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NOVEL NANOCOMPOSITE MEMBRANES FOR OSMOTICALLY DRIVEN PROCESSES: FABRICATION AND APPLICATION

by

SUNGIL LIM

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School of Civil and Environmental Engineering
Faculty of Engineering and Information Technology
University of Technology Sydney (UTS)
New South Wales, Australia

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Certificate of Authorship

I, **Sungil Lim** declare that this thesis, is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney. This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution. This research is supported by the Australian Government Research Training Program.

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Abstract

For osmotically driven membrane processes, including forward osmosis (FO) and pressure retarded osmosis (PRO), water permeate was selectively induced across a semi-permeable polymeric membrane by the osmotic pressure generated from the salinity gradient. Although both FO and PRO processes are mainly driven by the osmotic pressure difference increased by the more concentrated draw solution on the permeate site of the membrane, membrane orientations for the processes are mainly confirmed as the active layer facing the feed solution (AL-FS) for FO, and the active layer facing the draw solution (AL-DS) for PRO, respectively. Although the AL-FS orientation for FO is beneficial for controlling membrane fouling on the dense active layer, diluted internal concentration polarisation (ICP) inside a FO membrane would be a major obstacle to maintaining the osmotic driving force under FO operation. These processes have been widely used for a variety of water treatments and hybrid systems as a low-energy process. However, the processes still have some critical challenges for membrane development, which are related to the following aspects: water permeability, reverse solute diffusion, concentration polarisation, membrane fouling and membrane stability. Although many earlier studies developed various kinds of polymeric membranes at laboratory scale to produce outstanding performances for overcoming existing challenges in FO and PRO processes, most of them never produced their own scaled-up membrane modules for commercial applications. This study, therefore, initially targeted novel nanocomposite membrane development for FO and PRO processes using the dual-blade casting technique and two hydrophilic nanomaterials (graphene oxide and halloysite nanotubes). Subsequently, we selected the best strategy in our activities, and the selected one was further investigated for its commercial viability.

A novel, thin-film composite (TFC) forward osmosis (FO) membrane with dual-layered substrate support was manufactured by a double-blade casting technique using different polysulfone (PSf) concentrations for top (15 wt%) and bottom (7 wt%) substrate layers. Graphene oxide (GO), at the optimum loading of 0.25 wt.%, was incorporated into the substrate layer, and the dual casting approach resulted in a membrane support with an extremely porous bottom structure and a dense top skin layer on which the polyamide active layer was effectively formed, which is desirable for reducing the internal concentration polarisation (ICP) so that the optimum dual-layered GO nanocomposite membrane exhibited high water permeability and good ion selectivity enhanced by the presence of well-dispersed hydrophilic GO in the PSf substrate. The optimum FO membrane with a fabric backing support exhibited similar FO performances to a fabric-free one under the same compositions, so that this approach presents positive potential for commercial application. In addition, the dual-blade casting technique was also benchmarked to develop high-performance PRO membranes. The approach incorporates halloysite nanotubes (HNTs) into the bottom polymer substrate layer and GO on the top layer substrate, on which a thin polyamide active layer is formed. The fabricated membrane substrate showed highly desirable membrane substrate properties, such as a high porosity, opened-bottom surface, suitable top-skin surface morphology for subsequent polyamide (PA) layer formation and high mechanical strength, which are all desirable for high-performance PRO processes. The bottom substrate incorporated with HNTs presented high fouling resistance and antibacterial properties due to the HNT's loading to a closed morphology, enhanced negative charge density and nano-sized pins on the bottom surfaces for alleviating the growth of microorganisms. The overall results of this study, therefore, suggested an alternative approach for developing outstanding PRO membranes with high performance, fouling resistance and antibacterial properties.

As the demand for new HF TFC membranes for FO increases, outer-selective hollow fibre (OSHF) TFC membranes were designed and developed by the novel approach used in this study. Thin and porous HF membrane substrates comprising a dense and smooth outer surface were manufactured by manipulating the air-gap distance in the HF fabricating unit. Subsequently, the vacuum-assisted interfacial polymerisation (VAIP) was specially modified for formation of a PA layer on the outer surface of the HF membrane substrate. The experimental results confirmed that the membrane substrate should be a smooth layer with a molecular weight cut-off (MWCO) of less than 88 kDa for subsequent PA layer formation via VAIP. The optimum OSHF TFC membranes manufactured using the air-gap (6 cm) exhibited outstanding FO performance. Furthermore, the optimised membrane demonstrated higher fouling resistance and cleaning efficiency using a silica-alginate spiked feed solution due to the membrane's physico-chemical characteristics. Moreover, large-scale membrane modules (22.8 cm^2) were successfully produced under our methodology, so that we can expect strong scalability of our membranes at a commercial scale.

For further development of the OSHF TFC membranes, specific hydrophilic nanomaterials were used to prepare OSHF thin-film nanocomposite (TFN) membranes. This study focused on size-controlled graphene oxide (SGO) and schiff base network-1 (SNW-1) as COF for the TFN membranes. The novel hypothesis and related mechanisms were demonstrated based on theoretical and experimental studies. Under the VAIP process, most SGO and SNW-1 nanofillers in meta-phenylenediamine (MPD) solution diffused on the membrane surface were horizontally stacked on the outer surface due to the vacuum suction from inside to outside, so that the nanofillers could be effectively embedded into the PA selective layer for producing OSHF TFN membranes with extremely low material loading. In particular, SGO nanosheets were ideally incorporated into the thin PA layer under the optimum loading at 0.0005 wt%, so that the produced TFN membranes exhibited extremely high levels

of water flux due to enhanced free volume and hydrophilicity of the PA composite layer from GO. In particular, SGO membranes exhibited better water flux and ion rejection than those of bulk GO embedded membranes (BGO) due to less water pathways and high free volume inside the PA layer from SGO's small lateral size. In addition, SGO demonstrated strong fouling resistance and high cleaning efficiency using artificial wastewater due to the loose accumulation of foulants on the surface. Using SNW-1 nanoparticles, high permeable OSHF TFN membranes were also successfully developed in this study. Based on the above mechanisms, SNW-1 nanoparticles were also securely incorporated into a PA layer with a less detrimental effect on the PA layer's integrity. It is expected that the secondary amine groups in SNW-1 may chemically react with the acyl chloride groups in the TMC solution through covalent bonding to further improve the integrity of the PA composite layer. As a result, the optimum OSHF TFN membranes exhibited the highest water transport and ion selectivity, which may be attributable to the porous structures and hydrophilic nature of SNW-1. In addition, SNW-1 nanoparticles were well organized inside the thin and dense PA matrix with retaining the PA layer's integrity. Accordingly, the optimum TFN membranes exhibited stable FO performances under long-term operation (72 hours), indicating that the SNW-1 embedded OSHF TFN membranes are able to possess strong durability under FO operation.

Accordingly, our approaches can be valuable and practical for producing superior FO and PRO membranes with outstanding performance and fouling resistance among existing research, and commercial TFC and TFN membranes for their applications. Through my discussion, it is expected that the OSHF TFN GO membranes (as stated in Chapter 6) can be the best performing FO membranes that this thesis has studied in terms of the membranes' intrinsic transport properties and fouling potential for water treatment. In addition, this OSHF TFN membrane makes it easier to scale up membrane modules for commercial application compared to that of the flat-sheet membrane. The scaled-up OSHF TFN membrane module can

also be a suitable candidate for various osmotically driven processes such as aerobic or anaerobic osmotic membrane bioreactors (OMBR), fertiliser-drawn OMBR (FD-OMBR) or high-turbidity water treatment. Furthermore, based on my dual-blade casting studies we may consider developing dual-layered OSHF TFC or TFN membranes for FO or PRO applications using a triple-orifice spinneret. Finally, we strongly believe that the proposed novel approaches can provide bright insights into advance of FO processes, and our research team is planning to scale up the optimum membrane modules for various process applications and their commercialisation in the near future.

Keywords: *membrane; forward osmosis; pressure retarded osmosis, thin film composite; thin film nanocomposite; dual blade casting; outer selective; flat-sheet; hollow fiber; graphene oxide; halloysite nanotubes; covalent organic framework*

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1 Introduction

1.1 Research background

The world's population is growing rapidly and so are the issues related to fresh water, food and energy affecting the global economies (Montgomery and Elimelech, 2007, Shannon et al., 2008a, Tran et al., 2017). Among the three elements in the energy-water-food nexus, water is probably the most essential part for enhancing agriculture's productivity and global food security. The agriculture sector uses over 70% of the world's total fresh water consumption (Jury and Vaux, 2005, Tran et al., 2017). Nevertheless, water stress has been a severe issue for decades in many regions on our planet. The impact of climate change is further worsening water stress such as through unpredictable rainfall events, extreme weather conditions and frequent drought (Hughes, 2003, Mearns et al., 1996, Whetton et al., 1993). According to the International Energy Agency (2017), global electricity demand is envisaged to rise by 60% by 2040 with the projected electricity consumption of approximately 34,470 terawatt-hours in 2040 (Agency, 2017). Moreover, this demand has been increasing rapidly and is predicted to double in the next decades (Agency, 2017). The predicted trend is clear and understandable as the world population is rapidly increasing, however, the production of energy has been facing many challenging issues. Firstly, fossil fuel resources are being over exploited and are running out. Secondly, conventional energy production emits a huge amount of greenhouse gases changing the global climate. Lastly, more stringent regulations in electricity generation are increasing the cost of energy. Therefore alternative renewable energy sources have been utilized and exploited for power generation (Haas, 2008).

Many attempts have been made to develop technologies and policies for water and energy management to combat water-energy related issues. Osmotic driven processes which can be

applied in both water production and energy generation have recently attracted many research interests. For the water scarcity problem, using alternatives such as impaired water and unlimited saline water resources could be a salient solution (Shannon et al., 2008a). Desalination is one of the most reliable technologies for augmentation of limited fresh water sources (Shannon et al., 2008a). Currently available desalination technologies including reverse osmosis (RO) and thermal based processes are highly capital and energy intensive (Shon et al., 2008, Ng et al., 2006, McGinnis and Elimelech, 2008, Semiat, 2008) even though significant improvement in membrane and energy efficiency have been made in the last few decades. Forward osmosis (FO) has recently emerged as a novel process for various applications including for desalination. FO process is driven by the natural osmotic process without the need of high hydraulic pressure as for the RO process and hence the power consumption of FO is much lower than RO although they use similar salt rejecting membranes (McGinnis and Elimelech, 2008, Achilli et al., 2010, Tang et al., 2010, McGinnis and Elimelech, 2007, Choi et al., 2009, Lay et al., 2010). For power generation, free energy released during the mixing of different saline liquid streams could be harvested and exploited for power production by using membrane-based technologies such as reverse electro dialysis (RED) and pressure retarded osmosis (PRO) (Pattle, 1954a, Loeb, 1975, Yip and Elimelech, 2014). PRO has several advantages compared to RED with higher power density, higher efficiency and PRO is also more suitable for power extraction from high salinity gradients (Yip and Elimelech, 2014).

Osmotically driven processes utilize an osmotic pressure difference to drive the water transport through a semi-permeable membrane from a lower osmotic pressure solution (referred to as feed solution (FS)) to a higher osmotic solution (referred to as draw solution (DS)). The difference between FO and PRO processes is that while there is no pressure applied on the DS side

in the former, in a typical PRO process the DS side is pressurized with a specific value. The volume and hydraulic pressure of the diluted salty water are consequently increased which enables the generation of electricity when releasing the pressurized water through a hydro-turbine (Gerstandt et al., 2008, Loeb, 1976b, Thorsen and Holt, 2009). In addition, PRO is an environmentally friendly technology because no chemicals or greenhouse gas are facing released during power generation (Chung et al., 2012, Logan and Elimelech, 2012). Although these two processes offer a couple of advantages over the others in the field of water treatment and energy generation, there are still some challenges hindering their development of them. One of the challenges that both FO and PRO face a lack of suitable membranes (Chekli et al., 2016, Wang et al., 2018, Cath et al., 2006). Although membranes used in FO and PRO processes are differently designed and fabricated, the desired membranes must possess high performance in terms of high water flux, low reverse solute flux and high fouling resistance (Wang et al., 2018).

1.2 Research motivation

For osmotically driven processes including FO and PRO, water permeation is selectively induced through a semi-permeable polymeric membrane by the osmotic pressure produced from the salinity gradient between high-saline DS and low-saline FS. The driving force in these processes, which mainly depends on the osmotic pressure between DS and FS, enables natural diffusion of water molecules and ion molecules across a semi-permeable membrane. In particular, in PRO processes, specific hydraulic pressure below the osmotic pressure gradient should be applied into a draw stream to build-up the internal pressure from the osmotic driving force. Although these osmotically driven membrane processes have been widely suggested and applied

to a variety of water treatments with low-energy consumption, these processes still possess some critical challenges. These challenges for FO and PRO processes are related to concentration polarization, reverse solute diffusion, membrane fouling, membrane stability and regeneration of the DS.

Concentration polarization (CP) is a common and inevitable phenomenon in membrane-based water treatment processes including pressure and osmotically driven processes. When the driving force by an osmotic pressure between FS and DS occurs across a membrane, both external concentration polarization (ECP) and internal concentration polarization (ICP) can take place. Normally, the ECP occurs at the outer surface of an active layer, and ICP occurs within a porous membrane substrate. In FO processes, while the concentrated ECP can be minimized by controlling the hydrodynamic operating conditions such as cross-flow velocity, the diluted ICP cannot be simply mitigated through hydrodynamic operating conditions. ICP can be minimized by optimization of the intrinsic property of the membrane support layer such as through improving its structural properties, including porosity, pore size distribution, tortuosity and thickness (Ref). Recently, a few studies have introduced FO membranes with substrates which are thin with low S values, are highly porous with macro-voids, and have high wettability to minimize ICP and improve water permeability (Tiraferri et al., 2011, Xiao et al., 2015, Liu and Ng, 2014, Liu and Ng, 2015, Park et al., 2015, Han et al., 2012d). However, there is still a lack of novel approaches for highly porous membrane fabrication in order to ideally control the diluted ICP for alleviating loss of an osmotic pressure in FO processes.

For development of PRO membranes for energy harvesting, the CP should be considered as one of the critical obstacles for optimizing PRO processes. The ideal PRO membrane must thus possess a porous internal structure like an ideal FO membrane. However, the most important thing

for PRO membranes is mechanical stability to withstand a high hydraulic pressure in PRO. Thus, the ideal PRO membranes should have high water permeability, ion selectivity and strong mechanical strength, which together produce high power density (PD) at a high applied pressure. The thin, active layer of the PRO membrane must be supported by a strong and yet highly porous membrane substrate in order to have a high PD. However, a tradeoff exists between the substrate porosity and the mechanical strength of the membrane (Cheng et al., 2017h, Han et al., 2015). Further, the development of PRO membranes must also consider its resistance to fouling propensity (Lieu Le et al., 2017, She et al., 2017, Chen et al., 2017, Han et al., 2016f). When the membrane operates in the orientation with its active layer facing the draw solution (AL-DS), organic matter, scaling precursors and other foulants contained in the FS can easily foul the membrane surface facing the porous substrate, resulting in a significant PD decline (She et al., 2013, Thelin et al., 2013, Chen et al., 2015b, Han et al., 2016f, Lieu Le et al., 2017). Inorganic scaling such as that due to calcium salts can be controlled by adjusting pH and using anti-scalants. However, organic and colloidal fouling is a major concern in the PRO process; it can significantly reduce membrane permeability and hence PD due to the accumulation of foulants inside the membrane substrate (internal fouling) (Han et al., 2016f, Lieu Le et al., 2017).

Many academic studies on membrane fabrication have handled flat-sheet membranes with various novel approaches, however hollow fiber (HF) membranes have more practical potential to be commercialized due to high performance, high packing density per module, their self-supporting structure and less concern about scale-up from the laboratory (Ren et al., 2017, Zhong et al., 2013). Inner selective HF (ISHF) membranes where the PA selective layer is deposited on the lumen side of a membrane substrate have been mainly developed and employed for FO. (Zhong et al., 2013, Ong et al., 2015, Ren and McCutcheon, 2017). Since FO membranes are mainly

operated in active-layer-facing-feed-solution (AL-FS) orientation, the FS must be supplied into the bore side of ISHF membrane. In this orientation, the particulates in FS can clog the bore side of the membrane module resulting in the decline of FO performance, which can subsequently cause an increase in the pressure drop and external concentration polarization in the bore fluid. In addition, it is expected that the ISHF membranes possess relatively low surface area per a fiber due to their small inner diameter. One European company (Aquaporin inside^{TM}) has recently launched its commercial HF FO membrane modules possessing a thin-film selective layer incorporated with biomimetic aquaporin materials in the bore side as an ISHF membrane. Although the stated performance (water flux and reverse salt flux) of the HF FO module seems to be attractive for FO processes, particulate clogging and fouling in the bore side still remains a challenge due to the small inner diameter of the membrane, which is less than 200 μm. Thus, it is necessary to carefully consider the quality of FS for FO applications.

On the other hand, in comparison to ISHF membranes, outer-selective HF (OSHF) membranes have more practical potential for various FO applications because of (1) larger surface area per fiber, (2) less external concentration polarization (ECP), (3) less clogging foulants in the bore fluid, (4) lower fouling propensity and easier fouling control on the HF outer surface under AL-FS orientation, and (5) their suitability for application in sub-merged membrane processes like osmotic membrane bioreactor (OMBR) (Le et al., 2016, Ren and McCutcheon, 2015b, Cheng et al., 2017a). Under these advantages, the OSHF membranes may be therefore a suitable candidate for turbid water or wastewater treatment with less pretreatment steps.

Accordingly, this study has focused on these issues in osmotically driven membrane processes as aforementioned. Novel approaches for membrane fabrication were designed and

applied to developing promising FO and PRO membranes as suitable candidates for overcoming these challenges.

1.3 Objectives and scope of the research

Although earlier studies on development of FO and PRO membranes exhibited outstanding performance in laboratory-scale tests, there was no further scaled-up from fundamental research. It is thus essential to further focus on practical applications to be commercially available. In addition, future activities should produce novel breakthough approaches for advance of membrane fabrication. I have looked into the above research insufficiencies, and this study proposed to target the development of novel nanocomposite membranes for low-energy osmotically driven processes using novel casting techniques and various hydrophilic nanomaterials (graphene oxide (GO), size-controlled graphene oxide (SGO), halloysite nanotubes (HNTs) and Schiff-based network (SNW-1) covalent organic frameworks (COFs)). **Fig.1** illustrates the overall structures of research activities in the thesis.

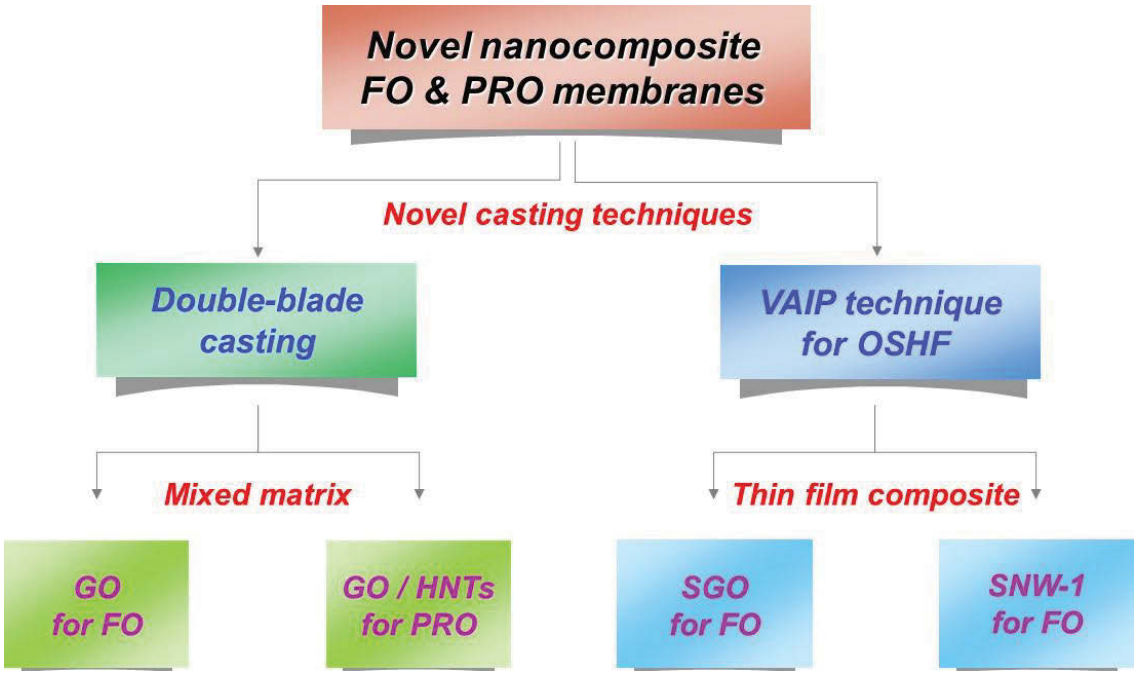


Figure 1 Overall structures of the study on development of novel nanocomposite membranes for osmotically driven processes.

The proposed scopes of this study are summarized into different segments:

- Application of novel casting techniques (Dual-blade casting techniques and vacuum-assisted interfacial polymerization, VAIP) to fabricating novel FO and PRO membranes
- Selection of promising nanomaterials (GO, HNTs and SNW-1) to produce nanocomposite FO and PRO membranes
- Development of novel FO and PRO membranes with outstanding performances and verification of suggested hypothesis and expected mechanisms in terms of improved performance based on theoretical and experimental studies.
- Investigation of thescaliabilty of developed novel FO and PRO membranes and their further applications to commercial FO and PRO processes.

1.4 Structure outline of the thesis

This research focuses on five main aspects for the development of novel nanocomposite membranes for osmotically driven processes (FO and PRO):

1) Dual-layered GO nanocomposite membrane substrates for FO applications,
2) Dual-layered GO/HNT nanocomposite membrane substrates for PRO applications
3) Outer-selective TFC membranes for FO applications (Osmotic membrane bioreactor)
4) Outer-selective TFN GO membranes for FO applications
5) Outer-selective TFN SNW-1 membranes for FO applications

The structure of the thesis is as belows:

- Chapter 1 presented the overall introduction including research background, motivation, main objectives and scope.

- Chapter 2 provides the motivation for novel FO and PRO membranes to overcome limitations and challenges in FO and PRO. In addition, it covers fundamental background and recently published literature about novel strategies and techniques for developing TFC FO and PRO membranes. Furthermore, characterization of PRO membranes such as physico-chemical properties, transport properties and performance tests are included in this chapter.

- Chapter 3 and Chapter 4 focused on the development of dual-layered nanocomposite membrane substrates for FO and PRO processes by using the double-blade casting technique. For dual-layered FO membranes, GO was mainly used as a nanofiller in order

to produce hydrophilic and porous membrane substrates for mitigating diluted ICP in FO processes. For dual-layered PRO membranes, GO for top layer and HNT for bottom layer were used to preprare the novel membrane substrates with highly porous, mechanically stable and anti-fouling characteristics.

- Chapter 5 focused on development of defect-free outer-selective hollow fiber (OSHF) TFC FO membranes for FO applications through the VAIP. This study provides practical guidelines for designing membrane substrate and organizing new methodologies of the VAIP with related mechanisms. In addition, this chapter reported the research progress of the novel OMBR process using our home-made OSHF FO membranes.

- Chapter 6 and 7 focus on development of novel OSHF thin-film nanocomposite (TFN) membranes using size-controlled graphene oxide (SGO) and Schiff-based network (SNW-1) as covalent organic frameworks (COFs), respectively. The unique characteristics of these hydrophilic nanofillers were attributed to altering the intrinsic transport properties of PA layer.

- Chapter 8 summarized the main findings and suggested concluding remarks.

2 Literature review

2.1 Introduction

There have been a number of review reports thus far on the development of either FO membranes or PRO membranes, however, none of them compiles and highlights the similarity and difference between these two membranes designated for FO and PRO processes. The objective of this review is, therefore, to comprehensively summarize the development of membranes for both FO and PRO processes aiming at the comparison and contrast of FO membrane and PRO membrane. This review initially introduces the basic background of osmotically driven process including FO and PRO with challenges and limitations. The following sections go over the recent developments focusing on aspects of material science, engineering membrane design, membrane fabrication techniques and membrane modification methods. Finally, a conclusion and recommendation are presented as a guide towards future development of novel membranes with high performance and durability.

2.2 Limitations and challenges of FO and PRO processes

2.2.1 Fundamental background of osmotically driven processes

As aforementioned in the introductory section, there are two main phenomena in osmotically driven processes including FO and PRO. Water permeation is selectively induced through a semipermeable membrane by salinity gradient and osmotic pressure difference between two solutions. The driving force in these processes is osmotic pressure induced by the difference of osmotic pressure between a less concentrated solution called FS and a highly concentrated solution

called DS. This driving force enables natural diffusion of water molecules through a membrane from FS to DS. Osmotically driven processes do not require the utilization of hydraulic pressure for the selective water permeation. This is one of the advantages of FO over pressure-driven membrane processes such as RO in **Fig. 2** and nano-filtration (NF), however, this technology has some the drawbacks. The net driving force gradually decreases over time due to the dilution of DS by water permeate and the concentration of FS as water molecules move to DS. In addition, a further process needs to be used to produce product water and regenerate DS using a DS recovery system. Nevertheless, FO has been successfully demonstrated in many previous studies to be suitable and effective when it is applied in a whole water treatment system.

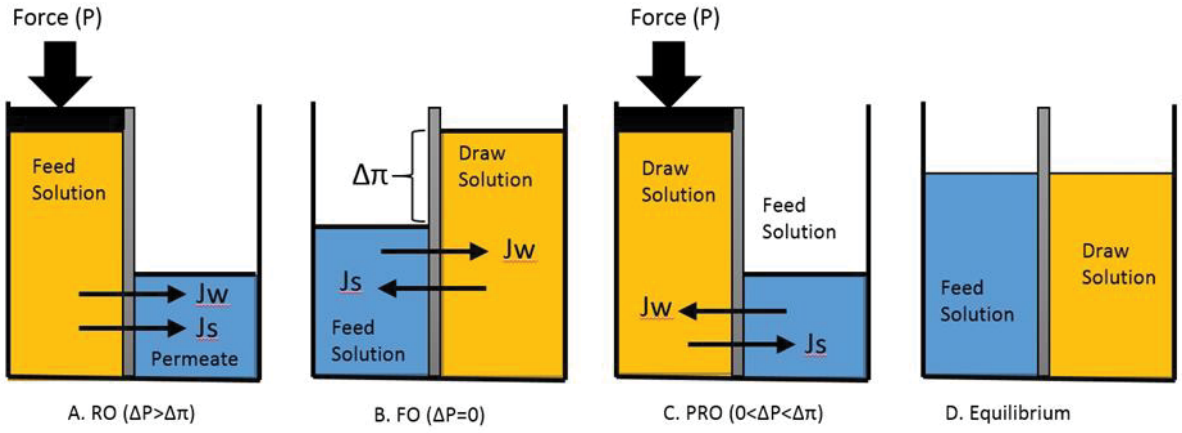


Figure 2 Reverse osmosis (RO), Forward osmosis (FO) and Pressure retarded osmosis (PRO).

PRO is a power generation system using membrane technology based on a salinity gradient. Free energy released during the mixing of two water streams with different salinity (e.g., river water and seawater or RO brine) can be harvested for generation of electricity. RO, PRO and FO processes have one thing in common. They all are membrane-based processes in which a semipermeable membrane must be used. The sole difference of these three processes is the

operating pressure applied shown in **Fig. 2**. In RO, the driving force is a hydraulic pressure above the osmotic pressure difference, applied to force water molecule in FS through the membrane. However, a net driving force in FO comes from the osmotic pressure difference between FS and DS without the application of hydraulic pressure. FS are naturally driven from feed stream to draw stream via osmotic pressure. For PRO, the hydraulic pressure less than the osmotic pressure is mainly applied into the draw stream, so that the net driving force is still occurred across a semi-permeable membrane. Subsequently, the internal pressure in a draw stream can be amplified by the water transport from FS to DS. The accumulated pressure is thus able to rotate a hydraulic turbine for energy harvesting.

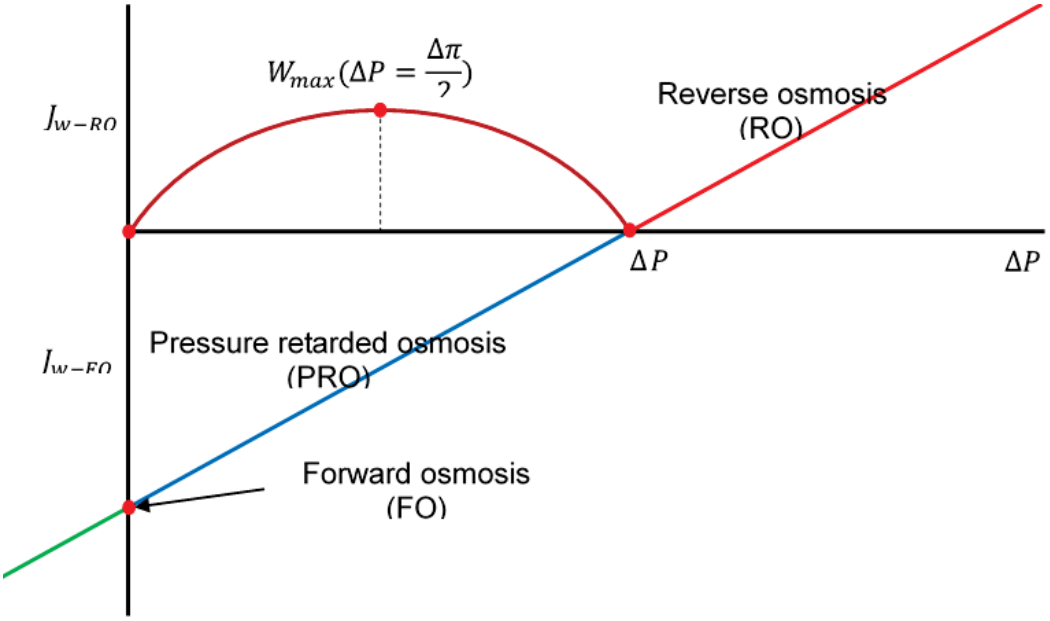


Figure 3 Relationship of water flux and pressure in RO, PRO, PAO and FO processes

Fig. 3 illustrates the water flux and solute flux directions in the RO, FO and PRO processes. For FO process, $\Delta P = 0$, while for RO process, $\Delta P > \Delta\pi$ and $0 < \Delta P < \Delta\pi$ in pressure retarted osmosis process. The calculation of water flux in FO, PRO and RO uses the following fundamental equation: (Cath et al., 2006)

$$J_w = A(\sigma\Delta\pi - \Delta P) \qquad \text{Equation 1}$$

Where A is the pure water permeability coefficient of the membrane, σ is the reflection coefficient, $\Delta\pi$ is the osmotic pressure differential across the membrane and ΔP is the applied hydraulic pressure gradient.

In the PRO process, power density, W (W/m^2), is the power per unit membrane area and it is equal to the product of the membrane water flux multiplied by the differential hydraulic pressure across the membrane according to the following equation:

$$W = J_w \Delta P \qquad \text{Equation 2}$$

Substituting **Eq.1** into **Eq.2** to give the following equation:

$$W = A_w(\Delta\pi - \Delta P)\Delta P \qquad \text{Equation 3}$$

Lee et al. investigated the impact of ΔP on W and J_w as shown in **Fig. 3** (Lee et al., 1981). It has been found that the power density reaches a maximum theoretical value, Wmax, when the hydraulic pressure is equal to the half value of the osmotic pressure gradient ($\Delta P = \Delta\pi/2$) across the PRO membrane. **Eq. 3** can be rearranged to calculate W_{max}:

$$W_{max} = A_w \frac{\Delta\pi^2}{4}$$ Equation 4

As illustrated in **Fig. 3**, three different membrane operating zones can be identified as ΔP increases from 0 to ΔP = π_{feed} i.e. FO, PRO and RO zones (Cath et al., 2006, Achilli et al., 2009a). In the FO zone, the hydraulic pressure is equal to zero (ΔP=0). Water flux, in this zone, is driven by the osmotic pressure gradient across the semipermeable membrane or in the direction of the osmotic pressure gradient.

2.2.2 Limitations and challenges of FO and PRO processes

Although osmotically driven membrane processes have been investigated for a variety of applications, FO is still facing some critical challenges. These relate to the following aspects: concentration polarization, membrane fouling, reverse solute diffusion, and the need for membrane development and the design of the draw solute. A recent study has indicated that both concentration polarization and reverse solute diffusion are the limiting factors in FO processes and pressure-retarded osmosis for power generation from salinity gradients by PRO (Yip and Elimelech, 2011).

2.2.2.1 Concentration polarization

Concentration polarization (CP) is a common and inevitable phenomenon in both pressure driven and osmotically driven membrane processes (Cath et al., 2006, McCutcheon and Elimelech, 2006, Zydney, 1997, Sablani et al., 2001, Thorsen, 2004, Kim and Hoek, 2005). In osmotically

driven membrane processes, concentration polarization is caused by the concentration difference between the FS and the DS through an asymmetric FO membrane as illustrated in **Fig.4**. Both external concentration polarization (ECP) and internal concentration polarization (ICP) can take place in FO and PRO processes. Generally, ECP occurs at the surface of the dense active layer of the membrane and ICP occurs within the porous support layer of the membrane. Both ECP and ICP are described further below.

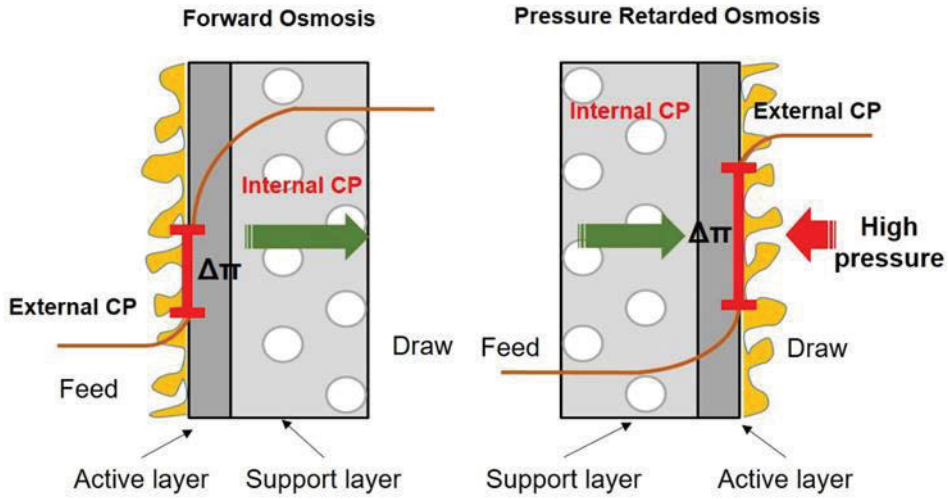


Figure 4 Illustration of ECP and ICP through asymmetric FO and PRO membranes

In FO and PRO processes, water flux can be theoretically modelled based on the film theory (Tiraferri et al., 2013, Altaee and Sharif, 2015), as follows:

$$J_w = \mathrm{A}_w \left[\frac{\pi_{D,b} exp^{(-J_w K)} - \pi_{F,b} exp^{\left(\frac{J_w}{k_F}\right)}}{1 + \frac{B}{Jw}\left[exp^{\left(\frac{J_w}{k_F}\right)} - exp^{(-J_w K)} \right]} - \Delta P \right] \qquad \text{Equation 5}$$

Where B is solute permeability coefficient, $\pi_{D,b}$ is the bulk osmotic pressures of the DS at the membrane surface and $\pi_{F,b}$ is the bulk osmotic pressures of the FS at the membrane surface.

k_F is the mass transfer coefficient defined by:

$$k_F = \frac{ShD_F}{d_{\mathrm{h}}} \qquad \text{Equation 6}$$

Where, Sh, D_F and d_h are the Sherwood number, diffusion coefficient of feed solutes and the hydraulic diameter, respectively. K is solute resistance to diffusion within the membrane support layer determined by:

$$K = \frac{t\tau}{D_{\mathrm{D}}\varepsilon} = \frac{\mathrm{S}}{\mathrm{D_D}} \qquad \text{Equation 7}$$

Where t, τ, ε and S are thickness, tortuosity, porosity and structural parameter of the support layer, respectively. D_D is the diffusion coefficient of the draw solute.

$$S = \frac{t\tau}{\varepsilon} \qquad \text{Equation 8}$$

2.2.2.1.1 External concentration polarization

In hydraulically pressure-driven process such as RO, only concentrative ECP occurs at the surface of membrane active layer. The only difference is that in osmotically driven processes such

as FO and PRO, ECP occurs at both sides of the membrane including concentrative and dilutive ECP depending upon the membrane orientation. Dilutive ECP occurs at the membrane surface being in contact with the DS while concentrative ECP occurs at the surface of the membrane facing FS. In the dilutive ECP phenomenon, osmotic pressure of DS at the interface between the membrane layer and DS is reduced, giving rise to the decline of the net driving force. However, in the concentrative ECP phenomenon, the net driving force declines due to the increase of FS's osmotic pressure at the interface between membrane and FS. However, the negative effect of ECP on the water flux can be mitigated by optimizing operating conditions such as enhancing turbulence or cross flow velocity of DS and FS or operating under the critical flux (Fried, 1997, Cath et al., 2006).

McCutcheon and Elimelech have modeled ECP in FO using boundary layer film theory (Fried, 1997, McCutcheon and Elimelech, 2006). The general equation for concentration polarization modulus in pressure-driven membrane processes can be expressed as (Fried, 1997)

$$\frac{C_m}{C_b} = \exp(\frac{J_w}{k_F}) \qquad \text{Equation 9}$$

where C_m and C_b are the concentrations of the FS at the membrane surface and in the bulk, respectively.

When the FS concentration is relatively low, the concentrations in **Eq. 9** can be replaced by the osmotic pressures. Therefore, the concentrative ECP modulus can be expressed as

$$\frac{\pi_m}{\pi_b} = \exp(\frac{J_w}{k_F}) \qquad \text{Equation 10}$$

where π_m and π_b are the osmotic pressures at the membrane surface and in the bulk where concentrative ECP occurs, respectively.

Similarly, the dilutive ECP modulus in FO can be expressed as

$$\frac{\pi_m}{\pi_b} = \exp(-\frac{J_w}{k_F}) \qquad \text{Equation 11}$$

where π_m and π_b are the osmotic pressures at the membrane surface and in the bulk where dilutive ECP occurs, respectively.

Therefore in the **Eq. 10** and **11**, both concentrative ECP and dilutive ECP have been taken into consideration (Mccutcheon and Elimelech, 2007) and denoted as a general term ECP. However, several important aspects must be realized in this equation. First, the mass transfer coefficients on the FS and DS sides are not the same because of the concentration gradient. Second, the model is based on the assumptions that the solute permeability coefficient is zero (i.e. the reflection coefficient σ = 1 (Su and Chung, 2011)), and that the FS and DS concentrations are relatively low because only then can the concentration be assumed to be equal to the corresponding osmotic pressure. Most importantly, this model is only suitable for a dense symmetric film rather than for an asymmetric membrane. Therefore, the application of this model is relatively limited. We must consider the situation that an asymmetric FO membrane is used as in practice, in which ICP effects are more important.

2.2.2.1.2 Internal concentration polarization

In osmotically driven membrane processes, one of the most critical phenomena is ICP. Similar to ECP, ICP also includes dilutive and concentrative ICP occur within the membrane support layer depending on the orientation of support layer to FS or DS. When the support layer faces the FS, concentrative ICP occurs due to the accumulation of FS's solute in the membrane support layer. On the other hand, dilutive ICP occurs when the membrane support layer faces the DS as DS is diluted by water permeate from FS within membrane support layer. Compared to ECP, ICP is even more severe by greatly reducing the net osmotic pressure in FO and PRO processes. It is generally recognized that this phenomenon leads to severe water flux decline in FO and PRO, resulting in low performance and less attractive FO and PRO (Mehta and Loeb, 1978c, Mehta and Loeb, 1978a, Gray et al., 2006, McCutcheon and Elimelech, 2006). Recently reported studies stated that more than 80% of water flux decline was attributed to ICP (Mehta and Loeb, 1978a, Mehta and Loeb, 1978c). Unlike ECP, ICP phenomenon takes place within the membrane support layer, therefore, adjusting operating condition such as enhancing flowrates of FS and DS, or creating turbulence and operating under the critical flux condition cannot mitigate the consequence of ICP.

The effect of ICP on FO water flux has been modeled by adopting the classical solution-diffusion theory (McCutcheon and Elimelech, 2006, Mccutcheon and Elimelech, 2007, Lee et al., 1981, Loeb et al., 1997). When the DS is placed against the membrane support layer (i.e. FO mode), dilutive ICP dominates the water flux (J_w), and it can be expressed (Loeb et al., 1997) as

$$J_w = \frac{1}{K} \ln \frac{A\pi_D + \mathrm{B}}{A\pi_F + \mathrm{B} + J_w} \qquad \text{Equation 12}$$

In the alternative membrane orientation (i.e. PRO mode), the effect of concentrative ICP on the water flux can be expressed (Loeb et al., 1997) by:

$$J_w = \frac{1}{K}\ln\frac{A\pi_D + \mathrm{B} - J_w}{A\pi_F + \mathrm{B}} \qquad \text{Equation 13}$$

Note that the structural parameter *S* is an important intrinsic parameter of a membrane because it determines the ICP in the membrane support by membrane thickness, tortuosity and porosity. Therefore, for a newly developed membrane, it is necessary to characterize the membrane structural parameter *S*. It is noteworthy that the PRO process is less affected by ICP than FO mode because highly concentrated DS faces the selective layer. Therefore, the water flux in PRO mode is mostly higher than that in FO mode under a same condition.

2.2.2.2 Lacking suitable membranes

Lacking an ideal membrane is one of the major hurdles that hinder the development of osmotically driven processes. Nowadays, several types of FO and PRO membranes have been developed including ceramic membrane, metal membrane and polymeric membrane. However, polymeric-based membranes are the most common. Based on membrane's morphology, osmotic-based membranes can be classified into three types as follows: (i) asymmetric; (ii) thin-film composite (TFC); (iii) others (biomimetic, self-standing). This paper focuses on reviewing the recent development of polymeric thin-film composite membrane for osmotically driven processes.

Table 1 presents several membranes developed for osmotically driven processes from 2010 to 2017. Although a myriad of efforts has been made on membrane development for those processes, however, a lack of suitable FO and PRO membranes remains a challenging issue to make FO and PRO commercialized and available on the market.

An ideal membrane for FO and PRO should have the followings essential characteristics(Cath et al., 2006, Miller and Evans, 2006): high solute rejection, high water permeability, high mechanical strength to support high hydraulic pressures, robust and stable under operating condition (temperature; alkaline or acidic FS and DS); and low fouling potential. To have these properties, FO and PRO membranes should be highly hydrophilic, thin, possessing a high-density selective layer, and a porous support layer. These factors will help the membrane achieve minimal ICP and deliver a high performance such as high water flux and solute rejection in FO and PRO processes. These requirements can be potentially achieved by designing novel membrane structures and using suitable materials.

Table 1 Recent development of TFC membrane for osmotically driven processes

Year	Application	Membrane configuration	Membrane Feature and Materials	Fabrication techniques		Ref
				Support layer	Active layer	
2010	FO (Water and wastewater treatment), and PRO (power generation)	Inner selective hollow fibre	Polyethersulfone (PES) support layer – Polyamide (PA) active layer	Non-solvent induced phase inversion (NIPS) using dry–jet wet spinning process	Interfacial polymerization (IP)	(Wang et al., 2010)
	FO (Water and wastewater treatment), and PRO (power generation)	Flat sheet	PES support layer - PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Lotfi et al., 2017)
2011	FO (Seawater desalination)	Inner selective hollow fibre	Polyethersulfone (PES) support layer - Double active layer with a Poly(amide–imide) (PAI) NF-like selective layer covered by a PA active layer	Non-solvent induced phase inversion (NIPS)	Inner selective layer: Interfacial polymerization (IP). NF-like outter selective layer: PEI cross-linking.	(Fang et al., 2012)
	FO (Seawater desalination)	Flat sheet	PES nanofibre support layer - PA active layer	Electrospun phase inversion	Interfacial polymerization (IP)	(Bui et al., 2011a)
	FO (Water desalination) and PRO (power generation)	Flat sheet	PESU-co-sPPSU 11 sulfonated PES support layer - PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Widjojo et al., 2011)
	FO (Water desalination) and PRO (power generation)	Flat sheet	Polyacrylonitrile (PAN) support layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Layer by Layer (LbL) assembly	(Saren et al., 2011)
	FO (Water desalination) and PRO (power generation)	Inner selective hollow fibre	PAI support layer - polyethyleneimine (PEI) NF-like active layer	Non-solvent induced phase inversion (NIPS)	Chemical post-treatment with PEI cross-linking	(Setiawan et al., 2011)

	FO (Water and wastewater treatment), and PRO (power generation)	Flat sheet	Polyester (PEST) nonwoven fabric - PES support layer - PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Yu et al., 2011)
2012	FO (Water desalination) and PRO (power generation)	Hollow fibre with outer and inner active layers	Dual PAI and PES substrate layer - PEI NF-like outer active layer and inner PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Fang et al., 2012)
	FO (Water desalination) and PRO (power generation)	Inner selective hollow fibre	PES support layer - PA active layer	NIPS using dry–jet wet spinning process	Interfacial polymerization (IP)	(Sukitpaneenit and Chung, 2012)
2013	FO (Seawater desalination and Lysozyme (LYS) and alginate (ALG) removal)	Flat sheet	Polysulfoner (PSf) support layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Gu et al., 2013)
	FO (Seawater desalination)	Inner selective hollow fibre	Multiwalled carbon nanotubes (MWCNTs) embeded Immobilizedpolyethyleneimine–PAI support layer – PEI active layer	NIPS using dry–jet wet spinning process	Chemical post-treatment with PEI cross-linking	(Goh et al., 2013)
	FO (Water desalination) and PRO (power generation)	Flat sheet	Polyethylene terephthalate (PET) nanofibres backing layer PSf support layer – PA active layer	Electrospun phase inversion	Interfacial polymerization (IP)	(Hoover et al., 2013)
	FO (Water desalination) and PRO (power generation)	Flat sheet	Polyvinylidene fluoride (PVDF) nanofibres support layer – PA active layer	Electrospun phase inversion	Interfacial polymerization (IP)	(Tian et al., 2013)
2014	FO (Water desalination) and PRO (power generation)	Flat sheet	PSf and sulfonated poly(phenylene oxide) support layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Zhou et al., 2014)
	FO (Seawater desalination)	Flat sheet	Polyvinyl alcohol (PVA) nanofibre support layer – PA active layer	Electrospun phase inversion	Chemical cross-linking via acid catalyzed glutaraldehyde	(Puguan et al., 2014)
	FO (Seawater desalination)	Flat sheet	PEST non-woven fabric backing layer - PSf support layer – PA/silicon dioxide (SiO_2) active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Niksefat et al., 2014)

	FO (Water desalination) and PRO (power generation)	Flat sheet	PSf–titanium dioxide (TiO_2) support layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Emadzadeh et al., 2014a)
2015	FO (Water desalination) and PRO (power generation)	Flat sheet	Multi-zoned nylon 6,6 MF support layer and nonwoven fabric backing layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Huang and McCutcheon, 2015)
2016	FO (Seawater desalination & Alginate and silica separation) PRO (power generation)	Flat sheet	PEST mesh-embedded double skinned PSf support layer – polydopamine (PDA) treated surface – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	(Liu et al., 2016)
Mass transfer modelling	Hollow fibre	PSf support layer – PA active layer	NIPS using dry–jet wet spinning process with dual-layer spinneret	Interfacial polymerization (IP)		(Lin, 2016)
2017	FO (Seawater desalination)	Flat sheet	PET & PVA nanofibres backing layer - PVDF support layer – PA active layer	Electrospun phase inversion	Interfacial polymerization (IP)	(Yasukawa et al., 2017)
	FO (Seawater desalination)	Flat sheet	Polyketone support layer – PA active layer	Non-solvent induced phase inversion (NIPS)	Interfacial polymerization (IP)	
	FO (Water desalination) and PRO (power generation)	Flat sheet	Sodium ion exchange resin (IER-Na) blended PSf support layer – PA active layer	NIPS with IER-Na blended PSf dope solution	Interfacial polymerization (IP)	(Zuo et al., 2017)

2.3 Recent activities for development of novel FO and PRO membranes

Many strategies have been investigated to tailor thin-film composite FO membranes which comprise of porous membrane substrates and polyamide (PA) active layer. Most TFC FO membranes have exhibited better performance with higher water flux and solute selectivity than symmetric FO membranes such as cellulose acetate based FO membranes (Lim et al., 2017). The TFC membrane substrate or active layer have been tailored to optimize themselves for FO operation. In particular, both the internal and external structure of the membranes have been modified to be more porous and hydrophilic enhancing the FO performance (Park et al., 2015, Liu and Ng, 2015, Akther et al., 2015). Although ICP is not able to be alleviated by the operating conditions, but can be controlled by modifying the structural porosity of the membrane substrate. That is, the membrane substrate should be ideally modified as porous as possible to minimize ICP. In addition, the addition of hydrophilic additives into a polymer solution plays an important role to form large internal pores in the phase inversion and to alleviate surface tension of water molecules to enhance water transport. In this chapter, recently developed technical strategies for preparing a membrane substrate were described in terms of how to control and modify membrane substrates for FO processes.

2.3.1 Hydrophilic materials

Most research and commercial TFC FO membranes are composed of polysulfone (PSf) or polyethersulfone (PES) polymers for the membrane substrate, which is also the traditional substrate for TFC membranes. They have outstanding characteristics of thermal stability, chemical resistance, and mechanical strength (Zhang et al., 2016c). In addition, these polymers can be

transformed to an asymmetric membrane substrate containing a finger-like porous internal structure and sponge-like dense top layer. The PES and PSf possess intrinsically hydrophobic nature. Some studies thus investigated to enhance their hydrophilicity. Some researchers suggested using hydrophilic polymers as a mother material or an additive for membrane fabrication. Sun et al. reported that the blending PSf and PES was a suitable strategy to modify the pore formation and chemical properties of the membrane substrate. The PSf polymer with the less polar PES additive was used to prepare high performance FO membranes, which possess porous internal structure, opened bottom surface as well as dense skin layer for desirable PA layer formation. However, the article reported that related mechanisms should be further investigated. For developing FO membranes, some literature focused on the effect of sulfonated polymers such as sulfonated PSf (sPSf), sulfonated polyphenylenesulfone (sPPSU), sulfonated poly(ether ketone) (SPEK), poly(arylene ether sulfone), and sulfonated poly(phenylene oxide) (SPPO), which are hydrophilic (Zhang et al., 2016c, Zhao et al., 2018, Ren et al., 2016, Widjojo et al., 2013, Han et al., 2016a, Yuan et al., 2017, Han et al., 2012b). **Fig. 5** presents the chemical structures of common PSf and these suggested materials. The intensity of polymer's hydrophilicity can affect the formation of membrane's pore structures, since hydrophilic polymers or additives can contribute to increasing the exchange speed of solvent and non-solvent in the phase inversion process so that the high exchange speed can force to form finger-like microvoids inside a membrane substrate underneath the thin dense layer (Park et al., 2015, Lim et al., 2017). In addition, sulfonic acid groups in these polymers may randomly penetrate into the backbone of the membrane substrate, and subsequently swell (Zhang et al., 2016c). Therefore, the sulfonated polymers can be suitable candidates for preparing porous membrane substrates for TFC FO membranes.

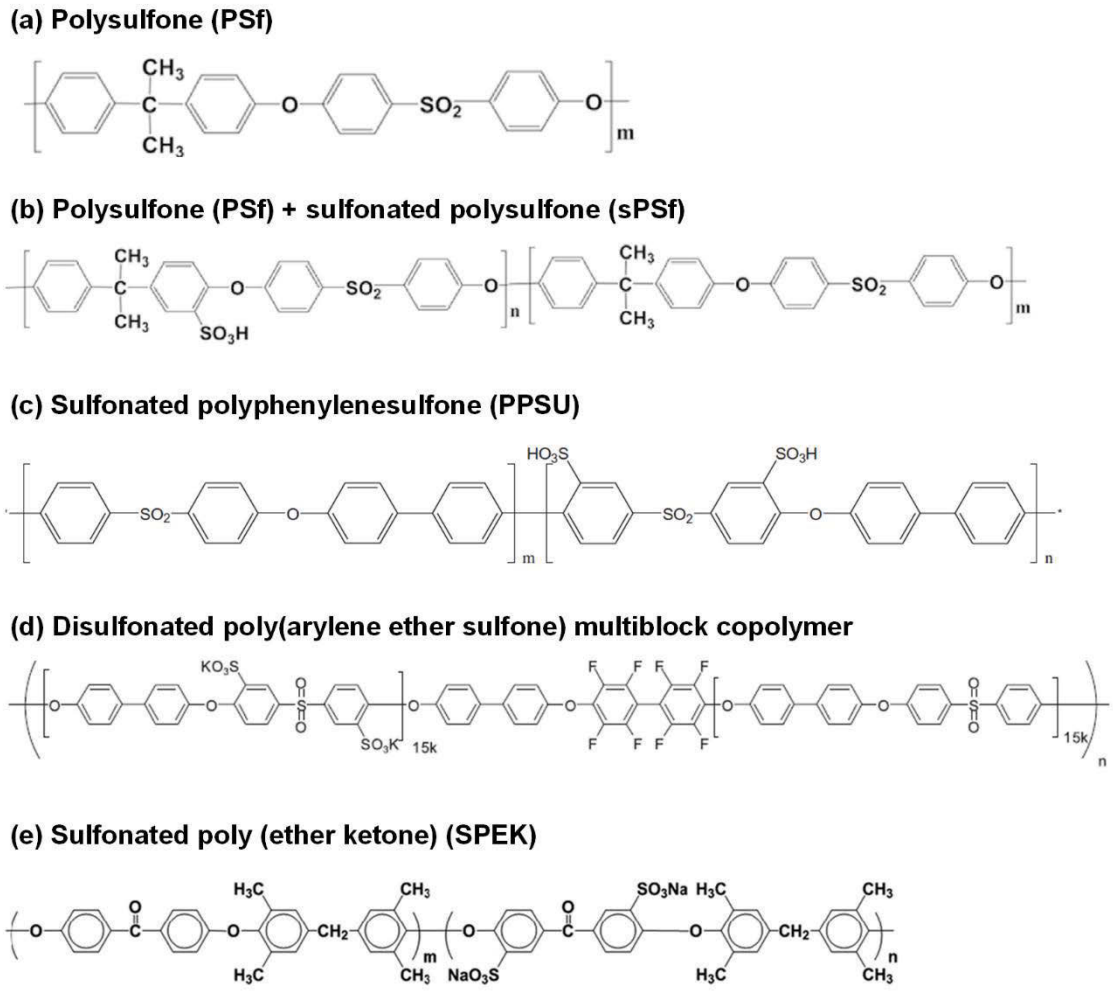


Figure 5 Chemical structures of hydrophilic sulfonated polymer materials what have been used for FO membrane development.

Although blending with sulfonated polymers is an attractive way to prepare FO membranes, the mechanical stability of the sulfonated membrane substrates may be sacrificed due to their porous and weak structures (Zhang et al., 2016c, Widjojo et al., 2013, Han et al., 2016a). To address this, Han et al. (Han et al., 2016a) proposed sPPSU-based FO membranes which is embedded with a polyethylene terephthalate (PET) fabric in order to enhance the mechanical

stability shown in **Fig.6**. The optimum sPPSU-based robust TFC membrane exhibited high water flux at around 30.5 $Lm^{-2}h^{-1}$ and reasonable specific reverse solute flux (SRSF) at around 0.2 g L^{-1} with its desirable tensile strength at 80.0 MPa. In addition, Zhao et al. produced mesh-embedded PSf/sPSf membrane substrates for a TFC FO membrane (Zhao et al., 2018). They used the robust woven fabric as a backing support in order to improve the membrane's mechanical stability. The best FO membranes with a SPSf content at 50% of the total polymer exhibited relatively high water flux at 31.8 $Lm^{-2}h^{-1}$ with good SRSF at 0.19 g L^{-1} using 1 M NaCl as DS and DI water as FS.

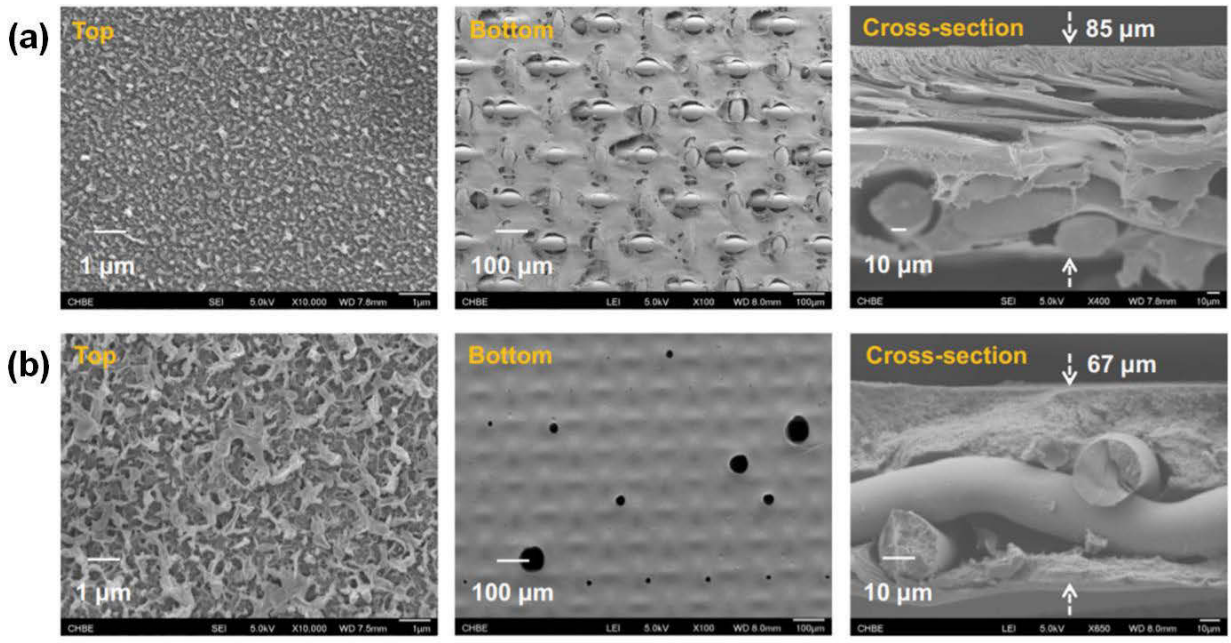


Figure 6 Morphological images (top, bottom and cross-section) of HTI TFC membrane (a) and sPPSU-based TFC membrane (b) (Han et al., 2016a).

Zhang et al. reported the new FO membrane substrate using the PSf polymer solution blended with the disulfonated poly(arylene ether sulfone) hydrophilic-hydrophobic multiblock copolymer (BFSH) (Zhang et al., 2016c). They proposed that sulfonic ion groups in the BFSH copolymer with hydrophilic and hydrophobic segments enhanced membrane's hydrophilicity, while the hydrophobic segments was used to enhance mechanical strength of the membrane substrate by controlling the water swelling and to improve the compatibility of the polymer structure. As a result, the optimum candidate (PFSH at 25 wt%) exhibited high water flux with less sacrifice of the tensile strength.

As another sulfonated material, Han et al reported the effect of sulfonated poly ether ketone (SPEK) for preparing hydrophilic FO membrane substrate (Han et al., 2012a). The authors mentioned that the SPEK polymer has many advantages such as high hydrolytic, thermal stability and less oxidization. In addition, the SPEK is commercially attractive due to its low cost and high applicability. In that study, they investigated the effect of blended SPEK material with a PSf polymer solution at the specific concentration. As a result, the SPEK played an important role to manipulate the intensity of membrane's hydrophilicity due to the sulfonic ion groups. By the addition of SPEK, de-mixing was delayed in the phase inversion process leading to a porous sponge-like structure without macro-voids. **Fig. 7** presents the morphological images of SPEK blended PSf membrane substrate (25 wt% SPEK) prepared in that study.

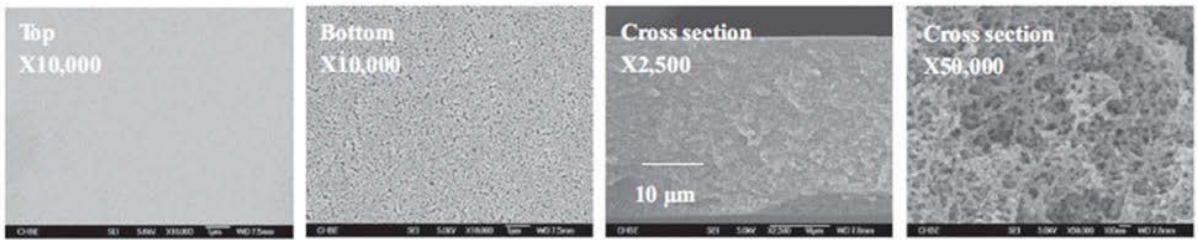


Figure 7 Morphological images (top, bottom and cross-section) of SPEK blended PSf membrane substrate (25 wt% SPEK) (Han et al., 2012b).

As a novel ketone-based polymeric material, polyketone (PK), which composes of the structural chains of 1-oxotrimethylne, was considered to prepare a porous membrane substrate for subsequent FO applications. Prof. Matsuyama and his colleagues reported that PK has a strong potential for membrane applications due to its strong mechanical property, good chemical and thermal resistance like other industrial-based materials (Yasukawa et al., 2015, Shibuya et al., 2017, Yasukawa et al., 2017). Using the PK polymer, they successfully produced membrane substrates. Interestingly, although the PK could not be dissolved by common organic solvents such as acetone, N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF) and N,N-dimethylacetamine (DMA), the best mixtures were prepared using resorcinol, NMP, methanol, acetone and hexane in order to well dissolve both PK and PSf polymers for the polymer solution. They prepared a series of membrane samples according to mixing ratio of the polymer solution and water. **Fig. 8** presents the morphological images of series of membrane samples observed by SEM analysis. In SEM observation, all of the PK membranes have a top dense layer and porous middle and bottom layer as similar to asymmetric polymeric structure. Most pores consist of a sponge-like structure with high porosity at over 80%, and these internal pores were quite well interconnected which is suitable for alleviating the hindrance of water and ion transport. For series

of samples, they manipulated the mixing ratio of ethanol and water in a coagulation bath in order to control a demixing ratio in the phase separation for tailoring membrane's porosity. As a SEM results, the membrane samples coagulated in the solution of the ratio of ethanol and DI water at 25/75 wt% (**Fig 8 (a) and (b)**) presented lower surface pore sizes than that in 35/65 wt% presented in **Fig. 8(c)** due to the delayed demixing ratio. However, the mean surface pores of the PK membranes were larger than those of common PSf and PES membrane substrates in the range of less than 30 nm, and these surface pores were randomly shaped and distributed. That is, the PK membrane could be classified as a microfiltration (MF) membrane, which is not a preferable surface morphology for a subsequent IP process. However, they produced the TFC FO membranes based on the PK membrane substrates under typical IP process. At this point, they suggested that there were strong adhesive interaction between the PK substrate and PA active layer based on expected chemical reaction as presented in **Fig.9**, so that the PA active layer was well deposited on the PK substrate, although the surface of the PK substrates were excessively loose. In the FO performance tests, the optimum membrane exhibited improved FO water flux at 29.3 $Lm^{-2}h^{-1}$ and decreased SRSF at 0.13 g L^{-1} using 0.6 M NaCl and DI water with the pressure resistance at 0.6 MPa in AL-FS orientation due to the lower *S* value of the PK membrane substrate at 280 μm, which implies that the intensity of ICP inside the membrane substrate was reduced. Based on this concept using the PK material, Shibuya et al. successfully produced porous hollow fiber membrane substrates for preparation of TFC FO membranes (Shibuya et al., 2017).

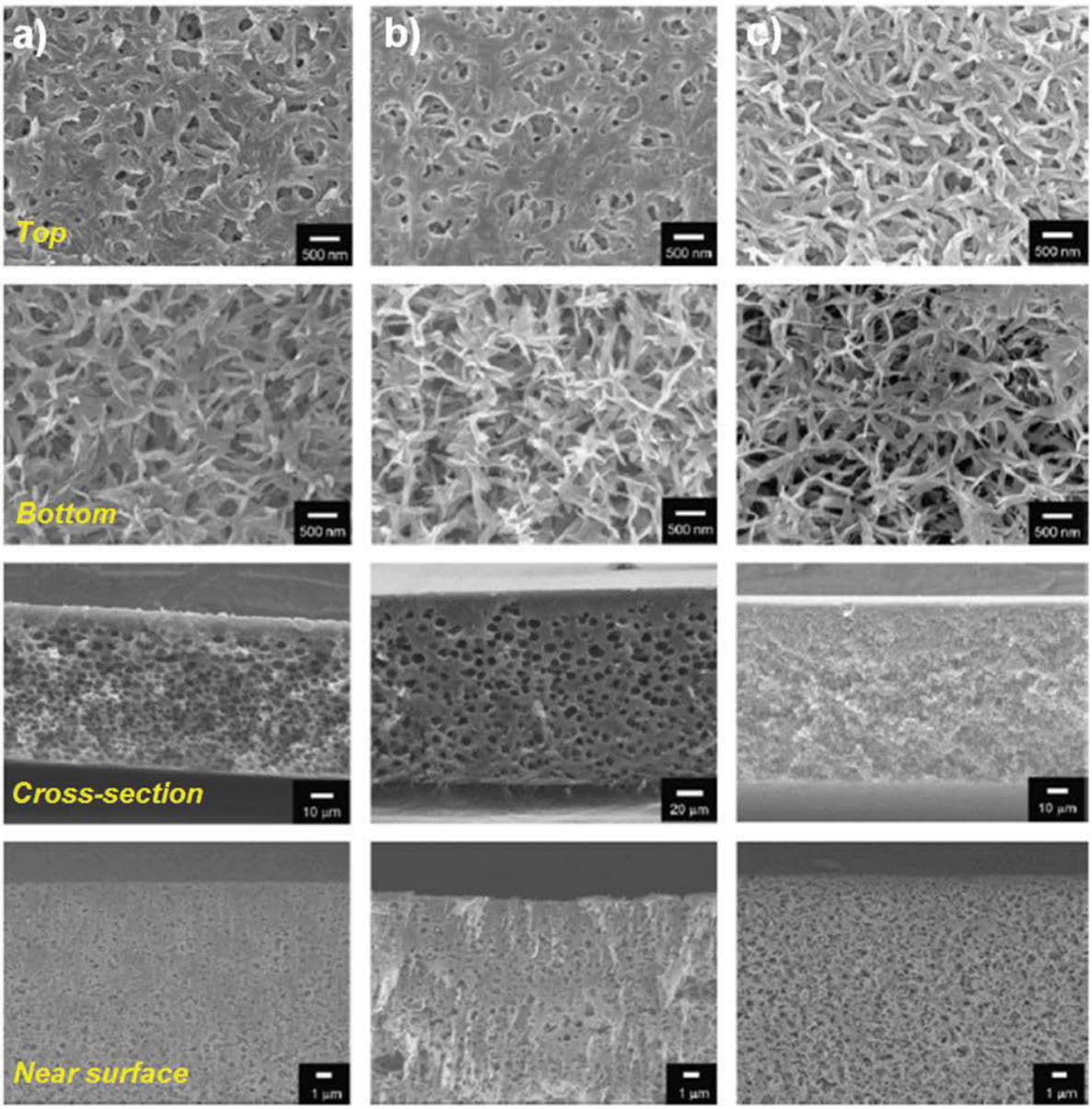


Figure 8 Morphological images (top, bottom and cross-section) of SPEK blended PSf membrane substrate according to various blending ratio (Yasukawa et al., 2015).

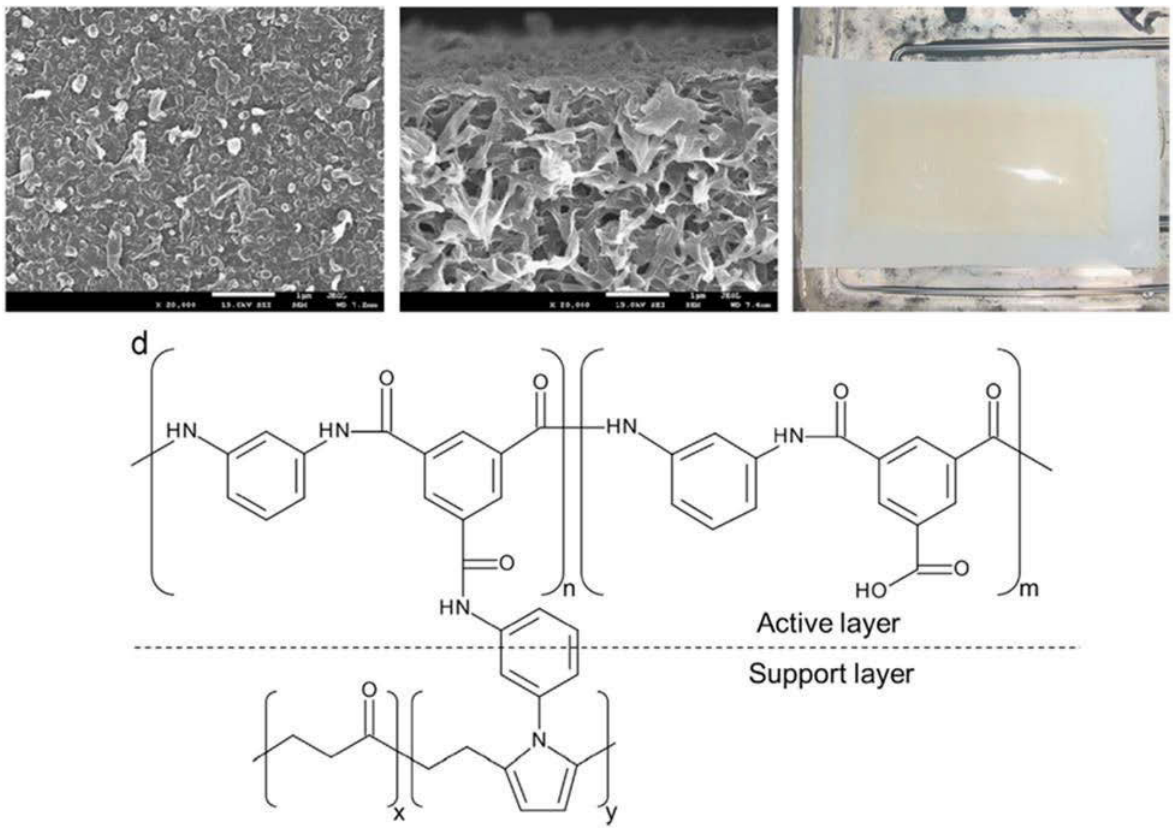


Figure 9 Morphological SEM images of top surface and cross-section of TFC-FO membranes using the PK (25/75) membrane substrate and expected chemical reaction between PK-based membrane substrate and PA active layer (Yasukawa et al., 2015).

Beyond the polymers considered in this chapter, other potential polymers such as polyacrylonitrile, polybenzimidazole, polyamide-imide, modified cellulose acetates (cellulose acetate butyrate, hydrophilic cellulose acetate propionate) have also been considered for FO membrane substrates (Ren and McCutcheon, 2015b, Setiawan et al., 2011, Ong et al., 2015).

2.3.2 Fabrication strategies

As an ideal membrane substrate, it should be highly porous, hydrophilic and thin for mitigating ICP under FO operation. In addition, the internal pores should be interconnected with low tortuosity. However, typical polymeric membranes prepared via a phase inversion process possess dense top layer and sponge-like pores inside the membrane substrates, which can be a big obstacle to break the ICP bottleneck in FO operation. To overcome this issue, several strategies have been investigated for developing extremely porous membrane substrates.

Song et al. used one of electrospinning technologies for developing porous TFC FO membranes, and they successfully produced scaffold-like nanofiber-based PES membrane substrates as presented in **Fig. 10(a)** (Song et al., 2011). The electrospinning system consists of a syringe-based polymer supplement system, inlet nozzle with positive charge, rotating drum as a collector, negatively conductive back-plate with negative charge and power generation system for supplying electricity illustrated in **Fig. 10(b)** (Woo et al., 2017). Using the electrospinning system, the authors prepared electrospun nanofiber (EN) TFC membranes which possess attractive characteristics for eliminating the ICP issue such as extremely high porosity, low tortuosity and its very thin layer. In addition, the internal pores of ENMs were ideally interconnected each other. **Fig. 10(c)** presents the morphological structure of the EN membrane substrate and EN TFC membrane. The average size of nanofibers are 50 to 150 nm, and the fiber's size can be tailored by the operating conditions.

For TFC EN membranes, it is challenging to produce an ideal PA selective layer due to EN membrane's surface morphology. Compared to common PSf membranes, EN membrane

substrates have rougher surfaces and randomly-shaped larger surface pores over at least 100 nm as a limitation (Liao et al., 2018). Thus, in the IP process, MPD monomer is immerged into the pores too much due to the large pore size, so that TMC monomer can be subsequently contacted and quickly reacted with the immersed MPD monomer. At this point, the reaction rate is accelerated by the excess MPD solution, so that PA layer can be thickly formed on the EN membrane substrate as shown in **Fig. 10(d)**. Although the active PA layer on the EN membrane substrate would be relatively thicker in most EN membrane studies, these studies presented great FO performances of the TFC-EN membranes, since their ENM substrates have superior characteristics for mitigating ICP and enhancing water transport.

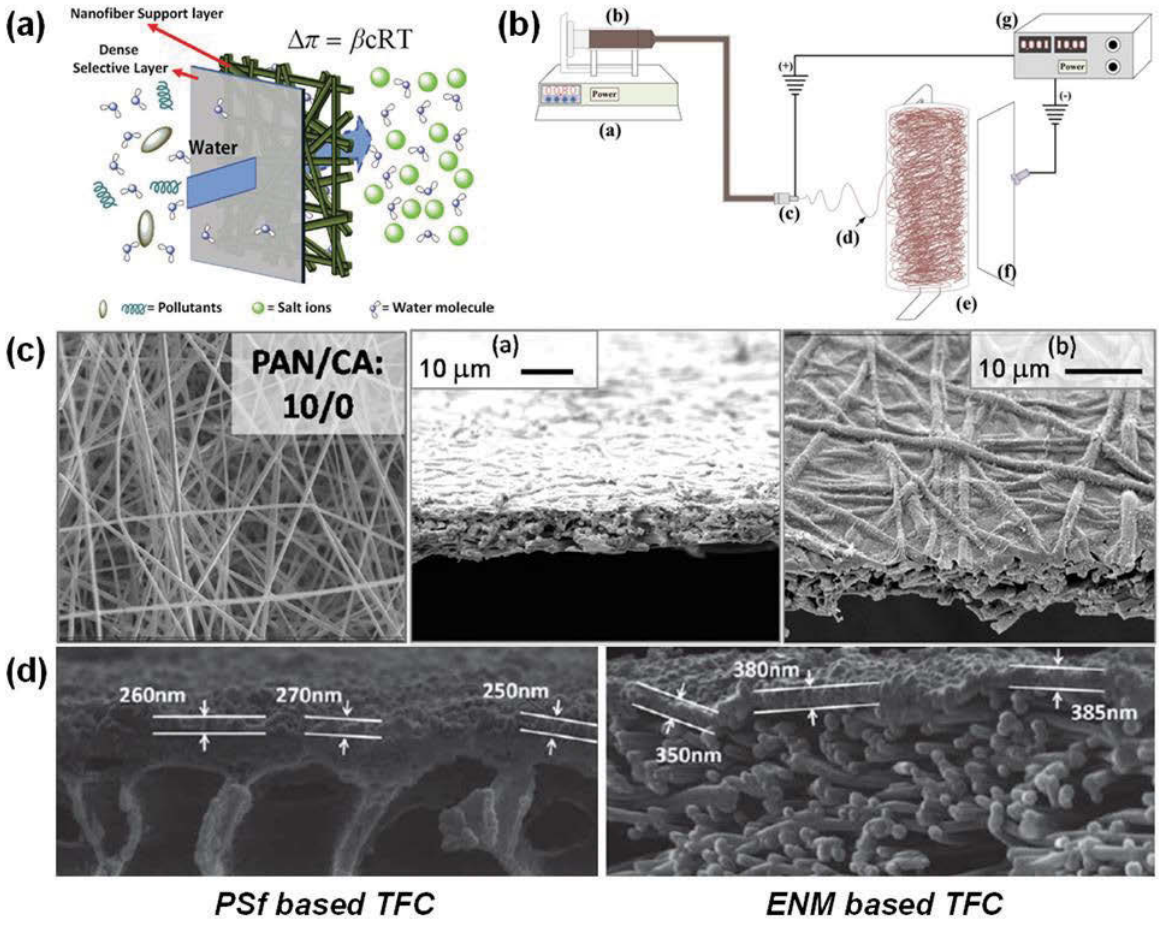


Figure 10 (a) Conceptual illustration of an ideal TFC membrane consisting of a scaffold-like nanofiber substrate and PA active layer, (b) schematic diagram of a typical electrospinning system for polymeric membrane preparation: syringe pump, syringe filled in polymer solution, nozzle, nanofiber, drum-shaped collector, and negatively-charged conductive plate with a power supply, (c) morphological images (Top surface, cross-section and deposited PA selective layer) of electrospun nanofiber membranes and (d) thickness of PA layer on the PSf substrate (left) and PSf-based ENM substrate (right) (Woo et al., 2017, Song et al., 2011, Bui and McCutcheon, 2013).

The mechanical stability of an EN matrix should be criticised to prepare a membrane substrate, as it may concern about the physical issue such as detaching and/or damaging nanofibers in a EN matrix and washing fibers away from the matrix via the hydraulic flow (Liao et al., 2018). Thus, it is required to strengthen each fiber and their physical interconnection in an EN matrix for further FO applications. Bui et al. (Bui and McCutcheon, 2013) produced hydrophilic and robust EN membrane substrates using polyacrylonitrile (PAN) and cellulose acetate (CA) as an additive in various blending ratios. They reported that these polymer components are compatible and miscible in an amorphous state but incompatible in a crystal state, so that it is expected that the miscible and compatible PAN/CA polymer mixture in liquid state was attributed to improving mechanical properties of the PAN/CA based EN mat. Furthermore, they also developed EN TFC FO membranes on the PET mesh in order to enhance the mechanical strength of the EN mats (Bui et al., 2011b).

Beyond those polymers for EN FO membranes, various polymer materials such as PSf, PES, PAN, polyvinyl alcohol (PVA), poly(vinylidene fluoride) (PVDF), polyetherimide (PEI), nylon 6,6 and others have been tested and investigated for FO applications as a key material for EN substrates, surface coating or additives (Park et al., 2018). In addition, the coaxial electrospinning technique using multiple polymer materials to tailor the intrinsic characteristics of the nanofibers themselves was applied (Shokrollahzadeh and Tajik, 2018, Shibuya et al., 2018). Furthermore, some hydrophilic nanomaterials have been incorporated into nanofibers in order to improve hydrophilicity and mechanical strength, and the operation, durability and fouling resistance. The detailed information will be further described in the following section (3.1.3).

For preparing dual-layered membrane substrates, co-casting and co-extrusion technique has been applied. The dual-layered membranes were simultaneously cast on the plate using two

different casting knives and materials. **Fig. 11** presents the conceptual illustration of dual-layered membranes and two representative methods for developing flat-sheet and hollow-fiber membranes (Xia et al., 2018). Like conventional single-layered membranes, the dual-layered membranes are also positively featured as (1) the casting process by a single-step phase inversion which is a more efficient and cost-effective technology to specially design composite membranes without any post treatment; (2) the ease of novel membrane development with tailoring membrane's characteristics for user's purpose; (3) the efficient application of novel and high-cost materials to improve membrane's performance (Xia et al., 2018, Li et al., 2004, He et al., 2002). However, the diffusion rate of two different materials should be carefully considered for being well sandwiched as one layer due to the concern about delamination issues (Xia et al., 2017, Setiawan et al., 2012a, Sun et al., 2010). Xia et al. (Xia et al., 2017) reported the relationship between adhesion and delamination of dual-layered membranes through manipulating the diffusion rate via a hydrophilic gradient illustrated in **Fig.12**. In case 1, the authors expected that no delamination would occur when the bottom layer is more hydrophilic than top layer or both top and bottom layer is extremely hydrophilic, as the hydrophilic bottom layer can absorb water from top to bottom layer due to the layer's strong affinity of water molecules in a phase inversion process. On the other hand, in the different scenario, if the bottom layer is more hydrophobic than top layer, water could not penetrate into the bottom layer due to its strong surface energy, so that the water would be stayed on the boundary of top and bottom layer, which causes to delaminate these layers in the phase inversion. Therefore, it is noteworthy to mention that the solvent/non-solvent exchange rate in dual-layer casting can significantly affect the mechanism of adhesion or delamination phenomenon for dual-layered membrane preparation.

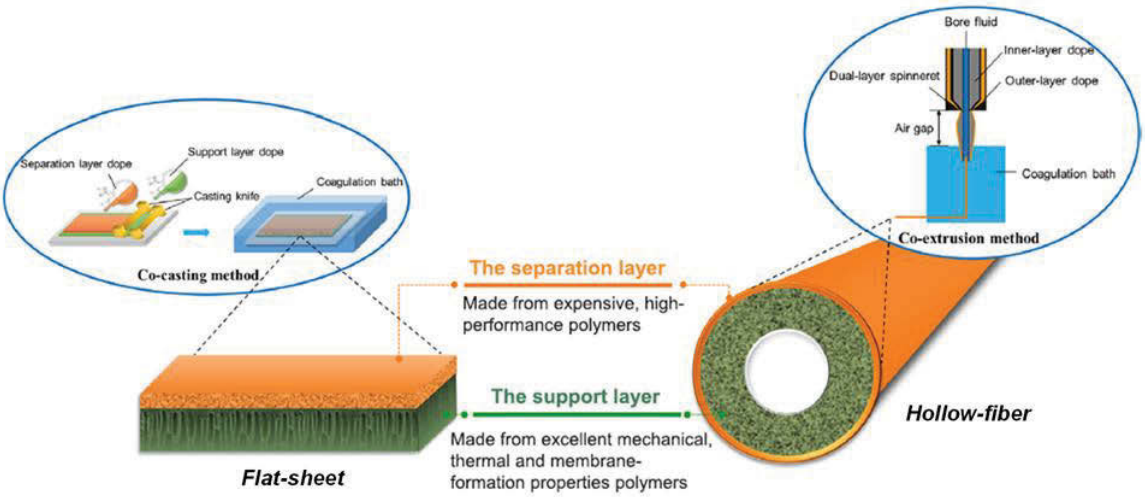


Figure 11 Conceptual illustration of dual-layered membrane and representative casting technologies for flat-sheet and hollow-fiber dual-layered membranes (Xia et al., 2018)

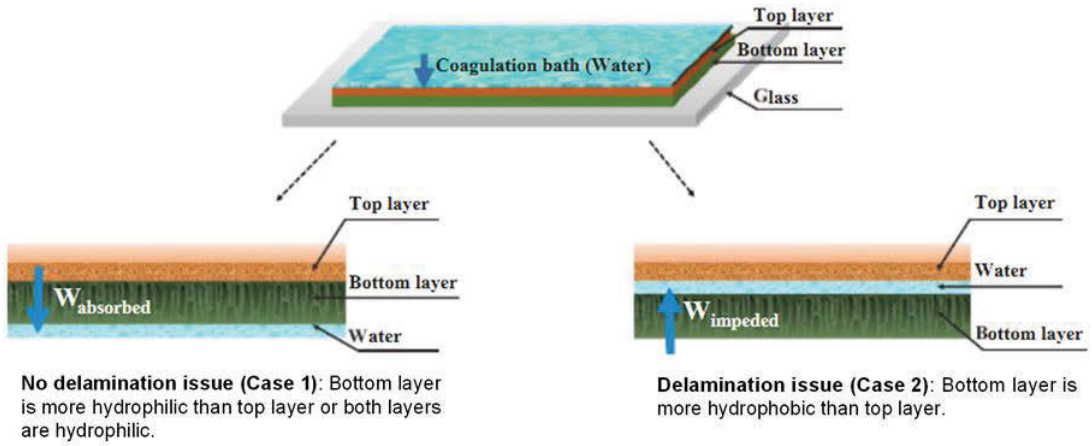


Figure 12 Conceptual illustration of dual-layered membrane and representative casting technologies for flat-sheet and hollow-fiber dual-layered membranes (Xia et al., 2018, Xia et al., 2017).

For FO processes, Yang et al. developed dual-layered HF membranes with dense skin layer like a common NF membrane using polybenzimidazole (PBI) and PES (Yang et al., 2009). The

PBI for the outer layer and PES for the inner layer were simultaneously cast using the triple spinneret presented in **Fig.13**. In particular, the PEI produced a dense outer structure with a small mean pore size (0.4 nm) and a narrow size distribution, which is suitable for a selective layer under FO operation. As a similar method above, Setiawan et al. launched PEI and PES based dual-layered HF membranes for FO processes. First of all, the dual-layered HF membrane substrate was prepared by using the triple spinneret with PAI (Torlon®) for outer layer and PES for inner layer. After that, a selective layer PEI polyeletrolyte was chemically cross-linked on the PAI outer surface as the post-treatment.

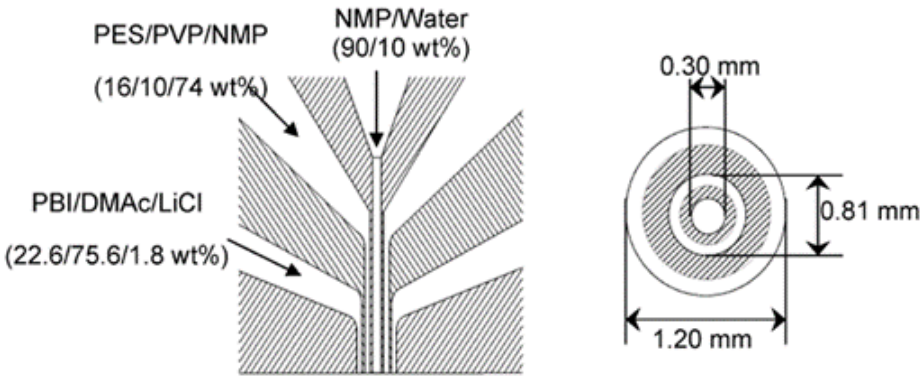


Figure 13 Design of the triple spinneret for preparing dual-layered HF membranes.(Yang et al., 2009).

In terms of flat-sheet FO membranes, Liu et al. proposed a dual-blade casting technique for fabricating dual-layered membrane substrates for FO application (Liu and Ng, 2014, Liu and Ng, 2015). For membrane fabrication, the one-step co-casting technique using two kinds of casting

blades was applied to produce double-layered polymeric membranes as presented in **Fig. 14**. As mentioned in early literatures, low concentrated polymer solution may produce highly porous membrane structures with very thin thickness under the phase inversion, which implies that produced membrane substrates may be properly used to reduce ICP in FO operation if the PA layer is able to be well deposited on the surface of the membrane substrate (Liu and Ng, 2015, Liu and Ng, 2014). Unfortunately, the membrane substrates produced by a low concentrated polymer solution may possess quite large pores on the surface, which may deteriorate PA active layer's integrity, even though it is attractive for ICP mitigation. That study thus investigated the effect of different casting solutions in membrane fabrication using the dual-blade casting technique. Two kinds of casting knives were serially positioned and simultaneously cast on the PET mesh. The casting thickness of the blade B was maintained at the zero clearance to fill the low-loaded PSf solution at 5 to 9 wt% (casting solution B) into open spaces of the PET mesh, while the opened gap of the blade A was set at 90 μm to fully cover the PET mesh using the high-loaded PSf solution at 10 wt% (casting solution A) as shown in Figure 11. The PET mesh was used as a backing support to enhance mechanical strength of the membrane substrate. In addition, the single-blade casting at a thickness of 90 μm using the casting solution A at 7 to 10 wt% was applied to prepare single-layered control membranes. Subsequently, the typical IP was conducted by the method in elsewhere (Han et al., 2017).

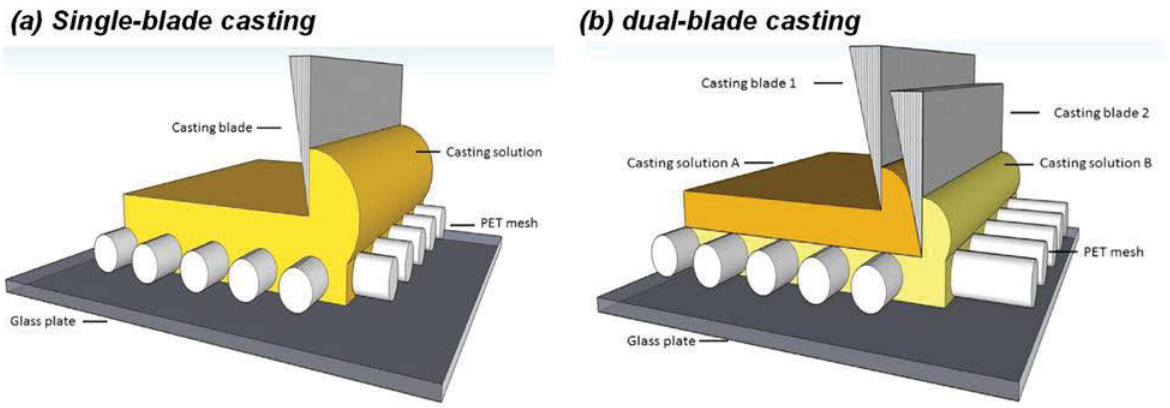


Figure 14 Conceptual illustration of single-blade casting for single-layered membrane (a) and dual-blade casting for dual-layered membrane (b) with a PET woven mesh (Liu and Ng, 2014).

With decreasing polymer loading, the authors reported that single-layered membrane substrates produced large pores on the top surface, which may impede the PA deposition via the IP. **Fig.15** shows the surface pores of the single-layered substrate using PSf at 8 wt% was much bigger at over 50 nm than those of dual-layered substrate less than 50 nm. This is because the polymer solution at low concentration causes to shrink the polymer structure in the precipitation process, so that the dual-layered membranes can be highly porous structure with macro-voids due to high intensity of the non-solvent inflow. However, under the co-casting approach, the SEM morphologies showed that dual-layered membrane substrates present relatively smooth and low porous surfaces, which is more desirable for subsequent IP than those of single-layered. This is because the top layer at 10 wt% of PSf was thin and dense on the support of low-concentrated bottom layer with a PET mesh in order to keep a desirable surface morphology for subsequent PA layer formation. In the FO performance test in **Fig.16**, decreasing the polymer concentration in single-layered membranes caused SRSF to rapidly increase, even though water flux was slightly

increased due to poor integrity of PA selective layer. On the other hand, for dual-layered membranes, the SRSF was quite good and stable in most series of samples because of secured surface morphology of the membrane substrate for subsequent PA formation. In addition, the water flux was gradually improved with decreasing polymer concentration of the bottom layer due to its extremely porous bottom layer which is suitable for mitigating ICP under FO operation.

Following that study, the same authors developed novel dual-layered mixed matrix membranes (MMMs) using hydrophilic colloidal silica. That study also applied the dual-blade casting technique to preparation of a membrane substrate. In particular, in that study they incorporated colloidal silica at extremely high concentrations (up to 4 wt%) into the bottom layer in order to increase the membrane porosity as well as hydrophilicity (Liu and Ng, 2015). As SEM results, single-layered MMMs (3 wt% of silica) presented an amount of colloidal silica on the top surface, and the silica on the top surface might subsequently deteriorate formation of PA layer, so that the FO performances of the MMM membranes deteriorated as well. However, for dual-layered MMM, although the colloidal silica was highly loaded in the membrane substrates, the surface morphology was well organized due to securing the top layer against incorporated colloidal silica. The FO water flux thus was improved as a function of silica concentration with retaining membrane's selectivity.

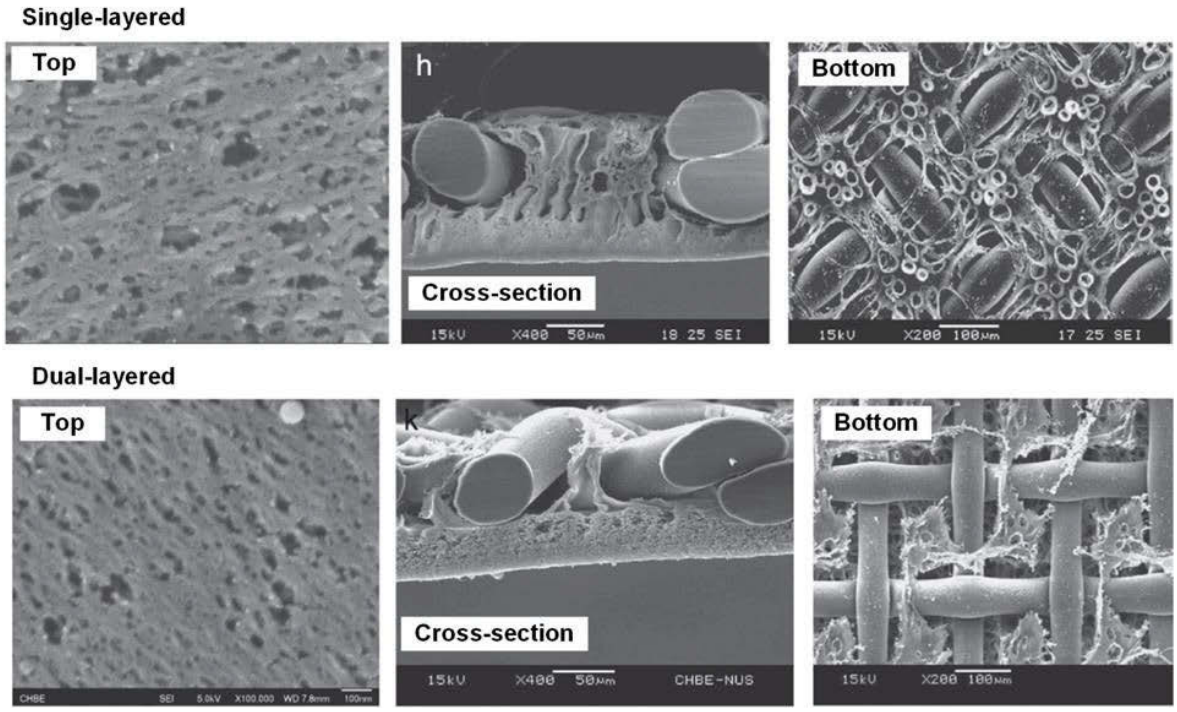


Figure 15 Morphological images (top, cross-section and bottom) of single and dual-layered membrane substrates with a PET woven mesh (Liu and Ng, 2014).

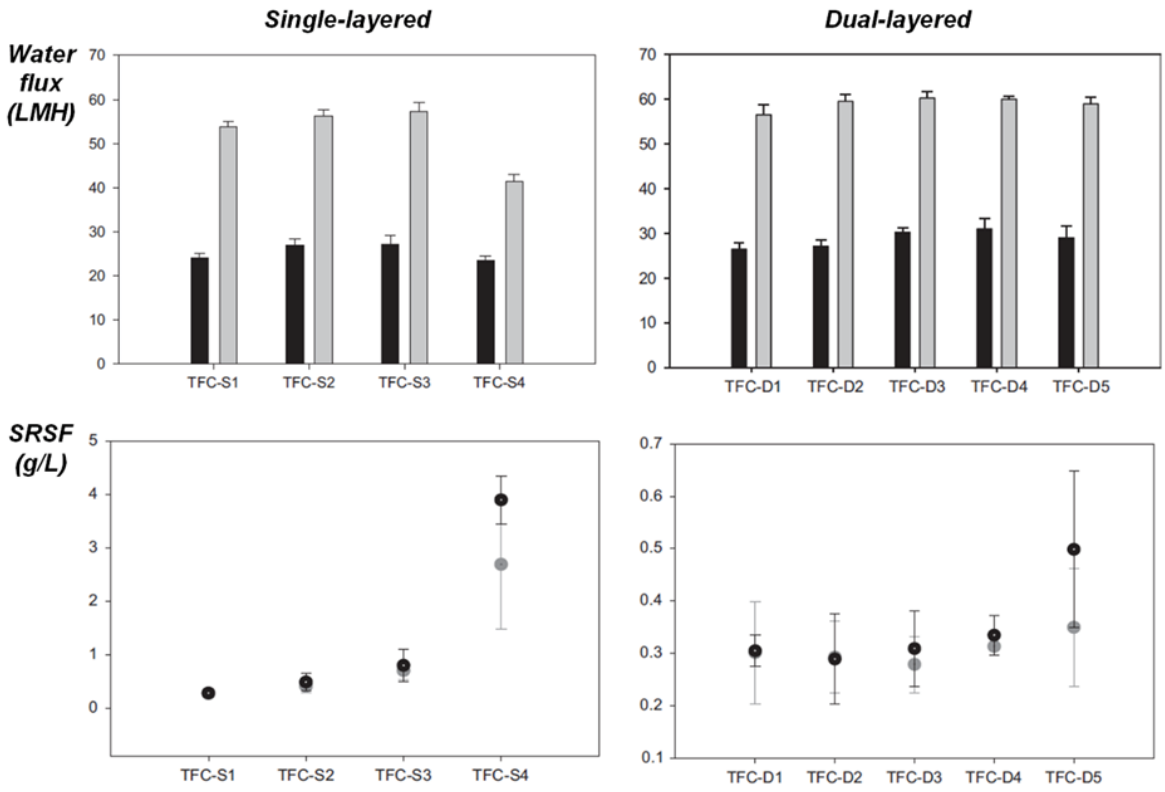


Figure 16 Key FO performances of single-layered and dual-layered TFC membranes under paring of 1M NaCl as DS and DI water as FS. (Liu and Ng, 2014).

As an another feasible strategy, Xiao et al. reported the sacrificial-layer approach to prepare porous PSf membrane substrate in order to reduce ICP in FO processes by using the dual-blade casting technology (Xiao et al., 2015). In that study, polyetheramine (PEI) and PSf was used for the bottom layer and top layer, respectively. In the co-casting, PEI/NMP solution was firstly cast on the glass plate using the casting knife at 100 µm, and PSf/NMP solution was then immediately cast on the PEI layer using the casting knife at 250 µm. The prepared dual-layered polymer film was subsequently immersed in the water bath for phase inversion. At the same time, the PEI bottom layer was peeled off in the whole structure. After that, PA layer was deposited on the surface of

the membrane substrate via a general IP process for a TFC membrane. The detailed procedure was described in **Fig. 17**. As shown in **Fig. 18**, dual-layered membrane substrates presented dense top surface which is similar with that of single-layered membrane containing surface pores less than 30 nm via the SEM analysis. The surface pore size was reasonable to form PA active layer on the surface of the membrane substrate. This is because the initial out-flow of solvent was significantly fast in the phase inversion so that it happened to form the dense skin layer via a quick gelation. The other section which is far from the interface observed slow out-flow of solvent, thus the porous structure near the bottom surface was formed. On the other hand, the dual-layered membranes clearly showed high porous internal structure as well as fully-opened bottom structure compared to the single-layered membrane which is attributed to the high inflow rate of water and exchange ratio of water and solvent, so that finger-like macro-voids were fully dominant inside the membrane substrate. In FO performances, as expected, the dual-layered membranes exhibited 10% and 30% higher water flux than those of the single-layered membranes using 0.5 M NaCl and 4 M NaCl DS, respectively. In addition, the S value of the dual-layered one at 167 μm was lower than that of the single-layered one at 241 μm, which implies that the dilutive ICP intensity of the dual-layered membrane would be lower than that of single-layered.

Therefore, these results demonstrated that the dual-blade casting is an interesting method to prepare a suitable membrane substrate for mitigating diluted ICP under FO operation. Based on these backgrounds, we have applied the dual-blade casting method to preparing novel FO membrane substrates possessing a porous internal structure, opened bottom layer and top dense layer for subsequent PA formation in chapter 3. After that, we also prepared robust and high permeable dual-layered membranes incorporated with GO and HNTs as a nanofiller for osmotic energy production in Chapter 4.

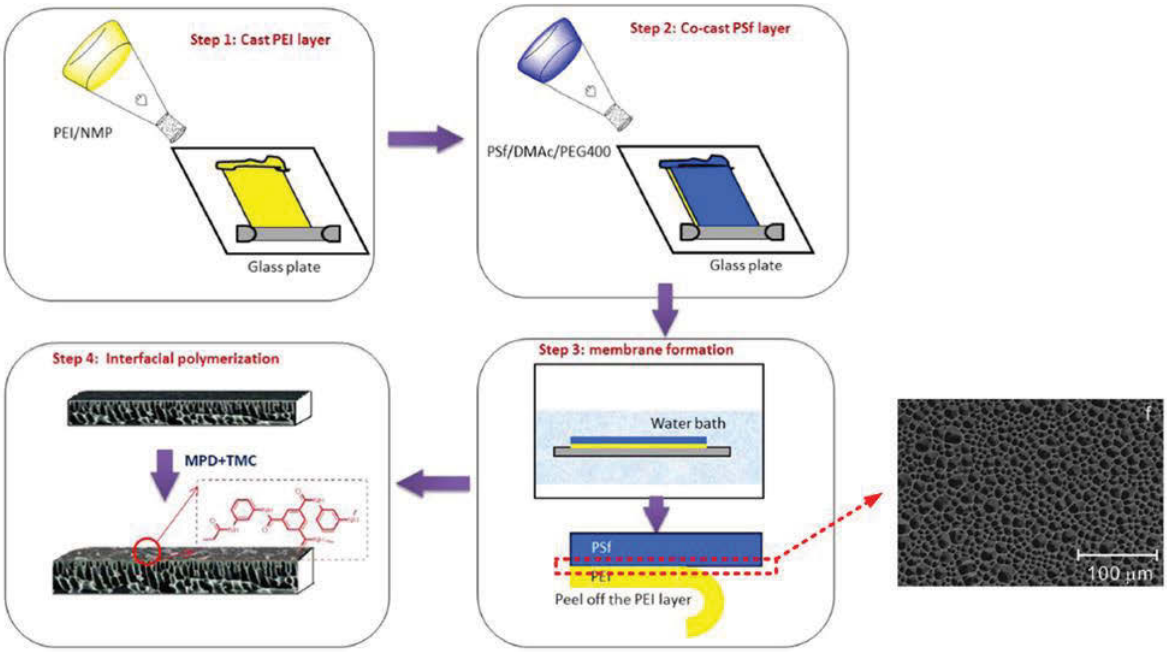


Figure 17 Schematic illustration of the experimental procedure of the sacrificial approach using PSf as a main polymer and PEI as a sacrificial polymer by the co-casting technology for preparing a porous membrane substrate with an opened bottom surface (Xiao et al., 2015).

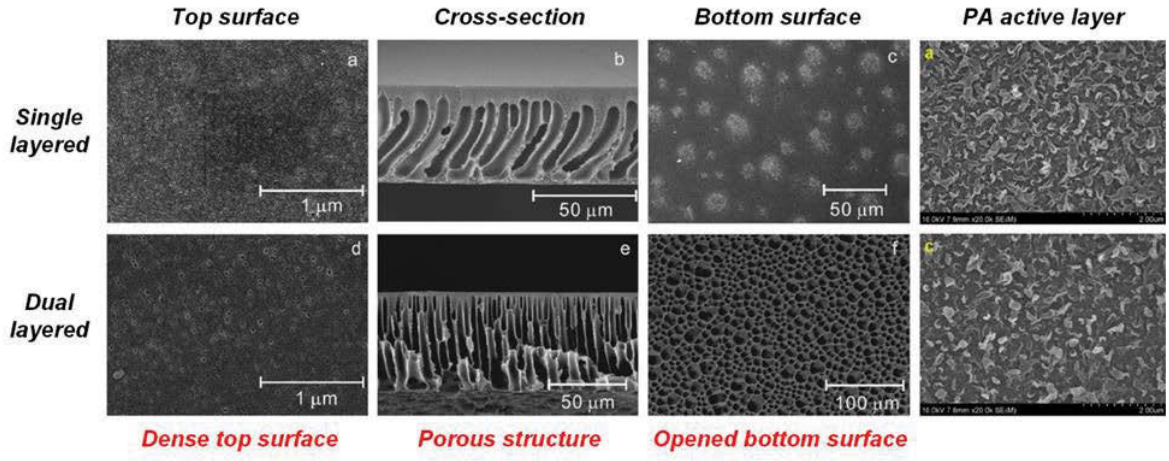


Figure 18 SEM morphological images (Top surface, cross-section and bottom surface) of PSf support layer produced by single-blade (bop line) and dual-blade (bottom line) casting method and PA active layer in TFC FO membranes.

As a novel fabrication technique for preparing thin active layers, the VAIP has been applied to developing outer-selective hollow fiber (OSHF) TFC membranes. The OSHF membranes have been attractive for the application of osmotically driven processes with its advantages of larger surface area, less ECP, less fouling propensity, easier to control foulants, and better to apply to sub-merged membrane processes as shown in **Fig. 19**. Nevertheless, most hollow fibre TFC FO membranes in previous literatures were inner-selective, which consist of the PA selective layer formed on the bore side of the membrane substrates, since it is easier to form defect-free PA layer with less external interferences for the IP process. On the other hand, for preparation of OSHF TFC membranes, it is difficult to form defect-free outer PA selective layer by the well-established interfacial polymerisation (IP) method. IP involves using amine monomer such as MPD, which is

first applied on the membrane support layer and the excess MPD is typically removed usually with the help of nitrogen-knife or nitrogen-purging. Acyl chloride monomer such as TMC is then applied; it cross-links with MPD to finally form a thin PA selective layer. The formation of defect-free ultra-thin PA selective layer on a flat-sheet and inner-selective hollow fibre membranes is easier as the IP is performed on only one side of the membrane surface and hence does not come in contact with any other surface. However, for a bundle of hollow fibre membranes containing thousands of fibres, the outer surface of each fibre, where PA layer is to be formed, is in direct contact with the outer surface of other fibres in the bundle. Hence, the challenge is in forming defect-free PA layer. The main difficulty lies in the removal of excess MPD monomer from the outer surface of the bundled fibre module before applying TMC monomer to form a defect-free ultra-thin PA selective layer. The presence of excess MPD monomer due to incomplete removal from the fibre surface results in pin-hole defects caused by droplets of the amine solution (Sun and Chung, 2013, Lau et al., 2012). Kumano et al. tried forming outer PA layer by passing a single hollow fibre membrane continuously through several monomer solutions but this approach is not only impractical for large scale fabrication but inevitably makes contact with the driving roller to form defects (Kumano, 1998).

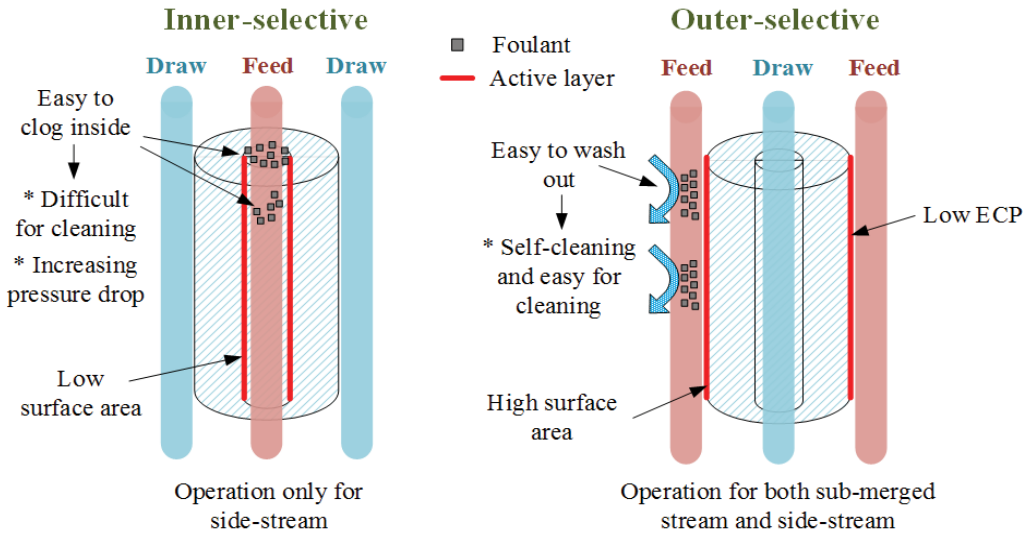


Figure 19 Expected behaviors of inner-selective and outer-selective hollow fibre membranes in FO processes

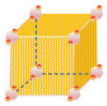
To overcome this issue, Sun and Chung, Cheng et al. and Le et al. recently applied the vacuum-assisted method to remove excess MPD from the outer surfaces of the bundled fibre module resulting in the formation of outer selective hollow fibre TFC membranes for PRO processes (Sun and Chung, 2013, Xue et al., 2015). Contrary to the OSHF membranes for PRO application, development of OSHF TFC membranes for FO faces many challenges. The primary one is that during the IP process, hollow fibers are likely to attach to one another (Cheng et al., 2017h, Cheng et al., 2017a). It therefore requires careful handling when conducting the IP process. Moreover, the OSHF PRO membranes must have a much thicker and stronger substrate to withstand applied hydraulic pressure unlike the OSHF FO membranes possessing thinner and weaker membrane substrates. This could lead to shrinkage of membrane substrate during the IP process. Thus, no study on development of OSHF membrane for FO process exists so far despite many of its attractive features.

2.3.3 Incorporation of hydrophilic nanomaterials

Polymer-based membranes has been widely used for various water treatment processes due to their performance, low cost and reasonable durability such as the ease of pore customization, higher flexibility and low costs and small carbon emission for membrane production. However, there are still challenges for polymeric membranes like trade-off between water permeability and ion selectivity, membrane fouling and mechanical stability for high performance, and energy efficiency. For overcoming existing limitations of TFC FO membranes, ideal membranes should control and alleviate the intensity of ICP via altering the membrane structure to be highly porous. In addition, the membranes should be highly hydrophilic and possess large free volume areas in a dense PA layer in order to enhance water permeability with less sacrifice of ion selectivity and to control membrane fouling. In addition, anti-biological properties are also required to mitigate biological fouling on the membrane. Many experts have investigated to develop novel FO membranes, and various organic, inorganic and bio materials were incorporated into polymer-based membrane matrices to produce hybrid polymeric membranes so as to alter the intrinsic properties of the major polymers among them. For example, as tabulated in **Table 2**, the various types of hydrophilic nanomaterials such as colloidal silica (SiO_2) nanoparticles (NPs), titanium dioxide (TiO_2) NPs, Zeolite, sodium hydroxide, functionalized carbon nanotubes (fCNTs), functionalized graphene (fGO), graphene oxide (GO), zinc oxide (ZnO), silver (Ag) NPs, halloysite nanotubes (HNTs), various frameworks (zeolitic imidazolate framework (ZIF), covalent organic framework (COF) and metal organic framework (MOF)), carbon quantum dots (CQDs) and others (Guo et al., 2014). In addition, aquaporin vesicles were used to produce biomimetic

membranes with incorporatating the vesicles into either a polymer matrix or a PA selective layer for enhancing water permeability, and recently the commercial manufacturer (Aquaporin A/S, Denmark) launched a commercial aquaporin-based biomimetic TFC FO membranes (Ren and McCutcheon, 2018, Li et al., 2017c). Accordingly, the addition of hydrophilic nanofillers has been considered as a promising tool for improving water permeability with retaining ion separation and mechanical strength of membranes themselves and modifying their surface properties to overcome above limitations of existing FO membranes.

Table 2 Representative nanomaterials for nanocomposite FO membranes according to different shapes.

Types	Spherical	plate	Tubular	Fiber	Frameworks
Shape					
Nanomaterials	SiO_2, TiO_2, ZnO_2, AgNP, CQDs	Graphene, GO, Zeolite, BN	CNTs, HNTs	Carbon nanofibers	ZIF, COF, MOF

Nanocomposite hybrid membranes are classified as a function of nanofiller's location inside a polymer matrix as (1) mixed matrix membranes (MMMs) (2) thin-film nanocomposite (TFN) membranes, and (3) surface deposited nanocomposite membranes. These nanocomposite membranes are illustrated in **Fig. 20**.

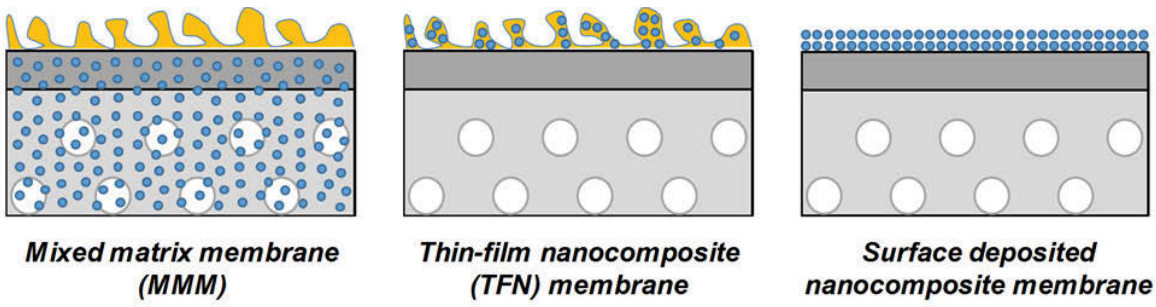


Figure 20 Types of nanocomposite membranes depending on the location of nanofillers in the TFC membrane matrix.

2.3.3.1 Modification of membrane structure and physico-chemical properties

For preparing MMMs, various nanomaterials are generally blended into a polymeric solution, which is a quite simple and practical method to produce hybrid nanocomposite membranes. In this approach for membrane development, nanomaterials are initially dispersed into a suitable solvent for preparing the polymer solution, dispersion property of the nanomaterials in the solvent is thus an important factor for producing MMMs, as the nanomaterials are able to easily lead to aggregate together due to their short collision distance and high surface area. In addition, the concentration of nanomaterials for loading should be carefully manipulated to be well distributed inside the polymer matrix. The MMMs for FO mainly use hydrophilic nanomaterials such as fCNTs, GO, HNTs, colloidal silica and others into the membrane substrates. The hydrophilic nanomaterials are able to positively contribute to form macro-sized finger-like voids inside a membrane substrate. As shown in Figure 17, the hydrophilic nanofillers incorporated in the polymer matrix attract water molecules into the matrix in phase inversion penetrating into the polymer matrix, which means that the exchange rate of solvent and non-solvent is increased as illustrated in **Fig. 21**. Therefore, the entire structure of the MMMs can be composed by finger-like structures and thin top dense layer. That is, the porosity of the membrane substrate can be significantly improved by the finger-like structure, and its diluted ICP in FO operation will be consequently dropped by the low S value. In addition, the intrinsic property of MMMs itself would be more hydrophilic than the neat polymer membranes, enhancing water transport across the membrane substrate. Furthermore, 1D nanomaterials such as nanofibers and nanotubes in a polymer matrix presented positive behavior for enhancing mechanical stability of the nanocomposite polymer matrix (Yin and Deng, 2015a, Liu et al., 2014). For 2D carbon nanosheets,

they played an important role in the polymer matrix to smoothen top surface of the membrane substrate in phase inversion process.

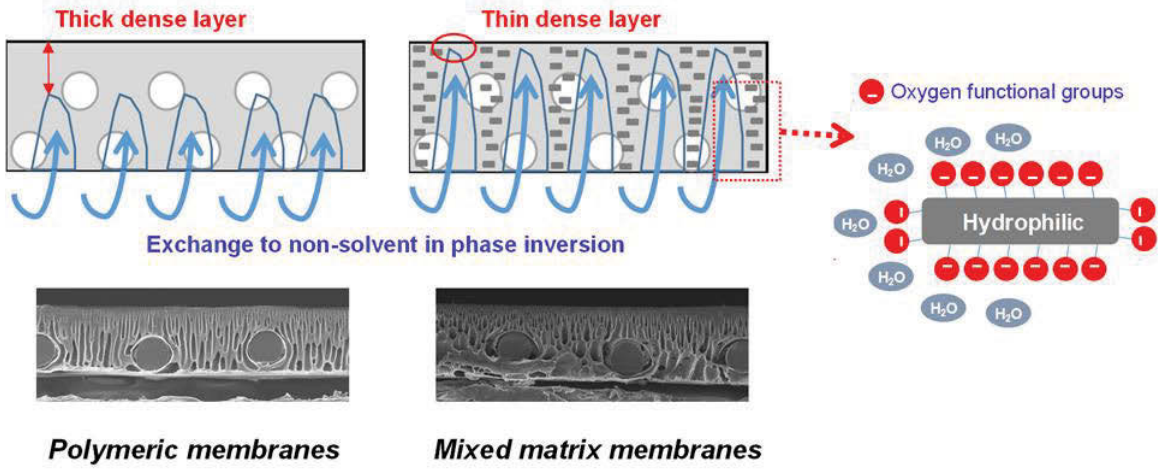


Figure 21 Comparison of the pore formation mechanism with polymeric membranes and mixed matrix membranes incorporated with hydrophilic nanofiller.

In the activities using GO nanosheets, Park et al. developed nanocomposite membrane substrates for TFC FO membranes using GO nanosheets. They embedded GO nanosheets into PSf membrane substrates as a function of GO loading from 0 to 1 wt% (Park et al., 2015). As mentioned above, GO nanosheets possess many advantages such as novel 2D atomic single-layer plates with extremely high aspect ratio, which emphasize a great interaction with the polymer matrix. In addition, GO has plenty of oxygen function groups on the surface and excellent stability against thermal and chemical damage. With these unique characteristics, GO nanosheets in the PSf solution affected the exchange rate of solvent and non-solvent in phase inversion, so that GO-loaded membrane substrates exhibited higher porosity, hydrophilicity and pure-water permeability

than those of neat PSf membranes. However, in the GO loading over 0.5 wt%, the viscosity of PSf/GO mixture was drastically increased, whereupon the demixing ratio between solvent and non-solvent might be retarded due to high kinetic hindrance in phase inversion. Thus, it contributes to form a relatively thick sponge-like structures above and beneath finger-like pores as presented in **Fig.22 (a)**. Furthermore, as shown in **Fig.22 (b)**, with an increase of GO loading, the surface of GO substrates was getting to be smoother, which is desirable for subsequent PA active layer formation. Of all experimental results, the optimum GO loading was confirmed at 0.25 wt% in series of membrane samples, and demonstrated significant improvement of the water permeability with no deterioration of its reverse solute diffusion via extremely low S value (191 μm).

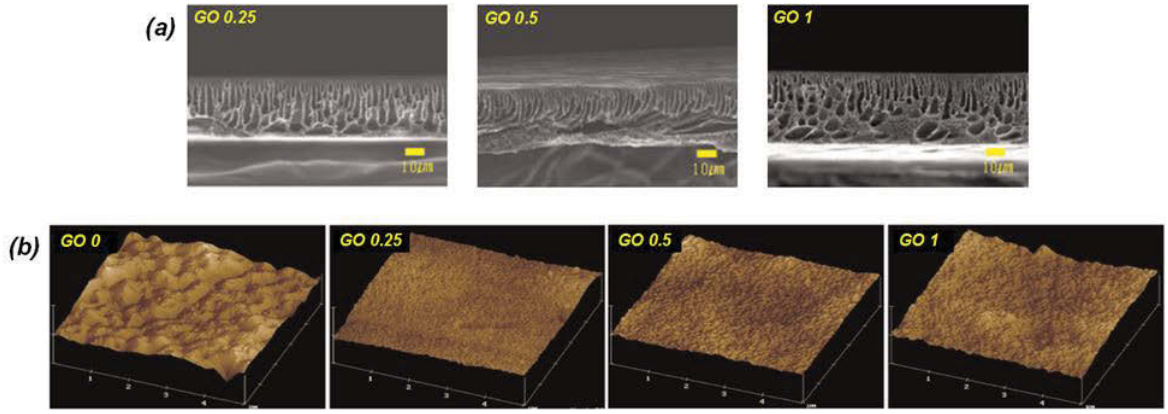


Figure 22 Cross-section SEM images (a) and topography (b) of series of GO incorporated membrane substrates according to GO loading from 0 to 1 wt% (Park et al., 2015).

By using the modified GO nanosheets, Wang et al. designed porous PES substrate using reduced GO (rGO) modified graphitic carbon nitride (CN/rGO) for preparing TFC FO membranes

(Wang et al., 2015). In particular, they emphasized that CN/rGO nanosheets consist of porous and curved dimensional structures with lamellar morphology. Furthermore, these nanosheets might contribute to enhancing the membrane wettability by their nitrogen-rich bonds as presented in **Fig.23**. This study demonstrated that improvement of the FO performance was attributed to the decline of ICP intensity through the porous membrane substrate incorporated with CN/rGO and membrane's hydrophilicity.

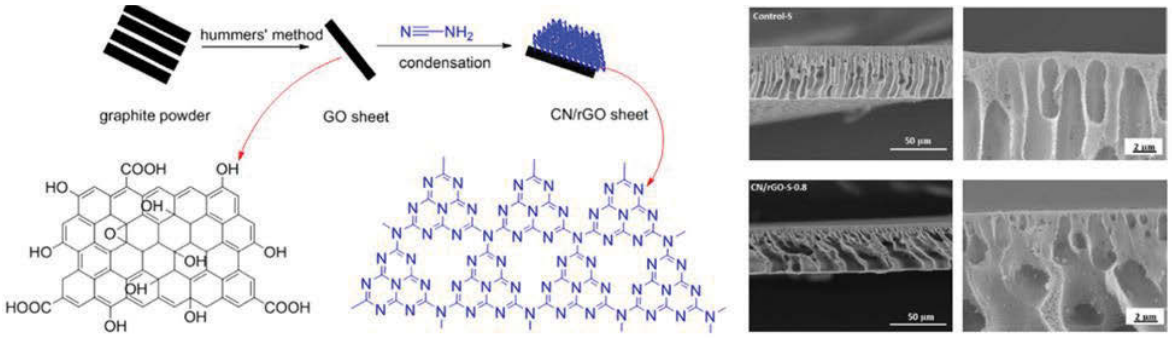


Figure 23 Schematic illustration of CN/rGO production (left) and internal morphology of Neat and optimum CN/rGO membrane substrate. (Wang et al., 2015)

As a novel nano-modifier, carbon nanotubes (CNTs), which consist of graphate lamellae rolled into the column shape have obtained strong attraction for membrane development due to its unique characteristics such as their high aspect ratio, smooth surface, and 1-dimentional (1D) tubular structure themselves with inner hollow cavities. Thus, CNTs are able to combine with the polymeric molecules inside the matrix and enhance water transport across a polymer matrix due to the expectation of super-fast water transport inside the tube by the super hydrophobic and

smooth wall of CNT itself (Sun et al., 2018, Baek et al., 2014). In addition, the CNTs inside a polymer matrix may produce nano- or micro-sized slits in the boundary of CNTs and polymer molecules due to their incompatibility (Lee et al., 2017). The gaps may contribute to enhanced water permeability of the polymer matrix. Furthermore, CNTs can enhance mechanical strength inside the mixed matrix, and they also possess great antibacterial property like GO nanosheets (Kang et al., 2009, Goh et al., 2013, Vatanpour et al., 2011). Although CNTs have amazing characteristics for membrane development, CNTs themselves are hydrophobic and easy to be aggregated due to the strong van der Waal's force, so that CNTs have poor dispersion property in most solvents. Therefore, some studies modify neat CNTs to be hydrophilically functionalized CNTs (fCNTs) by using sulfuric acid and nitric acid or using nitric acid with refluxing as shown in **Fig. 24 (a)** in order to improve the surface hydrophilicity and dispersion property (RSC) (Goh et al., 2013). Thus, **Fig. 24 (b)** shows the excellent water dispersion of modified fCNTs via the refluxing method using nitric acid. In addition, the hydrophilic fCNTs like other hydrophilic modifiers can play an important role to alter the demixing ratio of solvent and non-solvent in phase inversion for producing a porous membrane substrate as aforementioned. Wang et al. prepared PES/fCNTs composite membrane substrate to produce a high permeable TFC FO membrane (Wang et al., 2013). The membrane exhibited improved water flux and salt rejection under FO operation due to the effect of CNTs. In addition, the fCNT was effective in a polymer matrix for mitigating alginate fouling due to the electric repulsion to negatively charged alginates (Choi et al., 2015). For developing robust PRO membranes, Tian et al. synthesized PEI EN support incorporated with fCNTs in order to reinforce its mechanical strength (Tian et al., 2015). They emphasized that the reinforced EN substrate can support the PA active layer with increasing PA's mechanical stability for withstanding a high hydraulic pressure under PRO operation. As a result,

the optimum membrane exhibited the highest PD at 17.3 W/m^2 in series of membrane samples. In addition, they presented the long-term stability of the PRO membranes with a stable PD at 15.5 W/m^2.

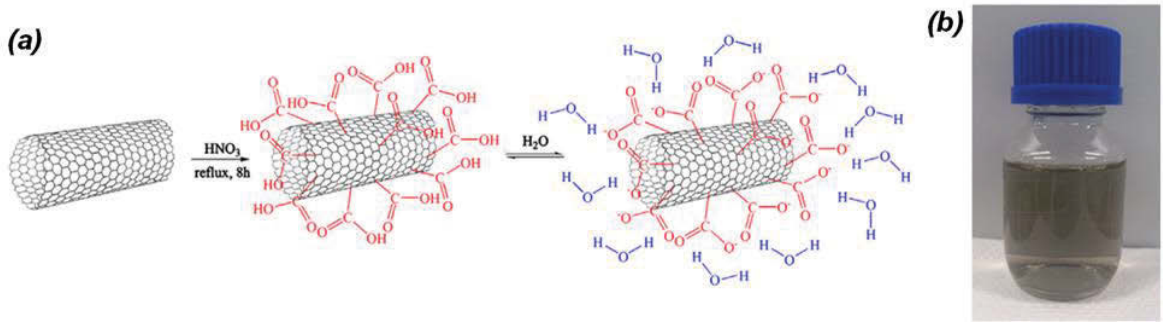


Figure 24 (a) Scheme of the chemical reaction of fCNTs via the refluxing method using nitric acid (left) and photo image of fCNTs dispersed aqueous solution (Goh et al., 2013)

As another tubular nanofillers, halloysite nanotubes (HNTs) are a naturally produced 1D nanotube which consists of alumina and silica composites as shown in **Fig. 25** (Liu et al., 2014, Ghanbari et al., 2016). The HNTs present nano-sized tubular structures with a large aspect ratio similar to kaolinite, a relatively low density of nanofillers. In addition, HNTs possess hydrophilic nature from hydroxyl groups on their surface such as siloxane, so that the characteristics contribute to produce relatively weak tube-tube interaction not like CNTs which have a big challenge to make dispersion in various solvents or water (Byrne and Gun'ko, 2010, Ghanbari et al., 2016, Liu et al., 2014, Ghanbari et al., 2015). In addition, HNTs are easily produced from natural mineral orgins that is abundant in the world, so that HNTs are much cheaper than other nanomaterials such as CNTs, GO and others (Liu et al., 2014). **Table 3** present the comparison of some nanofiller's prices

(Vahdat Vahedi, 2015). Furthermore, it has been reported that HNTs linked with polymer molecules are able to contribute to increased tensile, flexural strength and elastic modulus of polymer matrices.

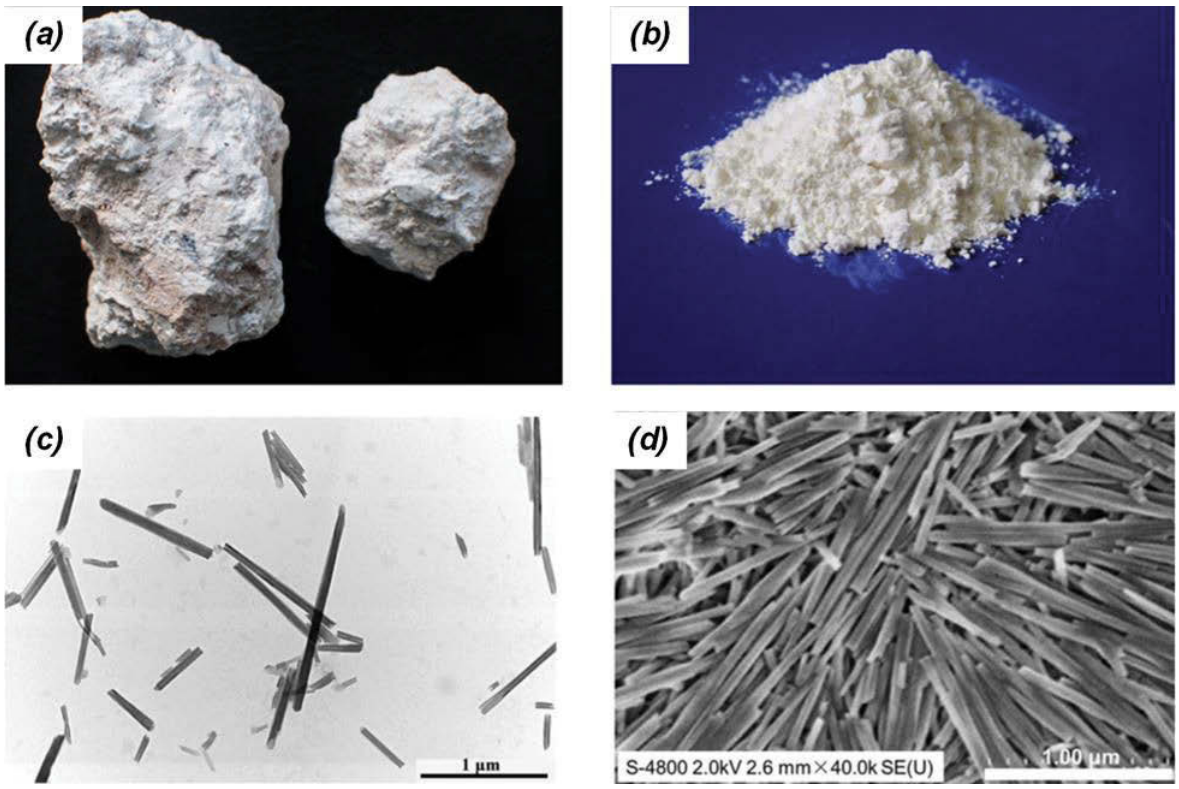


Figure 25 (a) The raw rock of HNT, (b) grinded HNT powder, (c) TEM image and (d) SEM image of HNTs (Liu et al., 2014)

Table 3 The comparison of filler's prices per one kilogram (kg) (Vahdat Vahedi, 2015)

Type of fillers	Price (US dollar per kg)
HNTs	2 – 20
Montmorrilonite	35 –200
CNTs	400 – 1000
Carbon black	1.1
Silica	2.2 – 4.2
Calcium carbonate	0.15 – 13.64
Polyprophylene (PP)	1.49 – 2.35
Polyethylene (PE)	1.38 – 2.42
Polyvinylchloride (PVC)	1.21 – 2.59

In a polymer-based mixture, there is no any requirement for HNTs to be chemically treated for improving their dispersion property in polymeric liquids for the membrane preparation. There is therefore less concern about nanofiller's aggregation in both polymer solution and polymer matrix. With the excellent dispersion of HNTs, it is expected that optimum HNT loading in a polymer matrix would be higher than those of other nanomaterials, so that the HNT's effect would be more featured. Furthermore, HNTs which possess 1D nano-sized tubular structure and negative charges on their surface play an important role to mitigate the attachment of foulants and biological growth on a membrane surface for a preparation of fouling resistance membranes (Kang et al., 2009). With the addition of HNTs into a polymer matrix, Ghanbari et al. proposed to develop MMMs in order to improve the porosity and hydrophilicity for mitigating diluted ICP in FO processes (Ghanbari et al., 2016). The HNT loading for development of the MMMs was manipulated from 0 to 1 wt%, and hydrophilicity, porosity and surface roughness of the membrane substrate were sensitively affected as a function of HNT's loading in the range. As shown in **Fig. 26**, it observed that the top layer of the neat membrane substrate presented tiny holes only with no

HNT fragments, and just two fragments were shown in the image of the MMMs with HNTs at 0.25 wt%. However, according to increasing HNT loading over 0.25 wt%, the number of HNT fragments were found on the top surface of the MMMs in the SEM images. At 1 wt%, the aggregated HNTs werer clearly shown on the surface, and it is also expected that the MMMs with a high HNT loading may form many enlarged voids or undesirable cracks. In addition, exposed HNTs on the top surface may deteriorate the integrity of the PA layer that will be subsequently deposited on the top surface of MMMs. In FO performance tests, the trends of water flux and salt rejection were well correlated with what it expected. Under the high loading of HNTs, although the water flux of the TFC membrane was significantly improved, the salt rejection decreased. However, at the optimum HNT loading, water flux of the FO membrane was significantly improved with no or less sacrifice of ion rejection. Based on these activities in literatures, it is expected that the addition of HNTs into a polymer matrix may positively improve membrane porosity, hydrophilicity and mechanical stability. In addition, fouling mitigation and anti-biological properties on the membrane surface may be improved with HNTs. Therefore, it is proposed that HNTs can be used as a promising modifier for developing not only high permeable membranes but also robust polymeric membranes such as RO or PRO membranes.

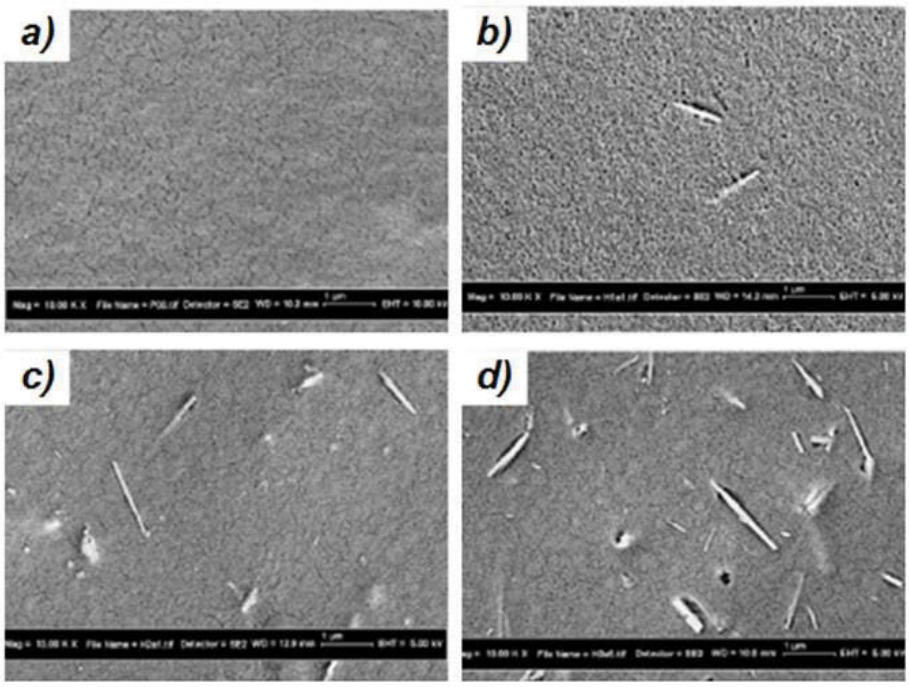


Figure 26 SEM images of the top surface of the MMMs with different loading of HNTs: (a) 0 wt% (b) 0.25 wt%, (c) 0.5 wt% and (d) 1 wt%.

Silica nanoparticles, metal-based nanoparticles such as silver (Ag) or titanium oxide (TiO_2) have been also used to prepare MMMs for OD membranes. These materials most commonly possess nano-sized structure, high hydrophilicity and excellent dispersion properties themselves, which are desirable for nanofillers to be embedded into a polymer matrix. In particular, silica nanoparticles have had a wide range of applications for membrane production due to their high stability, mechanical strength and non-toxic nature. Some studies used several silica nanoparticles to produce hydrophilic and porous EN membrane substrates for TFC FO membranes (Obaid et al., 2016, Bui and McCutcheon, 2016, Tian et al., 2017, Zhang et al., 2018). In particular, these were

mainly focused on developing silica-composite EN membrane substrates for preparing TFC FO membranes.

2.3.3.2 Thin-film nanocomposite (TFN) membranes

Most FO membranes consists of a thin active layer, porous support layer and backing support which are denoted as thin film composite (TFC) membranes. The TFC membranes have been developed and commercialized in both academia and industry areas for membrane-based water treatment processes, because these asymmetric membranes are able to specially design each layers (selective layer, support layer and backing support) for user's purpose through various techniques. For 30 years, many activities have been dedicated to improve water permeability, ion selectivity and membrane fouling of the TFC membranes. As mentioned above, the membrane substrate has been modified to be porous, hydrophilic and mechanically stable. In addition, the active layer has been altered by using various conditions and monomers in the interfacial polymerization and applying physico-chemical modification of an active surface. As an upcoming technology, hydrophilic nanomaterials has been applied to developing nanocomposite thin active layer. This is one effective approaches to alter intrinsic properties of a thin active layer. Thus, many studies have investigated various nanomaterials including zeolite, TiO_2, fCNTs, HNTs, SiO_2, GO, carbon quantum dots, Ag nanoparticles, colloidal silica, titanate nanotubes, various organic frameworks and others to be incorporated into the PA active layer (Ghanbari et al., 2015, Chae et al., 2015, Amini et al., 2013, Rajaeian et al., 2013, Yin et al., 2016, Ma et al., 2017, Zhang et al., 2017b, Tian et al., 2017, Ma et al., 2012, Emadzadeh et al., 2015). The nanomaterials have been dispersed either in aqueous MPD solution or organic TMC solution in the IP process. For TFN FO membranes, hydrophilic nanofillers have been used to enhance hydrophilic nature of the

PA active layer for improving water permeability and fouling mitigation. Thus, selected hydrophilic nanofillers as mentioned above are normally well dispersed in aqueous phase. Most studies for TFN FO membranes dispersed chosen nanofillers into aqueous MPD solution (Ma et al., 2012, Amini et al., 2013, Ghanbari et al., 2015). **Fig. 27** presents illustration of TFN membrane fabrication using nanofillers through the IP process (Yin and Deng, 2015a).

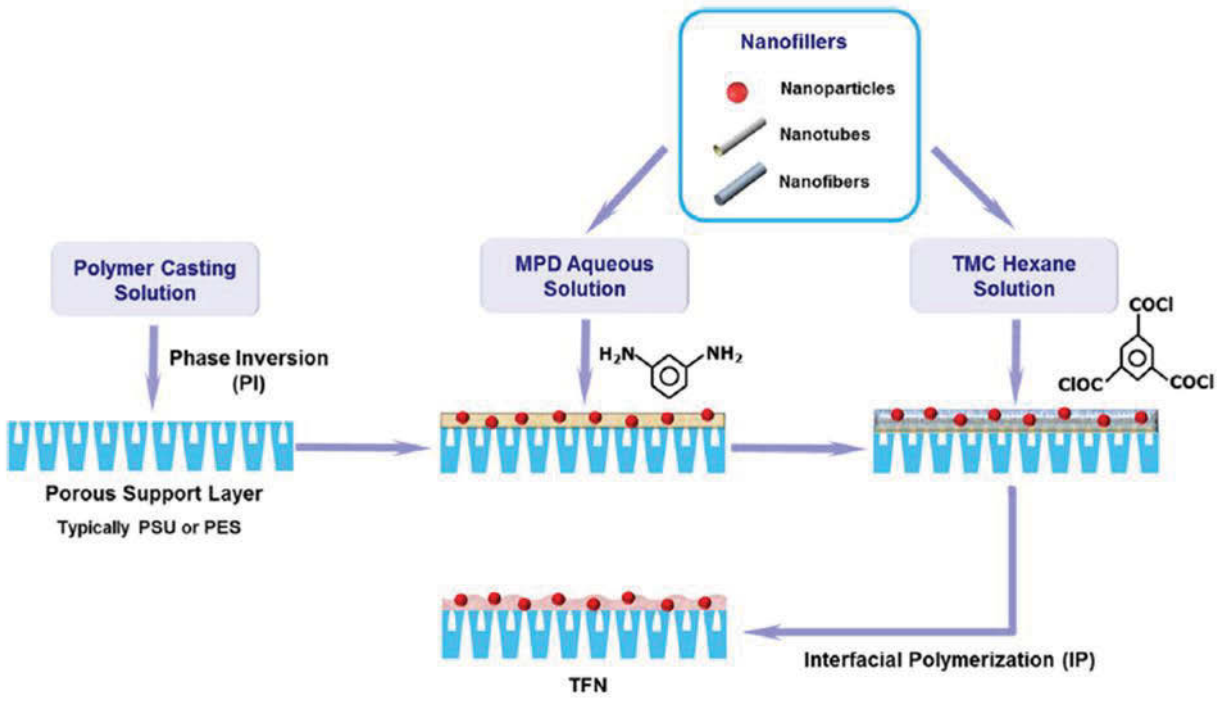


Figure 27 Illustration of TFN membrane fabrication using nanofillers through the IP process (Yin and Deng, 2015a)

The PA selective layer, which is used as a key barrier in TFC membranes, controls permeability, ion selectivity and fouling resistance. The incorporation of nanofillers into the PA layer can be an effective method to modify physico-chemical properties of the PA layer such as hydrophilicity, surface charge density, ratio of free-volume, water channels and cross-linking degree can be tailored by using various nanofillers. Ma et al. reported novel TFN membranes using

UiO-66 nanoparticles which is a kind of MOF (Ma et al., 2017). The incorporation of UiO-66 nanoparticles into the PA layer significantly changed the PA layer's morphology and hydrophilic nature, so that water flux improved 20.7 $Lm^{-2}h^{-1}$ compared to that of the neat TFC membrane at 16.5 $Lm^{-2}h^{-1}$ in FO operation using 1 M NaCl as DS and DI water as FS.

Generally, the hydrophilicity, cross-linking degree and thickness of thin PA layer are key parameters for controlling intrinsic transport properties of TFC membranes. However, there still exists the trade-off relationship between water permeability and solute permeability, which is an obstacle for further improving membrane performances. To break the trade-off, the PA layer may be modified for enhancing water permeability but also retaining ion selectivity. Thus it is necessary to find suitable nanofillers to control cross-linking degree, surface charge density, pore structures inside PA layer. For choosing the best nanofillers, intrinsic characteristics of nanofillers such as physical demension, internal structure, surface chemistry, dispersion property and compatibility with the thin PA layer should be also carefully considered. Introducing TFN membranes can be an effective solution to improve intrinsic transport properties to enhance hydrophilicity and to impart anti-fouling and anti-microbial properties via altering PA layer using various kinds of nanofillers (Yin and Deng, 2015a, Sun et al., 2018).

3 Dual-layered nanocomposite membrane based on polysulfone/graphene oxide for mitigating internal concentration polarization in forward osmosis

*** This chapter was published in *Polymer* (2017).**

3.1 Abstract

A novel TFC FO membrane with dual-layered substrate support was fabricated by a double-blade casting technique using different polysulfone (PSf) concentrations for top (15 wt%) and bottom (7 wt%) substrate layers. Graphene oxide (GO) was incorporated in the substrate layer, and the dual casting approach resulted in a membrane support with a highly porous bottom structure and a dense top skin layer on which the polyamide active layer was effectively formed. The dual-layered TFC PSf/GO membrane (TFC-PSf$_d$GO) exhibited high water permeability, and ion selectivity was enhanced by the presence of well dispersed hydrophilic GO in the PSf substrate. The TFC-PSf$_d$GO also exhibited the lowest specific reverse solute flux (J_s/J_v=0.19 gL^{-1}) and a more favorable structural parameter (S=130 μm) compared to GO-free membranes. Using deionized water as FS and 1 M NaCl as DS, TFC-PSf$_d$GO had J_v=33.8 Lm^{-2}h^{-1} and J_s=6.9 gm^{-2}h^{-1} under AL-FS mode, and J_v=61.5 Lm^{-2}h^{-1} and J_s=14.0 gm^{-2}h^{-1} under AL-DS mode. The potential of TFC-PSf$_d$GO for commercial application was further evaluated by fabricating it with a fabric backing support (denoted as TFC-PSf$_d$GO$_f$). Compared to TFC-PSf$_d$GO, TFC-PSf$_d$GO$_f$ exhibited only 14% decline in its water flux. The overall results reveal that, fabrication of TFC membrane support via co-casting approach along with GO incorporation produced high-performance TFC FO membranes which likely reduced the internal concentration polarization effects.

Keywords: *Forward osmosis; Dual-layered substrate; Graphene oxide (GO); Thin-film composite membrane; Internal concentration polarization (ICP)*

4 Dual-layered nanocomposite membrane incorporating graphene oxide and halloysite nanotube for high osmotic power density and fouling resistance

*** This chapter was published in *Journal of Membrane Science* (2018).**

4.1 Abstract

This study introduces a thin-film composite (TFC) membrane with a dual-layered nanocomposite substrate synthesized using a dual-blade casting approach for application in osmotic power generation by the pressure-retarded osmosis (PRO) process. The approach incorporates halloysite nanotubes (HNTs) into the bottom polymer substrate layer and graphene oxide (GO) on the top layer substrate, on which a thin polyamide active layer is formed. The fabricated membrane substrate showed highly desirable membrane substrate properties such as a high porosity, opened-bottom surface, suitable top-skin surface morphology for subsequent active layer formation and high mechanical strength, which are essential for high-performance PRO processes. At a GO loading of 0.25 wt% and HNT loading of 4 wt%, the power density (PD) of the nanocomposite membrane was 16.7 W/m^2 and the specific reverse solute flux (SRSF) was 2.4 $g\ L^{-1}$ operated at 21 bar applied pressure using 1 M NaCl as DS and deionized water as feed, which is significantly higher than the those for a single-layered or commercial PRO membrane. This membrane performance was observed to be stable in the pressure cycle test and under long-term operation. The membrane substrate with HNTs incorporated exhibited high fouling resistance to sodium alginate and colloidal silica foulants, with the PD decreasing by 17% after 3 h of operation, compared to a membrane substrate without HNTs and commercial PRO membranes, which

decreased by 26% and 57%, respectively. A fluorescence microscope study of the membranes subjected to feed water containing *Escherichia coli* confirmed the good antibacterial properties of the dual-layered TFC membrane. The study provides an attractive alternative approach for developing PRO membranes with high PD and fouling resistance.

Keywords: Dual-blade casting; nanocomposite membrane; graphene oxide; halloysite nanotube; pressure-retarded osmosis.

Sungil Lim, Myoung Jun Park, Sherub Phuntsho, Anne Mai-Prochnow, Anthony B Murphy, Donghan Seo, Hokyong Shon, "Dual-layered nanocomposite membrane incorporating graphene oxide and halloysite nanotube for high osmotic power density and fouling resistance", *Journal of Membrane Science* **564** (15), pp.382-393, 2018

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5 Defect-free outer-selective hollow fiber thin-film composite membranes for forward osmosis applications

*** This chapter was submitted to *Journal of Membrane Science* (2018).**

5.1 Abstract

This study presents the successful fabrication of a novel defect-free outer-selective hollow fiber (OSHF) thin-film composite (TFC) membrane for forward osmosis (FO) applications. Thin and porous FO membrane substrates made of polyether sulfone (PES) with a dense and smooth outer surface were initially fabricated at different air-gap distances. A modified vacuum-assisted interfacial polymerisation (VAIP) technique was then successfully utilised for coating polyamide (PA) layer on the hollow fiber (HF) membrane substrate to prepare OSHF TFC membranes. Experimental results showed that the molecular weight cut-off (MWCO) of the surface of the membrane substrate should be less than 88 kDa with smooth surface roughness to obtain a defect-free PA layer via VAIP. The FO test results showed that the newly developed OSHF TFC membranes achieved water flux of 30.2 L m^{-2} h^{-1} and a specific reverse solute flux of 0.13 g L^{-1} using 1M NaCl and DI water as draw and feed solution, respectively. This is a significant improvement on commercial FO membranes. Moreover, this OSHF TFC FO membrane demonstrated higher fouling resistance and better cleaning efficiency against alginate-silica fouling. This membrane also has a strong potential for scale-up for use in larger applications. It also has strong promise for various FO applications such as osmotic membrane bioreactor (OMBR) and fertiliser-drawn OMBR processes.

Keywords: Outer-selective; Thin-film composite; Hollow fiber; Forward osmosis; Vacuum-assisted Interfacial polymerisation

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Sungil Lim, Van Huy Tran, Nawshad Akther, Sherub Phuntsho and Ho Kyong Shon, "Development of defect-free outer-selective thin-film composite hollow fiber membranes for forward osmosis applications", Under review in *Journal of Membrane Science*, 2019

5.5 Application of the OSHF FO membrane for osmotic membrane bioreactor treating municipal wastewater

5.5.1 Introduction and aims

In this chapter, we successfully developed novel OSHF TFC membranes for FO processes with excellent performances. As aforementioned above, we demonstrated that the OSHF TFC membranes are the most suitable candidate for OMBR application. OSHF TFC membranes have the edge over the ISHF TFC membranes because of (i) more substantial surface area per fiber, (ii) less external concentration polarization (ECP), (iii) lower fouling propensity, and (iv) ease of fouling control (Cheng et al., 2017h, Le et al., 2016, Ren and McCutcheon, 2015a, Pathak et al., 2018). The objective of this study is to investigate the performance of novel OSHF TFC FO membrane for the first time in OMBR application and to assess different fouling mitigation strategies using these membrane modules. The OMBR system, which used side-stream OSHF TFC FO membrane modules, was operated under two operation regimes. Three fouling mitigation strategies were sequentially carried out during operation of each regime. The investigation focused on the performance of OSHF TFC membrane based on following key factors: (i) water flux, (ii) reverse solute flux or salinity buildup in the mixed liquor, (iii) removal of primary contaminants, and (iv) membrane fouling and efficiency of fouling control strategies. To the best of our knowledge, there has been no study investigating the performance of OSHF TFC FO membranes applied in OMBR.

Van Huy Tran, Sungil Lim, Nirenkumar Pathak, Nawshad Akther, Sherub Phuntsho, Dong Suk Han and Ho Kyong Shon, “Application of novel outer selective thin film composite hollow fiber forward osmosis membrane in osmotic membrane bioreactor treating municipal wastewater”, Under review in *Bioresource Technology*, 2019

6 Novel outer-selective hollow fiber (OSHF) thin-film nanocomposite membranes with size-controlled graphene oxide for forward osmosis applications

6.1 Abstract

In this paper, novel outer-selective hollow fiber (OSHF) TFN membranes incorporated with graphene oxide (GO) nanosheets were successfully developed using the vacuum-assisted interfacial polymerization (VAIP) technique. The GO loading was firstly optimized, followed by the performance comparison between bulk GO (BGO) nanosheets and size-controlled GO (SGO) nanosheets that are embedded into the PA selective layer. Experimental results confirmed that the optimum SGO loading was 0.0005 wt.% (5 g/m^3), which is much lower than the previous studies. Hence, the cost of GO used in TFN membrane production is significantly reduced using the VAIP technique. Optimum OSHF TFN membrane exhibited an excellent water flux at 39.0 Lm^{-2}h^{-1} and high solute selectivity (J_s/J_w at 0.16 g L^{-1}). Moreover, SGO TFN membranes showed better performance than those embedded with BGO and presented their high potential for fouling resistance in wastewater treatment. The overall experimental results showed that the existing trade-off between water permeability and reverse solute flux could be eliminated while enhancing fouling resistance when optimum loading of SGO is used for developing FO TFN membranes. This novel TFN membrane can be a decent candidate to emerging FO processes for desalination and water reclamation.

Keywords: Outer-selective; hollow fiber membrane; Thin-film nanocomposite (TFN); Graphene oxide (GO); Forward osmosis (FO)

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Sungil Lim, Kwanghyun Park, Van Huy Tran, Nawshad Akther, Sherub Phuntsho and Ho Kyong Shon, “Novel outer-active thin-film nanocomposite hollow fiber membranes with size-controlled graphene oxide for osmotic membrane bioreactor applications”, in preparation, 2019

7 Covalent organic framework (COF) based OSHF TFN membranes for forward osmosis applications

7.1 Abstract

In this study, we successfully developed a new outer-selective hollow fiber (OSHF) TFN FO membranes with amine-rich Schiff-based network (SNW-1) nanoparticles as kinds of covalent organic frameworks (COFs) by the vacuum-assisted interfacial polymerization (VAIP). The SNW-1 nanoparticles possess hydrophilic nature and porous internal structures which are desirable for producing highly permeable membranes. For fabricating defect-free TFN membranes, SNW-1 nanoparticles were horizontally accumulated and stacked on the outer surface of the HF substrate through the vacuum pressure in the VAIP. Furthermore, we expected that the covalent bonding between secondary amine (NH^{2-}) groups in SNW-1 and acyl chloride ($COCl^{-}$) in trimesoyl chloride (TMC) is able to positively affect the compatibility of SNW-1 with PA layer. As a result, the S10 sample with the loading at 0.001 wt. % exhibited the best FO performances with the highest water flux at 31.5 L m^{-2} h^{-1} and relatively low specific reverse solute flux (SRSF, J_s/J_w) at 0.18 g L^{-1} in series of TFN membranes. The optimum loading at 0.001 wt% was much lower than those in other TFN membranes (normally above 0.01 wt. %) due to the minimum loss of SNW-1 in VAIP. Also, the optimum TFN membrane presented an excellent stability of the FO performance for 72 h. Therefore, we believe that the best membrane in this study can be a promising and comparative candidate to optimize FO processes in the future.

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Sungil Lim, Nawshad Akther, Van Huy Tran, Tae-Hyeon Bae, Sherub Phuntsho and Ho Kyong Shon, "Development of outer-active thin-film nanocomposite hollow fiber membranes with covalent organic framework (SNW-1) for forward osmosis applications", in preparation, 2019

8 Conclusions and recommendations

This thesis aimed to develop novel nanocomposite membranes for osmotically driven membrane processes. The dual-blade casting technique for preparing highly porous membrane substrates and the VAIP technique for developing OSHF membranes were specially modified in this study. These novel approaches for membrane development significantly contributed to successfully preparing promising FO and PRO membranes. Furthermore, some hydrophilic nanomaterials were properly selected and subsequently applied to developing nanocomposite FO and PRO membranes.

8.1 Dual-blade casting technique for developing FO and PRO membranes

In this study, TFC FO and PRO membranes with dual-layered membrane substrates were fabricated by the double-blade casting technique using different polymer concentration for top and bottom layers.

For dual-layered FO membranes, the bottom substrate layer with low polymer concentration obtained the highly porous finger-like structure and opened bottom surfaces, which significantly helped reduce the ICP effect, and the top substrate layer with high polymer concentration produced a dense skin surface, which is desirable for subsequent PA layer formation. The overall dual-layered FO membrane substrate presented much higher porosity, purewater permeability compared to the single-layered one. To further improve FO performance, hydrophilic GO nanosheets at 0.25 wt% were incorporated into both layers, so that hydrophilicity and purewater permeability of GO-embedded substrates were further improved. As a result, the dual-layered GO membrane exhibited the highest water flux at 33.8 L m^{-2} h^{-1} and lowest SRSF at 0.19 g L^{-1} in a series of membrane samples including particle-

free single- and dual-layered membranes due to its lowest *S* value at 130 μm and strong hydrophilic nature.

For PRO membranes, dual-layered PES membrane substrates were prepared via the dual-blade casting technique in a way similar to those for FO membranes. However, to improve mechanical stability, the polymer concentrations for dual-layered PRO membranes were increased further than those for FO membranes, and the PET woven fabric was used as a backing support. Moreover, the approach further involved incorporating GO for top layer and HNTs for bottom layer in dual-layered membrane substrates, with a thin PA active layer on the GO composite layer. Overall, the optimum dual-layered GO / HNT nanocomposite membranes exhibited higher PD, lower SRSF and higher mechanical strength than single- and dual-layered PRO membranes made of a pure PES polymer, and commercial PRO membranes. The HNTs on the bottom layer played to enhance the resistance to membrane fouling due to the HNT's behaviors in the polymer matrix such as closing bottom surface, enhancing negative charges and performing as a nano blade when subjected to lab-scale fouling tests with sodium alginate and colloidal silica and biological tests with *E.Coli*.

The overall results of this study therefore provide promising approaches and effective guidelines using the dual-blade casting technique and hydrophilic nanofillers (GO and HNTs) for developing novel dual-layered nanocomposite FO and PRO membranes.

8.2 Outer-selective hollow fiber (OSHF) TFC FO membrane and its applications

Novel OSHF TFC FO membranes with high performance and fouling resistance were developed in this study. This study presented a practical guideline on how to fabricate the optimum OSHF TFC membranes for the first time. It started with designing outer surface morphology of HF membrane substrates as a function of air gap distance which was subsequently followed by a newly modified VAIP technique. Deploying this innovative approach, defect-free PA active layer was deposited on the outer surface of HF substrate for OSHF TFC membranes. Experimental results showed that optimum OSHF FO membranes were fabricated using the air-gap at 6 cm exhibited outstanding FO performances (water flux – 30.2 $Lm^{-2}h^{-1}$ and SRSF – 0.13 g L^{-1}) under 1M NaCl as DS and DI water as FS. Furthermore, the optimum membrane demonstrated higher fouling resistance and cleaning efficiency using the silica-alginate spiked solution due to membrane's physico-chemical characteristics. Moreover, there was a strong possibility to scale-up the large-scale membrane modules (22.8 cm^2) with similar FO performances with a small-scale one (6.5 cm^2). The membrane orientation, outstanding FO performances and their positive scalability prove that the novel OSHF TFC membrane can be the most suitable candidate for new emerging FO processes such as aerobic / anaerobic submerged osmotic membrane bioreactor (OMBR) or fertilizer-drawn OMBR hybrid processes for wastewater reuse.

Based on this fundamental study, we initiated studying the aerobic OMBR system for treating municipal wastewater using the large-scale OSHF TFC membrane modules. Prepared membrane modules exhibited excellent intrinsic transport properties which is similar with those of the small-scale membrane modules.

8.3 OSHF TFN FO membranes with hydrophilic nanomaterials

In this study we successfully developed novel OSHF TFN membranes using size-controlled GO (SGO) nanosheets and SNW-1 nanoparticles for FO applications. The novel hypothesis and related mechanisms for developing OSHF TFN membranes were demonstrated based on experimental results and analysis. Under the VAIP process, most nanofillers mixed with MPD solutions were properly accumulated and horizontally stacked on the outer surface of the HF membrane substrate. At this stage, the nanofillers were attached on the surface by the vacuum pressure from outside to inside, so that the particle loss in the VAIP was minimized due to attachment of nanofillers by the vacuum pressure from outside to inside compared to that in general IP. Thus, nanofillers could be efficiently used to prepare OSHF TFN membranes with an extremely low loading of nanofillers in the VAIP.

Using SGO nanosheets, defect-free PA composite layer was successfully deposited on the outer surface of the HF substrate. As expected in our hypothesis, SGO nanosheets were ideally incorporated into the thin PA layer, and the GO embedded TFN membranes exhibited improving permeability without trade-off of ion selectivity due to enhanced free-volume and hydrophilicity of the PA composite layer. The optimum loading of SGO nanosheets for OSHF TFN membranes was 0.0005 wt%, and the best TFN GO membranes resulted in the highest water flux at 38.9 $Lm^{-2}h^{-1}$ and SRSF at 0.13 g L^{-1} under pairing of 1M NaCl and DI water. In addition, the TFN GO membranes presented strong fouling resistance and high cleaning efficiency using the artificial wastewater due to the loose accumulation of foulants on the surface by the GO effects. Therefore, a frequent hydraulic flushing was considered for effective membrane cleaning for attached foulants on the surface with an outstanding flux recovery at around 98%. Furthermore, anti-biological activity on the PA composite layer may be expected due to GO's anti-biological nature. Compared to the TFN membrane embedded with bulk GO nanosheets, the SGO composite TFN membrane exhibited better water permeability while

maintaining its selectivity due to a shorter pathway for water transport inside PA layer from its small lateral size.

As another nanomaterials, porous SNW-1 nanoparticles were successfully applied to the development of high performance OSHF TFN membranes. Based on the hypothesis and expected mechanisms mentioned above, SNW-1 nanoparticles were properly incorporated into the PA layer with no deterioration of ion rejection under VAIP process. Especially, the secondary amine groups in SNW-1 might chemically reacted with the acyl chloride groups in the TMC solution via the covalent bonding. The expected reaction might strongly support to retain the integrity of the PA composite layer with SNW-1. In this study, the SNW-1 loading was manipulated and optimized in the extremely low range (0.0005 to 0.0015 wt%), as such S10 samples (SNW-1 loading at 0.001 wt%) exhibited the best FO performance with the highest water flux at 31.5 $Lm^{-2}h^{-1}$ and reasonable SRSF at 0.18 g L^{-1} in series of TFN membranes. The enhanced FO performances were attributed to the unique characteristics of SNW-1 like framework-based porous structure and amine-based hydrophilic property and good compatibility with PA composite layer. In addition, the best TFN membrane showed stable FO performances in the long-term operation for 72 h. This means that the SNW-1 incorporated OSHF TFN membranes demonstrated their strong durability for subsequent commercial applications.

Therefore, these findings proved that the novel OSHF TFN membranes embedded with SGO nanosheets or SNW-1 nanopraticles can be suitable candidates with superior FO performances and fouling resistance among existing TFC or TFN FO membranes for water and wastewater treatment. Also, we strongly believe that the proposed OSHF TFN membranes can provide bright insights for optimizing FO membrane processes in the near future.

8.4 Recommendations

All studies have investigated novel strategies how to develop outstanding FO or PRO membranes with high water flux, high ion selectivity and strong fouling resistance. New fabrication approaches were applied and combined to develop outstanding FO and PRO membranes such as dual-blade casting, VAIP for OSHF TFC membranes, incorporation of nanomaterials (GO, HNTs and SNW-1) into either a polymer matrix or thin PA layer. Although most technical approaches in the thesis produced interesting outputs for academic advance of FO and PRO membranes, I would like to conclude what approaches I recommend for commercial applications in future.

TFC membranes in academia or industry area consist of either flat-sheet or hollow fiber (HF) shapes, but HF membranes offer several advantages over the flat sheet membranes such as high packing density per module, self-supporting structure, and ease of both modulation and scaling-up compared to those of flat-sheet membranes. Based on my technical discussions, I am able to recommend that the OSHF TFN GO membranes presented in Chapter 6 is the most superior FO membranes in this thesis in the view of membrane performance, fouling potential, scalability and processability. Thus, I expect that if the large-scaled OSHF TFN GO membrane modules (tubular or submerged modules) are successfully developed, developed modules will be highly attractive for the application into the various membrane processes for osmotically driven water treatment such as aerobic / anaerobic osmotic membrane bioreactor (OMBR), fertilizer-drawn OMBR (FD-OMBR) or high-turbid water treatment. As another suggestion, I hope to highlight the strong potential of the dual-blade casting technique for membrane development. The approach is able to separately design top and bottom layer for the purpose. Thus, top surface and internal structures of OSHF membrane substrates can be customized, and further developed dual-layered ISHF or OSHF membranes using various nanofillers using a

triple-orifice spinneret may be developed. Therefore, I strongly believe that my recommendations for membrane development can offer significant impacts for advance of osmotically driven processes.

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