and low structural parameter may potentially be used for forward osmosis and pressure retarded osmosis application. Further improvement of the mechanical properties of electrospun nanofiber through post-treatment or parameters in electrospinning process should be systematically studied.

Fig. 2-7 Schematic illustration of nanofiber composite FO membranes. Adapted from Ref. (Song, Liu et al. 2011) with copyright permission.

2.2.3. Layer-by-layer (LbL) membranes

In 2011, LbL FO membrane was firstly reported by Qi et al. (Saren, Qiu et al. 2011) by using phase inversion method to fabricate the membrane substrate followed by base treatment to enhance the hydrophilicity and the charge density on the support layer (Fig. 2-8). Poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene-sulfonate) (PSS) were selected for the LbL assembly. A small structural parameter was achieved by tailoring the

membrane structure with thinner cross-section, higher porosity, high hydrophilicity, finger-like straight pore, which resulted in significantly reduction of internal concentration polarization. Both the water permeability and salt selectivity were tunable by controlling the number of polyelectrolyte.

Fig. 2-8 Schematic illustration of layer-by-layer assembly of PAH and PSS. This figure was reproduced from Ref. (Saren, Qiu et al. 2011) with copyright permission.

The procedures for preparing these LbL active layers are quite typical: soaking the negatively charged PAN membrane in PAH polycation solution followed by rinsing with deionized water to remove excess PAH and then soaking in to the PSS poly anion solution followed by rinsing with DI water to remove excess PSS. These two steps were repeated until the desired polyelectrolyte layers are obtained. Later, they reported chemical crosslinking of polyelectrolyte layers by using glutaraldehyde (GA) as the cross-linker (Qiu, Qi et al. 2011). High FO water flux of about 100 LMH was achieved by using high concentration of draw solution in the AL-DS orientation. As a result of high ionic strength of draw solution, severe solute reverse transport was observed for

the AL-DS orientation. However, the poor NaCl rejection remained a key limitation and restricted the application of these LbL membranes in the FO process.

Later, Qiu et al. reported a high flux LbL FO membrane by crosslinking chemically the layer-by-layer polyelectrolytes by glutaraldehyde (Qiu, Qi et al. 2011) as shown in Fig 2-9. A series of non-crosslinked and crosslinked LbL FO membranes were fabricated and characterized in term of intrinsic separation properties, FO performance, and substrate morphology.

Fig. 2-9 Schematic illustration of cross-linked layer-by-layer FO membranes. This figure was reproduced from Ref. (Qiu, Qi et al. 2011) with copyright permission.

Crosslinked LbL FO membranes had higher water permeability and better magnesium chloride rejection compared to non-cross-linked LbL FO membranes. On the other hand, LbL FO water flux as high as 100 L/m² h was achieved using 3 M MgCl₂ draw solution and distilled water as the feed solution in the AL-DS orientation. This clearly showed that the potential of cross-linked FO LbL to be used in the high flux FO application.

As shown in Fig. 2-10, Qi et al. also reported a novel double-skinned LbL FO membrane and studied their FO performance and membrane fouling (Qi, Qiu et al. 2012). In general, the bottom skin layer showed a lower hydraulic resistance and inferior solute rejection compared to the top skin layer when the same number of polyelectrolytes were deposited.

Fig. 2-10 Schematic illustration of the double-skinned xLbL FO membranes. This figure was reproduced from Ref. (Qi, Qiu et al. 2012) with copyright permission.

More recently, Duong et al. demonstrated that LbL polyelectrode membrane can achieve reasonable NaCl rejection by using double cross-linking method (Duong, Zuo et al. 2013) as shown in Fig. 2-11.

Fig. 2-11 Schematic illustration of layer-by-layer assembly and chemical crosslinking by glutaraldehyde and UV crosslinking. This figure was reproduced from Ref. (Duong, Zuo et al. 2013) with copyright permission.

The highly crosslinking LbL FO membranes were achieved firstly using glutaraldehyde chemical crosslinking followed by UV photo-crosslinking. Both the deposition time and salt concentration on the FO performance were studied to optimize the LbL condition. The PAH/PSS layers were cross-linked by GA and UV at different conditions and they reported that the FO water flux of $10.9 \text{ L/m}^2 \text{ h}$ and reverse salt flux of 8 GMH were achieved when using 0.3 M NaCl as the draw solution and distilled water as the feed water.

More recently, LbL hollow fiber membrane was reported by Wang et al. by using PES hollow fibre substrate followed by polyelectrolyte deposition (Liu, Fang et al. 2013) as shown in Fig. 2-12. In this work, different number of polyelectrolyte LbL layer was systematically studied and their FO performance was evaluated by using a variety of draw solution and deionized water as the feed solution. Excellent water flux and low ratio of salt flux to water flux can be achieved by

using low concentration of draw solution (Liu, Fang et al. 2013). These results suggested that LbL hollow fiber membrane could be potentially used for FO application and significantly reduce the regeneration of draw solution.

Fig. 2-12 (Left) Cross-section morphology of PES hollow fiber membrane substrate and (right) schematic illustration of layer-by-layer assembly on hollow fiber membrane. This figure was reproduced from Ref. (Liu, Fang et al. 2013) with copyright permission.

2.2.4. Rejection layer formed by post-modification

In 2011, Lauren et al. firstly showed that positively charged NF-like hollow fiber FO membranes with a positively charged rejection layer (Setiawan, Wang et al. 2011). The porous FO substrates were fabricated by wet-spinning of the polyamide-imide (PAI) dope solution followed by chemical post-modification with the polyethyleneimine (PEI) aqueous solution. The ATR-FTIR measurement proved that the reaction between PAI and PEI due to the disappearance of the peak of imide group while the enhancement of the peak of amide group. Based on the ATR-FTIR measurement, they proposed a feasible mechanism as shown in Fig. 2-13. It is important to note that the NF-like positively charged FO hollow fiber membranes have a double electric repulsions to the salt transport through the membrane in the AL-FS orientation, which resulted in high salt rejection. On the other hand, the positively charged NF-like rejection layer promote the salt transfer in the AL-DS orientation.

Fig. 2-13 Proposed mechanism between polyamide-imide and the polyethyleneimine. This figure was reproduced from Ref. (Setiawan, Wang et al. 2011) with copyright permission.

In 2012, Qiu et al. reported that the same method could be used to fabricate positively charged NF-like flat sheet FO membranes using polyamide-imide (PAI) to fabricate FO substrate via phase inversion followed by chemical post-modification with polyethyleneimine to form a NF-like thin salt rejection layer (Qiu, Setiawan et al. 2012) as shown in Fig. 2-14. The chemical post-modification was carried out by soaking the PAI substrate into the PEI aqueous solution for 120 minutes. The NF-like FO membranes showed high FO water and low reverse solute flux, which can be attributed to the formation of tight rejection layer on top of the PAI substrate.

Fig. 2-14 Morphology of the NF-like FO membranes after the chemical post-modification. This figure was reproduced from Ref. (Qiu, Setiawan et al. 2012) with copyright permission.

2.2.5. Thin film inorganic (TFI) membranes

In 2013, You *et al.* firstly reported a new type of FO membranes with inorganic rejection layer, they called this type of FO membranes as thin film inorganic (TFI) membranes (You, Tang et al. 2013) as shown in Fig. 2-15. TFI membranes consisted of microporous silica xerogels as rejection layer while stainless steel mesh as the supporting layer. The rejection layer was fabricated using layer-by-layer self assembly of microporous silica xerogels onto the commercial stainless steel mesh. Compared to the commercial CTA FO membranes, TFI FO membranes showed better FO performance, which could be attributed to thin-film microporous structure and hence reducing the effect of the internal concentration polarization. It is important to note that both the mechanical and chemical strength of TFI FO membranes is much better than the polymeric FO membranes.

Fig. 2-15 Schematic illustration of thin film inorganic (TFI) FO membranes. This figure was reproduced from Ref. (You, Tang et al. 2013) with copyright permission.

2.3 Concentration polarization

Although the aforementioned osmotic-driven FO membranes have a range of potential applications, there are several critical challenges have yet to be fully solved. One of the most challenging problems of FO membrane processes is the concentration polarization (CP), a prevalent problem occurred in both pressure-driven membrane processes, such as ultrafiltration (UF) and nanofiltration (NF) and osmotic-driven membrane processes, such as forward osmosis (FO) and pressure-retarded osmosis (PRO), which will significantly reduce the effective driving force across the membranes. In osmotic-driven membrane processes, CP can be further classified into (1) external concentration polarization (ECP), which occurs within the boundary layer between the bulk solution and membrane surface; (2) internal concentration polarization, which occurs within the porous supporting layer of the asymmetric FO membranes.

2.3.1 External concentration polarization (ECP) and modelling

The water flux in osmotic-driven membrane processes can be described by a general equation as shown in Eq (1).

$$J_v = A(\sigma\Delta\pi - \Delta P) \quad (1)$$

Where J_v is the FO water flux, A is the water permeability constant of the membrane, σ is the reflection coefficient, $\Delta\pi$ is the osmotic pressure difference across the membrane and ΔP is the applied hydraulic pressure difference across the membrane.

Assuming that an osmotic pressure gradient is created across an ideal FO membrane (ΔP is equal to 0), which is a thin symmetric membrane and completely retaining all the solute (i.e. $R = 100\%$ and $\sigma = 1$), the FO water flux can be simplified into Equation (2) in the absence of ECP (Fig. 2-16).

$$J_v = A(\pi_{draw} - \pi_{feed}) \quad (2)$$

Fig. 2-16 The FO water flux in the absence of ECP and ICP

In osmotic-driven membrane processes, a build-up of solute at the membrane surface occurs when the water molecules diffuse through the membranes (convective flow). This phenomenon is called external concentration polarization, which slightly decreases the osmotic driving force and thus reduces FO water flux (Fig. 2-17). External concentration polarization can be further

divided into (1) concentrative external concentration polarization (CECP), which occurs at the membrane surface facing feed solution; and (2) dilutive external concentration polarization (DECP), which occurs at the membrane surface facing draw solution. CECP is similar to the ECP in pressure-driven membrane processes; where feed solution flows through the membrane while rejected solute is accumulated at the membrane surface and hence decrease FO water flux due to reduce the osmotic driving force. On the other hand, feed solution that passes through the membrane will dilute the draw solution within the boundary layer, which results in the DECP phenomenon at the draw solution side.

Fig. 2-17 The FO water flux in the presence of ECP

Therefore, the effective osmotic pressures across the membrane in the presence of ECP should be expressed as

$$J_v = A(\pi_{m-draw} - \pi_{m-feed}) \quad (3)$$

The adverse effect of both CECP and DECP on the FO water flux can be reduced by increasing cross-flow velocity (CFV) or using flow promoters, such as spacers to create turbulence or eddy at the membrane surface. This is particular important for the high flux FO membranes because of the effect of ECP (i.e. the concentration polarization modulus) on decreasing FO flux is an exponential function as shown in Equation (4).

$$\frac{C_m}{C_b} = \exp\left(\frac{J_v}{k_m}\right) \quad (4)$$

Where C_m and C_b are the concentrations of solute at the membrane surface and in the bulk solution, J_v is the FO water flux, and k_m is the mass transfer coefficient. The ratio of $\frac{C_m}{C_b}$ is defined as concentration polarization modulus, which indicate the severity of the ECP on the membrane surface. The concentration of a solution can be used to calculate osmotic pressure of a solution using the van't Hoff equation:

$$\pi = \beta C_i R_g T \quad (5)$$

Where β is the dimensionless van't Hoff correction factor of solute that can be dissociated into ions in a solution (e.g. NaCl), C_i is the molar concentration of solute i solution, R_g is the universal gas constant, and T is the absolute temperature. When the concentration of the solution

is relatively low, the osmotic pressures can be used to replace the concentrations in the Equation 3 and thus the CECF modulus at the feed solution and DECF at the draw solution can be expressed as

$$\frac{\pi_{m-feed}}{\pi_{b-feed}} = \exp\left(\frac{J_v}{k_{feed}}\right) \text{ for CECF} \quad (6)$$

$$\frac{\pi_{m-draw}}{\pi_{b-draw}} = \exp\left(-\frac{J_v}{k_{draw}}\right) \text{ for DECF} \quad (7)$$

Where k_{feed} and k_{draw} are the mass transfer coefficient at the feed solution side and at the draw solution side, π_{m-feed} and π_{m-draw} are the osmotic pressures on the membrane surface at the feed solution side and at the draw solution side, and π_{b-feed} and π_{b-draw} are the osmotic pressures of the feed solution and the draw solution in the bulk.

By substituting Equations (6) and (7) in to Equation (3):

$$J_v = A \left(\pi_{b-draw} \exp\left(-\frac{J_v}{k_{draw}}\right) - \pi_{b-feed} \exp\left(\frac{J_v}{k_{feed}}\right) \right) \quad (8)$$

It is important to realize that there are several assumptions in this equation. First, the rejection of the ideal FO membrane is 100% and hence the solute permeability coefficient is equal to zero and the reflection coefficient is equal to one. Second, the mass transfer coefficient on the feed side is not equal to the mass transfer coefficients on the draw side because of the difference in the concentration gradient on each side. Last but not least, this model is based on the assumption that a thin symmetric membrane (i.e. cellulose triacetate FO membranes), and hence the application of this model is relatively limited. If an asymmetric FO membrane (i.e. thin film composite FO membrane) is used, then the effect of internal concentration polarization will be more important than the external concentration polarization.

2.3.2 *Internal concentration polarization (ICP)*

The main reason why traditional semi-permeable RO membranes cannot be used for FO application is because of the severe internal concentration polarization occurred inside the RO substrate layers (Loeb, Titelman et al. 1997, McCutcheon and Elimelech 2006, Tang, She et al. 2010), which significantly lower the theoretical osmotic pressure across the semi-permeable FO membranes. Unlike the external concentration polarization (ECP) occurred on the surface of pressure-driven membranes, such as reverse osmosis (RO) and nanofiltration (NF), which could be reduced by increasing flow rate, the effect of ICP occurred inside the substrate layer, which could not be reduced by increasing cross-flow or hydrodynamic condition. Therefore, the effective osmotic pressure is significantly lower than the bulk osmotic pressure difference across the semi-permeable FO membranes due to the effect of ICP in both active-layer-facing-draw-solution (AL-DS) and active-layer-facing-feed-solution (AL-FS) orientation (Fig. 2-16).

In AL-DS orientation, the convective FO water flux will cause the buildup of solute inside the FO substrate layer, which is referred to as concentrative ICP. In AL-FS orientation, the draw solution was diluted by the convective FO water flux at the draw solution-active layer interface, which is referred to dilutive ICP. Both dilutive and concentrative ICP will considerably reduce the effective osmotic pressure across the semi-permeable membranes and causing the FO water flux lower than my expectation.

Fig. 2-18 Schematic illustration of (a) concentrative ICP in AL-DS orientation and (b) dilutive ICP in AL-FS orientation across a semi-permeable FO membrane. This figure was reproduced from Ref. (Cath, Childress et al. 2006) with copyright permission.

2.4. Nanomaterials-based mixed matrix membrane in osmotic-driven membrane processes

In 2013, Ma et al. has firstly reported on the fabrication of zeolite-based nanocomposite membrane as FO substrate for reducing ICP as shown in Fig. 2-17 (Ma, Wei et al. 2013). They found that the addition of nano-sized zeolite particles into the polysulfone (PSf) substrate can significantly increase the water permeability for its selective layer. The zeolite-based nanocomposite substrate was prepared by using phase inversion method while the selective layer was fabricated by using interfacial polymerization method. The nanocomposite FO membranes with 0.5 wt% loading of zeolite nanoparticle showed higher water permeability compared to the traditional thin film composite membranes, which may be ascribed to the embedment of porous zeolite nanoparticle into the FO substrate and hence mitigate the effect of ICP of the FO

membrane substrate. For the first time, the addition of porous nanomaterials into the FO substrate was demonstrated as an effective way to control ICP.

Fig. 2-19 Schematic illustration of zeolite-based mixed matrix FO membranes and their FO performance. This figure was reproduced from Ref. (Ma, Wei et al. 2013) with copyright permission.

Very recently, Wang et al. reported that the addition of multi-walled carbon nanotube (MWCNT) into the polyethersulfone (PES) to fabricate FO substrate can improve the overall FO performance. The nanocomposite PES-MWCNT substrate was also prepared by the phase inversion method while the polyamide salt rejection layer was prepared by conventional interfacial polymerization. It is noteworthy that the tensile strength of the nanocomposite PES-MWCNT FO substrate was improved compared to the control PES substrate. The optimal nanocomposite FO membrane with 2.0wt% of MWCNT resulted in higher water permeability and better salt rejection compared to the control and commercial FO membranes. This can be attributed to the smooth selective layer and more open interior pore structure, which reduce the effect of internal concentration polarization.

Later, Emadzadeh et al. showed that the addition of titanium oxide (TiO_2) nanoparticles into the polysulfone (PSf) to prepare FO substrate can also enhance the overall FO performance (Emadzadeh, Lau et al. , Emadzadeh, Lau et al. 2014) as shown in Fig. 2-18. The PSf- TiO_2 nanocomposite FO substrates were also prepared by the phase inversion method while the polyamide selective layer was formed by interfacial polymerization between TMC and MPD. Upon addition of TiO_2 , both surface hydrophilicity and membrane porosity of the FO substrate were improved and finger-like pores were observed when increasing the loading of TiO_2 . Compared to the control thin film composite (TFC) membrane, the nanocomposite FO membranes with 0.5 wt% TiO_2 showed higher FO water flux and lower reverse solute flux. The enhancement of overall FO performance could be attributed to the addition of TiO_2 nanoparticles into the FO substrate, which lower the structural parameter and hence reduce the effect of internal concentration polarization.

Fig. 2-20 Schematic illustration of titanium dioxide-based mixed matrix FO membranes and their FO performance. This figure was reproduced from Ref. (Emadzadeh, Lau et al. 2014) with copyright permission.

2.5 Hypothesis/strategy

Recently, mixed matrix membrane (MMM) is an emerging research topic under membrane development area. Several membrane properties, such as permeability, selectivity, thermal and mechanical stability, can be potentially enhanced by incorporating nanomaterials such as zeolite (Jeong, Hoek et al. 2007, Lind, Ghosh et al. 2009, Lind, Jeong et al. 2009, Fathizadeh, Aroujalian et al. 2011, Ma, Wei et al. 2012, Ma, Wei et al. 2013), silica nanoparticle (Jadav and Singh 2009, Huang, Zhang et al. 2012, Wu, Tang et al. 2013), titanium oxide nanoparticle (Lee, Im et al. 2008), and silver nanoparticle (Lee, Kim et al. 2007, Kim, Hwang et al. 2012). For example, non-porous silica nanoparticle, which has a variety of advantages, such as high thermal and chemical stability, (Dai, Yang et al. 2012, Liu, Wang et al. 2012) has been reported to increase gas permeability without significantly decrease the selectivity of mixed matrix gas

separation membranes (Jang, Kim et al. 2011, Sharif, Koolivand et al. 2012, Shen and Lua 2012). The performance enhancement was believed due to the good compatibility between the polymer and the non-porous silica nanoparticle and they could be potentially used to fabricate not only gas separation, but also ultrafiltration and reverse osmosis MMM for industrial application. However, osmotic-driven membranes are strongly affected by ICP different from pressure-driven membranes. The hypothesis is that the mixed matrix strategy can be potentially effective in enhancing the mass transfer efficiency of FO membrane substrate and thus in controlling ICP. Nevertheless, the utilization of porous nanomaterials as the fillers for the preparation of mixed matrix FO membranes has not been reported in the open literature.

In Part 1, the main goal is to improve FO water flux by using porous nanomaterials-based mixed matrix membranes and porous matrix membranes as FO substrate as shown in Fig. 2-19. For the strategy of mixed matrix membranes (MMMs), SG particles were chosen as fillers for the fabrication of MMMs because of their high BET surface area, neutral pH, low trace metal content, tight particle size distribution, and different pore size are available. Firstly, SG particles were embedded into polyacrylonitrile (PAN) to cast MMMs with various SG loadings. Next, the effect of different pore size of SG particle will also be studied in a comprehensive way. Finally, the surface morphology, cross-section structure, intrinsic separation properties and FO performance of these SG-based mixed matrix FO membranes will be thoroughly investigated. For the study of porous matrix membranes, MOF particles were selected as fillers for the fabrication of PMMs because of their high water solubility, low solvent solubility, and commercial availability. Firstly, three different types of MOF particles were dispersed into PAN solution followed by non-solvent induced phase separation to obtain the PMM using water as the

mild etching solution. The relationship of bond dissociation energy (BDE) between metal ions and organic linker of MOF particles were systematically studied to establish the selection rule of fillers for PMMs.

Fig. 2-21 Schematic comparison between (a) commercial FO substrate vs mixed matrix substrate; and (b) mixed matrix substrate vs porous matrix substrate.

Chapter 3

Methodology

3.1 Materials and Chemicals

3.1.1 General materials and chemicals

All chemicals and materials were used as received unless otherwise stated. Polyacrylonitrile (PAN, Sigma–Aldrich, weight-averaged molecular weight $M_w \sim 150,000$, Lot# MKBD6325V) was used for the preparation of polymer dope solution due to its ease of processing, good chemical resistance, and reasonable mechanical strength. (Fu, Zhang et al. , Saren, Qiu et al. 2011). *N,N*-dimethylformamide (DMF, purity $\geq 99.8\%$, Merck) was used as solvent to dissolve PAN while lithium chloride (anhydrous LiCl, Merck) was added as the pore former to promote the formation of finger-like pore, respectively. Sodium hydroxide (anhydrous NaOH, purity $\geq 98\%$, Merck) was used to prepare alkali solution for base treatment of FO substrate to enhance membrane hydrophilicity and surface charge.

Silica gel (SiliaFlash® Irregular Silica Gels, SiliCycle Inc., Canada) was used as filler for the preparation of mixed matrix membranes due to its high thermal and chemical stability, high surface area, neutral pH, non-toxic, tunable particle and pore size, readily available in kilogram scale, commercial viable and well characterized properties. (Dai, Yang et al. 2012, Liu, Wang et al. 2012) According to the product characteristics provided by the SiliCycle, the particle size and pore size of silica gel ranged from 40 to 63 μm and 40 to 300 Å respectively. The measured particle size distribution of silica gel particle is shown in Fig. 3-1 and the experimental result is consistent with the information of silica particle size distribution provided by Silicycle Company.

Fig. 3-1 The particle size distribution of silica gel particles ranging from 40 -63 μm .

On the other hand, Basolite A100 (Aluminium terephthalate or MIL 53, product # 688738, produced by BASF, Sigma-Aldrich, Lot#STBC4615V), Basolite C300 (Copper benzene-1,3,5-tricarboxylate or HKUST-1, product # 688614, produced by BASF, Sigma-Aldrich, Lot#STBC4614V), Basolite F300 (Iron benzene-1,3,5-tricarboxylate or Fe-BTC, product # 690872, produced by BASF, Sigma-Aldrich, Lot#S61151V) were used as filler for the preparation of porous matrix membranes due to their relatively lower water stability compared to silica gel. These nomenclatures of metal-organic framework (MOF) particles are based on the information provided by the manufacturer. The letter indicates the metal ion of MOF particles (A: aluminium, Al, C: copper, Cu and F: iron, Fe), and the number represents their organic ligands

(100: terephthalate and 300: benzene-1,3,5-tricarboxylate). All types of fillers were used as received.

For the layer-by-layer (LbL) self-assembly, poly(allylamine hydrochloride) (PAH, $M_w \sim 112,000 - 200,000$, Polyscience, Lot# 639458) was used as positively charged polyelectrolyte and poly(sodium 4-styrene-sulfonate) (PSS, $M_w \sim 70,000$, 30 wt.% in H_2O , Sigma–Aldrich, Batch# 09622HH) was used as negatively charged polyelectrolyte for the formation of rejection layer. The ionic strength of the polyelectrolyte solution was controlled by adding sodium chloride (NaCl, 99%, Merck). Glutaraldehyde (GA, 25% in water, Sigma–Aldrich) was used as a coupling reagent to fabricate a cross-linked layer-by-layer (xLbL) selective layer on top of the FO substrate, which have relatively high FO water flux and reasonable solute rejection towards divalent ions. Therefore, they might have many potential applications in biomass concentration, food processing, and etc (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Qi, Qiu et al. 2012, Duong, Zuo et al. 2013).

3.2 Fabrication Methods

3.2.1 Fabrication of FO Membranes

3.2.1.1 Fabrication of FO substrate layer

The detailed procedure for the fabrication of SG-based FO nanocomposite substrates can be found elsewhere (Lee, Qi et al. 2014). To achieve good dispersion of the silica gel particles, different amounts (0.0 wt.%, 0.25 wt.%, 0.50 wt.%, 1.0 wt.% and 2.0 wt.% based on the dope solution) of dry filler particles were added into DMF followed by ultra-sonication of the solution for 1 h. The time of ultra-sonication can be adjusted until a good dispersion of particle is

observed. The upper bound of silica gel in the dope solution is 2.0 wt.% because further increasing the amount of silica gel might result in particle aggregation inside the membranes, which can be observed from optical microscopy and more details will be discussed in Chapter 4. PAN (18 wt.%) and LiCl (2 wt.%) were then added into the DMF solution followed by stirring for at least 24 h at 60 °C until a homogeneous solution was obtained. The polymer solution was then cooled down to room temperature overnight without stirring to completely remove any gas bubbles. A casting knife was set at a gate height of 150 µm (Elcometer Pte. Ltd., Asia) was used to cast the polymer solution onto a clean glass plate. The thin polymer film was then solidified in a coagulation water bath at room temperature. The resulting FO substrate was then immersed into a 1.5 M NaOH solution for 1.5 h to partially hydrolyze the surface of FO substrate (Qiu, Qi et al. 2011).

3.2.1.2 Fabrication of FO rejection layer

The detailed procedure for xLbL rejection layer preparation can be found elsewhere (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Qi, Li et al. 2012, Qi, Qiu et al. 2012). Briefly, the rejection layer was formed by alternatively soaking the FO nanocomposite substrate into the PAH and PSS solution for 15 min followed by soaking the substrate into the DI water after each polyelectrolyte soaking step. Based on the optimization of xLbL layers performed in previous studies (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011), the PAH/PSS treatment was repeated three times to prepare a rejection layer with reasonable rejection properties for FO applications. xLbL FO membranes were then cross-linked by soaking the membranes in a 0.1 wt.% GA solution for 30 min followed by soaking with DI water for 5 min to remove excess GA. To give an example, the resulting FO membranes were designated as (M0.00, M0.25, M0.50, M1.00, and M2.00

based on the wt.% of SG filler). Table 3-1 shows the compositions of polymer dope solution for SG-based FO substrates and active layer.

Table 3-1 Flat-sheet SG-based mixed matrix membranes with different SG loading.

Membrane	Substrate				Active Layer	
	PAN (wt.%)	DMF (wt.%)	LiCl (wt.%)	SG (wt.%)	PAH (g/L)	PSS (g/L)
M0.00	18	80.00	2.0	0.00	1.0	1.0
M0.25	18	79.75	2.0	0.25	1.0	1.0
M0.50	18	79.50	2.0	0.50	1.0	1.0
M1.00	18	79.00	2.0	1.00	1.0	1.0
M2.00	18	78.00	2.0	2.00	1.0	1.0

For porous matrix membrane, MOF-based FO membranes were labelled as Control, PMM_{F300}, PMM_{A100}, and PMM_{C300}, respectively, according to the type of MOF particles used. Table 3-2 shows the composition of polymer dope solution for MOF-based FO substrates and active layer.

Table 3-2 MOF-based porous matrix membranes with different types of MOFs.

Membrane	Substrate				Active Layer	
	PAN	DMF	LiCl	MOF	PAH	PSS
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(g/L)	(g/L)
Control	18	80	2.0	0.0	1.0	1.0
PMM _{F300}	18	79	2.0	1.0	1.0	1.0
PMM _{A100}	18	79	2.0	1.0	1.0	1.0
PMM _{C300}	18	79	2.0	1.0	1.0	1.0

3.3 Characterization Methods

3.3.1 Characterization of filler particles

Micromeritics ASAP 2020 instrument (USA) was used to obtain the nitrogen sorption isotherm of filler particles at $-196\text{ }^{\circ}\text{C}$ (Huang, Zhang et al. 2012). The sample was degassed in a vacuum oven for 6 h at $200\text{ }^{\circ}\text{C}$ to remove the gases and vapors absorbed on the sample surface before the measurement. By plotting the volume of nitrogen adsorption against the relative pressure, the specific surface area, pore diameter, and pore volume of silica gel was calculated using multiple point Brunauer-Emmett-Teller (BET) equation.

$$\frac{1}{\left[V_a \left(\frac{P_0}{P} - 1 \right) \right]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

where V_a is volume of gas absorbed at standard temperature and pressure and V_m is volume of gas absorbed at standard temperature and pressure to produce an apparent monolayer on the sample surface. P is partial vapor pressure of adsorbed gas in equilibrium with the surface at 77.4K and P_0 is saturated pressure of adsorbed gas. C is dimensionless constant that is related to the enthalpy of adsorption of the adsorbed gas on the powder sample. To give an example, the silica gel with different pore size were named as SG_{F40} , SG_{F60} , SG_{F90} , and SG_{F300} and their nominal pore size, measured pore size, and BET surface area were summarized into Table 3-3.

Table 3-3 The properties of different pore size and BET surface area of silica gel filler.

SG ^a	Nominal Pore Size (Å)	Measured Pore Size (Å)	BET Surface Area (m ² / g)
SG _{F40}	40	58	433
SG _{F60}	60	59	424
SG _{F90}	90	106	318
SG _{F300}	300	173	68

^a All the SG particles have comparable particle sizes, with each ranging from 40 - 63µm.

3.3.2 Characterization of FO membranes

The surface and cross section morphological structures of the prepared FO membranes were characterized by field emission scanning electron microscope (FESEM, JSM-7600F, USA) (Qi, Li et al. 2012). A freeze-dryer was used to dry all the membranes samples at room temperature for at least 12 h followed by coated with a uniform platinum layer before observation. Element mapping was detected with the FESEM microscope equipped with energy-dispersive X-ray spectroscopy (EDX) (Ma, Wei et al. 2012). The surface roughness of the membrane samples was tested by atomic force microscope (AFM, Park Systems XE-100, Korea). Attenuated total reflection - fourier transform infrared spectra (ATR-FTIR, Shimadzu Prestige-21, Japan) was used to confirm the functional group on the membranes. OCA contact angle goniometer system (DataPhysics Instruments GmbH, Germany) was used to measure contact angles of the membranes and the measurement was repeated 8 times on 3 different membrane samples with the elimination of the highest and lowest two values before averaging and calculating the standard deviation.

In order to determine the residual amount of MOFs inside the PMM membrane, the PMM samples were digested with a mixture of concentrated nitric acid and concentrated hydrochloric acid in the ratio of 3:1 for 6 hours followed by topping up the concentrated acid solution to 10 mL with water. By measuring the dry mass (m_{dry}) and wet mass (m_{wet}) of membrane samples, the membrane porosity (ε) can be calculated according to following equation (Sukitpaneenit and Chung 2009, Wei, Qiu et al. 2011):

$$\varepsilon = \frac{(m_{wet} - m_{dry}) / \rho_w}{(m_{wet} - m_{dry}) / \rho_w + m_{dry} / \rho_m} \times 100\%$$

where ρ_w and ρ_m are the density of water (1.0 g/cm³) and the density of PAN (1.18 g/cm³). It was assumed that all the pores in the membrane and silica gel were completely filled with water.

The methods for determining intrinsic separation properties such as pure water permeability, salt rejection, and salt permeability can be found elsewhere (Tang, She et al. 2010, Wei, Qiu et al. 2011). Briefly, all the membranes were tested in a pressurized cross flow filtration setup using an applied pressure of 5 bars and the feed water temperature remained at 25 °C by a circulating cooling system. The effective membrane area was 42 cm². A relatively high cross flow velocity of 20 cm/s and diamond-shaped feed spacers (34 mils) were used to reduce the concentration polarization of feed solutes. By measuring the amount of permeate, the water permeability coefficient A of membranes was determined. The rejection R were determined by conductivity measurements (Ultra Meter IITM 4P, Myron L Company, CA) with the difference between the feed water (5 mM MgCl₂) and permeate water. The dextran rejection was determined by gel permeation chromatography (GPC, Varian Company, USA) with the difference between the feed

water and permeates water. The reported values of A and R are the average value of at least three replicates and the solute permeability coefficient B was calculated from the rejection and the permeate flux. The choice of parameters used for determining the intrinsic separation properties are selected based on their importance in the evaluation of overall membrane performance. The values of A , R , and B were calculated according to the following equations:

$$A = \frac{J_v}{\Delta p}$$

where J_v is the permeate water flux and Δp is the applied pressure.

$$R = 1 - \frac{C_p}{C_f}$$

where C_p is the conductivity of permeate and C_f is the conductivity of feed.

$$B = J_v \left(\frac{1}{R} - 1 \right)$$

where J_v is the permeate water flux and R is the salt rejection.

For the evaluation of FO performance, a small piece of membrane with the effective membrane area of 60 cm² was used in each FO test for both the active-layer-facing-DS (AL-DS) and active-layer-facing-FS (AL-FS) orientations. Concentrated MgCl₂ solutions (0.1, 0.3, 0.5, 1.0, or 3.0 M) were used as draw solution (DS) and the feed solution (FS) was either 10 or 100 mM NaCl solution and DI water. The range of draw solution and feed solution concentrations were chosen based on the concentration of solute from fresh water to seawater brine. NaCl was selected as the feed solute due to its pervasive existence in seawater and wastewater. On the other hand, MgCl₂ was selected as the draw solute because of the MgCl₂ has high water solubility and high diffusion coefficient (Achilli, Cath et al. 2010, Zhao, Zou et al. 2012). The structural parameter (*S* value) of the FO membranes was determined by using the equation in the previous study (Saren, Qiu et al. 2011, Tiraferri, Yip et al. 2013):

$$S = \frac{D}{J_v} \ln \left\{ \frac{C_{draw} - J_v / (A \cdot \beta R_g T) + J_s / J_v}{C_{feed} + J_s / J_v} \right\} \quad (\text{AL-DS orientation})$$

$$S = \frac{D}{J_v} \ln \left\{ \frac{C_{draw} + J_s / J_v}{C_{feed} + J_v / (A \cdot \beta R_g T) + J_s / J_v} \right\} \quad (\text{AL-FS orientation})$$

where *D* is the solute diffusion coefficient; *S* is the structural parameter of the support layer; *C_{draw}* and *C_{feed}* are the concentrations of draw solution and feed solution, *J_s* is the solute flux (determined from FO experiments); *β* is the van't Hoff coefficient; *R_g* is the universal gas constant; *T* is the absolute temperature.

Silica gel-based mixed matrix forward osmosis membranes

Chapter 4: Energy-dispersive X-ray spectroscopy (EDX) was used for the image and it is showing the presence of silica gel (i.e. the Si element) in the FO support layer.

Chapter 4

Synthesis and characterization of silica gel - based mixed matrix forward osmosis membranes based on layer-by-layer assembly

4.1 Introduction

As mentioned in Chapter 2, forward osmosis (FO) can potentially reduce the energy consumption of current technologies by up to thirty percent by using the osmotic pressure difference between a low concentration feed solution (FS) and a high concentration draw solution (DS) as the driving force to move water through a semi-permeable membrane (Cath, Childress et al. 2006, Zhao, Zou et al. 2012). Compared to high pressure-driven reverse osmosis (RO) and nanofiltration (NF) membrane processes, FO process has been reported to have several advantages including (1) low energy consumption and higher fouling resistance, (2) high rejection of a variety of solutes, and (3) low operating cost because of the utilization of high osmotic pressure difference instead of the high pressure difference across the membranes as the driving force (McCutcheon, McGinnis et al. 2005, Achilli, Cath et al. 2009, Lee, Boo et al. 2010). Hence, FO process has been employed in a wide range of applications such as wastewater treatment (Holloway, Childress et al. 2007, Cornelissen, Harmsen et al. 2008, Achilli, Cath et al. 2009, Lay, Zhang et al. 2011), seawater desalination (Kessler and Moody 1976, McCutcheon, McGinnis et al. 2005, McGinnis and Elimelech 2007), food processing (Petrotos, Quantick et al. 1998, Torreggiani and Bertolo 2004), and valuable product concentration (Torreggiani and Bertolo 2004, Zou, Gu et al. 2011).

Comprehensive reviews of FO technology have been provided by Cath et al. (Cath, Childress et al. 2006), Zhao et al. (Zhao, Zou et al. 2012), and Chung et al. (Chung, Li et al. 2012). Existing commercial FO membranes are based on triacetate (CTA) chemistry and polyamide (PA) chemistry (Wei, Qiu et al. 2011). These membranes have relatively low water permeability and are prone to hydrolysis and biodegradation. Therefore, one of the highest priorities in the research area of FO is to develop high performance FO membranes (Chou, Shi et al. 2010, Su, Yang et al. 2010, Wang, Shi et al. 2010, Yip, Tiraferri et al. 2010, Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Tiraferri, Yip et al. 2011, Wei, Liu et al. 2011, Wei, Qiu et al. 2011, Chou, Wang et al. 2012, Qi, Li et al. 2012, Qi, Qiu et al. 2012). Generally, FO membranes are synthesized by phase inversion method (Yang, Wang et al. 2009, Sairam, Sereewatthanawut et al. 2011) followed by either interfacial polymerization (Wang, Shi et al. 2010, Yip, Tiraferri et al. 2010, Tiraferri, Yip et al. 2011, Wei, Liu et al. 2011, Wei, Qiu et al. 2011, Chou, Wang et al. 2012) or layer-by-layer (LbL) (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Qi, Li et al. 2012, Qi, Qiu et al. 2012), with a dense rejection layer on top of a porous support layer. One of the major limitations for these asymmetric composite FO membranes is the internal concentration polarization (ICP), a specific and serious problem in FO process (Loeb, Titelman et al. 1997, Cath, Childress et al. 2006, Gray, McCutcheon et al. 2006, McCutcheon and Elimelech 2006, Tang, She et al. 2010). In reality, the actual effective osmotic concentration difference will be significantly lower than the theoretical bulk osmotic concentration difference across the rejection layer (McCutcheon and Elimelech 2006). Concentrative ICP occurred when the active layer faces the draw solution (AL-DS), the solutes were concentrated in the membrane porous substrate. Alternatively, dilutive ICP occurred when the active layers face the feed solution (AL-FS), the draw solution was diluted in the support layer. In general, a smaller structural parameter S , which means thinner

membrane, smaller tortuosity, and higher porosity of membrane) can reduce the severity of ICP during the FO process.

Recently, mixed matrix membrane (MMM) is an emerging topic under membrane development area. Several membrane properties, such as permeability, selectivity, thermal and mechanical stability, can be potentially enhanced by incorporating nanomaterials such as zeolite (Jeong, Hoek et al. 2007, Lind, Ghosh et al. 2009, Lind, Jeong et al. 2009, Fathizadeh, Aroujalian et al. 2011, Ma, Wei et al. 2012, Ma, Wei et al. 2013), silica nanoparticle (Jadav and Singh 2009, Huang, Zhang et al. 2012, Wu, Tang et al. 2013), titanium oxide nanoparticle (Lee, Im et al. 2008), and silver nanoparticle (Lee, Kim et al. 2007, Kim, Hwang et al. 2012, Liu, Qi et al. 2013). For example, silica nanoparticle, which has a variety of advantages such as high thermal and chemical stability, inexpensive and commercially viable, tunable particle and pore size (Dai, Yang et al. 2012, Liu, Wang et al. 2012), has been reported to increase gas permeability without significantly decrease the selectivity of mixed matrix membranes (Jang, Kim et al. 2011, Sharif, Koolivand et al. 2012, Shen and Lua 2012). The performance enhancement was believed due to the good compatibility between the polymer and the silica nanoparticle and they could be potentially used to fabricate not only gas separation, but also ultrafiltration and reverse osmosis MMM for industrial application. For example, addition of hydrophilic silica nanoparticles into a hydrophilic polymer such as cellulose triacetate will give a good compatibility due to the formation of hydrogen bonding (McCutcheon and Elimelech 2008). Unlike pressure-driven membranes, FO water flux is strongly affected by ICP. The mixed matrix approach can be potentially effective in enhancing the mass transfer efficiency of membrane substrate and thus in

controlling ICP. Nevertheless, the utilization of silica gel (SG) as the filler for the preparation of mixed matrix FO membranes has not been reported in the open literature.

The objective of current study is to increase membrane porosity and hence improve FO performance by using SG-based mixed matrix membranes as FO substrate layers. First of all, SG fillers were embedded into polyacrylonitrile (PAN) to cast MMMs with various SG loadings. The morphology, structure and performance of these SG-based mixed matrix FO membranes were systematically characterized. This is the first report systematically studying the synthesis and characterization of SG-based mixed matrix membranes for FO application based on layer-by-layer assembly.

4.2 Results and discussion

4.2.1 Characterization of silica gel particles

The FESEM image and the nitrogen adsorption and desorption isotherms showed that the SG particles are mono-dispersed micro-particles with a narrow particle size of ca. 60 μm and there are relatively ordered nano-pore channel (6 nm) in the particle (Fig. 4-1). The specific surface area for SG is 542 m^2/g calculated by using the Brunauer-Emmett-Teller (BET) method.

Fig. 4-1 Nitrogen sorption isotherm of silica gel and the inset is the FESEM micrographs of silica gel.

4.2.2 Characterization of physical and chemical properties of SG-based mixed matrix FO membranes

4.2.2.1 Morphology, thickness and porosity of SG-based mixed matrix FO membranes

Both top view and cross section images of pure PAN substrate (M0.00) and SG-based mixed matrix FO substrates (M1.00) were shown in Fig. 4-2 (a) to (d). Basically, no major difference was observed on the top substrate surface. The cross-sectional images (Fig. 4-2 (c) and (d)) showed that less pores were observed without the SG particle (M0.00) while more straight finger-like pores were observed with SG particles (M1.00). From Fig. 4-2 (e) and (f), the presence of SG was observed using FESEM and further confirmed by both EDX and FTIR analysis (Fig. 4-3).

Fig. 4-2 FESEM micrographs of the membranes substrate. (a) Top surface and (c) cross-section of M0.00 substrates; (b) top surface and (d) cross-section of M1.00 substrates; (e) and (f)

FESEM and EDX image of M1.00 substrate confirmed that SG particle was successfully incorporated into the membranes.

One potential explanation is that the hydrophilic SG filler might facilitate the formation of pores due to decreased interfacial energy between solvent (DMF) and water during phase inversion separation (Huang, Zhang et al. 2012). As a result, a highly porous substrate (porosity of >70% based on gravimetric measurement) was obtained as shown in Table 4-2. Substrate with high porosity and low tortuosity are generally favored in FO application to minimize structural parameter S . The overall thickness of membrane substrate was $\sim 55\ \mu\text{m}$, which is comparable to the thickness of commercial HTI FO membranes ($40 - 90\ \mu\text{m}$) but is significantly thinner than that of conventional TFC RO membranes ($150\ \mu\text{m}$) (Saren, Qiu et al. 2011). According to previous study, the thin cross-section, high porosity and straight pore can reduce the structural parameter of the FO membranes and thus to minimize their ICP (Wei, Liu et al. 2011, Wei, Qiu et al. 2011). In the current study, the optimal SG-based mixed matrix FO membranes (M1.00) had a relatively low S value ($0.25\ \text{mm}$, compared to $0.36\ \text{mm}$ for the pure PAN membrane M0.00).

Table 4-1 Membrane thickness, membrane porosity, surface roughness, and contact angle of SG-based mixed matrix FO membranes with different loading of silica gel.

Membrane	Membrane Thickness (μm)	Membrane Porosity ϵ (%)	Surface Roughness R_a (nm)	Contact Angle ($^\circ$)	Structural Parameter (mm)
M0.00	56 ± 1	67 ± 1	15 ± 1	34 ± 2	0.36 ± 0.03
M0.25	52 ± 1	73 ± 5	21 ± 2	28 ± 1	0.44 ± 0.01
M0.50	55 ± 1	78 ± 4	33 ± 3	26 ± 2	0.28 ± 0.02
M1.00	54 ± 1	79 ± 1	36 ± 8	30 ± 1	0.25 ± 0.01
M2.00	59 ± 1	80 ± 3	15 ± 1	33 ± 1	0.34 ± 0.01

4.2.2.2 ATR-FTIR spectra of SG-based mixed matrix FO membranes

Fig. 4-3 showed the ATR-FTIR spectra of the pure PAN membrane (M0.00) and the SG-based mixed matrix FO membranes (M2.00). The FTIR spectra of PAN and NaOH-treated PAN have been reported in Qiu et al. (Qiu, Qi et al. 2011) and Phuoc et al. (Duong, Zuo et al. 2013). For both of the membranes, the absorption peaks at 1560, which correspond to the $-\text{COONa}$ stretching. The presence of the $-\text{SO}_3$ group of the PSS polyelectrolyte at 1006, 1035, and 1126 cm^{-1} and $-\text{CH}=\text{N}-$ group of the PAH polyelectrolyte at 1627 cm^{-1} indicated that the xLbL film was successfully deposited onto the SG-based mixed matrix FO membranes. Furthermore, a new peak at $\sim 1050 \text{ cm}^{-1}$, which is attributed to the Si-OH stretching, indicates that the SG particles were successfully incorporated in the PAN membranes (Huang, Zhang et al. 2012). Its low peak intensity was likely due to the relatively low loading of silica (2 wt.%).

Fig. 4-3 FTIR spectra of pure PAN membranes (M0.00) and SG-based mixed matrix FO membrane (M2.00). A new peak at $\sim 1050\text{ cm}^{-1}$ was due to the Si-OH stretching of silica gel.

4.2.2.3 FESEM and AFM characterization of SG-based mixed matrix FO membranes

Top view of both FESEM and AFM of SG-based mixed matrix FO membranes after xLbL synthesis is shown in Fig. 4-4. As the loading of silica gel in the polymer dope solution increases, surface roughness of the SG-based mixed matrix FO membranes also increases. The AFM root-mean-square (RMS) roughness, which is an indication of the mean roughness height, was significantly increased from 15 nm (M0.00) to 36 nm (M1.00), which showed greater nodular appearance on the surface of SG-MMMs. This might be due to the presence of SG cause the variation of surface roughness of SG-based mixed matrix FO membranes under different

loading. However, the increased surface roughness may potentially affect the fouling propensity of the membrane (Gu, Wang et al. 2013, Wei, Qiu et al. 2013). There is no much difference between PAN and SG-based mixed matrix FO membranes in term of hydrophilicity and all of the membranes are quite hydrophilic with the contact angle of about 30°.

Fig. 4-4 FESEM and AFM characterization of (a) M0.00, (b) M0.25, (c) M0.50, (d) M1.00 and (e) M2.00.

4.2.3 Effect of SG loadings on intrinsic separation properties of SG-based mixed matrix FO membranes

The effect of SG loadings on intrinsic membrane separation properties, such as water permeability and salt rejection of SG-based mixed matrix FO membranes, was measured by using pressurized cross flow filtration test. The relationship between SG loading and water permeability of the SG-based mixed matrix FO membranes was shown in Fig. 4-5.

Fig. 4-5 Effect of different silica gel loading on (a) the pure water permeability of the membranes substrate after NaOH treatment, (b) the performance of RO after xLbL synthesis. (c) Optical images of the support layer and the particle size distribution ranging from 55 – 89 μm for

(ii) to (v). Testing conditions: DI water or 5 mM MgCl_2 as the feed solution; applied pressure: 5 bars, error bar was based on the standard deviation of 3 replicate measurements.

The water permeability of pure PAN substrate is $14.9 \text{ L/m}^2 \text{ h bar}$. With the increment of in SG loading, the SG-based mixed matrix FO substrate showed higher water permeability and an optimal of $24.5 \text{ L/m}^2 \text{ h bar}$ was attained for M1.00, which can be partially attributed to the nanoporous nature of the SG particles (Fig. 4-1). In addition, the SG particles may affect the phase inversion process to facilitate the formation of finger-like pore structure of the membranes due to the hydrophilic surface of SG fillers (Huang, Zhang et al. 2012). Further increasing SG loading to 2.0 wt.% had negative impacts on the SG-based mixed matrix FO membrane permeability, eg. $12.5 \text{ L/m}^2 \text{ h bar}$ for M2.00. This might be explained by increased risk of particle agglomeration at excessive SG loading as shown in Fig 4-5 (c), which lead to less effective water transport in the substrate (Shen, Ruan et al. 2011, Huang, Zhang et al. 2012).

As shown in Fig 4-5(b), SG-based mixed matrix FO membranes showed same trend to that the water permeability of FO substrate. The water permeability of M0.00 is $1.85 \text{ L/m}^2 \text{ h bar}$. With the increment of SG loading, the SG-based mixed matrix FO membranes showed higher water permeability and an optimal of $3.79 \text{ L/m}^2 \text{ h bar}$ was attained for M1.00. Further increasing SG loading to 2.0 wt.% had negative impacts on the SG-based mixed matrix FO membrane permeability, e.g. $2.26 \text{ L/m}^2 \text{ h bar}$ for M2.00. The current study showed reduced MgCl_2 rejection at increased SG loading, which might be due to the formation of a less tight rejection layer. The salt rejection decreased from initial 91% for M0.00 to 66% for M2.00, which resulted in a drastic

increase of B value from 2.6×10^{-7} m/s to 16.6×10^{-7} m/s. The ratio of solute permeability to water permeability (B/A ratio) also increased as the loadings of silica gel increased as shown in Table 4-3. Further study is needed to optimize the B/A ratio in order to reduce solute reverse diffusion and to achieve a better performance FO processes (Cath, Childress et al. 2006, Zhao, Zou et al. 2012).

Table 4-2 Intrinsic separation properties of SG-based mixed matrix FO membranes with different silica gel loading^a.

Membrane	Water permeability after NaOH treatment ^b	Water permeability A after xLbL synthesis ^b		MgCl ₂ Rejection ^c (%)	Salt Permeability B ^c (×10 ⁻⁷ m/s)	B/A ^c (kPa)
	(L/m ² h bar)	(L/m ² h bar)	(×10 ⁻¹² m/s Pa)			
M0.00	14.9 ± 0.4	1.85 ± 0.10	5.2 ± 0.3	91	2.6 ± 0.4	49.6
M0.25	16.3 ± 0.9	3.50 ± 0.11	9.7 ± 0.3	84	9.0 ± 1.6	92.4
M0.50	22.3 ± 0.4	3.35 ± 0.08	9.3 ± 0.2	83	9.6 ± 1.6	102
M1.00	24.5 ± 0.9	3.79 ± 0.17	10.5 ± 0.5	76	16.9 ± 1.1	161
M2.00	12.1 ± 0.7	2.26 ± 0.13	6.3 ± 0.4	66	16.6 ± 5.8	262

^a The experiment errors are reported as the standard deviation of at least 3 repeated measurements.

^b Measured at an applied pressure of 5 bar with ultrapure water as feed water in the pressurized cross flow filtration testing mode.

^c Measured at an applied pressure of 5 bar with 5 mM MgCl₂ as feed water in the pressurized cross flow filtration testing mode.

4.2.4 FO performance

4.2.4.1 Effect of SG loadings on FO performance of SG-based mixed matrix FO membranes

Fig. 4-6 demonstrates different SG loadings on FO performance of SG-based mixed matrix FO membranes. By using 0.5 M MgCl₂ as DS and DI water as FS, the FO water flux is tested for

both AL-DS and AL-FS orientation. Without SG loading, the xLbL membrane (M0.00) had an FO water flux of 40.8 L/m² h in AL-DS and 17.5 L/m² h in AL-FS.

Fig. 4-6 Effect of silica gel loading on (a) FO water flux, and (b) ratio of solute flux over water flux of SG-based mixed matrix FO membranes. Testing conditions: 0.5 M MgCl₂ as the draw solution and DI water as the feed solution, error bar was based on the standard deviation of 3 replicate measurements.

The much lower flux in AL-FS can be attributed to the dilution of draw solution in the membrane substrate in this orientation (McCutcheon and Elimelech 2006, Tang, She et al. 2010). The embedment of SG particles increased the FO water flux initially for a SG loading up to 1.0 wt.% and further increase SG loading caused the water flux reduction. This might be explained by increased risk of particle agglomeration at excessive SG loading, which lead to less effective water transport in the substrate (Shen, Ruan et al. 2011, Huang, Zhang et al. 2012). In addition, this result is consistent with the water permeability *A* of SG-based mixed matrix FO membranes, where the membrane with the optimal water permeability also had the optimal FO water flux (M1.00). For the AL-FS orientation, the same trend was also observed, where once again the SG-

PAN membrane (M1.00) showed the highest water flux. With a 0.5 M MgCl_2 as the DS and DI water as the FS, M1.00 had water flux of 77.9 $\text{L/m}^2 \text{ h}$ in AL-DS and 28.6 $\text{L/m}^2 \text{ h}$ in AL-FS. The water flux of the pure PAN membrane (M0.00) were significantly lower than these values, suggesting that the incorporation of SG particles as an effective approach for enhanced FO water flux performance.

The J_s/J_v ratio of SG-MMMs is shown in Fig. 4-6 (b) for both the AL-DS and AL-FS orientation. The term J_s/J_v ratio represents the effective solute concentration reverse diffused through an FO membrane. When evaluating FO membranes, both water flux and solute flux need to be considered at the same time. Previous studies have revealed that lower J_s/J_v value is preferred to avoid excessive fouling and solute accumulation in FO processes, less severe membrane fouling as well as decreased the replenishment cost where DS regeneration is needed (Qiu, Qi et al. 2011, Saren, Qiu et al. 2011, Qi, Li et al. 2012, Qi, Qiu et al. 2012). The SG-based mixed matrix FO membranes were observed that (1) a very small value of J_s/J_v ratio was obtained ($<0.3 \text{ g/L}$), (2) J_s/J_v ratio was slightly higher in AL-FS compared to AL-DS, and (3) J_s/J_v ratio remain nearly constant for a SG loading up to 1.0 wt.% and further increase SG loading resulted in slightly higher J_s/J_v ratio in both AL-DS and AL-FS. The SG-based mixed matrix FO membrane (M2.00) has the highest J_s/J_v ratio in both AL-DS and AL-FS. The high J_s/J_v value can be contributed to the low solute rejection by the membrane and the corresponding high B/A value. With a 0.5 M MgCl_2 DS and DI water FS, M2.00 had J_s/J_v ratio of 0.12 g/L in AL-DS and 0.25 g/L in AL-FS. The J_s/J_v ratio of the pure PAN membrane (M0.00) was slightly lower than these values, suggesting that the incorporation of excess SG particles decreased the selectivity of SG-based mixed matrix FO membranes. Therefore, it is very crucial to optimize the SG loading because of

excess SG particles (eg. from 1 wt.% to 2.wt.% in this study) may dramatically increase the solute flux and decrease the water flux at the same time (ie. the J_s/J_v ratio increased).

4.2.4.2. Effect of draw solution and feed solution concentrations on FO performance of SG-based mixed matrix FO membranes

The FO water performance of SG-based mixed matrix FO membrane (M1.00) is presented in Fig. 4-7 for a variety of DS concentrations (0.1, 0.3, 0.5, 1.0, 2.0, 3.0 M MgCl_2) and FS concentrations (0, 10, 100 mM NaCl).

Fig. 4-7 Effect of draw solution and feed solution concentration on FO water flux of SG-based mixed matrix FO membranes (M1.00). (a) Effect of DS concentration (0.1 – 3.0 M MgCl_2) using DI water as FS; and (b) effect of FS concentration (0-100 mM NaCl) using 1 M MgCl_2 as DS. Error bar was based on the standard deviation of 3 replicate measurements.

Regardless of the membrane orientation, higher the concentration of the DS resulted in higher the FO water flux for the SG-based mixed matrix FO membranes due to the larger osmotic

pressure as the driving force across the membrane. In AL-DS orientation, the FO water flux of SG-based mixed matrix FO membrane (M1.00) was 20 L/m² h for a 0.1 M MgCl₂ and it increased to 77.9 L/m² h at 0.5 M MgCl₂ as a result of increased the osmotic driving force. The highest FO water flux of 121 L/m² h was achieved by using the 2.0 M MgCl₂ as the DS and DI water as the FS, this clearly demonstrates the potential of SG-based mixed matrix FO membranes for high flux FO application. However, further increase the concentration of DS to 3.0 M MgCl₂ did not result in additional gain in water flux. This is consistent with prior studies (McGinnis and Elimelech 2007, Xu, Peng et al. 2010) that ICP increases and FO efficiency decreases at higher DS concentrations.

The FO water performance of SG-based mixed matrix FO membrane (M1.00) is presented in Fig. 4-7 (b) for various FS concentrations using 1.0 M MgCl₂ DS. Regardless of the membrane orientation, higher FS concentration decreased the osmotic pressure driving force across the membrane and hence decreased the water flux of the SG-based mixed matrix FO membranes. With a 1.0 M MgCl₂ as the DS and DI water as the FS, M1.00 had water flux of 117 L/m² h in AL-DS and 41 L/m² h in AL-FS. These values were significantly higher than those of the commercial HTI membranes, which had water flux of 36.3 L/m² h in AL-DS and 15.8 L/m² h in AL-FS, under the same testing condition. However, further increasing the FS concentration from 10 mM to 100 mM NaCl solution, the FO water flux decreased sharply from 106 L/m² h to 65.4 L/m² h in AL-DS orientation and the FO water flux decreased slightly from 37.4 L/m² h to 33.8 L/m² h in AL-FS orientation.

4.3. Conclusions

In summary, SG-based mixed matrix FO membranes with different SG loadings were systematically synthesized and characterized in this study. SG-based mixed matrix FO membranes can significantly enhance FO water flux probably due to both the *nanometer pores* in the SG particles and enhanced *substrate porosity* upon embedment into the membrane substrate layer. Both the intrinsic separation properties and surface chemistry and of SG-based mixed matrix FO membranes were enhanced by various SG loadings. The highest FO water flux of 121 L/m² h was achieved by using the 2.0 M MgCl₂ as the DS and DI water as the FS. The current study demonstrates the potential of use of MMMs for improving the substrate porosity and mass transfer coefficient as well as the rejection layer properties. This opens an additional dimension for ICP control in osmotic-driven membrane processes but there is no previous study about the pore size of filler particle and their potential effects on FO performance. Therefore, the next interesting research question is that how does the different pore size of filler affect the overall FO performance?

Chapter 5

Mesoporous Silica Gel–Based Mixed Matrix Membranes for Improving Mass Transfer in Forward Osmosis: Effect of Pore Size of Silica Gel

5.1 Introduction

As mentioned in the conclusion of Chapter 4, there is limited study about the pore size of filler particle and their potential effects on FO performance. Inspired by the great success of nanocomposite membranes for reverse osmosis applications (Lind, Ghosh et al. 2009, Yin, Kim et al. 2012), Ma et al. developed microporous zeolite loaded thin film nanocomposite (TFN) FO membranes and demonstrated their significantly higher water permeability and thus FO water flux as a result of different zeolite loading (Ma, Wei et al. 2012). In a typical TFN design, the pore size of the porous nanoparticles is chosen to be smaller than the hydrated radius of target solutes to maintain or even enhance solute rejection (Lind, Ghosh et al. 2009, Yin, Kim et al. 2012).

In parallel to the development of TFN FO membranes, recent studies have shown that the loading of porous fillers to FO substrates are highly effective in enhancing FO performance (Ma, Wei et al. 2013, Wang, Ou et al. 2013, Lee, Qi et al. 2014). These porous particles in these mixed matrix substrate (MMS) are shown to provide preferential water paths, which effectively enhances the mass transfer in the membrane support layer and mitigates internal concentration polarization (ICP) (Ma, Wei et al. 2013). Unlike nanoparticle fillers for TFN rejection layers where smaller particle pore size is favored due to solute rejection considerations (Lind, Ghosh et

al. 2009, Yin, Kim et al. 2012), fillers for mixed matrix substrate (MMS) with large pores are presumably more effective “water channels” due to their much reduced hydraulic resistance. The hypothesis is that pore size of the fillers might play a critical role on their effectiveness in enhancing FO performance. Unfortunately, there is lack of guiding principle for the selection of porous filler in term of pore size for fabricating mixed matrix FO substrate.

Therefore, the objective of current study is to systematically study the effect of pore size of porous fillers on the physiochemical properties, intrinsic separation properties, and FO performance of mixed matrix FO membranes. More specifically, silica gel (SG) particles with a variety of pore size were incorporated into polyacrylonitrile (PAN) to prepare the SG-based mixed matrix membranes (MMMs) due to their hydrophilic nature and a variety of pore size are commercially available. This is the first study to systematically investigate the effect of pore size of porous filler on SG-based mixed matrix FO membranes.

5.2 Results and discussion

5.2.1 Characterization of silica gel particles

The nitrogen adsorption and desorption isotherms of different pore size of silica gel is shown in Fig. 5-1. The measured pore size and BET surface area are presented in Table 3-3. For the different pore size of silica gel, the nominal pore size ranged from SG_{F40} (40 Å) to SG_{F300} (300 Å). The measured pore size agreed reasonably well with the nominal pore size. Larger pore size of silica gel was generally associated with smaller BET surface area. For example, SG_{F300} had the largest nominal pore size (300 Å) but also the smallest BET surface area (68 m²/g).

Fig. 5-1 Nitrogen sorption isotherm of different pore size of silica gel.

5.2.2 Characterization of physical and chemical properties of SG-based mixed matrix FO membranes with different pore size

The intrinsic properties of SG-based mixed matrix FO membranes with different pore size are shown in Table 5-1. The membrane thickness was not significantly influenced by the pore size of SG particles. The average thickness of SG-based mixed matrix membrane (42 - 49 μm) was similar to the thickness of commercial available HTI cellulose acetate FO membranes (50 μm) but was much thinner than HTI TFC FO membranes (100 μm) and traditional TFC RO membranes (150 μm) (Wei, Qiu et al. 2011, Ren and McCutcheon 2014). In all cases, the incorporation of SG particles had positive effect in improving the hydrophilicity of the substrate.

The contact angle of SG-loaded substrates ranged from 33-47°, as compared to 54° for the control without SG addition. The SG-based mixed matrix FO membranes were also more hydrophilic compared to the commercial HTI CA FO membranes (contact angle ~ 62°). The beneficial effect of nanoparticle loading on hydrophilicity enhancement is consistent with prior studies (Ma, Wei et al. 2012, Emadzadeh, Lau et al. 2014) and it is expected the increased substrate hydrophilicity could enhance FO water flux.

Table 5-1 Membrane thickness, contact angle, membrane bulk porosity, substrate water permeability, membrane water permeability salt rejection, and structural parameter of SG-based MMMs with different pore size of silica gel particles ^a

Membrane	Membrane Thickness (μm)	Contact Angle ($^{\circ}$)	Membrane Bulk Porosity (%)	Substrate Water Permeability ^b ($\text{L}/\text{m}^2 \text{ h bar}$)	Membrane Water Permeability ^b ($\text{L}/\text{m}^2 \text{ h bar}$)	Salt Rejection ^c (%)	Structural Parameter (mm)
Control	42 ± 2	54 ± 4	80 ± 2	171 ± 18	5.4 ± 0.6	83 ± 3	0.36 ± 0.03
F40	43 ± 1	47 ± 3	78 ± 2	218 ± 6	9.2 ± 1.2	80 ± 3	0.22 ± 0.01
F60	46 ± 1	39 ± 2	77 ± 4	244 ± 23	9.4 ± 0.7	74 ± 6	0.19 ± 0.02
F90	43 ± 1	33 ± 3	78 ± 3	307 ± 17	9.9 ± 0.5	68 ± 2	0.17 ± 0.01
F300	49 ± 1	42 ± 4	79 ± 2	273 ± 12	8.9 ± 0.6	76 ± 4	0.24 ± 0.01

^a The experiment errors are reported as the standard deviation of at least 3 repeated measurements.

^b Measured at an applied pressure of 5 bar with ultrapure water as feed water in the pressurized cross flow filtration testing mode.

^c Measured at an applied pressure of 5 bar with 5 mM MgCl_2 as feed water in the pressurized cross flow filtration testing mode.

5.2.3 Effect of different pore size of SG on intrinsic separation properties of SG-based mixed matrix FO membrane

Adding SG particles to the substrate had no obvious effect on the membrane bulk porosity. Nevertheless, the substrate pure water permeability (PWP) was substantially increased for the SG-loaded substrates. For the substrate F90, its PWP was nearly double of that of the control. Since both substrates had similar thickness and bulk porosity, the enhanced PWP was most likely attributed to increased surface porosity (ε_s) and/or reduced pore tortuosity (τ). According to the classical Hagen-Poiseuille equation, the substrate PWP is proportional to the ratio of ε_s / τ . The water permeability of the resulting xLbL membranes (A value) followed a similar trend to that of the substrate PWP as shown in Fig. 5-2 (a), suggesting an important dependence of the rejection layer properties on the substrate pore structure. This observation is consistent with previous studies, (Pendergast, Nygaard et al. 2010, Ma, Wei et al. 2013) which can be partially attributed to the reduced effective water transport distance through the rejection layer for a substrate with higher PWP. The solute rejection decreased as the membrane permeability increased, showing a typical permeability-selectivity tradeoff (Freeman 1999, Tang, Kwon et al. 2009). This observation suggests that salt rejection of a mixed matrix membrane is sensitive to the pore size of the SG particles even though these particles are only present in the membrane substrate and not in the rejection layer. Therefore, additional research studies are needed to further investigate the mechanisms involved and further study is needed to optimize the salt rejection of SG-based of mixed matrix FO membrane without compromising the water permeability.

Fig. 5-2 The effect of different pore size of SG-based mixed matrix FO membranes on (a) substrate water permeability and A value; (b) substrate water permeability and S value; and (c) the plot of A value against the $1/S$ value. Testing conditions: DI water as the feed solution;

applied pressure: 10 bars, error bar was based on the standard deviation of 3 replicate measurements.

It is also interesting to note the substantially reduced structural parameter (S) for the SG-based mixed matrix FO substrates as shown in Table 5-1. Structural parameter is a critical FO membrane property, with a lower S value preferred for controlling ICP in the FO substrate. In the current study, the S value was reduced from 0.36 mm (control) to 0.17-0.24 mm (MMMs) as a result of SG loading. In all cases, the SG-based mixed matrix FO substrates had much lower S values compared to the commercial HTI FO membranes (0.47 mm for CTA membrane and 0.62 mm for TFC membrane). (Wei, Qiu et al. 2011, Ren and McCutcheon 2014) While their S value was similar to that of the-state-of-the-art FO membranes supported by highly porous nanofiber substrates, (Song, Liu et al. 2011, Huang and McCutcheon 2014) MMMs generally offer much better mechanical stability (Pendergast, Nygaard et al. 2010, Hoek, Ghosh et al. 2011) that can potentially allow these membranes to be used for more demanding applications such as pressure retarded osmosis (Achilli and Childress 2010, She, Hou et al. 2013) and pressure assisted osmosis (Blandin, Verliefde et al. 2013).

The effect of filler pore size (d_{filler}) on S value is shown in Fig. 5-2 (b). Increasing d_{filler} up to 90 Å (F90) helped to reduce the S value, which is consistent with the hypothesis that the mesoporous silica gels with larger d_{filler} are more effective in enhancing mass transfer in the substrate since they are more permeable to water and solutes. Nevertheless, the S value increased from 0.17 ± 0.01 mm to 0.24 ± 0.01 mm when d_{filler} was further increased from 90 Å (F90) to 300 Å (F300). One plausible explanation is that, at very large filler pore size, the polymer molecules can enter into the filler pores to result in partial pore blockage and therefore reduced effectiveness of the fillers. Fig. 5-3 shows the nitrogen adsorption and

desorption isotherms of clean F300 silica gels and that of F300 fillers separated from a polymer dope solution by centrifugation.

Fig. 5-3 Nitrogen adsorption and desorption isotherm of silica gel F300 before and after pore-filled by polymer.

The results clearly indicate a significant reduction of both the filler pore size from 17 nm to 15 nm and BET surface area from 68 m²/g to 54 m²/g, which providing a direct support to the hypothesis of pore blockage in the filler particles. The current study seems to suggest that the optimal d_{filler} value is dependent on the competing effects of the reduced resistance to water/solute transport for larger pore size and the simultaneously increased risk of blockage of filler pores by the polymer chains. Based on the observation of the current study, an

optimal filler pore size of ~ 9 nm is recommended. It is worthwhile to note that this optimal value may depend on the properties of the polymer dope and the filler particles. For example, classical theory predicts that the liquid (or in this case the polymer dope) entry pressure into a pore is given by $4\gamma\cos\theta / d_{filler}$, where γ is surface tension of the polymer dope and θ is the contact angle. Thus, a more viscous polymer dope with higher surface tension may lead to a higher optimal d_{filler} value. Further studies are required to better understand the effect of polymer dope properties on the optimal filler pore size.

Both substrate PWP and S values are presented in Fig. 4-2 (b) as a function of filler pore size. Clearly, PWP and S value were strongly correlated. The PWP curve and S value curve were nearly mirror images to each other. As discussed earlier in the section, the substrate PWP is proportional to the ratio of ε_s / τ . Meanwhile, based on classical ICP theory, (McCutcheon and Elimelech 2007, Tang, She et al. 2010) S value is proportional to tortuosity, and it is inversely proportional to the substrate porosity. Recent research further reveals that the S value is generally dominated by the skin layer contribution as a result of much lower surface porosity compared to the average bulk porosity. (Chou, Shi et al. 2010, Wang, Wicaksana et al. 2010, Ma, Wei et al. 2013) Thus, it is reasonable to expect a strong dependence of S value on τ / ε_s , which explains the inverse relationship between substrate PWP and S value. Fig. 5-2 (c) plots the water permeability (A value) of SG-based mixed matrix FO membranes as a function of $1/S$ value. A value and S value are two key parameters dictating the FO water flux. A linear relationship between the A value and $1/S$ was observed. The current study clearly demonstrated that the feasibility of using mixed matrix substrates to simultaneously increase A value and reduce S value by enhancing the substrate mass transfer.

5.2.4 Effect of different pore size of SG particles on FO performance of SG-based mixed matrix FO membranes

Fig. 5-4 demonstrates the effect of different pore size of SG on FO water flux and the J_s/J_v ratio of SG-based mixed matrix FO membranes.

Fig. 5-4 The effect of different pore size and of silica gel loading on (a) FO water flux and (b) the ratio of salt flux over water flux of SG-based mixed matrix FO membranes. Testing conditions: 0.5 M $MgCl_2$ as the draw solution and DI water as the feed solution, error bar was based on the standard deviation of 3 replicate measurements.

The FO water flux was tested for both AL-DS and AL-FS orientations using 0.5 M $MgCl_2$ as DS and DI water as FS. Without the presence of SG particle in the substrate, the control membrane had an FO water flux of 78.1 $L/m^2 h$ in AL-DS. A lower flux of 28.7 $L/m^2 h$ was obtained in AL-FS due to the more severe dilutive ICP in this orientation.(Cath, Childress et al. 2006) For both AL-DS and AL-FS orientations, the FO water flux of the control membrane was significantly lower than those values of the SG-based MMM membranes, suggesting that the incorporation of SG particles is an effective approach for enhanced FO water flux performance. The optimal FO water flux was obtained for the filler pore size of 90

$\text{\AA}$, and further increasing d_{filler} to 300 $\text{\AA}$ caused an FO water flux reduction. As explained in the previous section, the pores of SG particle could be clogged with polymer due to the large pore of SG particle, which lead to less effective water transport inside the substrate.

Fig. 5-5 The effect of different number of xLbL layers of SG-based mixed matrix FO membranes (F90) on (a) water permeability and salt rejection; (b) FO water flux; (c) FO solute flux; (d) the ratio of solute flux over water flux of SG-based mixed matrix FO membranes. Testing conditions: (i) 5.0 mM MgCl_2 as the feed solution for (a); (ii) 0.5 M MgCl_2 as the draw solution and DI water as the feed solution for (b), (c), and (d). Error bar was based on the standard deviation of 3 replicate measurements.

The effect of different number of xLbL layers on water permeability, FO water flux, FO solute flux, the ratio of solute flux over water flux of SG-based mixed matrix FO membranes (F90) is presented in Fig. 5-5. One of the main advantages of xLbL method is that FO water

flux and FO solute flux solute can be finely adjusted but there is always a trade-off between these two parameters. As shown in Fig. 5-5(a), increasing in salt rejection by ~30%, decreasing in water permeability by ~ 62%. A similar trend is also observed between FO water and FO solute flux as shown in Fig. 5-5 (b) and (c). As a result, the ratio of solute flux over water flux is remained almost the same value as shown in Fig. 5-5 (d).

The FO water flux of SG-based mixed matrix FO membranes (F90) is presented in Figure 5-6 for a variety of DS concentrations (0.1, 0.3, 0.5, 1.0, 3.0 M MgCl_2) and FS concentrations (0, 10, 100 mM NaCl). From the viewpoint of driving force, higher the concentration of the DS should result in higher the FO water flux for the SG-based mixed matrix FO membranes. This is because of the larger osmotic pressure was created across the membrane regardless of the membrane orientation. In AL-DS orientation, the FO water flux of SG-based mixed matrix FO membranes (F90) was 42.3 $\text{L/m}^2 \text{ h}$ for a 0.1 M MgCl_2 and it increased to 117.2 $\text{L/m}^2 \text{ h}$ at 0.5 M MgCl_2 as a result of increased the osmotic driving force. The highest FO water flux of 126 $\text{L/m}^2 \text{ h}$ was achieved by using the 1.0 M MgCl_2 as the DS and DI water as the FS, this clearly demonstrates the potential of SG-based mixed matrix FO membranes for high flux FO application. However, further increase the concentration of DS to 3.0 M MgCl_2 did not result in additional gain in FO water flux. This is consistent with prior studies (McGinnis and Elimelech 2007, Xu, Peng et al. 2010) that ICP increases and FO efficiency decreases at higher DS concentrations. The membrane also worked well at higher FS concentration (82.5 $\text{L/m}^2 \text{ h}$ and 67.4 $\text{L/m}^2 \text{ h}$ in AL-DS orientation and 46.2 $\text{L/m}^2 \text{ h}$ to 41.2 $\text{L/m}^2 \text{ h}$ in AL-FS orientation using 10 mM or 100 mM NaCl solution as FS concentrations and 1.0 M MgCl_2 as DS).

Fig. 5-6. The effect of different concentration of (a) DS concentration; and (b) FS concentration of SG-based mixed matrix FO membranes (F90). Testing conditions: (a) concentration of draw solution (0.1 – 3.0 M MgCl_2) using DI water as FS; (b) concentration of feed solution (0 - 100 mM NaCl) using 1 M MgCl_2 as DS.

SG-based mixed matrix FO membranes with different pore size of SG particles were systematically fabricated and characterized in this current study. The pore size of SG particles played an important role in the current study. For SG particles with larger pore size (up to ~ 9 nm), the corresponding membrane had higher water permeability as well as lower structural parameter than the SG particles with smaller pore size. This clearly indicates the importance of water transport through the internal pores of the SG particles, which provide additional pathways (i.e., shortcuts) for water molecules to pass through the support layer (Fig. 5-6).

While earlier works have focused on the use of micro-porous fillers ($d_{\text{filler}} < 2 \text{ nm}$), (Ma, Wei et al. 2013) the current study clearly demonstrates the beneficial effect of larger d_{filler} . Unlike the case of TFN membranes where the fillers are designed in such a way that they retain solutes while allowing water to permeate through them, larger d_{filler} is preferred for fillers to

the membrane substrate as the latter is designed to be conduits to both water and solute molecules.

Fig. 5-7 Proposed mechanism for the enhanced FO water flux in SG-based mixed matrix FO membranes.

Nevertheless, caution should be exercised to avoid overly large filler pores to prevent their intrusion by polymer dope as shown in Fig. 5-7. The current study shows that a simultaneous improvement of membrane water permeability and reduction in structural parameter can be realized by the porous filler based MMM approach, thereby providing an additional degree of freedom to FO performance enhancement. A similar strategy might be used for the fabrication of SG-based mixed matrix pressure-retarded osmosis (PRO) membranes to control the ICP effect in the PRO substrate. Compared to FO, PRO has great requirement of membrane mechanical stability (Achilli and Childress 2010, She, Hou et al. 2013). In this regard, the MMM approach is more promising approach (say compared to nanofiber based approach) for preparing membranes to greater mechanical strength. Existing works showed that mixed matrix strategy could significantly enhance not only the tensile strength but also

the toughness of the membrane for a variety of applications, such as pervaporation and direct methanol fuel cells (Adoor, Sairam et al. 2006, Jaafar, Ismail et al. 2011).

5.3 Conclusions

In summary, SG-based mixed matrix FO membranes with different pore size of SG particles were systematically fabricated and characterized in this current study. SG-based mixed matrix FO membranes with optimal pore size (90 Å) can enhance water permeability and FO water flux probably due to both the nanometer pores of the hydrophilic SG particles and hence enhanced the mass transfer of water inside the membrane substrate layer. The highest FO water flux of 126 L/m² h was achieved by using the 1.0 M MgCl₂ as the DS and DI water as the FS. The current study demonstrates the importance of pore size of filler in mixed matrix FO membranes for improving the mass transfer coefficient of the substrate layer. Since the pore size of filler particles plays an important role in FO performance, the next interesting research question is that can these filler particles be removed to further increase membrane bulk porosity and hence controlling the ICP in FO process?

Metal-organic framework-based porous matrix forward osmosis membranes

Chapter 6

Fabrication of highly porous matrix membranes (PMM) using metal-organic frameworks (MOFs) as green template for water treatment

6.1 Introduction

As mentioned in the conclusion of previous chapter, the pore size of filler particles plays an important role in FO performance, the next interesting research question is that can these filler particles be removed to further increase membrane bulk porosity and hence controlling the ICP in FO process? In this chapter, a fundamental study about the removal of these filler particles as a “green template” to further increase membrane bulk porosity (Chapter 6) and hence controlling the ICP in FO process via the formation of macro-pores in the FO substrate (Chapter 7) will be discussed in details. First of all, it is important to realize that the FO substrate can be considered as UF membrane that is a pressure-driven membrane processes. In pressure-driven membrane processes, such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), an external pressure is applied on the solution at one side of the semi-permeable membrane, which serves as a driving force to separate water effectively from the pollutant in the feed solution (Petersen 1993, Van Der Bruggen, Vandecasteele et al. 2003). In general, the permeate flux of water, J_v is directly related to the driving force, ΔP , times the water permeability coefficient, A . The water permeability coefficient is mainly determined by the membrane structure, such as porosity, pore diameter, and tortuosity. In theory, an ideal membrane is expected to have highly porous but very thin and low tortuosity structure. Therefore, higher porosity of membrane will result in higher water permeability coefficient and therefore the higher flux of the membrane processes. Previous studies showed that a

variety of additives such as LiCl, polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) were added into the polymer dope solution in order to promote the pore formation (Guillen, Pan et al. 2011). However, all these additives can easily dissolve in the polar organic solvent such as *N,N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP), and was removed during the non-solvent induced phase inversion (NIPS), which resulted in lower porosity. Alternatively, mixed matrix membrane (MMM) is an emerging strategy to enhance several intrinsic membrane properties of pressure-driven membranes. For example, water permeability, anti-fouling property, thermal and mechanical stability of pressure-driven membranes can be potentially enhanced by incorporating nanomaterials such as zeolite (Jeong, Hoek et al. 2007, Bae, Liu et al. 2009, Lind, Ghosh et al. 2009, Fathizadeh, Aroujalian et al. 2011, Ma, Wei et al. 2012, Kiesow, Marczewski et al. 2013, Ma, Wei et al. 2013), silica nanoparticle (Jadav and Singh 2009, Huang, Zhang et al. 2012, Wu, Tang et al. 2013), titanium oxide nanoparticle (Lee, Im et al. 2008), and silver nanoparticle (Kim, Hwang et al. 2012, Liu, Qi et al. 2013). However, poor dispersion of the filler in the polymer matrix and incompatibility issue between the polymer and filler might result in poor selectivity of the MMMs (Shi, Yang et al. 2012, Zornoza, Tellez et al. 2013). Herein, the use of benign metal-organic frameworks (MOFs) as green template was proposed for the formation of macro-pores to enhance porosity and interconnectivity of the water treatment membranes.

The basic idea is to construct a porous matrix membrane (PMM) using MOF particles as green template, *which initially cannot dissolve in the polar organic solvent but can be easily washed away by water*. This porous matrix strategy might potentially further improve the porosity of the membranes after removal of these particles (Fig. 6-1). In addition, compared to conventional etching methods, such as the removal of silica nanoparticle by hydrofluoric

acid or the removal of gold nanoparticle by potassium iodide, this strategy uses only water as the etching solution, which is low cost, environmental-friendly and easily available. MOFs were chosen as the green templates because of some of MOFs have relatively low water stability compared to zeolite and silica gel but relatively high stability in organic solvents. Firstly, the dispersion of MOF as filler was studied by embedding less water soluble MOF (F300, iron benzene-1,3,5-tricarboxylate) into polyacrylonitrile (PAN) as a negative control. Secondly, two types of hydrophilic MOF (A100, aluminium terephthalate and C300, copper benzene-1,3,5-tricarboxylate) were chosen, which is relatively lower water stability than the F300 as the green template. Lastly, the morphology and structure of MOF-based PMMs were systematically characterized by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), and atomic force microscopy (AFM). The hypothesis is that the performance enhancement of osmotic-driven membrane process is due to the mass transfer coefficient of the PMM increased in FO substrate, which can be considered as an ultrafiltration (UF) membrane for proof-of-concept.

Fig. 6-1 Schematic representation of my strategy compared with traditional mixed matrix membranes.

6.2 Results and discussion

6.2.1 Characterization of MOF and water stability test

Firstly, the morphology information and water stability of MOF (A100, C300, and F300) in pure water were shown in Fig. 5-2. A100 is a grey powder while F300 is an orange powder as observed by naked eyes. Both A100 and F300 showed as irregular shaped fine particle under the observation of FESEM. On the other hand, C300 is a blue powder and stone-like particle under the observation of FESEM. Both A100 and C300 showed relatively low water stability and can be completely dissolved in pure water compared to F300, which showed relatively high water stability and can only partially dissolved in aqueous solution.

Fig. 6-2 The FESEM characterization of MOF. (a) A100, (b) C300, (c) F300. The inset is the camera image of MOF. (d) The water stability of MOF in pure water.

6.2.2 Fabrication of PMMs

The preparation of PMMs is outlined in Fig. 6-3. MOFs were firstly dispersed in the DMF by ultra-sonication of the solution for 1 hour. Polymer and LiCl were then added into the DMF solution followed by stirring for at least 24 h at 60 °C until a homogeneous solution was obtained. A casting knife was used to cast the polymer solution onto a clean glass plate. The polymer film was then immersed into the tap water bath at room temperature followed by soaking in continuous flow water bath to remove the MOF as well as the excess solvent inside the membrane. The advantages of this strategy including: 1) MOFs were used as green template, which can be easily removed by water without using toxic chemical, strong acid or base; 2) the fabrication process is under mild condition: neutral pH, at room temperature and under atmospheric pressure; 3) the processes is environmental-friendly, which minimizes the use of chemicals and reduces the impact on the environment; 4) the strategy is compatible with the current membrane manufacturing processes without extra steps or modification; 5) MOFs is commercial viable, low cost and could be easily scale-up.

Fig. 6-3 Schematic diagram of the preparation of PMMs.

6.2.3 Characterization of MMMs and PMMs

Fig. 6-4 showed the FESEM and EDX images of cross sections of PMMs and MMMs. The separation performance and the porosity of the PMMs compared with the control were shown in Fig. 6-5.

Fig. 6-4 FESEM micrographs of cross-section of (a) control, (b) PMM_{F300}, (c) PMM_{F300}, inset: enlarged image of F300, which cannot be completely remove under neutral condition, (d) EDX image of the enlarged image, (e) PMM_{A100}, (f) PMM_{C300}.

The cross-section images of a control, which represent the commercial UF membrane and a negative control (F300), which represent MOF-based MMM were shown in Fig. 6-4 (a) and (b). The presence of MOF (F300) can still be observed using FESEM and further confirmed by EDX analysis (Fig. 6-4 (c) and (d)). These results proved that the MOF were successfully incorporated into the polymer matrix and good dispersion was achieved after ultra-sonication. Correspondingly, the marginal increased in water permeability and membrane porosity were observed in Figure 6-5 (a) and (b). This might be explained by the partial dissolution of F300 under neutral pH condition (Henninger, Habib et al. 2009, Jeremias, Khutia et al. 2012).

More importantly, the successful removal of MOF particle was confirmed by FESEM as shown in Fig. 6-4 (e) and (f). Significant amount of macro-pores was created in the polymer matrix. As a result, a highly porous PMM_{C300} with porosity of $83 \pm 2\%$ based on gravimetric measurement was obtained as shown in Fig. 6-5 (b). Generally, a membrane substrate with high porosity is more favored due to increase the mass transfer of water in pressure-driven membrane processes. Indeed, the highly porous matrix ultrafiltration membranes (PMM_{A100} and PMM_{C300}) generally showed higher water permeability without compromising the rejection of dextran. The highest water permeability of $260.5 \text{ L/m}^2 \text{ h bar}$ was achieved for PMM_{C300}, which probably due to the combination of enhanced porosity and interconnectivity of the ultrafiltration membranes. It is important to note that the dextran rejection did not significantly change between control and highly porous PMM after removal of MOF in the substrate layer, which means the membrane selectivity remain unchanged. The overall results clearly show that the removal of MOFs in the polymer matrix substantially enhanced the porosity and is a promising strategy for better separation performance of pressure-driven membranes.

Fig. 6-5 Effect of different types of MOF on the performance of pressure-driven ultrafiltration membranes (a) the pure water permeability and dextran rejection of the ultrafiltration membranes; (Testing conditions: DI water or dextran solution as the feed

solution; applied pressure: 5 bars) and (b) membrane porosity. Error bar was based on the standard deviation of 3 replicate measurements.

In order to determine the residual amount of MOFs inside the PMM membrane, the PMM samples were digested with a mixture of concentrated nitric acid and concentrated hydrochloric acid in the ratio of 3:1 for 6 hours followed by topping up the concentrated acid solution to 10 mL with water (Please refer to Chapter 3). Precipitates were observed at the bottom of the bottles after the PMM samples were dissolved in the acid solution. Inductively coupled plasma (ICP) analysis, which can determine metal ions in aqueous solutions down to part per millions (ppm) or even part per billions (ppb) level, was used to determine metal concentration in the aqueous phase. Indeed, the PMM_{F300} has the highest residual percentage of iron (24.0 ± 6.9 wt%). In comparison, PMM_{A100} has significantly lower residual percentage of aluminum (8.4 ± 0.6 wt%) and PMM_{C300} has the lowest residual percentage of copper (3.8 ± 0.4 wt%) among the three PMM samples. It is noteworthy that the order of membrane water permeability (PMM_{F300} < PMM_{A100} < PMM_{C300}) coincides with the reverse order of water stability and residual percentage of MOF (MOF_{F300} > MOF_{A100} > MOF_{C300}). Thus, one reasonable explanation for the highest water permeability of PMM_{C300} is the higher water solubility of C300. The enhanced pore connectivity in addition to improved porosity is likely responsible to the marked increased in membrane water permeability. However, other important parameters, such as the loading, shape, and size of MOF particles, water stability of MOFs, and other types of water soluble MOFs or other kinds of nanomaterials should be further optimized to enhance of the performance of PMM membranes. Table 6-1 compares the FO performance of the current study with other FO membranes in literature.

Table 6-1 Comparison of FO performance of the current study with other FO membranes in literature

Membranes	J_v (L/m ² h)	J_s (g/m ² h)	J_s/J_v (g/L)	FS	DS: MgCl ₂ (M)	orientation	Temp. (°C)	Reference
PMM _{C300} ^a	44	21	0.47	DI	0.5	AL-FS	25 ± 1	current study
	107	18	0.17	DI	0.5	AL-DS	25 ± 1	
xLbL2.5 ^b	17.2	2.0	0.120	10 mM NaCl /DI	0.5	AL-FS	23 ± 1	(Liu, Qi et al. 2013)
	39.3	3.1	0.071	10 mM NaCl /DI	0.5	AL-DS	23 ± 1	
xLbL3-3 ^c	42.3	12.0	0.284	DI	0.5	AL-DS	22 ± 0.5	(Qi, Qiu et al. 2012)
	35.5	N.A.	N.A.	10 mM NaCl	0.5	AL-DS	22 ± 0.5	
xLbL ^d	30.0 ^m	5.8	0.193 _m	DI	0.5	AL-FS	23	(Qiu, Qi et al. 2011)
	60.0 ^m	3.5	0.058 _m	DI	0.5	AL-DS	23	
HTI ^e	15.8	1.2	0.074	DI	1	AL-FS	23 ± 1	(Wei, Qiu et al. 2011)
	36.3	7.6	0.209	DI	1	AL-DS	23 ± 1	

^a J_v values were obtained by using 0.5 M MgCl₂ as draw solution and DI water as feed solution.

^b J_v values were obtained by using 0.5 M MgCl₂ as draw solution and DI water or 10 mM NaCl as feed solution.

^c Cross-linked double-skinned NF-like flat sheet FO membranes

^d Cross-linked NF-like flat sheet FO membranes

^e Commercial flat sheet thin film FO membrane.

6.3 Conclusion

In summary, MOF-based PMMs were systematically synthesized and characterized in this study. PMMs can significantly enhance water permeability in pressure-driven membrane processes probably due to the removal of MOF particles in the polymer matrix, which enhanced membrane porosity and interconnectivity of the membrane. More importantly, the current study demonstrates MOFs as green template might have good potential for not only pressure-driven membranes processes but also for carbonaceous nanofiber membranes for selective filtration and separation of nanoparticle, or osmotic-driven membrane process, such as forward osmosis (FO) and pressure-retarded osmosis (PRO).

Chapter 7

Metal-organic framework – based porous matrix membranes for improving mass transfer in forward osmosis membranes

7.1 Introduction

As mentioned in the conclusion of Chapter 6, metal-organic frameworks (MOFs) were used as green template to fabricate porous matrix membranes that might have good potential for not only pressure-driven membrane processes but also for osmotic-driven membrane processes. In this chapter, PMMs were used as FO substrate layer for improving mass transfer in FO process. First of all, it is important to realize that MOFs are highly crystalline and highly porous compounds, consisting of metal ions or clusters coordinated with rigid organic ligands to form three-dimensional networks (Tanh Jeazet, Staudt et al. 2012, Zornoza, Tellez et al. 2013). Recently, MOF-based mixed matrix membranes (MMMs) have been successfully developed and the fabrication of MOF-based MMMs generally involves: (1) the dispersion of MOF particles in the organic solvent; (2) addition of polymer powder or pellets followed by continuous stirring to obtain the homogeneous solution; (3) casting the polymer solution in a petri dish or on a glass plate by doctor blade followed by natural evaporation (Zornoza, Tellez et al. 2013). MOF-based MMMs are mainly used in gas separation and purification because of their tunable and small pore size, which could be used as molecular sieves to selectively pass through certain types of gas molecules (Ren, Jin et al. 2012, Tanh Jeazet, Staudt et al. 2012, Hao, Li et al. 2013).

Other applications such as pervaporation (Liu, Li et al. 2011, Shi, Yang et al. 2012, Liu, Jin et al. 2013, Hua, Ong et al. 2014) and solvent resistant nanofiltration (SRNF) (Basu, Maes et al. 2009, Sorribas, Gorgojo et al. 2013, Siddique, Rundquist et al. 2014) have also been reported in the literature. In 2009, Basu et al. reported MOF-based MMMs for SRNF application and all the membranes showed higher permeability but lower rejection against dye molecule. This might be attributed to poor compatibility between MOF and the polymer used. In 2011, Liu et al. studied MOF/silicon rubber MMMs for organophilic pervaporation and reported outstanding performance enhancement for the recovery of bio-alcohol (Liu, Li et al. 2011). This might be ascribed to the super-hydrophobic surfaces and internal porosity of MOF, which selectively absorb alcohol and provide alternative pathways for the transport of bio-alcohol through the membranes. On the other hand, Sorribas et al. studied MOF-based thin film nanocomposite (TFN) membrane for organic solvent nanofiltration (OSN) and showed significant enhancement in solvent flux, such as methanol (MeOH) and tetrahydrofuran (THF). They pointed out that the larger the pore size and porosity of the MOF, the greater the enhancement effect of solvent permeability.

However, there are several serious challenges preventing MOF-based MMMs from realizing industrial applications. One of the most critical problems is the relatively low water stability for most of MOF particles compared to zeolites and silica gel due to the weak coordination bonds between metal cluster and organic linkers (Zornoza, Tellez et al. 2013). This unique problem of MOF severely limited the application of MOF-based MMMs for aqueous phase separations, such as pressure-driven ultrafiltration (UF) membrane processes. Recently, Lee et al. [12] proposed the concept of porous matrix membranes (PMMs) by using MOF particles as a green template. Compared to traditional design of MMMs, PMMs can increase the membrane porosity (ϵ) and the interconnectivity of the UF membrane (Lee, Tang et al.

2014). As a result, the overall separation performance was significantly enhanced in term of pure water permeability (PWP) and this might be attributed to the improvement of mass transfer coefficient of the UF membrane.

In the current study, the use of porous matrix approach to make a better porous matrix substrate (PMS) for forward osmosis (FO) process was proposed. As mentioned in the Chapter 2 of this thesis, FO is one of the most promising osmotic-driven membrane technologies with lower energy requirement compared to the pressure driven membrane processes. However, the effect of internal concentration polarization (ICP) is one of the most critical Achilles' heels in FO process. The severity of ICP can be determined using structural parameter (S value), which is mainly related to the intrinsic membrane properties, such as membrane wettability, pore structure, membrane thickness and tortuosity of the FO substrate. In the current study, the main objective is to improve mass transfer efficiency and hence control ICP through the incorporation of MOF particles as removable fillers into FO substrate, where the hypothesis is that porous matrix substrate (PMS) will help to reduce structural parameter (i.e. smaller S value) in FO process. Furthermore, porous matrix strategy is more beneficial to the overall performance of osmotic-driven membrane processes than pressure-driven membrane processes due to the enhancement of porosity and reduction of tortuosity at the same time. Nevertheless, the study of using PMM approach for the preparation of PMS for FO membrane processes so far had not been applied in osmotic-driven membrane process.

Therefore, the main objective of current study is to study the use of PMS as FO substrate for controlling the ICP effect (i.e. smaller S value) and hence improving mass transfer efficiency (i.e. higher FO water flux). More specifically, the effects of MOF particles on the

physiochemical properties, intrinsic separation properties, and FO performance of MOF-based PMMs will be systematically studied as well. MOF particle with different water stability was incorporated into polyacrylonitrile (PAN) to prepare the MOF-based PMS followed by the formation of rejection layer via layer-by-layer (LbL) self-assembly to prepare the MOF-based PMM. In this study, three different MOF was selected because of their different water stability. Iron-based MOF particle (F300) is relatively more stable in the water than aluminum-based MOF particle (A100) and copper-based MOF particles (C300), which was used to fabricate MOF-based PMM (PMM_{F300}) and used as an example of PMM with partially removal for comparison with MOF-based PMMs with totally removal (PMM_{A100} and PMM_{C300}). This is the first report systematically studying the fabrication of MOF-based PMS for improving mass transfer efficiency and hence controlling the ICP effect based on LbL self-assembly.

7.2 Results and discussion

7.2.1 Characterization of physical and chemical properties of MOF-based porous matrix FO membranes

The general properties of the MOF-based PMS, such as contact angle and structural parameter (S value) are shown in Table 7-1. The structural parameter is related to the intrinsic membrane properties, such as membrane porosity, membrane tortuosity and membrane thickness. Both the hydrophilicity (measured by contact angle) and membrane porosity are essential properties for the fabrication of FO substrate with smaller S value. For example, a more hydrophilic FO substrate with higher porosity and lower tortuosity can help in reducing the effect of ICP.

Table 7-1 Membrane thickness, contact angle, surface roughness, membrane porosity and structural parameter of MOF-based PMS with different type of MOFs. The average pore sizes of MOF particles are generally smaller than 2 nanometers (Furukawa, Cordova et al. 2013).

Membrane	Membrane Thickness (μm)	Contact Angle ($^{\circ}$)	Surface Roughness (nm)	Membrane Porosity (%)	Structural Parameter (mm)
Control	49 ± 1	44 ± 4	17 ± 1	73 ± 4	0.36 ± 0.03
PMS _{F300}	57 ± 2	29 ± 3	13 ± 3	76 ± 3	0.24 ± 0.04
PMS _{A100}	56 ± 1	28 ± 3	9 ± 3	81 ± 3	0.21 ± 0.02
PMS _{C300}	50 ± 2	29 ± 2	5 ± 2	85 ± 2	0.19 ± 0.02

All the MOF-based PMS are more hydrophilic (contact angle $\sim 30^{\circ}$) compared to the control membrane (contact angle $\sim 44^{\circ}$) and the commercial FO membranes (contact angle $\sim 62^{\circ}$). In addition, the membrane thickness was only slightly affected by the porous matrix approach. The average thickness of MOF-based mixed matrix membrane and MOF-based porous matrix membrane ranged from 49 - 57 μm . It is important to note that the overall performance of FO process, such as FO water flux, could be enhanced with a more hydrophilic and thinner FO substrate. In all cases, the surface roughness of substrates is relatively small compared to the control substrate as shown in Fig. 7-1.

Fig. 7-1 AFM micrographs of MOF-based PMS (a) Control, (b) PMS_{F300}, (c) PMS_{A100}, (d) PMS_{C300}

7.2.2 Effect of different types of MOF particle on intrinsic membrane properties

Fig. 7-2 shows the effect of different types of MOF particles on the intrinsic membrane properties, such as membrane bulk porosity, and S value. Firstly, it is important to note that MOF-based PMS has higher membrane bulk porosity than the control membrane as shown in Fig. 7-2 (a).

Fig. 7-2 (a) The membrane bulk porosity of the resulting MOF-based mixed matrix FO membrane and MOF-based porous matrix FO membranes and the dash line represents the membrane bulk porosity of control; (b) the percentage of removal and bond dissociation energies of MOF particles; (c) the plots the membrane bulk porosity as a function of $1/S$ value; (d) the plots the A value of MOF-based FO membranes as a function of $1/S$ value. Error bar was based on the standard deviation of 3 replicate measurements.

The membrane bulk porosity ranged from 76-85%, as compared to ~70% of the control membrane. Both the enhancement of membrane wettability and membrane porosity are helpful to overall FO performance, such as FO water flux. Furthermore, these results consistent with the hypothesis, which is to increase mass transfer efficiency of the FO

substrate for both water and solute through the formation of macro-pores inside the FO substrate (Do, Tang et al. 2012, Emadzadeh, Lau et al. 2014).

Secondly, it is also critical to note that the membrane bulk porosity is related to bond dissociation energy (BDE) between metal ions and organic ligands as shown in Fig. 7-2 (b). Bond dissociation energy is defined as the change in standard enthalpy when a chemical bond is broken, which is equivalent to the stability of a chemical bond. In MOF particles, the BDE represents the binding strength of the coordination bond between the metal cluster and the organic ligand. A smaller BDE means a lower water stability or higher pH sensitivity of MOF particles. Based on the inductively coupled plasma analysis, a higher percentage of removal was observed for MOF particles with lower BDE when these MOF-based PMS were leached in acidic solution (Low, Benin et al. 2009, Lee, Tang et al. 2014). For MOF particles with BDE lower than 200 kJ/mol, the corresponding MOF-based PMM had percentage of removal higher than 90% and hence higher membrane bulk porosity (>80%). For instance, MOF_{F300} has higher bond dissociation energy (334.0 ± 6.0 kJ/mol) between the iron and oxygen bond (Fe-O) compared to bond dissociation energy of MOF_{A100} (166.7 ± 12.0 kJ/mol) between the aluminum and oxygen bond (Al-O) and bond dissociation energy of MOF_{C300} (133.9 ± 11.6 kJ/mol) between the copper and oxygen bond (Cu-O) (Luo 2002). As a result, the PMM_{F300} had the lowest removal percentage of MOF particles (76 ± 6.9 wt%) compared to PMM_{A100} (91 ± 0.6 wt%) and PMM_{C300} (96 ± 0.4 wt%). These results clearly indicate a significant enhancement of membrane bulk porosity is attributed to higher percentage of removal of MOF particles, providing consistent evidence for the formation of macro-pores inside the FO substrate. Furthermore, the current study seems to suggest that lower bond dissociation energy of MOF particles generally gives a higher percentage of removal inside the substrate and hence higher membrane bulk porosity. Based on the results of the current study, the suitable MOF particles with BDE < 200 kJ/mol is recommended for the fabrication of PMMs.

It is worthwhile to note that this porous matrix strategy may depend on the intrinsic properties of the polymer dope and the MOF particles, such as hydrophobic and/or charge interaction. Further systematic studies are required to understand the potential effect of different surface chemistry of MOF particles on the dispersion of MOF particles inside the polymer matrix and hence the overall membrane bulk porosity.

Thirdly, Fig. 7-2 (c) plots membrane bulk porosity against $1/S$ value. Both membrane bulk porosity and S value are two key parameters predicting the overall FO performance, such as FO water flux. According to classical ICP model, S value is given by π/ε , where τ is the membrane tortuosity, t is the membrane thickness, and ε is the membrane porosity. In Fig. 7-2 (c), the diagonal line is a reference line, where the slope of the line passing through the origin thus represents average membrane tortuosity (τ) and membrane thickness (t). Assuming that the membrane thickness has no significant difference, the gradient of the line might be used to estimate the change of membrane tortuosity with respect to the membrane bulk porosity and S value. A linear relationship between the membrane bulk porosity and $1/S$ was observed for MOF-based PMM. In all cases, increased membrane porosity led to increased value of $1/S$ (i.e., increased membrane bulk porosity helped to reduce the S value), which is consistent with the hypothesis that the formation of macro-pores in the substrate layer can be favorably to control ICP due to enhancement of membrane porosity of the substrate layer. Compared to gradient of the MOF-based PMM, the slope of the control membrane is steeper and further away from the reference line. This suggests that the MOF-based PMM help to reduce membrane tortuosity and hence a larger $1/S$ value is observed (i.e. smaller S value). Combining the Fig. 7-2 (a) and (c), it can be concluded that the formation of macro-pores inside the MOF-based PMS provides higher membrane porosity and lower

membrane tortuosity than control membrane, thus the S value of MOF-based PMM is lower than the control membrane. It is worthwhile to note that the discussion above assumed uniform porosity and tortuosity for the entire substrate. In reality, porosity and tortuosity properties can change significantly over the cross-section of an asymmetric substrate (Wang, Wei et al. 2012, Ma, Wei et al. 2013). While a more detailed mathematical treatment is beyond the scope of the current study, the bulk values of porosity and tortuosity in the current study provide an equal basis for comparing the PMMs with their control.

Indeed, the reduced structural parameter (S value) for the MOF-based PMS is observed as shown in Table 7-1. Structural parameter is a direct indicator of the severity of ICP in FO substrate, with a lower S value is preferred for controlling ICP in the FO substrate. In the current study, the S value was reduced from 0.36 mm (control) to 0.24 mm (MMM_{F300}) and further decreased to 0.21 mm (PMM_{A100}) and 0.19 mm (PMM_{C300}). In all cases, the MOF-based FO substrates had much lower S values compared to the commercial HTI FO membranes (0.47 mm for CTA membrane and 0.62 mm for TFC membrane) (Wei, Qiu et al. 2011, Ren and McCutcheon 2014). Compared to the S value reported in the current literature, the reported S value is comparable to the FO substrate prepared by electrospinning (0.11 mm) (Song, Liu et al. 2011, Huang and McCutcheon 2014) and much better than the current-state-of-the-art phase inversion method (0.67 – 0.71 mm) (Wei, Qiu et al. 2011). It is also important to highlight that this method is facile and simple, where the membrane porosity is controllable and tunable through the careful selection of the filler as well as the etching condition. Since all the membranes are similar in the thickness, the current study clearly demonstrated that the feasibility of using porous matrix strategy to simultaneously increase membrane bulk porosity and reduce membrane tortuosity (i.e. smaller gradient compared to the control) at the same time and hence controlling the effect of ICP (i.e. smaller S value).

PMMs generally offer much higher membrane bulk porosity and lower tortuosity (Pendergast, Nygaard et al. 2010, Hoek, Ghosh et al. 2011) that can potentially allow these membranes to be used for more demanding applications such as pressure assisted osmosis (PAO) (Blandin, Verliefde et al. 2013) and pressure retarded osmosis (PRO) (Achilli and Childress 2010, She, Hou et al. 2013), although careful optimization is needed to be exercised for maintaining mechanical stability and avoiding excessive membrane compaction.

7.2.3 Effect of different types of MOF particle on intrinsic separation properties

Fig. 7-3 shows the effect of different types of MOF on intrinsic separation properties. Fig. 7-3 (a) plots the substrate water permeability and membrane water permeability (A value) of the resulting MOF-based PMMs and Fig. 7-3 (b) membrane water permeability (A value) and salt rejection of the resulting MOF-based PMMs. Compared to the control membrane, MOF-based PMS had no obvious increase in the membrane thickness but the substrate pure water permeability (PWP) was substantially improved for the MOF-based PMS. For the substrate of PMS_{C300}, its PWP was nearly 63% higher than the substrate of control. Since both substrates had similar thickness, the enhanced PWP was most likely attributed to increased and membrane bulk porosity (ε).

According to the classical Hagen-Poiseuille equation, the PWP of FO substrate is proportional to the membrane bulk porosity, which proved that the hypothesis is valid and proof-of-concept. On the other hand, the membrane water permeability (A value) of the resulting MOF-based PMMs (after surface modification via LbL self-assembly) followed a same trend to that of the substrate PWP as shown in Fig. 7-3 (a). This suggests that a strong correlation between the water permeability of rejection layer and water permeability of

substrate layer. This observation is consistent with previous studies (Pendergast, Nygaard et al. 2010, Ma, Wei et al. 2013), which can be partially attributed to the increased surface porosity of the substrate layer (ε_s) and hence reduced effective water pathway through the rejection layer. However, increased surface porosity of the substrate layer might cause ‘defect’ of the rejection layer during the LBL process. As a result, the salt rejection was slightly affected upon the enhancement of membrane water permeability as shown in Fig. 7-3 (b).

Fig. 7-3 Effect of different types of MOF the performance of pressurized cross flow filtration after xLbL synthesis. (a) The substrate water permeability and membrane water permeability (A value) of the resulting MOF-based PMMs; (b) membrane water permeability (A value) and salt rejection of the resulting MOF-based PMMs. (Testing conditions: 5 mM MgCl₂ as the feed solution; applied pressure: 9 bars, error bar was based on the standard deviation of 3 replicate measurements)

7.3.4 Effect of different types of MOF particle on FO performance

Fig. 7-4 demonstrates the effect of different type of MOF particles on FO water flux and the J_s/J_v ratio of MOF-based PMMs.

Fig. 7-4 Effect of different types of MOF on (a) FO water flux, and (b) ratio of solute flux over water flux of MOF-based mixed matrix FO membranes and porous matrix FO membranes. Testing conditions: 0.5 M MgCl_2 as the draw solution and DI water as the feed solution, error bar was based on the standard deviation of 3 replicate measurements.

For both AL-DS and AL-FS orientations, the FO water flux was tested using 0.5 M MgCl_2 as draw solution (DS) and deionized water as feed solution (FS). For the AL-DS orientation, the control membrane had an FO water flux of 78.1 $\text{L/m}^2 \text{h}$. For AL-FS orientation, a lower FO flux of 28.7 $\text{L/m}^2 \text{h}$ was achieved due to the more severe dilutive ICP in this orientation (Cath, Childress et al. 2006). For both AL-DS and AL-FS orientations, the FO water flux of the control membrane was significantly lower than those values of the MOF-based PMMs, suggesting that the porous matrix strategy is an effective approach for enhanced FO water flux performance. The optimal FO water flux was obtained for the MOF-based porous matrix FO membranes (PMM_{C300}) with the smallest BDE. It is noteworthy that the order of membrane FO water flux ($\text{PMM}_{\text{F300}} < \text{PMM}_{\text{A100}} < \text{PMM}_{\text{C300}}$) coincides with the reverse order of bond dissociation energies of MOF ($\text{MOF}_{\text{F300}} > \text{MOF}_{\text{A100}} > \text{MOF}_{\text{C300}}$). As explained in the previous section, the enhanced FO performance might be explained by the formation of

macro-pores inside the PMMs, which increase the mass transfer efficiency and more effective water/solute transport inside the PMM substrate. The J_s/J_v ratio followed a similar trend, suggesting a moderate loss of solute rejection at increased substrate porosity.

The effect of different concentration of draw solution and feed solution on FO water flux of MOF-based PMM (PMM_{C300}) is presented in Fig. 7-5.

Fig. 7-5 Effect of (a) draw solution concentration and (b) feed solution concentration on FO water flux of MOF-based mixed matrix FO membranes and porous matrix FO membranes. Testing conditions: 0.1 – 3.0 M MgCl_2 as the draw solution and 10 mM, 100 mM NaCl solution or DI water as the feed solution, error bar was based on the standard deviation of 3 replicate measurements.

A variety of DS concentrations (0.1, 0.3, 0.5, 1.0, 3.0 M MgCl_2) and FS concentrations (0, 10, 100 mM NaCl) were used to test the FO performance. Regardless of the membrane orientation, higher the concentration of the DS should result in higher the FO water flux for the MOF-based PMMs. This could be explained by the fact that the larger osmotic pressure was created across the membrane. In AL-DS orientation, the FO water flux of MOF-based

porous matrix FO membranes (PMM_{C300}) was 33.7 L/m² h for a 0.1 M MgCl₂ and it increased to 107.4 L/m² h at 0.5 M MgCl₂ as a result of increased the osmotic driving force. Further increase the concentration of DS to 3.0 M MgCl₂ results in additional gain in FO water flux. This is consistent with prior studies (McGinnis and Elimelech 2007, Xu, Peng et al. 2010) that ICP increases and FO efficiency decreases at higher DS concentrations. The highest FO water flux of 132.7 L/m² h was achieved by using the 3.0 M MgCl₂ as the DS and DI water as the FS, which clearly demonstrates the potential of MOF-based porous matrix FO membranes for high flux FO application. The membrane also performed reasonably well at higher FS concentration (99.7 L/m² h and 79.7 L/m² h in AL-DS orientation and 46.2 L/m² h to 43.9 L/m² h in AL-FS orientation using 10 mM or 100 mM NaCl solution as FS concentrations and 1.0 M MgCl₂ as DS).

7.2.5 Proposed mechanism and implications.

Fig. 7-6 demonstrates the importance of water transport through the macro-pores inside the FO substrate, which provide direct pathways for water molecules to pass through the support layer with lower resistance and shorter tortuosity. Unlike the traditional concept of mixed matrix approach, where MMMs are designed in such a way that water molecules have to pass through either the narrow internal pore of fillers (d_{filler}) or passing around the surface of the filler.

Fig. 7-6 Schematic comparison between (a) mixed matrix membrane and (b) porous matrix membrane. The importance of water transport through the macro-pores inside the FO substrate is shown, which provide additional pathways for water molecules to pass through the support layer with lower resistance and shorter tortuosity.

As a result, water molecules will face either higher hydraulic resistance due to the water molecule have to enter a narrow internal pore of the micro-porous filler, such as zeolite in TFN study ($< 2\text{nm}$) or longer tortuosity due to the water molecule have to pass around the outer surface of filler. In the current study, porous matrix approach indicates the importance of water/solute transport through the macro-pores inside the FO substrate, which provide more efficient and direct pathways for water molecules to pass through the support layer with lower resistance (Fig. 7-6). The porous matrix approach is more effective in enhancing mass transfer efficiency of water/solute compared to mixed matrix approach (Yin, Kim et al. 2012, Lee, Qi et al. 2014). This might be attributed to the water/solute is not necessary to enter the pore of filler or pass around the fillers, which significantly reduced water pathway and hence shorter the tortuosity of the membrane (Jeong, Hoek et al. 2007). Furthermore, the enhanced

pore connectivity inside the substrate layer in addition to improved membrane bulk porosity is partially responsible to the significant increase in FO water flux due to control the effect of ICP and hence smaller S value.

Noticeably, the BDE between metal ions and organic linker of MOF particles played an important role in the current study. For example, MOF_{C300} has the lowest bond dissociation energy (133.9 ± 11.6 kJ/mol) between the copper and oxygen bond (Cu-O) compared to bond dissociation energy of MOF_{A100} (166.7 ± 12.0 kJ/mol) between the aluminum and oxygen bond (Al-O) and bond dissociation energy of MOF_{F300} (334.0 ± 6.0 kJ/mol) between the iron and oxygen bond (Fe-O) (Luo 2002). On top of the BDE, there are some other important considerations for the selection of filler: (a) charge density between the metal ion and choice of organic linker, such as the valence of the metal ion or the electron withdrawing and electron donating group on the organic linker; (b) the filler should be easily removed using environmental-friendly condition; (c) the compatibility between filler and polymer; (d) the filler must be well-dispersed inside the polymer matrix (Mahajan, Burns et al. 2002, Low, Benin et al. 2009, Lee, Tang et al. 2014).

Lastly, the current study provides an additional degree of freedom to further increase the mass transfer efficiency and hence control the effect of ICP in the FO substrate through the porous matrix approach due to the simultaneous improvement of membrane bulk porosity and reduction in membrane tortuosity. A similar strategy might be feasible for the fabrication of MOF-based porous matrix pressure-assisted osmosis (PAO) membranes or MOF-based porous matrix pressure-retarded osmosis (PRO) membranes to control the effect of ICP in the substrate (Oh, Lee et al. 2014). Existing works had showed that porous matrix strategy could

significantly enhance the membrane bulk porosity for a variety of potential applications, such as pressure-driven membrane processes such as ultrafiltration membrane (Lee, Tang et al. 2014).

7.3 Conclusions

In summary, MOF-based PMMs with different types of MOF particles were systematically fabricated and characterized in this current study. MOF-based porous matrix strategy can enhance not only the membrane bulk porosity but also decrease the membrane tortuosity at the same time. This might be probably due to both the formation of macro-pores in the FO substrate layer and hence enhanced the mass transfer of water inside the FO substrate layer. The bond dissociation energy between metal ions and organic ligands of MOF particles played an important role for the general selection of fillers of PMMs. The highest FO water flux of $132 \text{ L/m}^2 \text{ h}$ was achieved by using the 3.0 M MgCl_2 as the DS and DI water as the FS. The current study demonstrates the importance of membrane bulk porosity and membrane tortuosity of MOF-based PMMs for improving the mass transfer coefficient and hence controlling the effect of ICP in the FO substrate layer. This might potentially provide an additional strategy for ICP control in osmotic-driven membrane processes, such as PAO and PRO. However, it is critical to realize that external concentration polarization (ECP) also affects the overall performance of FO membrane, especially in the configuration of spiral wound membrane module. Therefore, the next interesting research question is that can the side effect of ECP be reduced using a better design of FO feed spacer?

Part 2: Fabrication of 3D Printed Spacers

(Ongoing study and collaborative work with Wen See Tan)

Chapter 8 (Ongoing study and collaborative work with Tan Wen See)

Fabrication of 3D printed feed spacers in spiral wound membrane modules for osmotic-driven membrane processes

8.1 Introduction

In this chapter, the external concentration polarization issue associated with osmotic-driven membrane processes (ODMP) will be addressed using 3D printed spacers. Osmotic-driven membrane processes, such as forward osmosis (FO) or pressure-retarded osmosis (PRO) technology is one of the promising and advanced desalination technologies for the separation of salt from water in producing clean water to meet the future water demand. For more details about osmotic-driven membrane processes, the reader may refer to the Chapter 2. It is important to note that the configuration of spiral wound modules (SWM) is generally accepted by desalination industry as the standard design for not only reverse osmosis (RO) and nanofiltration (NF) process but also for forward osmosis (FO) and pressure retarded osmosis (PRO) due to its large membrane surface area per unit volume. Nevertheless, these spiral wound membrane modules suffer from severe external concentration polarization (accumulation of retained solutes, colloids, organic compounds, and biological matter) on the membrane surface, which eventually leads to irreversible membrane fouling and scaling on the membrane surface in SWM as shown in Fig. 8-1. In addition, the narrow spacer-filled channels of a SWM are associated with serious problems such as feed channel pressure drop from feed inlet to concentrate outlet (the loss of pressure owing to flow through the spacer-filled feed channels of spiral-wound module) and membrane damage due to the presence of feed spacers when they are tightly pressed against the rejection layer of membrane during the

manufacturing process. In summary, these major challenges of spiral wound membrane modules are shown in Fig. 8-1.

Fig. 8-1 The primary challenges of spacer in spiral wound membrane modules: pressure loss, concentration polarization, and membrane fouling.

Among these critical challenges, membrane fouling is one of the most challenging issues where a thin film of foulant is gradually deposited on a membrane surface or feed channel spacer (Meng, Yang et al. 2008). Membrane fouling can cause severe flux decline and require more driving force, either a higher osmotic pressure or transmembrane pressure to maintain the same flux, which is predicted to result in a 30% energy penalty for the desalination process (Field, Wu et al. 1995). Membrane fouling has two implications. First, it introduces an additional hydraulic resistance through the formation of a deposit layer on membrane. Second, the fouling layer causes the cake-enhanced osmotic pressure phenomenon, whereby

the back-diffusion of solutes from the membrane surface to the bulk solution is hindered and thus leads to an increase in the concentration polarization (Hoek and Elimelech 2003). Since membrane fouling is strongly influenced by the external concentration polarization, improved feed spacer design can mitigate membrane fouling in the FO process and can provide an opportunity for higher FO water flux.

One of the important roles of FO feed spacers is to improve the mass-transfer coefficient (k) at the boundary layer by creating eddies or mixing. Optimizing the mass transfer in a SWM is critical for reducing the external concentration polarization and to permit use of higher FO water flux for the next generation of ultra-permeable membranes, such as aquaporin FO membranes. The concentration polarization modulus (M) is an exponential function of the operating flux (J) and mass transfer-coefficient (k), i.e. $M = \exp(J/k)$. However, there is a trade-off between mass transfer and pressure loss, since both terms are a function of FO spacer properties and Reynolds number (Re), a dimensionless group that is a measure of the convective to diffusive transport of the flow, where $k = f(\text{spacer geometry}, \sim Re^{0.5})$ and $\Delta P_{CH} = f(\text{spacer geometry}, \sim Re^{1.8})$. More importantly, severe external concentration polarization will lead to FO membrane fouling but most of the previous studies claimed that external concentration polarization is not critical in FO process. In addition, FO feed spacer may create localized dead spots with poor mass transfer that can initiate fouling and hence influence membrane fouling patterns (Suwarno, Chen et al. 2012). Therefore, the main objective of this study is to fabricate a 3D printed FO feed spacer with higher mass transfer coefficient and lower pressure drop, thereby reducing membrane fouling. First of all, 3D printing technology is selected as a tool for fabrication of FO feed spacer due to its capability to create 3D object with freeform design (Chua and Leong 2014, Lee, Tan et al. 2016). A systematic approach is proposed to optimize one of the most important design parameters of

FO spacers in SWMs to mitigate the membrane fouling, namely *mesh length between spacer filaments* and more detailed description of the parameters of 3D printed FO feed spacers are shown in Fig. 8-2.

Fig. 8-2 The concept of unit cell (i.e. a *primary building unit*) of 3D printed FO feed spacers. (a) top view and (b) side view of a unit cell; (c) four unit cells (2x2) can be considered as a *secondary building unit* (i.e. a parallelogram-type mesh) with a spherical node at the intersection of two spacer filaments. The definitions of various parameters are following:

d_n = Diameter of the spherical node;

d_f = Diameter of the spacer filament

l_m = Mesh length between spacer filaments

θ = Mesh angle between spacer filaments

The hypothesis is that feed spacer with smaller mesh length will lead to higher mass transfer but also higher pressure drop along the feed channel. In order to verify the hypothesis, a pressurized cross-flow filtration is conducted to understand the relationship between mesh length and spacer performance followed by a FO fouling experiment to demonstrate the important role of spacer in fouling pattern (i.e. a FO cell with and without spacer). The rationale and overview of this study is summarized as below. Firstly, the presence of large organic compounds (i.e. foulants), such as dextran or polyelectrolyte, in the feed solution requires a FO feed spacer with good mass transfer to reduce external concentration polarization, which is more severe due to lower back diffusion for these large organic compounds. Secondly, a better FO feed spacer can have better fouling control especially in the active-layer-facing-feed-solution (AL-DS) orientation due to the lower external concentration polarization. Lastly, the fouling pattern on the membrane surface will also be strongly affected by the 3D printed spacers.

8.2 Theory

8.2.1 General intrinsic properties of feed spacers

Spacer filament ratio (SFR) is defined as the ratio between mesh length (l_m) and node diameter (d_n) and determined by:

$$SFR = \frac{l_m}{d_n} = \frac{\text{mesh length}}{\text{node diameter}}$$

The *mass transfer coefficient* (k) can be estimated using the experimental data based on modified film models and the equation of osmotic pressure. First of all, the water flux (J) of an ultrafiltration (UF) membrane can be correlate to osmotic pressure on the wall ($\Delta\pi_w$) using the dextran solution as the feed solution as shown in the following equations (Da Costa, Fane et al. 1991, Da Costa, Fane et al. 1994).

$$J = L_p(\Delta P_{TM} - \Delta\pi_w) \text{ (Find } \Delta\pi_w)$$

where L_p is the water permeability coefficient of membrane and ΔP_{TM} is the transmembrane pressure across the membrane. The water permeability coefficient was calculated for the test of pure water permeability (PWP) based on the assumption that the reflection coefficient is equal to 1 (i.e. 100% rejection and hence the concentration of permeate is equal to 0).

Next, the value of osmotic pressure on the wall ($\Delta\pi_w$) can be used in the equation of osmotic pressure to estimate the value of concentration of dextran on the wall (C_w) as shown in the following equation.

$$\Delta\pi_w = 0.0867C_w + 2.98C_w^2 + 89.8C_w^3 \text{ (Find } C_w\text{)}$$

Finally, the estimated value of C_w can be used in the modified film model to estimate the value of *mass transfer coefficient* (k) as shown in the following equation.

$$J = k \ln \left(\frac{C_w}{C_b} \right) \text{ (Find } k\text{)}$$

where C_b is the concentration of dextran solution in the bulk solution.

The pressure drop along the feed channel (ΔP_{CH}) is measured by the pressure transducer between the inlet and outlet of the pressurized cross-flow cell.

Voidage is defined as the void volume fraction and determined by (Da Costa, Fane et al. 1991, Da Costa, Fane et al. 1994):

$$\varepsilon = \frac{V_{total} - V_{spacer}}{V_{total}} = \frac{\text{void volume}}{\text{total volume}}$$

Four unit cells of spacer (2x2) can be considered as a secondary building unit (i.e. a parallelogram type mesh) with a spherical node at the intersection of two spacer filaments as shown in Fig. 8-2(c). In this case, the diameter of spacer filaments and the mesh length of spacer filaments are same ($d_{f1} = d_{f2} = d_f$; $l_{m1} = l_{m2} = l_m$) and hence the volume of spacer (V_{sp}) will be given by:

$$V_{sp} = \frac{4}{3}\pi \left(\frac{d_n}{2} \right)^3 + \pi \left(\frac{d_f}{2} \right)^2 \times l_m \times 2$$

The first term represents the volume of spherical node and the second term represents the volume of spacer filaments.

The total volume of spacer (V_{total}) is the product of the mesh area and the spacer thickness:

$$V_{total} = S_{mesh} \times h_{sp}$$

where

$$S_{mesh} = (l_m + d_n)^2 \times \sin \theta \text{ and } h_{sp} = d_n$$

and h_{sp} is the overall thickness of spacer, which is equal to the diameter of the spherical node.

So

$$V_{total} = (l_m + d_n)^2 \times \sin \theta \times d_n$$

and

$$\varepsilon = 1 - \frac{\frac{4}{3}\pi\left(\frac{d_n}{2}\right)^3 + \pi\left(\frac{d_f}{2}\right)^2 \times l_m \times 2}{(l_m + d_n)^2 \times \sin \theta \times d_n}$$

The surface area of 3D printed feed spacer (S_{sp}) can be calculated by:

$$S_{sp} = \pi d_n^2 + 2\pi d_f l_m - \pi d_f^2$$

The first term represents the surface area of spherical node, the second term represents the surface area of spacer filaments, and the third term represents the overlapping area between the spherical node and the spacer filaments. The calculated volume and surface area of 3D printed FO feed spacers with different mesh length are shown in Table 8-1.

Table 8-1 The geometric parameters of one-unit cell of 3D printed spacer with different mesh length.

Spacer – l_m (mm)	d_f (mm)	d_n (mm)	θ (°)	SFR	V_{total} (mm ³)	V_{sp} (mm ³)	ε	S_{sp} (mm ²)
ML – 7.5	1.0	2.5	90	3	250.0	12.27	0.95	36.52
ML – 5.0	1.0	2.5	90	2	140.6	16.20	0.88	52.23
ML – 2.5	1.0	2.5	90	1	62.5	20.12	0.67	67.93

l_m = Mesh length between spacer filaments

d_f = Diameter of the spacer filament

d_n = Diameter of the spherical node

θ = Mesh angle between spacer filaments

SFR = Spacer filament ratio

V_{total} = Total volume of the unit-cell

V_{sp} = Volume of the spacer

ε = voidage in spacer-filled channel

S_{sp} = Surface area of the spacer

8.3. Experimental

8.3.1 Materials and Methods

All membranes and materials were used as received unless otherwise stated. GE Osmonics Ultrafilic UF MW Membrane (YMMWSP3001, 305 x 305 mm, STERLITECH Corporation) and Cellulose Triacetate (CTA, Hydration Technology Innovations) FO membrane were used to characterize the performance of 3D printed feed spacer in terms of mass transfer, pressure drop and membrane fouling. VeroWhitePlus (RGD 835, Stratasys, SDS-06124, UN3082) was used as the printing inks for the fabrication of 3D printed FO feed spacer due to its good chemical resistance, and reasonable mechanical strength. Dextran, from *Leuconostoc* spp. (T-500, $M_w \sim 500,000$, CAS#: 9004-54-0, $(C_6H_{10}O_5)_n$, Sigma-Aldrich) was used as solute to measure mass transfer while humic acid (PGS 10, CAS# 1415-93-6, CAS# 68131-04-4, technical grade, Sigma-Aldrich) was used as foulant to prepare the feed solution, respectively. In the current study, performance of feed spacer was design and studied using three different 3D printed spacers with different mesh length (denoted as ML-2.5, ML-5.0, ML-7.5, see Fig. 8-3) while the draw spacer was remained unchanged in all experiments.

Fig. 8-3 The CAD design of 3D printed feed spacers with different mesh length (l_m) but same total area. (a) $l_m = 2.5$ mm (b) $l_m = 5.0$ mm (c) $l_m = 7.5$ mm. Total area: 360 mm x 60 mm.

The geometrical parameters of these 3D printed spacers are summarized in Table 8-1. Briefly, 3D printed spacer ML-7.5 has the longest mesh length while the 3D printed spacer ML-2.5 has the shortest mesh length. The pressurized cross-flow setup was firstly used to calculate the pure water permeability (L_p) using the following conditions:

- (a) Membrane = GE Osmonics Ultrafilic UF MW Membrane;
- (b) Temperature = 25 ± 0.5 °C;
- (c) Applied pressure = 0 - 10 bar;
- (d) Flow rate = 0 - 2.0 L/min.
- (e) Feed solution = DI water (for L_p) or dextran solution (1 – 10 g/L)

First of all, the UF membrane was compressed at 10 bar and a crossflow rate of 1.0 L/min for 12 hours with Milli-Q water before the measurement of pure water permeability. Before each experimental conditions, flux was set to the desired value and the system was left to equilibrate for 1 h. The permeation flux was calculated based on the mass of permeate at fixed interval while the pressure drop was measured based on a digital pressure transducer. For test runs with dextran solution as the feed solution, the desired concentration was achieved by the addition of concentrated dextran solution to reach the final concentration of 10 g/L and the system was left to equilibrate for another 1 h.

For FO fouling experiment, the water flux was calculated by the weight changes of feed solution at fixed interval using DI water as the feed solution and 1 M NaCl solution as the draw solution. Then the fouling test was started by the addition of the fouling agent to the feed tank. Unless otherwise stated, the following experimental conditions were used for all FO experiments:

- (a) Membrane = CTA FO membrane;
- (b) Temperature = 25 ± 0.5 °C;
- (c) Orientation = AL-FS (FO mode);
- (d) Draw Solution = 1 M NaCl solution;
- (e) Feed Solution = DI water (for baseline) or Dextran solution (10 g/L) or humic acid solution (20 mg/L) and CaCl_2 solution (1 mM);
- (f) Flow rate = 0.4 – 0.8 L/min for feed channel and 0.4 L/min for draw channel.

8.4 Results and discussion

Fig. 8-4 The camera picture of 3D printed feed spacers with different mesh length (ML) but same total area. Total area: 360 mm x 60 mm; Material used: VeroWhitePlus.

All 3D printed feed spacers were successfully fabricated based on the CAD design with high dimensional accuracy and uniformity as shown in Fig. 8-4. The total areas of 3D printed feed spacers are consistent, which is about 360 mm x 60 mm. In this study, VeroWhitePlus RGD 835 was used as the printing inks for the fabrication of 3D printed FO feed spacer due to its good chemical resistance and reasonable mechanical strength.

Fig. 8-5 The plot of water flux versus (a) transmembrane pressure (Feed = DI water or 10 kg/m^3 dextran solution, Flow rate = 1 L/min); (b) flow rate (Feed = DI water or 10 g/L dextran solution, $\Delta P_{\text{TM}} = 10 \text{ bar}$).

Fig. 8-5 shows the relationship of permeate flux with transmembrane pressure (TMP or ΔP_{TM}) and flow rate for 3D printed spacers using DI water or 10 kg/m^3 dextran solution as feed solution and constant flow rate (1 L/min). In all cases, the water flux of membrane increases when the TMP increases from 0 bar to 25 bar or flow rate increases from 0 L/min to 2.0 L/min . For the pure water permeability (PWP) test, water flux increases linearly with respect to TMP. Based on the slope of this linear line, the water permeability coefficient of membrane is about $10.8 \text{ L/m}^2 \text{ h bar}$. Next, 10 g/L dextran solution was used as feed solution for the following cases. Compared to the case that without any spacer in the test cell (i.e. empty channel), enhancement of permeate flux is observed due to the presence of 3D printed spacers when the flow rate increases but there is only a slight difference between 3D printed spacers with different mesh length when the TMP increases. It is interesting to note that 3D printed spacers with smaller mesh length give higher water flux than 3D printed spacer with larger mesh length (Permeate flux: $\text{ML-2.5} > \text{ML-5.0} > \text{ML-7.5} > \text{w/o spacer}$), which is consistent with the hypothesis. However, the difference among

3D printed feed spacers is quite small and hence further computational fluid dynamics (CFD) simulation is required to get the optimized mesh length.

Fig. 8-6 The plot of concentration polarization modulus (C_w/C_b) as a function of (a) transmembrane pressure (Feed = 10 kg/m³ dextran solution, Flow rate = 1 L/min); (b) flow rate (Feed = 10 kg/m³ dextran solution, ΔP_{TM} = 10 bar).

Fig. 8-6. shows another way of comparing the performance of 3D printed spacers in term of concentration polarization modulus (CPM or C_w/C_b). In this figure, the variation of estimated C_w/C_b is plotted against a range of (a) TMP from 2.5 bar to 10 bar; and (b) flow rate from 0.5 L/min to 2.0 L/min. It is critical to note that higher value of C_w/C_b means higher concentration polarization on the membrane surface and hence greater potential for membrane fouling. In both cases, the empty channel has the highest concentration polarization along the feed channel compared to the 3D printed spacers. When 3D printed spacers with different spacers are compared, the effect of flow rate is more significant than the TMP in term of CPM. When the TMP increases, the CPM also increases that can be attributed to the higher convective flow and hence accumulation of more dextran on the membrane surface. It is interesting to note that the

trend of CPM for different flow rate is the reverse trend for different TMP (i.e. higher the flow rate, lower the CPM but higher TMP, higher the CPM). This can be explained by the higher shearing force on the membrane surface and hence lower concentration of solute on the membrane wall (i.e. scouring effect) is observed. A similar trend is observed again in terms of concentration polarization modulus (i.e. CPM: ML-2.5 < ML-5.0 < ML-7.5 < w/o spacer).

Fig. 8-7. The plot of (a) mass transfer coefficient as a function of flow rate; (b) the correlation between mass transfer coefficient and pressure drop for 3D printed feed spacers with different mesh length. (Feed = 10 kg/m^3 dextran solution, $\Delta P_{\text{TM}} = 10 \text{ bar}$).

When 3D printed spacers with different spacers are tested under different flow rate, there is a large difference in terms of mass transfer coefficient (MTC or k_m) but a general trend is observed again (i.e. MTC: ML-2.5 > ML-5.0 > ML-7.5 > w/o spacer) as shown in Fig. 8-7 and Table 8-2. The flow rate of feed solution increases, the mass transfer coefficient of solutes also increases. It is because mass transfer is a function of flow rate and independent of TMP. For the 3D printed feed spacer with the smallest mesh length, the mass transfer coefficient is also the highest that is consistent with the hypothesis. However, it is also important to note that there is a trade-off

between mass transfer and pressure drop. Compared to empty channel, all the 3D printed feed spacers give higher mass transfer coefficient but also higher pressure drop along the feed channel and hence further optimization in terms of other geometry and dimensions of spacer parameters is required.

Table 8-2 Summary of typical experimental data at Flow rate = 2 L/min, and $\Delta P_{TM} = 10$ bar.

Spacer – ML (mm)	ΔP_{CH} (kPa)	$\Delta \pi$ (kPa)	C_w (kg/m ³)	k (10 ⁶ m/s)
w/o spacer	8.9	842	446	1.25
ML – 7.5	9.9	645	404	2.87
ML – 5.0	13.6	598	393	3.28
ML – 2.5	15.8	511	371	4.05

These observations are consistent with the hypothesis that feed spacer with smaller mesh length leads to higher pressure drop along the feed channel. To further understand about the relationship between the external concentration polarization and membrane fouling, ML-7.5 is chosen as the typical 3D printed FO feed spacer due to its lowest pressure drop with reasonable mass transfer for the FO fouling test.

Fig. 8-8 A comparison of FO test cell with 3D printed feed spacer (ML-7.5) and without any spacer (i.e. empty channel) in terms of FO water flux under fouling conditions. (a) Feed Solution = DI water; (b) Feed Solution = 10 g/L Dextran solution; (c) 20 mg/L humic acid solution and 1 mM CaCl_2 solution; (d) The flow rate of feed channel was increased from 0.4 L/min to 0.8 L/min while the flow rate of draw channel was fixed at 0.4 L/min throughout the experiment. Membrane = CTA FO membrane; Temperature = 25 ± 0.5 °C; Orientation = AL-FS (FO mode); Draw Solution = 1 M NaCl.

As shown in fig. 8-8, the variation of FO water flux is plotted against accumulated time with different types of fouling conditions. FO test cell with ML-7.5 and without any spacer (i.e. empty channel) are compared in term of FO water flux under four different fouling conditions: (a) feed solution = DI water; (b) feed solution = 10 g/L Dextran solution; (c) feed solution = 20 mg/L humic acid solution and 1 mM CaCl_2 solution; (d) The flow rate of feed channel was increased from 0.4 L/min to 0.8 L/min while the flow rate of draw channel was fixed at 0.4 L/min throughout the experiment. First of all, DI water was used as feed water for 24 hours to get a baseline for comparison and ML-7.5 gives a slightly higher FO water flux than the empty channel. Next, high concentration of dextran solution (10 g/L) was used as feed water but there is no change in term of FO water over > 24 hours compared to the baseline. It is because both the FO membrane and dextran macromolecule are hydrophilic compounds and hence no interaction between them even though at the high concentration.

The feed solution was then changed to 20 mg/L humic acid solution and 1 mM CaCl_2 solution. The purpose of small amount of calcium chloride solution is to increase the interaction between FO membrane and humic acid. As a result, FO water flux decreases in both cases but FO water flux of empty channel (i.e. without spacer) decreases more significant than the FO water flux of spacer-filled channel. This result clearly demonstrates that the important role of FO feed spacer to maintain the higher water flux and empty channel has lower FO water flux due to more severe external concentration polarization and hence higher fouling tendency on the membrane surface.

Lastly, the effect of flow rate along the feed channel on the reversible membrane fouling was also studied. When the flow rate increased from 0.4 L/min to 0.8 L/min, the FO water flux of

spacer-filled channel was recovered back to almost initial FO water flux but the FO water flux of empty channel only recovered slightly. These results indicate that FO fouling in spacer filled channel is reversible and the fouling layer can be washed away at higher flow rate compared to empty channel. In summary, these preliminary results clearly demonstrate that the important role of FO feed spacer is to increase mass transfer and disturb external concentration polarization on the membrane surface and hence higher FO water flux was observed.

Based on these preliminary results, a proposed mechanism is shown in Fig. 8-9. FO test cell without any feed spacer (i.e. empty channel) may create localized dead spots with poor mass transfer that can initiate external concentration polarization and hence membrane fouling as shown in Fig. 8-10 (a). However, 3D printed FO feed spacer with contact-point design may significantly reduce the localized dead spots with better mass transfer that can reduce the accumulation of foulant on the membrane surface and hence influence membrane fouling patterns.

Fig. 8-9 (a) The comparison of fouling pattern between FO test cell without spacer (left) and FO test cell with 3D printed FO feed spacer (right); (b) proposed mechanism for the observed fouling pattern on the membrane surface.

8.5. Conclusion

In this study, FO feed spacer with three different mesh length were successfully designed and fabricated using 3D printing technology. The main conclusion is that the 3D printed feed spacers with smaller mesh length can give better mass transfer but also higher pressure drop along the spacer-filled feed channel. In addition, the 3D printed spacers have smaller concentration polarization modulus compared to empty channel and hence higher FO water flux under membrane fouling test. However, further optimization and studies, such as CFD simulation and real-time monitoring of membrane fouling, are required to better understand the role of 3D printed feed spacers during the process of membrane fouling. Nevertheless, the fabrication of FO feed spacer with mesh length using 3D printing is proven to be feasible, which open up a new research area in osmotic-driven membrane process and might contribute significantly to the overall FO performance in terms of mass transfer, pressure drop and membrane fouling.

Chapter 9

Conclusions and recommendations

9.1 Conclusions

Fabrication and characterization of porous materials-based mixed matrix membranes and porous matrix membranes and 3D printed feed spacers were systematically studied. The physical properties, chemical properties, surface morphology, intrinsic separation properties and FO performance of (a) MMMs and PMMs; and (b) 3D printed feed spacers were investigated in details. The major findings and conclusions are summarized as following:

(1) SG-based mixed matrix FO membranes with different SG loadings were systematically synthesized and characterized in this study. SG-based mixed matrix FO membranes can significantly enhance FO water flux probably due to both the nanometer pores in the SG particles and enhanced substrate porosity upon embedment into the membrane substrate layer. Both the intrinsic separation properties and surface chemistry and of SG-based mixed matrix FO membranes were enhanced by various SG loadings. The highest FO water flux of $121 \text{ L/m}^2 \text{ h}$ was achieved by using the 2.0 M MgCl_2 as the DS and DI water as the FS. The current study demonstrates the potential of MMMs for improving the substrate porosity and mass transfer coefficient as well as the rejection layer properties.

(2) SG-based mixed matrix FO membranes with different pore size of SG particles were systematically fabricated and characterized in this chapter. SG-based mixed matrix FO

membranes with optimal pore size (90 Å) can enhance the water permeability and FO water flux probably due to both the nanometer pores of the hydrophilic SG particles and hence enhanced the mass transfer of water inside the membrane substrate layer. The highest FO water flux of 126 L/m² h was achieved using the 1.0 M MgCl₂ as the DS and DI water as the FS. The current study demonstrates the importance of pore size of filler in mixed matrix FO membranes for improving the mass transfer coefficient of the substrate layer. This might potentially provide an additional parameter for ICP control in osmotic-driven membrane processes.

(3) MOF-based PMM were systematically synthesized and characterized in this study. PMMs can significantly enhance water permeability in pressure driven membrane processes probably due to the removal of MOF particles in the polymer matrix, which enhanced membrane porosity and interconnectivity of the membrane. More importantly, the current study demonstrates MOFs as green template might have good potential for not only pressure-driven membranes processes but also for carbonaceous nanofiber membranes for selective filtration and separation of nanoparticle, or osmotically-driven membrane process, such as forward osmosis (FO) and pressure-retarded osmosis (PRO).

(4) FO feed spacer with three different mesh length were successfully designed and fabricated using 3D printing technology. The main conclusion is that the 3D printed feed spacers with smaller mesh length can gives better mass transfer but also higher pressure drop along the spacer-filled feed channel. In addition, all the 3D printed spacers have smaller concentration polarization modulus compared to empty channel and hence higher FO water under membrane

fouling test. However, further optimization and studies, such as CFD simulation and real-time monitoring of membrane fouling, are required to better understand the role of 3D printed feed spacers during the process of membrane fouling.

9.2 Recommendations

In order to better understanding about the nanocomposite membranes and 3D printed feed spacers, future research areas should focus on understanding the mechanism of water/solute transport inside the substrate layers as well as on the membrane surface. Based on the current study, I would like to suggest the directions of future research works as following:

(1) The effect of smaller particle size of silica gel particles and its effect on the overall membrane performance. In addition, the effect of different shapes of silica gel particles, such as spherical, square, and rectangular, is worthwhile to study because the current study is based on the irregular shape silica gel particles. The hypothesis is that regular shape silica gel particles might give a smoother surface of the FO substrate and hence less defect formation that will influence the overall FO performance.

(2) The surface chemistry of the silica gel particles and the compatibility between the silica gel particles and the polymer molecules. Good compatibility between the filler particles and polymers played an important role in the overall membrane performance. However, this compatibility problem was not studied in detailed in the SG-based mixed matrix FO membranes. For example, Liu *et al.* reported that double-blade co-casting technique for flat-sheet silica-polysulfone mixed matrix FO substrate but the compatibility issue between the silica particles and polysulfone was not addressed in their papers. (Liu and Ng 2015, Liu, Ong et al. 2016)

(3) *In situ* generation of filler particles during the preparation of polymer dope solution or after phase inversion. For example, one-pot synthesis is a common method in the organic synthesis. Similar concept can potentially be applied in the mixed matrix membranes using MOF nanoparticles as fillers and polyamide polymer dope solution (Liu, Wang et al. 2014, Campbell, Davies et al. 2015).

(4) The relationship between the pore size the silica gel particles and the molecular weight of polymer is one of the most important consideration for the fabrication of mixed matrix membranes. In addition, further optimization of skin layer is also very important (Liu and Ng 2015, Liu, Ong et al. 2016). Although imperfect porous substrate layer will cause defects on the skin layer, the link between porous substrate and the rejection properties of the skin layer is still not very clear. More attention should be paid to maintain the salt rejection due to the fact that highly porous substrate put higher demand to the active layer to reject the salt.

(5) The selection of 3D printing technologies for fabrication of FO feed spacers and the impact of different 3D printing technologies on the performance enhancement in terms of mass transfer, pressure, drop, and fouling tendency.

(6) The selection of 3D printing materials for fabrication of FO feed spacers and the impact of different 3D printing materials on the performance enhancement in terms of mass transfer, pressure, drop, and fouling tendency.

(6) The relationship between the geometry of spacer node and the pressure drop along the feed channel. The motivation is that feed spacer with different geometry of node will lead to different kind of form drag and hence different degree of pressure drop along the feed channel.

(7) The relationship between the geometry of spacer filament and the pressure drop along the feed channel. The inspiration is that feed spacer with different geometry of spacer filament will lead to different kind of form drag and hence different degree of pressure drop along the feed channel.

Appendices – A1

A PERSPECTIVE ON 3D PRINTED MEMBRANE: DIRECT/INDIRECT FABRICATION METHODS VIA DIRECT LASER WRITING

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Abstract

This conference paper mainly comprises three parts: (1) a brief introduction to the current state of research; (2) a clear description of the additive manufacturing technique and fabrication methods; (3) a brief description of the structure-performance relationship. The idea is based on the notion that membranes with 'controlled architecture' could achieve enhanced performance, and that additive manufacturing techniques, also known as 3D printing, have a great potential in fabricating membranes with controlled architecture.

Keywords: Membrane; Spiral wound module; 3D printing; Additive manufacturing; Rapid prototyping

A1. Introduction

The research of 3D printed (3DP) membranes is pioneered by Professor Dr.-Ing. Matthias Wessling and his co-workers at the Chemical Process Engineering (CVT)/Aachener Verfahrenstechnik (AVT), and the DWI - Leibniz Institute for Interactive Materials at the RWTH Aachen University, Germany. To date, the major developments focus on module and device fabrication with typical 3D printers with high resolution (~30 µm). Their work is mainly based on a common liquid-based 3D printing technique, called Digital Light Processing (DLP), which could be used for a variety of applications. In 2014 Wessling *et. al.*

proposed a novel approach to directly print via the DLP technique a ladder-shaped polydimethylsiloxane (PDMS) membrane, which is not feasible to produce with traditional machining techniques (Femmer, Kuehne et al. 2014). PDMS is one of the common polymers used in gas-liquid-contactors due to its high permeability for various gases. In gas-liquid contactors, it is important to note that membrane surface geometry plays an important role in their performance and hence PDMS membranes fabricated by 3DP technique with sheet-like 'triple-periodic minimal surfaces' (TPMS) architectures gave a better performance relative to conventional membrane geometries.

Wessling and his co-workers have also developed a new sacrificial lithography technique to produce a tri-continuous TPMS-PDMS membrane with a complex geometry via a sacrificial resist (Femmer, Kuehne et al. 2015). Compared to flat-sheet and hollow-fiber membranes, these TPMS-PDMS membranes give a better boundary-layer mass transport due to the improved hydrodynamics. In addition, TPMS-PDMS membranes with different shapes were created to systematically study their structure-performance relationship in terms of heat transfer and pressure drop. In this study non-geometrical influences were prevented and other effects decreasing membrane performance, such as concentration polarization, were identified (Femmer, Kuehne et al. 2015). Furthermore, based on the 3DP method, a PDMS membrane device with mixers based on a staggered herringbone structure was fabricated via soft lithography to increase mass transport and reduce pressure drop (Femmer, Eggersdorfer et al. 2015). This herringbone structure was designed as a static mixer to induce secondary flows such as Dean vortices and Taylor flows, which significantly reduce the concentration polarization on the membrane surface in a microfluidic gas-liquid contactor. These studies demonstrate the potential benefits of 3D printed membrane macrostructures ($>30\text{ }\mu\text{m}$). However, to apply the 3D printing approach to print a microporous membrane requires 3D printers with submicron resolution (W. S. Tan 2014, Lee, Tan et al. 2016). The interesting research question is, '*Can 3D printing produce prototypes of such idealized membranes?*'

A2. Direct Laser Writing

Direct laser writing (DLW) is one of 3D printing techniques that can directly print a three-dimensional membrane with well-defined sub-micron pores. This DLW technique was recently developed by Prof. Dr. Martin Wegener from Karlsruhe Institute of Technology (KIT), Germany for the fabrication of nanostructures such as photonic crystals. A new spin-off company, called Nanoscribe, is currently selling this advanced 3D laser lithography system and photoresists materials. This DLW technique is based on a laser light source for two-photon polymerization (TPP) of photoresist. The system is called *Photonic Professional GT* with the unique possibilities to fabricate microporous membranes with feature sizes down to 500 nm. Typically, there are two types of scanning modes: Piezo mode and Galvo mode. The Piezo scanning mode is a fixed-beam moving-sample (FBMS) method with x-y-z-movement and a writing field up to $300 \times 300 \times 300\text{ }\mu\text{m}^3$. On the other hand, the Galvo scanning mode is a moving-beam fixed-sample (MBFS) method with only x-y-movement and for which the writing field depends on the

objective. The key difference between the Piezo and Galvo modes is that Piezo mode can achieve arbitrary 3D trajectories with an optimized speed to accuracy ratio while the Galvo mode can print only the object layer-by-layer with a higher speed but lower accuracy. For the fabrication process the overview of the whole process mainly consists of three steps: (a) design structure; (b) choice of materials; and (c) membrane fabrication. Based on this DLW technique, two fabrication methods, (a) direct method and (b) indirect method, can be used to fabricate a membrane with different pore size and pore shape (Figure 1).

Figure A1-1 The schematic diagram of (a) direct method via direct laser writing (DLW) and (b) indirect method via phase separation μ -molding (PS μ M).

A3. Direct and Indirect Fabrication

For the direct method, a microporous membrane with a well-defined sub-micron pore structure is designed using computer-aided design (CAD) software followed by the direct fabrication of these membranes using the DLW technique. For the indirect method, a μ -mold, which consists of a microarray with different size and shape, is fabricated by the DLW technique followed by the phase separation μ -molding (PS μ M) to produce these membranes (Vogelaar, Barsema et al. 2003, Vogelaar, Lammertink et al. 2005). PS μ M is one of the novel microfabrication methods based on phase separation of a polymer solution and a broad range of materials has been structured, including both polymers and inorganic materials. An ideal microporous membranes would have surface isoporosity, be highly porous, possibly with interconnected pores and with tunable surface chemistry (Fane, Wang et al. 2015). However, the feasibility of fabricating an ideal microporous membrane with different pore size and shape via direct/indirect methods based on the DLW technique still remains untested.

A4. Investigation of Structure-Performance Relationship

It is important to understand the structure-performance relationship of microporous membranes because these membranes are not only the basis for microfiltration (MF) and ultrafiltration (UF) separations, but also are integral to other membrane processes where they provide a substrate layer for thin film composites for nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), and pressure-retarded osmosis (PRO) membranes. It is well-recognized that the overall performance of these membranes is critically dependent on the substrate morphology and property, such as membrane porosity (Chandler and Zydney 2006). From a theoretical point of view, the membrane porosity is defined as the volume of pores divided by the volume of the whole membrane. In this study the membrane porosity is determined by the pore size, pore shape and interconnectivity of the membrane; however, controlling these pore characteristics in a well-defined manner is still almost impossible based on the traditional fabrication methods, such as non-solvent-induced phase separation (NIPS) or thermally-induced phase separation (TIPS). In the new approach microporous membranes with well-defined pore structure and morphologies could be fabricated and characterized to understand the structure-performance relationship in terms of permeability and fouling tendency.

For the first step, microporous membranes will be designed by computer-aided design (CAD) software such as Autodesk Inventor and Solidwork. It is important to note that there is an additional option for microporous membranes with either interconnected pores or two different shape/size pores on the same membrane for the direct method via DLW technique (Figure 2).

Figure A1-2 The CAD design of 3DP membranes with either interconnected pores or two different shape/size pores (left) (Ho and Zydney 1999) and (right) the schematic diagram of phase separation hierarchical-molding (PSHM).

On the other hand, a new concept, called "phase separation hierarchical molding" (PSHM), is proposed based on the indirect method of phase separation μ -molding. It is critical to note that a hierarchical-structured mold, which consists of a nanoarray as the secondary structures (nanostructures) and a

microarray as the primary structures (microstructures), could be fabricated via DLW technique followed by the phase separation hierarchical-molding (PShM) to obtain an asymmetric membrane with hierarchical pores.

To establish the structure-permeability relationship, the number of pores is fixed while the pore diameter is varied for the same total membrane area. Next, a suitable photoresist is chosen based on the desired optical, chemical, physical, and pre-and-post processing properties. For the last step a reasonable writing mode will be selected based on the objective after which the 3DP microporous membrane will be fabricated. In summary, the three key considerations of the whole process development in DLW techniques are design parameters, materials parameters and process parameters. It is also critical to bear in mind that there are several disadvantages of the DLW technique based on the direct/indirect methods compared to the conventional NIPS and TIPS fabrication techniques, such as (1) a small membrane area ($<300 \times 300 \mu\text{m}^2$); and (2) a relatively time-consuming process to achieve a complex structure that depends on scanning mode.

A5. Conclusion

In summary, this conference paper briefly describes the recent research and development of 3DP membranes in the first part followed by the description of the DLW technique and the direct and indirect methods for the fabrication of the 3D printed membrane in the second and third part. In the last part, the importance of structure-performance relationship of 3D printed membranes is also briefly described. If the 3DP microporous membrane with controlled architecture via the direct/indirect fabrication methods using DLW technique can be fabricated successfully, then this will be a significant breakthrough in 3DP membranes in term of resolution from micrometer scale to submicron or even nanometre scale. For the scientific benefits and applicability of the results, the knowledge generated from this fundamental study will help us to better understand the structure-performance relationship of microporous membranes. For the economic benefits and applicability of the results, the impact of this research will be significant for advancement of the membrane industries in Germany, not only for MF and UF membranes but also for other types of membranes, such as NF, RO, FO, and PRO.

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