Liquid and Gas Permeation Studies on the Structure and Properties of Polyamide Thin-Film Composite Membranes

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Abstract

This research was undertaken to improve the understanding of structure-property-performance relationships in crosslinked polyamide (PA) thin-film composite (TFC) membranes as characterized by liquid and gas permeation studies. The ultrathin PA selective layer formed by interfacial polymerization between meta-phenylene diamine and trimesoyl chloride was confirmed to contain dense polymer matrix regions and defective regions in both dry and hydrated states.

The first part of this research studied the effect of non-selective convection through defective regions on water flux and solute flux in pressure-assisted forward osmosis (PAFO). Through systematic comparison with cellulose triacetate (CTA) and PEBAX-coated PA-TFC membranes, the existence of defects in pristine, hydrated PA-TFC membranes was verified, and their effects were quantified by experimental and modeling methods. In the membrane orientation of selective layer facing the draw solution, water flux increases of up to 10-fold were observed to result from application of low hydraulic pressure (1.25 bar). Convective water flux through the defects was low (< 1% of total water flux for PA-TFC membranes) and of little consequence in practical FO or reverse osmosis (RO) applications. However, it effectively mitigated the concentration polarization in PAFO and therefore greatly increased the diffusive flux through the dense regions.

The second part of this research characterized the structures of the PA material and the PA selective layer by gas adsorption and gas permeation measurements. Gas adsorption isotherms (N\textsubscript{2} at 77K, CO\textsubscript{2} at 273K) confirmed the microporous nature of PA in
comparison with dense CTA and polysulfone materials. Gas permeation through the commercial PA-TFC membranes tested occurred primarily in the defective regions, resulting in Knudsen gas selectivity for various gas pairs. Applying a Nafion coating layer effectively plugged the defects and allowed gas permeation through the dense PA regions, which significantly decreased gas permeance and increased gas selectivity. Specifically, high He and H$_2$ selectivity against CO$_2$ suggests the potential applications of this membrane in He recovery and CO$_2$ capture in pre-combustion.

Finally, the dense PA matrix was modified with two types of novel nanofiller to improve desalination performance in RO. A series of dense, nano-sized (1-3 nm) polyhedral oligomeric silsesquioxanes (POSS) with different functional groups were systematically incorporated into the PA matrix by physical blending or chemical fixation. The free volume of the PA matrix increased with addition of POSS, leading to water flux increases of up to 67 %, while maintaining high NaCl rejections. The effects of adding microporous, hydrophobic zeolitic imidazolate framework-8 (ZIF-8) nanoparticles into PA are presented in the last chapter. A 162 % water flux increase was achieved without decreasing NaCl rejection. This interesting result can be attributed to a less crosslinked PA structure and to the intrinsic desalination properties of ZIF-8.
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1. Introduction

1.1. Synthetic membrane technologies

World energy consumption reached 524 quadrillion British thermal units (Btu) in 2010, which is expected to increase to 820 quadrillion Btu in 2040 [1]. Out of the globally delivered energy in 2010, the industrial sector consumed 52.4 % [1]. A significant fraction of energy in industry was used in separation processes, which drives the demand to improve process energy efficiency and develop alternative technologies [2]. Emerging synthetic membrane-based separation techniques can save energy compared to conventional separation techniques such as distillation, crystallization, adsorption, etc., because they avoid thermodynamically imposed efficiency limitations on heat utilization in thermal-based separation techniques [2]. Moreover, membrane units are advantageous in their modular system design, scale-up, ease of operation, and low maintenance.

A synthetic membrane is a layer of organic or inorganic material, which serves as a selective barrier between two phases and is impermeable or semi-permeable to specific molecules when exposed to the action of a driving force. As shown in Figure 1.1, when a multi-component feed contacts the membrane, component B preferably permeates through it over component A, resulting in enrichment of B in the permeate and enrichment of A in the retentate.
Synthetic membranes are commonly categorized as macroporous (> 50 nm), mesoporous (2-50 nm) and microporous (dense, < 2 nm) based on their pore diameter. These characteristics directly determine the membrane processes and the applications, which range from large-scale civil and industrial projects (e.g., potable water production, wastewater treatment and gas separation) to domestic products (e.g., tap-water filter and hemodialysis filters). Global synthetic membrane market were 16.5 billion USD in 2012, and 9.4 % annual growth is expected through 2019, reaching 29.3 billion USD [3].

1.2. **Polyamide thin-film composite membranes**

Over one third of the world’s population lives in water-stressed areas and this figure is predicted to increase to two thirds by 2025 because of population growth, industrialization, pollution, and climate change [4]. Seawater accounts for more than 97 % of global water resources, and potentially offers an unlimited, steady source of potable water through desalination. Traditional multi-stage flash thermal distillation (MSF) desalination technology requires high energy input. After 70 years of research and development, the alternative, more energy-efficient, membrane-based RO technology has already surpassed MSF in global desalination capacity: 44 % RO vs. 40 % MSF [5]. Most of the MSF plants are located in the Middle East regions with abundant and relatively
inexpensive energy sources [5]. Currently, RO covers about 80 % of newly contracted desalination capacity [6].

The first reported RO membrane by Reid and Breton in 1959 was a hand-cast thin symmetrical cellulose acetate (CA) that demonstrated 98 % NaCl rejection; however, the permeate flux was less than 0.01 L/m²·h [7]. Loeb and Sourirajan [8, 9] developed a new phase inversion method for preparation of integrally-skinned asymmetric CA membranes that reduced the selective layer thickness to 0.1-0.2 µm. This led to at least a 10-fold increase in water flux, making the RO process economically practical for the first time. The development of polyamide (PA) thin-film composite (TFC) membranes was another major milestone in RO history [10]. Cadotte patented the first PA-TFC membrane prepared by interfacial polymerization (IP) [11]. It had exceptional desalination performance compared to other RO membranes available at that time. An ultra-thin PA selective layer (~ 100-200 nm) was synthesized in situ on top of a mesoporous support layer (~ 40 µm, normally polysulfone), backed by a structural support layer (~ 120 µm, normally nonwoven polyester), as shown in Figure 1.2. This multilayer membrane configuration minimizes resistance to water transport while providing the strength to withstand the high hydraulic pressures (up to 60 bar) applied in the RO process. The typical PA layer is synthesized by contacting an aqueous solution of m-phenylene diamine (MPD) with an immiscible organic solution containing trimesoyl chloride (TMC). Polymerization occurs at the solution interface, as depicted in Figure 1.3.
Figure 1.2. Schematic of the cross-section of a generic thin-film-composite membrane.

Figure 1.3. Schematic of polyamide layer formation by interfacial polymerization between $m$-phenylene diamine and trimesoyl chloride.

Most RO membrane manufacturers now use similar IP chemistry and production methods for their membranes. Therefore, most commercial membranes have similar desalination performance. Table 1.1 lists examples of state-of-the-art commercial RO membranes from some of the top manufacturers. PA-TFC membranes account for $\sim 91\%$ of global RO membrane sales [12]. Asymmetric cellulose triacetate (CTA) hollow-fiber membranes hold a distant second spot. Although the Toyobo CTA hollow fiber module
has twice the permeate flow rate of PA-TFC spiral-wound modules, the membrane-area-normalized water flux of CTA is around one-tenth of that of PA-TFCs.

**Table 1.1.** Desalination properties of some state-of-the-art SWRO membrane modules.

<table>
<thead>
<tr>
<th>Membrane module brand name</th>
<th>Material &amp; module</th>
<th>Permeate flow rate (m³/d)</th>
<th>NaCl rejection (%)</th>
<th>Test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow Filmtec 8-in. SW30ULE-440i</td>
<td>PA-TFC spiral-wound</td>
<td>45.4</td>
<td>99.7</td>
<td>3.2 % NaCl, 55.2 bar, 8% recovery</td>
</tr>
<tr>
<td>Hydranautics 8-in. SWC6 MAX</td>
<td>PA-TFC spiral-wound</td>
<td>50</td>
<td>99.8</td>
<td>3.2 % NaCl, 55.2 bar, 10% recovery</td>
</tr>
<tr>
<td>Toray 8-in. TM820L-440</td>
<td>PA-TFC spiral-wound</td>
<td>43.5</td>
<td>99.75</td>
<td>3.2 % NaCl, 55.2 bar, 8% recovery</td>
</tr>
<tr>
<td>Toyobo 16-in. HL10255SI</td>
<td>Cellulose triacetate hollow-fiber</td>
<td>95</td>
<td>99.6</td>
<td>3.5 % NaCl, 53.9 bar, 30% recovery</td>
</tr>
</tbody>
</table>

PA-TFC membranes were primarily developed to desalinate water by RO; however, their intrinsically fast water transport and excellent rejection of monovalent and multivalent solutes make them promising in other emerging processes, e.g., forward osmosis (FO) and pressure retarded osmosis (PRO). Different from RO, where osmotic pressure of a solution is overcome by hydraulic pressure, FO and PRO use the osmotic pressure difference between two solutions to drive the spontaneous diffusion of solvent from a less concentrated solution to a more concentrated solution [13]. The applications of FO technology vary from potable water production to emergency desalination bags. PRO has been proposed to generate electricity by harnessing osmotic pressure differences to produce pressurized flow – essentially RO in reverse. Of the materials and membranes developed for these processes, PA-TFCs show superior water flux and solute rejection.
Commercial RO membranes have been adapted to FO applications by simply coating a hydrophilic layer onto the supports [15].

PA-TFC membranes are also potentially useful for gas separations. Louie et al. applied a polyether-polyamide block copolymer coating on top of six types of commercial RO PA-TFC membranes, which showed high selectivity for permanent gases (He, H₂) over CO₂ [16]. Lee et al. reported a facilitated transport behavior of humidified gases through piperazine-based PA-TFC commercial nanofiltration (NF) membranes for CO₂ capture [17].

Despite the commercial success of PA-TFCs for RO and their potential in other applications, the intrinsic properties of these PA materials and the selective PA layer have not been fully characterized. Chapter 2 provides a detailed review of experimental and modeling studies characterizing PA-TFC membranes. The PA selective layer is generally considered as dense and defect-free because of the excellent NaCl rejections in RO and the self-terminating reaction mechanism of the IP technique. However, the substructures of this layer are difficult to analyze through cross-section imaging techniques because the average thickness is typically less than 200 nm. Moreover, the ultrafast reactivity of the monomers and crosslinking nature of the materials make it difficult to study the film formation mechanism and intrinsic material properties. This impedes the development of next-generation high-flux RO membranes and the applications of PA-TFC membranes in other areas. Recent developments in advanced membrane imaging techniques have revealed that the PA selective layer is not homogenous, but consists of dense nodular structures at the bottom and relatively open structures reaching outward, as shown in Figure 1.4 [18]. Applications of PA-TFC membranes in gas separations [16] and PRO
[19] also produced experimental results that contradict the assumption that PA selective layers are dense and defect-free.

Figure 1.4. Cross-section transmission electron microscopy image of a PA-TFC RO membrane [18].

This study aims to deepen the understanding of the structure-property-performance relationships of the PA selective layer through novel characterization methods and modification techniques, and to improve their separation performance.

1.3. Research hypotheses and experimental plans

This research aims to answer three main questions regarding the characteristics of the selective layer of PA-TFCs:

i. Is the selective layer of a PA-TFC membrane heterogeneous?

ii. How does selective layer heterogeneity of PA-TFCs influence liquid and gas permeation properties?

iii. How can the selective layer of PA-TFCs or the process be modified to improve performance in liquid and gas permeation applications?
Following these three questions, the hypotheses below are made:

i. The selective layer of a PA-TFC membrane contains dense polymer matrix regions and defective regions in both dry and hydrated states, as shown in Figure 1.5.

![Figure 1.5. Proposed selective layer structure of a PA-TFC membrane.](image)

ii. In liquid permeation, defective regions allow hydraulic pressure-driven, non-selective convection. In pressure-assisted forward osmosis, the non-selective convection through defective regions can mitigate concentration polarization and increase diffusive water flux through the dense polymer matrix, as shown in Figure 1.6.
**Figure 1.6.** Proposed water flux through the dense polymer matrix regions and the defective regions of a PA-TFC membrane in (a) forward osmosis and (b) pressure-assisted forward osmosis (draw solution and feed solution represent solutions with relatively higher and lower concentrations, respectively. The arrows represent water flux directions. In forward osmosis, defects in hydrated state have no separation ability, resulting in no water flux through these regions. In pressure-assisted forward osmosis, hydraulic pressure is applied, and non-selective convection through defects can mitigate concentration polarization and increase the diffusive water flux through the dense polymer matrix).
iii. In gas permeation, gas permeates through defects in preference to dense regions. As shown in Figure 1.7a, gas permeation primarily occurs in defective regions in the pristine dry PA-TFC membrane, resulting in low gas selectivity. After plugging the defects with a thin coating layer, gas permeation occurs in both coated defective regions and dense polymer matrix regions (Figure 1.7b), which increases gas selectivity.

![Figure 1.7](image)

**Figure 1.7.** Proposed gas permeation routes in (a) pristine and (b) coated PA-TFC membrane (red layer represents a thin coating layer plugging the defects).

iv. Increasing the free volume of the dense PA matrix by physical blending or chemical fixation of nanofillers can increase RO performance. As shown in Figure 1.8, water permeates through both dense and defective regions in RO.
Non-selective convection through defective regions is detrimental in RO because the desired product is potable water with low salinity. In this study, the nanocomposite concept was employed to modify the dense PA matrix regions to improve RO performance.

![Proposed water flux through dense polymer matrix regions and defective regions of a PA-TFC membrane in reverse osmosis.](image)

**Figure 1.8.** Proposed water flux through dense polymer matrix regions and defective regions of a PA-TFC membrane in reverse osmosis.

### 1.4. Dissertation overview

Chapter 1 briefly introduces synthetic membrane technologies and applications of PA-TFC membranes. Chapter 2 is a literature review on interfacial polymerization, membrane transport theories, thin-film-nanocomposite membranes and polymers of intrinsic microporosity. Chapter 3 presents a novel process to utilize convection through defects to improve overall membrane performance, and a modified solution-diffusion with defects model describing membrane transport under process conditions. Chapter 4 presents gas adsorption and gas permeation studies on PA material and PA-TFC membranes. Chapter 5 and Chapter 6 present two new methods to increase the free
volume of the dense PA matrix using nanocomposite TFCs to improve RO desalination performance. Chapter 7 provides conclusions and recommendations for future work.
References


2. Literature Review

2.1. Interfacial polymerization

Interfacial polymerization (IP) refers to the polycondensation reaction of monomers at the interface of two solutions. This low temperature synthetic route was first developed in the 1940s to 1960s as an alternative to the high temperature melt-condensation procedure to produce condensation polymers, such as polyamides, polyurethanes, and polycarbonates [1]. A comprehensive review of the early history, applications and mechanisms of IP technology is given in Condensation polymers by interfacial and solution methods by Morgan [1]. Reactions employed in this technique typically require high reactivity between the monomers, e.g., acyl chloride with amine or phenol. Many reactions have kinetic rates estimated to be $10^2$-$10^6$ L/mol·s. Principles obtained from these early studies generally apply to the $m$-phenylene diamine (MPD) and trimesoyl chloride (TMC) system to synthesize an aromatic PA selective layer in RO thin-film composite (TFC) membranes. So far this is the most important commercial application of IP technology [2]. This section discusses the principles of IP reactions and also highlights IP technology developments relevant to desalination.

2.1.1. Mechanism of polymer formation

In the IP process, the polymer or film generally forms where the monomers first contact each other. Whether this happens at the interface, the aqueous phase or the organic phase depends on the solubility differences of monomers in the solvents. PA is generally believed to form in the organic phase because the diamine monomer has a high partition
tendency into the organic phase, whereas the acyl chloride has very little solubility in water. The mass transfer of diamine into the organic phase is the rate-controlling step at all concentrations because of the fast reaction rate. Once diamine diffuses into the organic phase, excess acyl chloride acylates the diamine at both ends, forming acyl chloride-terminated oligomers. Subsequent diamine continues to couple with the oligomers until a layer of high molecular weight polymer is formed. Hydrogen chloride formed during the condensation reaction is extracted into the aqueous phase. The heat released during the reaction is absorbed by the solvents, possibly causing local movement to affect film morphology.

Early modeling studies were based on the aliphatic PA Nylon-6, 10 [3-5] where the thickness of the linear polymer layer could reach ~250 µm. This enabled characterization of molecular weights, polydispersity and the reaction rate at different monomer concentrations and with different solvent systems. Enkelman et al. [3] assumed that the rate-limiting step of Nylon-6, 10 film formation was diamine diffusion, and that reaction termination was from amidation and hydrolysis of acyl chloride. A correlation between film thicknesses and diamine concentrations was obtained. An uneven molecular weight distribution and uneven functional group distribution within the film were predicted. Karode et al. [4, 5] assumed that the reaction for Nylon-6, 10 film formation mainly occurred in a ~10 nm thick reaction zone on the organic side of the interface and proposed a spinodal decomposition and nucleation mechanism for PA precipitation.

It is important to note that formation of aromatic crosslinked PA in desalination membranes is distinctly different from that of Nylon-6, 10 in its fast film formation, ultra-low film thickness and difficulty in characterizing molecular weights.
Sundet [6] proposed two-step film formation kinetics for the MPD/TMC system: fast condensation into highly branched PA particles, followed by aggregation of particles by amidation to a low density matrix. Isolated PA layer, obtained by dissolving the polysulfone support, was characterized with small-angle x-ray scattering and electron microscopy. A tightly packed 5-10 nm PA dense nodule structure on one surface was observed. However, the imaging quality was relatively poor and sample preparation steps were not described in detail. Based on images in the paper, the dense nodules observed in electron microscopy could be platinum and carbon coating materials.

Freger et al. [7] studied the MPD/TMC system for RO membrane PA layer formation, and predicted fast formation of a dense core film with finite thickness followed by a slow continuous polymerization on either side of the core, which results in higher concentration of amine end groups on the aqueous side and higher concentrations of hydrolyzed acyl chlorides on the organic side. The drawback of this model is that a theoretical reaction zone of least 5 µm must be assumed to match the actual observed thickness of the PA layer. Further studies by Freger [8] and Song et al. [9] generally describe the MPD/TMC IP reaction as a combination of different stages: i) a fast initial stage to form the dense incipient layer on the organic side of the interface; ii) a slow growth stage where the film continues to densify by crosslinking, and the diffusion of monomers – especially the amine – to the reaction sites is greatly hindered by the newly-formed film; iii) reaction termination caused by increased PA thickness and density.

The studies above deepen understanding of the polymer formation mechanism in the IP process, and provide guidelines for optimizing the production and quality of bulk
polymers (e.g., Nylon) and PA selective layer, which are discussed in the following section.

2.1.2. Experimental studies on PA selective layer formation by IP

Experimental studies on the properties of the PA selective layer in desalination membranes can be generally categorized into: i) new polymer chemical structures based on novel monomers, ii) effects of reaction conditions, e.g., additives, solvents and co-solvents, iii) effects of post treatment, and iv) membrane characterization.

Since the MPD/TMC aromatic PA membrane [10] was first commercialized by Filmtec under the trade name FT-30, many PA-based membranes with slightly modified structures were synthesized with different monomers and commercialized by different companies [11-14]. A detailed review of this subject was given by Petersen [2]. New PA structures continued to be reported with novel, custom-synthesized monomers. However, current commercial RO membranes are primarily based on the MPD/TMC chemistry and commercial NF membranes are based on piperazine/TMC/isophthaloyl chloride.

2.1.2.1. Effects of reaction conditions and post-treatment

The properties of the PA selective layer are greatly influenced by the reaction conditions and post-treatment [15-17]. By tailoring these parameters a wide range of membranes has been developed for different desalination applications using similar MPD/TMC chemistry. The effects of certain membrane formation variables on desalination performance are qualitatively predictable. For example, lower monomer concentrations and shorter reaction time are expected to result in thinner selective layers and, therefore, higher water flux at the expense of lower solute rejection [17]. However, the effects of
other variables are more difficult to predict. A selection of interesting findings and novel membrane preparation procedures are listed as follows.

Ghosh et al. [16] prepared and characterized PA membranes using four different organic solvents: hexane, heptane, cyclohexane and Isopar™. By correlating desalination performance with organic solvent properties, e.g., viscosity, surface tension, etc., their study suggested that a solvent with higher MPD diffusivity and lower MPD solubility formed a thinner and more heavily crosslinked structure to offer higher water flux with good solute rejection. High MPD diffusivity in the organic solvent contributes to high water permeability because fast protonation of MPD can form a thin film structure. Both MPD diffusivity and solubility influence crosslinking extent through competition between protonation of MPD and hydrolysis of TMC.

Kong et al. [18, 19] investigated the effects of a co-solvent, acetone, in the organic phase (hexane) on the properties of PA membranes. Membrane water flux increased almost 4-fold with slightly decreased NaCl rejection when 2% acetone was added to the hexane. The membrane surface became smoother than the pristine PA membrane, and slightly enlarged hollow voids within the selective layer were observed in cross-section transmission electron microscopy (TEM) images. These membrane property changes were attributed to the increased miscibility between the two phases caused by acetone addition, resulting in a larger IP reaction zone. In addition, the MPD diffusion rate into the hexane phase almost doubled when 2% acetone was added, producing a thinner dense layer [19].
Kwak et al. [20] studied the effects of adding dimethyl sulfoxide (DMSO) in the aqueous phase on the morphology and molecular structures of PA membranes. Surface roughness and surface area increased with increasing DMSO concentration. The increased miscibility between the phases was believed to induce a “fluctuating interface”; water permeability increased because of increased membrane surface area. Kim et al. [21] characterized these PA materials with positron annihilation lifetime spectroscopy (PALS) and concluded that the aromatic crosslinked PA formed by MPD/TMC chemistry was comprised of network pores with diameters of 4.2 - 4.8 Å and aggregate pores with diameters of 7.0 - 9.0 Å, as shown in Figure 2.1. The addition of DMSO increased the size and number of network pores, and the size of aggregate pores, whereas the number of aggregate pores decreased.
Figure 2.1. Schematic of proposed network pores and aggregate pores in aromatic polyamide synthesized by reaction of \(m\)-phenylene diamine and trimesoyl chloride [21].

2.1.2.2. Polyamide thin-film characterization

Studies in PA thin-film membrane characterization can be generally divided into two categories. The first approach is to evaluate physical properties of the selective layer, e.g., hydrophilicity [22], surface charge [23, 24], surface morphology [25, 26], chemical composition [27, 28] etc., and to correlate these with separation performance, e.g., water flux and solute rejection, fouling propensity, etc. The second direction is to apply novel characterization methods to study the substructures of the selective layer and their formation mechanism.

The aromatic PA membranes prepared by MPD/TMC typically exhibit irregular ridge-and-valley surface morphology, as shown in Figure 2.2. How these features are formed and how they contribute to water flux is still not fully understood. One explanation for
this morphology is that heat released from the exothermic condensation reaction causes local fluctuations in the interface, and the polymer is formed fast enough to precipitate along the fluctuated interface. This indicates that the outer surface is the effective desalination area, and water flux would increase with increasing surface roughness. Kwak et al. [29] observed a positive correlation between these two factors among four aromatic PA membranes. Increasing the surface roughness has been used as an empirical guideline to enhance the desalination performance of membranes in industry [30] and academic research [18]. However, in the study of Kwak et al. [29], the chemical structure differences between PA materials prepared with different monomers were not taken into account when correlating water flux and surface roughness. In addition, inconsistent correlations between these two parameters were reported with commercial PA-TFC RO membranes [31]. To fully understand the factors governing desalination performance, the substructure of the PA selective layer is of particular interest.

Figure 2.2. Surface scanning electron microscopy image of a commercial ESPA-3 RO membrane.
Chai et al. [32] used light reflectometry and pendent-drop tensiometry to study the real-time film growth by MPD and TMC at the interface of two solutions with no polymeric membrane support and managed to capture images of film growing towards the organic phase and film formation within relatively short time (< 1 s). SEM images of the surfaces towards the aqueous phase showed the existence of voids. However, the surfaces towards the organic phase were slightly smoother than the typical surfaces of PA membranes formed on a support, suggesting that the porous support has an influence on the selective layer surface morphology.

Ghosh et al. [33] investigated the influences of support layer hydrophilicity and pore size on the resulting membrane morphology and desalination performance, and proposed a “volcano-like” amine “eruption” mechanism for the formation of a rough surface. The concave interface of water in hydrophilic pores and the repelling effect of hydrophilic pores towards the organic phase generally reduced the amine “eruption”, forming a relatively smoother surface. This also resulted in more PA growth inside the pore instead of outward growth, which increased the effective selective layer thickness, causing reduced water flux. However, no direct evidence was provided to support the tendency of PA growth inside hydrophilic pores.

Freger [34] characterized the PA selective layer using TEM techniques and concluded that this thin layer was of nanoscale heterogeneity: a negatively charged carboxyl-rich sublayer was formed on top of a positively charged carboxyl-free sublayer. This claim generally agrees with the selective layer formation mechanisms proposed by Freger [8] and Song et al. [9]. However, in the TEM images, the carboxyl-free sublayer was about
200-300 nm thick and distinctively different in shape and appearance compared to the carboxyl-rich sublayer.

Pacheco et al. [35] isolated the PA selective layer from the polysulfone support using chloroform and obtained cross-section and project-area TEM images of this layer. The isolated PA layer towards the support side did not show the carboxyl-free region reported by Freger [34]; the carboxyl-free region observed by Freger may have been an artifact of the sample preparation process. Instead, this surface was a dense base of nodular PA, while the ridge-and-valley structure on the top surface consisted of a relatively open and loose PA extending outward from the base.

Yuan et al. [36] studied selective layer formation in real time using an optical contact angle measuring device with an aliphatic di-hydroxyl methyl diethanolamine in the aqueous phase and TMC in the organic phase. The relatively slow layer formation (~ 5-30 min) and increased layer thickness (~ 10-60 µm) compensated for the limited frame rate and magnification of the digital camera. A rough surface with layers of hollow bubbles was obtained and a layer-by-layer membrane formation mechanism was proposed to explain the rough surface. This study confirmed the interfacial film growth towards the organic phase and the heterogeneity of the layer formed. However, the differences between this system and that of MPD/TMC should be noted when applying this mechanism to explain the ridge-and-valley structures in MPD/TMC PA membranes.

Lee et al. [37] characterized the water vapor sorption and free volume cavity size of isolated PA materials from commercial RO membranes as function of water activity. One
gram of PA from Dow Filmtec SW30 membrane was estimated to have $2 \times 10^{21}$ sorption sites for water.

The thin-film characterization studies listed above help to understand the PA layer formation mechanism and the substructures within the layer, which can shed light on water and solute separation mechanisms and provide guidelines to tailor the intrinsic PA structure to improve desalination performance.

2.1.3. Polyamide thin-films in osmosis processes and gas separations

Osmosis is solvent diffusion across a selective membrane from a less concentrated solution to a more concentrated solution driven by osmotic pressure difference between the solutions. Early researchers proposed several prototype applications to utilize this driving force. Neff [38] patented the use of concentrated ammonium bicarbonate solution to desalinate seawater and then recycle the draw solution by heat to produce potable water. Kravath et al. [39] proposed to use a glucose solution to desalinate seawater for emergency water supply. Petrotos et al. [40] proposed sodium chloride brine to concentrate tomato juice and Kessler et al. [41] proposed fertilizer salts for irrigation of soil. Loeb [42] investigated energy production using the osmotic pressure difference between river water and a saline source, e.g. a salty lake, in a process termed pressure-retarded osmosis (PRO). However, these proposed processes were hindered by low water fluxes with commercial RO membranes. The thick, sponge-like support layer designed to withstand high hydraulic pressure in RO results in severe concentration polarization in other osmotic processes, significantly reducing the osmotic pressure difference across the selective layer [43]. Many efforts were devoted to develop thinner and more porous
supports to reduce internal concentration polarization while retaining similar PA selective layer chemistry and formation procedures [44-46], because the PA layer is generally considered sufficient to retain the solutes while allowing water to permeate. However, the substructure of the selective layer can potentially influence concentration polarization in the osmotic processes under hydraulic pressure.

Membranes can also potentially reduce energy consumption and simplify operations in gas separation applications [47]. The selective layer material requires high selectivity and moderate-to-high gas permeability to achieve efficient separation. The excellent thermal and mechanical stability and good chemical resistance of PA materials make them attractive to prepare high-performance gas separation membranes. However, linear PA materials generally exhibit low gas permeability because of high cohesive energy density, strong propensity towards efficient polymer chain packing, and semi-crystalline morphology [48]. By introducing bulky substituents to disrupt chain packing, gas permeability of the linear aromatic polyisophthalamide can be increased, with corresponding decreases in selectivity [49, 50].

Petersen et al. [51] prepared PA-TFC gas separation membranes based on IP between a terephthaloyl chloride (TPC) with long aliphatic side chains, and 1,2-ethylene diamine, MPD and Jeffamine T403, respectively. The aliphatic side chains were found essential to form a pressure-resistant layer on top of the porous support. Fully aromatic PA formed with MPD showed the highest gas permeance and medium selectivity; crosslinked aromatic-aliphatic PA formed with Jeffamine showed CO₂/N₂ and CO₂/CH₄ selectivity of 24 and 11, respectively, with high CO₂ permeance, demonstrating the potential of using IP to prepare cross-linked gas separation membranes. A silicone coating was applied on
top of a continuously formed PA layer to fill small defects. An MPD/TMC PA film was also prepared and showed Knudsen selectivity for O₂/N₂.

Zhao et al. [52] synthesized a fixed carrier PA membrane by IP between trimethylene tetramine and TMC for CO₂/CH₄ separation, and reported a CO₂/CH₄ selectivity of 94 at 1.1 bar feed pressure with 10/90 (volume) CO₂/CH₄ mixture. Increasing feed pressure to 5.1 bar decreased selectivity to 41.

Sridhar et al. [53] prepared a PA-TFC membrane by IP between MPD and isophthaloyl chloride (IPC), and reported a permeance of 15 GPU for CO₂ and 52 GPU for H₂S with selectivity of 14 and 49 for CO₂/CH₄ and H₂S/CH₄, respectively.

Li et al. [54] investigated CO₂ separations using PA-TFC membranes formed by IP between TMC and two aliphatic diamines containing different ethylene oxide (EO) groups. A crosslinked polydimethylsiloxane (PDMS) was first coated on a porous polysulfone support; then the organic solution, and finally the aqueous solution were coated to form the IP film. Short EO chains improved the mechanical properties of PA films and simplified optimization of reaction conditions to improve CO₂ permeance and CO₂/gas selectivity in syngas and natural gas purification and flue gas CO₂ capture. Wang et al. [55] prepared PA-TFC membranes using a similar technique but with additional sodium 3,5-diaminobenzoate in the aqueous phase. The optimized membranes showed 5831 GPU of CO₂ permeance with a CO₂/N₂ selectivity of 86 when tested with CO₂/N₂ mixture feed (15/85 by volume) and 1.1 bar feed pressure. Furthermore, excellent oxidation and acid resistance was demonstrated. Economic evaluation of this membrane type for CO₂ capture in flue gas appeared to be competitive against a typical chemical
absorption process. Facilitated transport of CO$_2$ through a commercial nanofiltration membrane (Dow Filmtec NF3838-30 FF) was reported by Lee et al. [56] with humidified feed.

Louie et al. [57] tested commercial aromatic crosslinked PA-TFC RO membranes in gas separations. All dry PA membranes were confirmed to have defects as indicated by Knudsen diffusion of gases. After the membranes were coated with a polyether-polyamide block copolymer PEBAX® 1657, the selectivity increased more than 2-fold, generally exceeding the selectivity of PEBAX® itself. In addition, the coated membranes became selective for H$_2$ and He over CO$_2$, whereas PEBAX® was CO$_2$-selective. This indicates the intrinsic separation properties of the dense PA matrix.

Albo et al. [58] verified the Knudsen gas selectivity of commercial PA-TFC RO membranes, and observed a 6-fold increase in He permeance and 6-fold increase in He/N$_2$ selectivity at 150 °C. The increase in permeance and selectivity was attributed to an activated diffusion mechanism through the dense PA matrix. PA membranes were proposed as alternative material for high-temperature separation processes.

### 2.2. Membrane transport theories

Many models have been proposed to describe water and solute transport through PA-TFC membranes. Generally these models can be categorized into: i) irreversible thermodynamics (IT), ii) solution-diffusion (SD), and iii) pore-flow (PF). IT models [59, 60] treat the membrane as a “black box” in which relatively slow processes proceed near equilibrium. These models do not provide insights into the mechanisms of transport or the structures of membranes.
In SD models [61], the membrane is assumed to be dense, and separation of solute from water is achieved by differences in solubility and diffusivity of solute and water within the membrane. Water and solute move through the dense membrane by diffusion between interstitial spaces of polymer chains or polymer nodules. In PF models [62-64], the membrane is assumed porous, and separation is achieved by selective pores. Water and solute move through the pores by diffusion and convection. Wijmans et al. [61] comprehensively compared the fundamental differences between the SD models and the PF models. For example, the chemical potential gradient across the membrane is expressed only as a concentration gradient in the SD models, while in the PF models it is as a pressure gradient only. The debate about whether PA-TFC RO membranes are dense or porous continues. However, SD models are more popular for describing and predicting RO membrane performance because of their simplicity and wide applicability [61]. This section briefly introduces the SD model and SD with defects model, which are described in detail in the following chapter. In addition, the concepts of concentration polarization, Knudsen diffusion and the series resistance model are included.

2.2.1. Solution-diffusion model

According to the SD model, transport of water or solute across a membrane generally include: i) absorption of a component from the feed into the membrane; ii) diffusion through the membrane; iii) desorption of the component from the membrane to the permeate. By balancing the chemical potential of the bulk solution and the membrane surfaces at the feed side and the permeate side and rearranging Fick’s law, expressions for water flux $J_w$ and solute flux $J_s$ in RO can be obtained as follows [61]:
\[ J_w = A(\Delta p - \Delta \pi) \]  
\[ J_s = B(C_{\text{feed,}s} - C_{\text{permeate,}s}) \]

where \( A \) is the water permeability coefficient, \( B \) is the solute permeability coefficient; \( \Delta p \) and \( \Delta \pi \) are the hydraulic pressure difference and osmotic pressure difference between the feed solution and the permeate solution, respectively; \( C_{\text{feed,}s} \) and \( C_{\text{permeate,}s} \) are solute concentrations at the selective layer surfaces on the feed solution side and the permeate solution side, respectively. \( A \) and \( B \) are defined as:

\[ A = D_w K_w c_w v_w / lRT \]  
\[ B = D_s K_s / l \]

where \( D \) is Fick’s law diffusion coefficient, \( K \) is the sorption coefficient, \( c \) is molarity, \( v \) is molar volume, \( l \) is membrane thickness, \( R \) is the ideal gas constant, and \( T \) is absolute temperature.

Solute rejection \( R \) is a practical term to characterize the ability of the membrane to separate solute from water. It is defined as:

\[ R = (1 - C_{\text{permeate}} / C_{\text{feed}}) \times 100 \% \]

where \( C_{\text{permeate}} \) and \( C_{\text{feed}} \) are the solute concentrations of the bulk permeate and feed solution, respectively.

### 2.2.2. Solution-diffusion with defects model

In the SD with defects model [12, 65], water and solute transport through the membrane is a parallel process of diffusion through the polymer and non-selective convection through open channels or pores.

\[ J_w = A(\Delta p - \Delta \pi) + L_d \Delta p \]
\[ J_s = B(C_{\text{feed,s}} - C_{\text{permeate,s}}) + L_d \Delta p C_{\text{feed,s}} \]  

(2.7)

where \( L_d \) is the convective flow permeability coefficient.

### 2.2.3. Concentration polarization

Concentration polarization is a common phenomenon in membrane-based separations. It can be generally divided into external concentration polarization (ECP) and internal concentration polarization (ICP). Concentration at the external surface of the membrane selective layer can be concentrated or diluted by convection.

Concentrative ECP is caused by convection that pulls solute from the bulk solution to the surface of the selective layer; water permeates through, leaving the solute behind [66]. Concentration at the membrane surface, \( C_m \), can be estimated by:

\[ \frac{C_m}{C_b} = \exp \left( \frac{J_w}{k} \right) \]  

(2.8)

where \( C_b \) is the bulk concentration and \( k \) is the solute mass transfer coefficient.

Dilutive ECP is identical to concentrative ECP except that here convection pulls the solute away from the selective layer. In this case \( C_m \) is estimated by:

\[ \frac{C_m}{C_b} = \exp \left( - \frac{J_w}{k} \right) \]  

(2.9)

Note that \( k \) is closely related to the flow conditions, e.g. whether it is laminar or turbulent, and the geometry of the flow channel. Through optimization of these parameters, ECP can be mitigated.
ICP refers to concentration polarization within the membrane porous support. ICP is generally not significant when water and solute transport is in a co-current mode, e.g., in RO; however, ICP can be significant when water and solute transport is in a counter-current mode [67], e.g., in FO where water diffuses from the less concentrated solution to the more concentrated solution, and solute diffuses in the opposite direction. ICP can be quantified as the solute resistance to diffusion within the porous support, given by:

$$K = \frac{\tau t}{D_s \varepsilon}$$  \hspace{2cm} (2.10)

where $\tau$, $t$ and $\varepsilon$ are the tortuosity, thickness and porosity of the porous support, and $D_s$ is the diffusion coefficient of solute in water.

### 2.2.4. Knudsen diffusion

Knudsen diffusion describes gas molecule transport within mesopores (~2-50 nm), in which the gas molecules collide more frequently with pore walls than with each other. It occurs when the mean free path of the gas molecule is larger than the pore diameter, $d_p$. The molar flow rate $N_p$ of a gas transported through a cylindrical pore via Knudsen diffusion [68] is,

$$N_p = \frac{\rho d_p^2 D_p}{3(2pRTM)^{0.5}l_p}$$  \hspace{2cm} (2.11)

where $M$ is the gas molar mass and $l_p$ is the pore length.

Therefore, the Knudsen selectivity of gases $\alpha_{ij}$ can be directly calculated from the molar masses of the gases, irrespective of membrane materials.
\[ a_{ij} = (M_j / M_i)^{0.5} \]  

(2.12)

2.2.5. Series resistance model

The series resistance model [69] is generally used to describe the gas permeation properties of composite membranes. Each portion of the composite membrane is described as a resistance to gas flow, similar to the effects of a series of resistors on electrical current. For a given PA-TFC membrane (permeance \( J_{\text{pristine}} \)), and a coating layer with given thickness \( l_{\text{coating}} \) and permeability \( P_{\text{coating}} \), the permeance of the composite membrane, \( J_{\text{coated membrane}} \), can be predicted by:

\[ J_{\text{coated membrane}} = \left( \frac{1}{J_{\text{pristine}}} + \frac{l_{\text{coating}}}{P_{\text{coating}}} \right)^{-1} \]  

(2.13)

2.3. Thin-film-nanocomposite membranes

Nanotechnology offers a new route to improve polymeric membrane performance. In gas permeation, nanoporous inorganic materials, e.g., zeolites, exhibit high permeability and high selectivity because of their interconnected mono-sized micropores. However, because of their crystalline and brittle structure, it is very difficult to prepare defect-free membranes from these materials. On the other hand, a simple way to utilize the properties of these nanoporous inorganic materials is to form a membrane by mixing them with polymers; these are termed as mixed-matrix membranes (MMMs) [70, 71]. Nano-sized, dense inorganic fillers, e.g., silica, can also be incorporated into polymeric materials to enhance gas permeation performance by disrupting the polymer chain packing [72, 73].

A similar concept has been applied in PA membranes for water desalination. Jeong et al. [74] prepared the first PA thin-film-nanocomposite (TFN) membranes by adding 50-150
nm zeolite 4A nanoparticles in the organic phase to be incorporated into the PA selective layer during interfacial polymerization. Under optimized conditions, TFN membranes yielded ~ 81% higher water flux than pristine PA membranes while maintaining high NaCl rejection. In addition, TFN membranes were reported to be more hydrophilic, smoother and more negatively charged than the pristine PA membranes. Proposed mechanisms for the increased water flux include: i) fast water transport through the zeolite pores; ii) increased membrane affinity to water; and iii) fast water transport through the voids between zeolite and PA.

Lind et al. [75] investigated the influence of zeolite 4A crystal size on the properties of PA-TFN membranes and concluded that smaller zeolites were beneficial for improving water permeance. Larger zeolites increased selective layer thickness, and a “template” effect of zeolite on PA film growth was proposed. Using x-ray photoelectron spectroscopy (XPS), reduced crosslinking of the PA surface layer was observed when zeolite was added.

Huang et al. [76] studied the effects of zeolite incorporation routes on TFN membranes, and concluded that adding zeolite from the organic phase was more favorable than from the aqueous phase. The aqueous route resulted in most zeolite particles located at the bottom region of the selective layer and barely influenced surface crosslinking extent; the organic phase resulted in more zeolites residing at the middle and top region of the selective layer, exposing them as water channels to generate higher water permeance. Contradicting the studies from Lind et al. [75], increased PA layer crosslinking was reported with the organic route and the proposed reason was increased reaction temperature caused by heat release from zeolite hydration.
Huang et al. [77] investigated the instability of zeolite 4A in TFN membranes when tested with acidic feed solution and feed containing multivalent cations, and proposed an alternative filler, silicalite-1 zeolite, which is stable under these feed conditions. In addition, a 233 % water permeance increase was achieved with silicalite-1, much higher than the 70 % water permeance increase with zeolite 4A. The proposed reasons are (i) increased hydrophilicity of membrane surface, (ii) relatively larger pores in silicalite-1 (5.6 Å against 4.2 Å in zeolite 4A), and (iii) weak H-bond interactions between water molecules and the silicalite-1 framework.

Other porous fillers, e.g., silica [78], Cu-BTC metal-organic framework [79], and ordered mesoporous carbon [80] were also incorporated into PA-TFN membranes, yielding higher water permeance. However, it should be noted that these fillers do not have intrinsic separation capacity for NaCl and H2O, e.g., the internal pore sizes of silica, Cu-BTC and ordered mesoporous carbon are 30 Å, 9 Å and 10-30 Å, respectively.

Another porous filler type, carbon nanotubes (CNT), demonstrated fast internal water transport and excellent desalination capacity [81, 82]. Water is not in direct contact with the hydrophobic CNT pore walls and, therefore, there is essentially no friction for water passing through [81, 82]. Ratto [83] first incorporated CNT with an outer diameter 8 Å into PA-TFN membranes, and reported a 233 % water permeance increase while maintaining high NaCl rejection. Following work focused on outer surface modifications of CNT to achieve better dispersions in membranes. Zhao et al. [84] grafted carboxylic acid groups to CNT outer surfaces with mixed acids and achieved high dispersion of CNT in the aqueous solution. Resulting TFN membranes showed a ~ 80 % water permeance increase with slightly decreased NaCl rejection. Higher chlorine resistance
and better antifouling properties against inorganic and protein foulants were also reported. Lee et al. [85] modified the CNT surfaces with a bio-inspired dopamine solution and incorporated the CNT from the aqueous phase. Higher water permeance increase was observed with modified CNT than with unmodified CNT. A water permeance increase was observed with increasing operating pressure, which is cited as the evidence of water molecule diffusion through the embedded CNT pores.

Dense fillers were also incorporated into the PA selective layer. Silver [86] and TiO₂ [87] nanoparticles improved the antifouling properties of TFN membranes. However, water permeance was barely influenced, presumably because these relatively large particles (~50-100 nm for silver and ~30 nm for TiO₂) had negligible effects on the polymer structures. With ~3 nm silica, water permeance increases of up to 134 % were achieved while maintaining NaCl rejection [88]. Small nanoparticles efficiently disrupt polymeric chain packing and increase free volume and, therefore, water sorption and diffusion. A polyhedral oligomeric silsesquioxane (POSS) ammonium salt similar in size to the silica above was also incorporated into the TFNs, and a 35 % water permeance increase was reported [89]. Moon et al. [90] prepared a TFN membrane using similar chemistry and procedures and, based on molecular simulation, reported increased free volume resulting from incursion of POSS into the PA matrix.

### 2.4. Polymers of intrinsic microporosity

Microporous materials are defined as solids containing interconnected pores less than 2 nm in size [91]. With the development of microporous materials, the micropores region is further divided into supermicropores (0.7-2 nm), ultramicropores (0.4-0.7 nm) and
submicropores (< 0.4 nm). Up to now, there are mainly two classes of inorganic materials used in industry as microporous materials: crystalline zeolites [92] with well-defined surface composition, and amorphous activated carbons [93] with poorly-defined surface chemistry.

Most traditional polymers do not form solids with classical microporosity because their conformation mobility allows the constituent macromolecules to fill space efficiently. In order to limit packing to introduce microporosity into the polymer matrix, methods such as crosslinking of rigid polymer backbones [94, 95] and introduction of bulky substituents [96-99] have been employed. Crosslinked network polymers are developed primarily to target applications in catalysis and adsorption. Non-crosslinked microporous materials and solution-processible polymers of intrinsic microporosity (PIMs) [100, 101] with rigid and contorted backbones can be formed into membranes with excellent gas separation properties [102, 103].

Zhao et al. [104] prepared a 2-D porous organic framework based on the nucleophilic substitution of cyanuric chloride, as shown in Figure 2.3. N2 adsorption reveals that the network polymer has a BET surface area of 183 m²/g and a narrow pore size distribution centered around 11.8 Å.

Considering the highly crosslinked and rigid network in the PA RO membrane separation layer (Figure 2.1), the aromatic PA could have intrinsic microporosity. Qian et al. [105] characterized the crosslinked PA prepared by TMC and piperazine with CO2 adsorption at 273 K, and reported a BET surface area of 105 m²/g.
Figure 2.3. Synthesis and structure of PAF-6 [104].
References


3. Solution-Diffusion with Defects Model for Pressure-Assisted Forward Osmosis

Abstract

An osmosis transport model is presented that combines the standard internal and external concentration polarization equations in the forward osmosis (FO) field with the selective layer transport equations first proposed by Sherwood in 1967. The Sherwood model describes water flux as the sum of a solute-selective, diffusive component driven by the sum of osmotic pressure and hydraulic pressure differences, and a nonselective, convective component driven by hydraulic pressure difference only. This solution-diffusion with defects (SDWD) model and the solution-diffusion (SD) model were compared against data collected using polyamide thin-film-composite (PA-TFC) and integrally-skinned asymmetric cellulose triacetate (CTA) membranes, evaluated in various configurations. When tested with pure water on the porous support side and 1.5 M (\(\pi = 72.7\) bar) sodium chloride solution on the selective layer side, applying 1.25 bar of hydraulic pressure to the porous support side increased water flux by an order of magnitude for PA-TFC membranes, but had negligible effect on CTA membrane flux. These large flux variations can be explained by the SDWD model, but not the SD model. To confirm the existence of defects, a PA-TFC membrane was coated with a uniform, highly water-permeable, nonselective polymer. After coating to block convection through defects, the influence of hydraulic pressure on water flux through this membrane
essentially disappeared. Water flux through these defects is low (< 1% of total water flux for PA-TFC membranes) and of little consequence in practical FO or reverse osmosis (RO) applications. But in pressure-assisted forward osmosis (PAFO) or pressure-retarded osmosis (PRO), convective transport through defects affects the solute concentration difference across the membrane selective layer, increasing or decreasing water flux through defect-free regions. The presence of defects may explain why membrane power density in PRO is lower than that predicted based on FO and RO tests.

3.1. Introduction

In general, two membrane types are used for industrial desalination: (i) polyamide thin-film composite (PA-TFC) and (ii) integrally-skinned asymmetric cellulose acetate or triacetate (CTA). Though fabricated of different materials by different methods, they share the standard asymmetric membrane morphology, with an ultrathin, solute-selective layer at one surface of a porous support. Both have been used in reverse osmosis (RO) for decades, desalinating water by forcing it through the selective layer under a hydraulic pressure greater than the saline water’s osmotic pressure. In recent years interest has grown in potentially using these membrane types for other osmotic processes, including pressure-retarded osmosis (PRO) for power generation and forward osmosis (FO) for desalination. In FO, differences in osmotic pressure provide the driving force for water flux; applied hydraulic pressure differences are generally assumed to be negligible. However, flux in FO may be influenced by superimposing a hydraulic pressure difference onto the osmotic pressure difference – pressure applied inadvertently, as a side-effect of
circulating water through membrane modules [1, 2], or deliberately, in a process termed pressure-assisted forward osmosis (PAFO) [3-5].

Given an asymmetric membrane, either side may be exposed to a hydraulic pressure \( p \) and/or osmotic pressure \( \pi \). Figure 3.1 shows the four possible permutations.

**Figure 3.1.** Schematic of four possible permutations with higher osmotic pressure \( \pi \) and/or higher hydraulic pressure \( p \) on either side of an asymmetric membrane (SL-FS means selective layer facing the feed side; SL-DS means selective layer facing the draw side).

i) Higher \( p \) and higher \( \pi \) on selective layer side. If \( p > \pi \), this is reverse osmosis; if \( p < \pi \), this is pressure-retarded osmosis.

ii) Higher \( p \) on selective layer side, higher \( \pi \) on porous support side. This is PAFO (SL-FS) as applied in previous work [3-5].

iii) Higher \( \pi \) on selective layer, higher \( p \) on support. This is PAFO (SL-DS) as investigated here. In FO applications, this configuration may suffer from fouling problems – though a dual-skin membrane [6, 7] might improve practicality. As a tool to
investigate transport through the selective layer of asymmetric membranes, it has great value.

iv) Higher $p$ and higher $\pi$ on porous support side. This configuration is impractical because of membrane fouling and mechanical integrity issues.

Water and solute flux through these membranes is described by combining a model for transport through the selective layer with the convection-diffusion equation applied across the porous support and boundary layers adjacent to it. The solution-diffusion (SD) model has become the standard selective layer transport model [8-11], but others have been proposed, including irreversible-thermodynamics models [12, 13], pore-flow models [14-16], and modified SD models [17]. For CTA, it is commonly accepted that the Loeb-Sourirajan process can make defect-free asymmetric RO membranes [18], but for PA the evidence is more ambiguous. Defects were detected in RO tests of commercial PA-TFC membranes (BW30 and SW30 from Dow FilmTec) [19], and gas permeation tests demonstrated the presence of selective layer defects in dry samples of commercial RO membranes [20, 21]. Such defects may be associated with the PA selective layer’s irregular ridge and valley structure [22] and the extremely fast and complex reaction kinetics of the layer formation mechanism [23].

Nearly all previous publications in PRO, FO, and PAFO assume that transport through the selective layer occurs by solution-diffusion [2, 24, 25]. (The only exception is Fang et al. [26] who modeled FO transport using irreversible thermodynamics.) In the SD model, the driving force for water flux $J_w$ is the net pressure difference across the selective layer, $\Delta \pi + \Delta p$, where $\Delta p$ is approximately zero in FO, negative in PRO and positive in PAFO.
The driving force for solute flux through the selective layer is concentration difference across it, proportional to $\Delta \pi$.

$$J_w = A(\Delta \pi + \Delta p)$$

$$-J_s = B\left(C_{\text{draw},s} - C_{\text{feed},s}\right)$$

where $A$ is the water permeability coefficient, $B$ is the solute permeability coefficient, and $C_{\text{draw},s}$ and $C_{\text{feed},s}$ are solute concentrations at the selective layer surfaces on the draw solution side and the feed solution side, respectively.

Thus, the SD model predicts that low hydraulic pressure ($\Delta p << \Delta \pi$) has little effect on water flux, producing negligible change in concentration polarization and solute flux. However, previous work reported experimental results that conflicted with this model. Coday et al. [2] found that hydraulic pressure had negligible influence on water flux, but measured much lower reverse solute flux under PAFO conditions than could be explained by the SD model. In PRO mode it was reported that solute permeability appears to increase when hydraulic pressure is applied [27-31]. As a practical consequence, membranes operated under actual PRO conditions often produce less power than predicted by permeability coefficients measured under FO conditions [27, 30, 32]. In the SD model, solute permeability is an intrinsic property of the selective layer material. Why would this property change with pressure? Explanations have been offered that include stretching or deformation of the selective layer, and damage or blocking associated with compression of the membrane porous support against module spacers when hydraulic pressure is applied [2, 27-30].
Here, we offer another explanation for the above discrepancies: the selective layer contains permanent defects that permit nonselective convective transport. The driving force for convection through these defects is not a function of $\Delta \pi + \Delta p$, but of $\Delta p$ alone [17, 19].

$$J_w = A(\Delta p + \Delta \pi) + L_d \Delta p$$ (3.3)

$$-J_s = B\left(C_{\text{draw},s} - C_{\text{feed},s}\right) - L_d \Delta p C_{\text{feed},s}$$ (3.4)

where $L_d$ is the convective flow permeability coefficient. Under FO conditions, $\Delta p = 0$, so convection through defects is zero. Under PAFO or PRO conditions, hydraulic pressure opens a parallel pathway through defects in the selective layer, which leads to passage of low-salinity (PAFO) or high-salinity (PRO) water. As a result, solute concentration on the porous support side of the selective layer can increase or decrease, resulting in changes in water flux.

Figure 3.2 illustrates schematically how selective layer defects may influence steady-state concentration profiles and therefore osmotic pressure driving force. Three sets of conditions are shown. Solid black lines show concentration profiles at zero hydraulic pressure (FO conditions). If hydraulic pressure is applied on the side indicated in each figure, and if the selective layer obeys the SD model, concentration profiles will change as shown by the blue dotted lines. Applying hydraulic pressure will change the net driving force, changing the water flux, changing the concentration gradients – increasing concentration polarization in response to the higher water flux in (a) and (b), and reducing concentration polarization in response to the lower flux in (c). Two general
statements can be made regarding concentration profile behavior under the SD model: 1) The osmotic pressure difference across the selective layer will adjust to any hydraulic-pressure-induced water flux change by attenuating it. In FO cases (a) and (b), increased flux caused by $\Delta p$ will be partially offset by a decrease in $\Delta \pi$; in the PRO case (c), decreased flux caused by $\Delta p$ will be partially offset by an increase in $\Delta \pi$. 2) If $\Delta p \ll \Delta \pi$, all the changes discussed above will be negligible, because the only driving force for flux in the SD model is $\Delta p + \Delta \pi$.

Dashed red lines in Figure 3.2 show possible concentration profiles if the selective layer contains defects. If defects are ubiquitous enough that concentration on both sides of the selective layer can be considered uniform – in other words, if defects are close enough to each other that concentration along any vertical line is constant – the problem can be analyzed in one dimension. In Figure 3.2a, hydraulic pressure transports water and solute through defects from right to left by convection. Low-salinity water will be drawn from the source at right to replace it. The solution that passes through the defects will reduce the concentration at the left surface of the selective layer. Therefore, downstream of the selective layer concentration polarization will increase when flux increases, but upstream of the selective layer convection through defects will have the opposite effect, reducing concentration polarization. The magnitude of this effect depends of course on the number and size of defects, or more precisely on the ratio of convective flux through defects to diffusive flux through defect-free regions. If convection through defects is high, the dashed red line in Figure 3.2a may drop below the black line, increasing the osmotic pressure difference across the selective layer, thereby increasing diffusive water flux through the defect-free regions. Because convection is driven by $\Delta p$ alone, concentration
profiles and therefore diffusive water flux may change dramatically even in cases where $\Delta p << \Delta \pi$.

If the SD model is applied to describe a membrane with defects, solute permeability coefficient $B$ will appear to increase with hydraulic pressure. However, the intrinsic permeability of the defect-free regions of such a membrane does not change. Rather, application of hydraulic pressure triggers transport of solute via a parallel pathway. The importance of this additional pathway depends on the operating conditions. For example, it is clearly negligible in FO where $\Delta p = 0$; but potentially important in PAFO and PRO.

Figure 3.2. Schematics of osmotic pressure profiles through thin-film-composite membranes in PAFO and PRO (black solid lines represent the profiles in FO; blue dotted lines 1-6 represent the possible profiles in PAFO and PRO according to the SD model; red dashed lines 1’-6’ represent the possible profiles in PAFO and PRO according to the SDWD model).
3.2. Membrane transport models

Water and solute flux through composite membranes can be obtained by combining a selective layer transport model with the convection-diffusion equation applied across the porous support. Expressions for water flux are derived by equating the solute flux across the selective layer and support layer. Equations for composite membranes with selective layers described by the SD and SDWD models are listed below.

3.2.1. SD model

\[
J_w = A \left[ \frac{\pi_{\text{draw},m} - \exp(J_w K) \pi_{\text{feed},m}}{1 + \frac{B}{J_w} \left[ \exp(J_w K) - 1 \right]} \right] + \Delta p \tag{SL-DS} \]

\[
J_w = A \left[ \frac{\pi_{\text{draw},m} - \exp(J_w K) \pi_{\text{feed},m}}{\exp(J_w K) + \frac{B}{J_w} \left[ \exp(J_w K) - 1 \right]} \right] + \Delta p \tag{SL-FS} \]

where \( \pi_{\text{draw},m} \) and \( \pi_{\text{feed},m} \) are the osmotic pressures at the outer surfaces of the composite membrane on the draw and feed side, respectively. \( K \) is the solute resistance to diffusion within the porous support, given by:

\[
K = \frac{\tau t}{D_s \varepsilon} \tag{3.7}
\]

where \( \tau, t \) and \( \varepsilon \) are the tortuosity, thickness and porosity of the porous support, and \( D_s \) is the diffusion coefficient of solute in water. The set of equations above is identical to the PRO model proposed by Lee et al. [24]
3.2.2. SDWD model

\[
J_w = A \left[ \frac{1 + \frac{L_d \Delta p}{J_w} \left[ \exp(J_w K) - 1 \right]}{1 + \frac{B + L_d \Delta p}{J_w} \left[ \exp(J_w K) - 1 \right]} \left( \pi_{\text{draw}, m} - \exp(J_w K) \pi_{\text{feed}, m} \right) + \Delta p \right] + L_d \Delta p \quad \text{(SL-DS)}
\]

(3.8)

\[
J_w = A \left[ \frac{\exp(J_w K) + \frac{B}{J_w} \left[ \exp(J_w K) - 1 \right]}{\pi_{\text{draw}, m} - \left( \exp(J_w K) - \frac{L_d \Delta p}{J_w} \left[ \exp(J_w K) - 1 \right] \right) \pi_{\text{feed}, m}} + \Delta p \right] + L_d \Delta p \quad \text{(SL-FS)}
\]

(3.9)

Note that when \( L_d = 0 \), Eq. 3.8 and 3.9 reduce to Eq. 3.5 and 3.6.

3.2.3. Concentrative and dilutive external concentration polarization

ECP is generally considered of less influence to FO performance than ICP. However, at the high fluxes generated under some PAFO conditions, ECP may be influential. Concentrative ECP is caused by convection that pulls solute from the bulk solution to the surface of the selective layer; water permeates through, leaving the solute behind [33].

Concentration at the membrane surface, \( C_m \), can be estimated by:

\[
\frac{C_m}{C_b} = \exp \left( \frac{J_w}{k} \right)
\]

(3.10)

where \( C_b \) is the bulk concentration and \( k \) is the mass transfer coefficient; \( k \) is related to the Sherwood number \( Sh \) by:
\[ k = \frac{ShD_t}{d_h} \]  \hspace{1cm} (3.11)

where \( d_h \) is channel hydraulic diameter. In a rectangular channel, \( Sh \) can be calculated [34] by:

\[ Sh = 1.85 \left( \frac{ReSc \ d_h}{l} \right)^{0.33} \]  \hspace{1cm} (laminar flow) \hspace{1cm} (3.12)

\[ Sh = 0.04Re^{0.75} Sc^{0.33} \]  \hspace{1cm} (turbulent flow) \hspace{1cm} (3.13)

where \( Re \) is the Reynolds number, \( Sc \) is the Schmidt number, and \( l \) is channel length.

Dilutive ECP is identical to concentrative except that here convection pulls the solute away from the selective layer. In this case \( C_m \) is estimated by:

\[ \frac{C_m}{C_b} = \exp \left( -\frac{J_w}{k} \right) \]  \hspace{1cm} (3.14)

### 3.3. Experimental and methods

#### 3.3.1. Chemicals and membranes

DI water (18.2 MW cm resistivity at 25 °C) was used throughout the experiments. NaCl was from Fisher Scientific (CAS No. 7647-14-5, purity \( \geq 99.5\% \)). A polyether-polyamide block copolymer PEBAX® 1657 was purchased from Arkema Inc. (Philadelphia, PA, USA), and its general structure can be found in ref. [35].

Four commercial membranes and one PEBAX-coated RO membrane were used, as outlined in Table 3.1. Membranes are labeled in the form of A-B, where A is the
application and B is the membrane material and structure. For example, SW-PA is a seawater RO membrane with PA-TFC material and structure. SW-PA and BW-PA were purchased from Sepro Membranes, Inc. (Oceanside, CA, USA). FO-CTA-1 and FO-CTA-2 were kindly provided by Hydration Technology Innovations (HTI, Albany, OR, USA). FO-CTA-1 is cellulose triacetate (CTA) with an embedded polyester screen mesh; FO-CTA-2 is CTA cast onto a non-woven backing. Their general properties and structural images can be found in previous papers [36, 37]. For reference, Table 3.1 also lists water flux and NaCl flux of these membranes, measured under brackish water RO conditions using Sterlitech cross-flow cells.

**Table 3.1.** Membranes used in this study.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Label</th>
<th>Material</th>
<th>Manufacturer</th>
<th>Performance *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$J_w$ (L/m²·h)</td>
</tr>
<tr>
<td>Seawater RO</td>
<td>SW-PA</td>
<td>PA TFC</td>
<td>Sepro RO4</td>
<td>15.1</td>
</tr>
<tr>
<td>Brackish water RO</td>
<td>BW-PA</td>
<td>PA TFC</td>
<td>Sepro RO1</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>BW-PA-coat</td>
<td>PA TFC</td>
<td></td>
<td>13.8</td>
</tr>
<tr>
<td>FO</td>
<td>FO-CTA-1</td>
<td>CTA</td>
<td>HTI a</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>FO-CTA-2</td>
<td>CTA</td>
<td>HTI b</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* Test conditions: 2000 ppm NaCl solution as feed; pressure = 15.5 bar; temperature = 23°C; membrane area = 33.5 cm²; cross-flow mode with a velocity of 0.37 m/s. a membrane for cartridge type products with embedded mesh; b membrane for pouch products with nonwoven support.
The PEBAX-coated membrane (designated BW-PA-coat) was prepared by dip-coating the selective layer of BW-PA using a 1 wt. % PEBAX ethanol/water (70/30 volume ratio) solution, followed by drying in an oven at 60 °C for 10 h.

Prior to all tests, PA-TFC membranes were soaked in isopropanol for 10 min and then in water for at least 30 min to wet the pores of their porous supports; CTA membranes were soaked in water for 30 min to remove any glycerin. They were not compacted under hydraulic pressure.

3.3.2. Experimental setup

Figure 3.3 shows a schematic of the laboratory-scale apparatus used for all tests in this study. The cross-flow membrane cell allows feed and draw solutions to flow across opposite sides of the membrane. Each channel has dimensions of 2.8, 50 and 100 mm height, width and length, respectively. Three layers of diamond mesh feed spacers (fiber diameter ~ 0.4 mm, thickness of each layer ~ 0.8 mm, opening size ~ 2.6 mm) were used on both sides to increase mixing. Feed and draw solutions were operated in co-current mode with cross-flow rates of 0.15 and 0.05 m/s, respectively. A heat exchanger maintained the feed and draw solutions at 23 °C. A digital balance interfaced with a computer was used to monitor the weight of the draw solution, from which the water flux was calculated. A calibrated conductivity meter in the feed tank was used to determine the solute concentration and obtain the solute flux. Detailed calculation methods for water and solute flux were reported in previous work [38]. The hydraulic pressure on the feed side was generated by a pump and controlled by a valve.
3.3.3. Experimental methods

All tests in this study were carried out in the apparatus shown in Fig. 3. Three tests were performed to determine the parameters of the models: $A$, $B$ and $K$ in the SD model, and $A$, $B$, $K$ and $L_d$ in the SDWD model, as shown in Figure 3.4. These tests included:

1. pure water permeability (DI water on both sides, Figure 3.4i),
2. low pressure PRO/RO (2000 ppm NaCl solution on high-pressure side, and DI water opposite, Figure 3.4ii),
3. FO (0.5, 1.0 and 1.5 M NaCl draw solutions, DI water feed, Figure 3.4iii).
Figure 3.4. Schematic of the parameter determination procedures for the SD and SDWD model.

After determining all parameters, model fits were evaluated using data collected under PAFO test conditions. These tests used draw solutions of 0.5, 1.0 or 1.5 M NaCl, and feed solutions of DI water or 2000 ppm NaCl. Applied hydraulic pressure in PAFO tests was varied from 0.25 to 1.7 bar, with the upper limit restricted by the range of the pressure transducer.

3.4. **Results and discussion**

3.4.1. **Transport parameter determination**

3.4.1.1. **Pure water permeability tests**

With no solute on either side, osmotic pressure is zero everywhere and water flux is proportional to hydraulic pressure in both models. The water permeability coefficients $A$
in the SD model (Eq. 3.1) and $A + L_d$ in the SDWD model (Eq. 3.3) were obtained by linear fits to plots of water flux vs. hydraulic pressure (Figure 3.5). As shown in Figure 3.5, BW-PA exhibits the highest $A$, and PA membranes have higher $A$ than CTA membranes. Coating BW-PA with PEBAX reduced $A$ by ~80%.

**Figure 3.5.** Pure water permeability test (DI water on both sides of membrane; hydraulic pressure on porous support layer side).

Pure water permeability tests were repeated with hydraulic pressure on either side of the membrane, first applied on the selective layer side and thereafter on the porous support side. No significant difference in water flux could be measured (Figure 3.6) which confirms the mechanical stability of membranes over this pressure range, i.e., applying pressure to the porous support side does not stretch the selective layer or detach it from the support. However, applying higher pressures to the porous support side of PA-TFC membranes caused the delamination of their polysulfone layer from the nonwoven
backing and mechanical failure. SW-PA and BW-PA broke at 1.25 bar and 1.7 bar, respectively. FO-CTA-1 and FO-CTA-2 were able to withstand 1.7 bar.

Figure 3.6. Effect of membrane orientation on water flux under hydraulic pressure (DI water on both sides of membrane; experiments with hydraulic pressure on selective layer side of membrane were carried out first, followed by experiments with hydraulic pressure on porous support layer side).

3.4.1.2. Low pressure PRO/RO tests

2000 ppm NaCl solution was circulated on the selective layer side of the membrane and DI water on the porous support side. A low hydraulic pressure range was chosen to minimize the confounding effects of membrane compaction and concentration polarization (when $J_w$ is low, $C_{feed,s} \approx C_{feed,b}$, the concentration of the bulk feed solution).

$J_w$ and $J_s$ were obtained at different hydraulic pressures.

Figure 3.7 shows $J_w$ as a function of hydraulic pressure. At low pressures, water permeated from the DI water side to the NaCl solution side, as in PRO, because osmotic
pressure (~1.6 bar) was higher than hydraulic pressure. However, positive water fluxes, from the NaCl solution side to the DI water side, were observed at pressures lower than 1.6 bar for all membranes tested. One possible reason is that $\Delta \pi$ was reduced by NaCl diffusion across the selective layer. Another possible explanation is convection through defects, driven by $\Delta p$ rather than $\Delta p - \Delta \pi$.

![Graph showing water flux in low pressure PRO/RO tests](image)

Figure 3.7. Water flux in low pressure PRO/RO tests (2000 ppm NaCl solution on selective layer side and DI water on porous support side; hydraulic pressure applied on NaCl solution side; water flux from NaCl solution side to DI water side is defined as positive).

The $B$ parameter in the SD model was obtained with Eqs. 3.1 and 3.2 by substituting $\Delta \pi$ with $iRT\left(C_{\text{draw,s}} - C_{\text{feed,s}}\right)$ (the Morse equation, where $i$ is the dimensionless van’t Hoff factor, $R$ the gas constant, and $T$ absolute temperature), and the values of $J_w$ and $J_s$ measured at zero hydraulic pressure. $L_d$ in the SDWD model was obtained by the method of Eriksson [19], using the following equation:
\[ J_s = B \left( C_{\text{feed},s} - C_{\text{permeate},s} \right) + L_d \Delta p C_{\text{feed},s} \]

(3.15)

\( L_d \) was found by plotting \( \frac{J_s}{C_{\text{feed},s}} \) against \( \Delta p \) (Figure 3.8). With \( L_d \) known, \( A \) and \( B \) in the SDWD model were obtained using Eqs. 3.3 and 3.4. Results are listed in . High \( L_d \) for polyamide membranes (BW-PA = 0.49 and SW-PA = 0.21) confirms the presence of defects in PA-TFC RO membranes. Notably, these \( L_d \) values are higher than those reported by Eriksson at RO operating pressures [19]; compaction may reduce \( L_d \). Convection through these defects could be efficiently blocked by the PEBAX coating (BW-PA-coat = 0.01). The \( L_d \) value of FO-CTA-2 is effectively zero (0.02), indicating no defects. FO-CTA-1, a much thinner membrane with embedded mesh, shows significant evidence of defects, with \( L_d = 0.26 \).

![Figure 3.8.](image)

**Figure 3.8.** \( L_d \) parameter determination by plotting \( \frac{J_s}{C_{\text{feed},s}} \) against \( \Delta p \) in low pressure PRO/RO test (2000 ppm NaCl solution on selective layer side and DI water on porous support side; hydraulic pressure applied on NaCl solution side).
3.4.1.3. FO tests

Draw solution (0.5 M, 1.0 M or 1.5 M NaCl) was circulated on the selective layer side and DI water on the support side. As shown in Figure 3.9, water fluxes across FO-CTA membranes were more than four times those across SW-PA and BW-PA. Commercial RO membranes suffer from severe ICP in FO due to their thick and spongy porous support layers. $K$ parameters in both models were obtained by fitting FO experimental data with Eq. 3.5 and 3.8, as listed in Table 3.2.

Figure 3.9. FO water flux (draw solution: 0.5 M, 1.0 M and 1.5 M NaCl solutions with osmotic pressures $\pi$ of 22.8 bar, 46.7 bar and 72.7 bar, respectively; DI water feed; SL-DS orientation; note that the SD and SDWD modeling results for SW-PA, BW-PA and BW-PA-coat are overlapping each other).
Table 3.2. Parameters for FO and PAFO modeling

<table>
<thead>
<tr>
<th></th>
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<th>SDWD model</th>
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<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>K</td>
<td>A</td>
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<td>0.22</td>
<td>0.27</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Units: \( A \) (L/m\(^2\)·h·bar), \( B \) (L/m\(^2\)·h), \( K \) (m\(^2\)·h/L), \( L_d \) (L/m\(^2\)·h·bar).

3.4.2. PAFO tests

3.4.2.1. SL-DS with DI feed

This test was performed with 1.5 M NaCl DS on the selective layer side (SL-DS orientation), DI water and hydraulic pressure on the feed side (Figure 3.2a). Water flux and reverse NaCl flux as a function of hydraulic pressure are shown in Figure 3.10.

For PA-TFC membranes SW-PA and BW-PA, with increasing hydraulic pressure, water fluxes increased dramatically, whereas NaCl fluxes decreased to essentially zero. Water flux across BW-PA increased from 3 to more than 50 L/m\(^2\)·h when hydraulic pressure increased from 0 to 1.25 bar. SW-PA water flux increased from 5 L/m\(^2\)·h at 0 bar to 30 L/m\(^2\)·h at 1 bar. In both SD (Eq. 3.1) and SDWD (Eq. 3.3) models, the overall water flux \( J_w \) can be split into two components: osmosis-driven water flux \( J_{w,\pi} \) (\( A\Delta\pi \) in SD and SDWD) and hydraulic-driven water flux \( J_{w,p} \) (\( A\Delta p \) in SD and \( (A+L_d)\Delta p \) in SDWD).
With $J_w$ and $J_{w,p}$ at each hydraulic pressure known, $J_{w,\pi}$ can be obtained. The ratio $J_{w,\pi}/J_{w,\pi,p=0} = \Psi$ can be defined to evaluate the effect of hydraulic pressure on osmosis driving force: (i) if $\Psi > 1$, concentration polarization is reduced by hydraulic pressure; (ii) if $\Psi \approx 1$, concentration polarization is barely influenced by hydraulic pressure; (iii) if $\Psi < 1$, concentration polarization is increased by hydraulic pressure. For BW-PA, $\Psi$ is 12 at 1.25 bar hydraulic pressure; for SW-PA, $\Psi$ is 5 at 1 bar.

This unusual behavior of PA-TFC membranes cannot be explained by the SD model, because low hydraulic pressure should have little influence on the driving force $\Delta P + \Delta \pi$ and, hence, the water flux (Figure 3.11). In contrast, predictions from the SDWD model correspond better with the experimental data, validating the hypothesis that these PA separating layers contain defects. Defects also help explain the lower reverse NaCl flux in PAFO. As shown in Eq. 3.4, solute passage by convection from the feed to the draw solution through defects decreases the overall solute passage from the draw to the feed side.
Figure 3.10. Experimental results of (a) water flux and (b) salt flux with pressure in PAFO test (1.5 M NaCl draw solution, DI water feed, SL-DS).
Figure 3.11. Comparison of experimental and modeling results in PAFO for BW-PA and SW-PA membranes (modeling conditions: 1.5 M NaCl draw solution with an osmotic pressure of 72.7 bar, DI water feed, SL-DS).

Figure 3.12a shows the calculated ECP and ICP for BW-PA as a function of hydraulic pressure in PAFO using the SDWD model. With zero hydraulic pressure, ICP is the dominating resistance, with $\pi_{feed,s} \sim 68$ bar out of 72.7 bar total osmotic pressure difference. When hydraulic pressure is applied, convection through defects decreases reverse NaCl flux, and therefore ICP; the resulting higher water flux increases ECP.
Figure 3.12. Calculated ECP and ICP in PAFO for (a) BW-PA and (b) FO-CTA-2 membranes using the SDWD model (modeling conditions: 1.5 M NaCl draw solution with an osmotic pressure $\pi_{\text{draw,b}} = 72.7$ bar, DI water feed, SL-DS; $\pi_{\text{draw,s}}$ and $\pi_{\text{feed,s}}$ are the solute concentration at the surface of selective layer on the draw solution side and feed solution side, respectively; $\Delta\pi$ is the osmotic pressure difference across the selective layer).
To further investigate PA-TFC defects, the surface of BW-PA was dip-coated with a uniform, nonselective PEBAX layer to block the defects (Figure 3.13a and Figure 3.13b). After PEBAX coating, the surface roughness dropped from $62 \pm 14$ nm to $19 \pm 4$ nm based on the AFM results in Figure 3.13c and Figure 3.13d. Figure 3.10 shows the results from PAFO tests for BW-PA-coat. Higher water flux and lower NaCl flux were no longer observed. The osmosis-driven water flux ratio $\Psi \approx 1$ indicates little osmotic pressure profile change with hydraulic pressure. Both SD and SDWD modeling results fit the experimental data (Figure 3.14).
Figure 3.13. Cross-section SEM images of (a) BW-PA and (b) BW-PA-coat membranes and surface 3D AFM images of (c) BW-PA and (d) BW-PA-coat membranes (SEM images were acquired with FEI-Magellan at an accelerating voltage of 5 kV; samples were sputter-coated with a uniform layer of approximately 2 nm iridium. AFM images were acquired with an ICON Veeco microscope in the tapping mode under ambient conditions, using commercial silicon TM AFM tips model MPP12100).
Figure 3.14. Comparison of experimental and modeling results in PAFO for BW-PA-coat, FO-CTA-1 and FO-CTA-2 membranes (modeling conditions: 1.5 M NaCl draw solution with an osmotic pressure of 72.7 bar, DI water feed, SL-DS).

In contrast to the results from PA-TFC membranes discussed above, experimental water and NaCl fluxes for CTA membranes were barely influenced by pressure (Figure 3.10). For both membranes Ψ≈1, indicating little concentration profile change with hydraulic pressure. Both models fit the experimental data (Figure 3.14). For FO-CTA-2, the modeling results nearly overlap with each other due to the low convective contribution \( (L_d) \) to water flux. Figure 3.12b shows ECP and ICP, which barely change with hydraulic pressure according to the SDWD model.

FO-CTA-1 is an interesting case because it does not show water flux enhancement or NaCl flux decrease even though \( L_d \) is relatively large. Other properties of this membrane attenuate the effect of \( L_d \): (i) both \( K \) and \( A \) are low for FO-CTA-1, so ICP is not the controlling resistance to water flux; (ii) high \( B \) leads to high solute flux into the support. Convection through defects is insufficient to mitigate the NaCl flux by diffusion from the
draw to the feed side at low hydraulic pressure (1.7 bar). A previous study by Blandin et al. [5] showed enhanced water flux across this membrane under hydraulic pressure of 6 bar.

### 3.4.2.2. SL-DS with salt in feed

In additional PAFO (SL-DS) tests, 2000 ppm NaCl feed was used with 1.5 M NaCl draw solution (Figure 3.15). The membranes exhibited similar water flux vs. hydraulic pressure trends as with DI water feed. Both BW-PA and SW-PA outperformed FO-CTA-2 in water flux. BW-PA achieved 20 L/m²·h at 1.25 bar, almost three times as high as FO-CTA-2.

Figure 3.16 shows BW-PA performance (experimental data and SDWD model) in PAFO (SL-DS) with different draw and feed concentrations. The SDWD model can successfully predict PAFO performance over a broad range of operating conditions.

![Figure 3.15](image-url)

**Figure 3.15.** Experimental results of water flux with hydraulic pressure in PAFO tests (1.5 M NaCl draw, 2000 ppm NaCl feed, SL-DS).
Figure 3.16. Comparison between experimental and SDWD modeling results in PAFO for BW-PA membrane under different operating conditions (SL-DS; “1.5 M NaCl - DI” means 1.5 M NaCl draw and DI water feed).

3.4.2.3. SL-FS with DI feed

Most previous FO studies involving hydraulic pressure used the SL-FS orientation [1-4, 39]. As depicted in Figure 3.2b, the probable outcome in this orientation is enhanced concentration polarization when hydraulic pressure is applied. This section examines this issue by both experimental and theoretical methods.

The effects of membrane orientation on water flux in PAFO for BW-PA and FO-CTA-2 membranes are shown in Figure 3.17. For FO-CTA-2 in both orientations, experimental results show little change in water flux with increasing hydraulic pressure. However, the osmosis-driven water flux ratio $\Psi$ was $\sim 0.8$ at 1.8 bar hydraulic pressure in the SL-FS orientation, indicating more severe concentration polarization. From the SDWD model,
\( \Delta \pi \) decreased from \( \sim 7 \) bar to 6 bar when hydraulic pressure increased from 0 to 1.8 bar (Figure 3.18). For BW-PA, water flux increased with increasing hydraulic pressure in both orientations. However, the increase in SL-FS was less significant than that in SL-DS. Moreover, \( \Psi \) decreased to 0 at 0.5 bar hydraulic pressure in SL-FS, which indicates that the additional increase in water flux was generated only by hydraulic pressure. This agrees with the modeling results in Figure 3.18 (black line).

Interestingly, in SL-FS orientation with DI feed, both the SD and SDWD models fit the BW-PA water flux data well (Figure 3.17, red solid and dashed lines). In SL-FS orientation, ICP is less affected by defects because hydraulic-driven water flux either through defects or defect-free regions reduces the concentration near the inner selective layer similarly (line 3 and 3’ in Figure 3.2b). With DI feed, ECP on the selective layer side is negligible (line 4 and 4’ in Figure 3.2b). However, with salty feed (e.g. 2000 ppm NaCl), the SDWD model predicts slightly higher water flux (4.5 L/m\(^2\)·h) than the SD model (2.7 L/m\(^2\)·h) at 1.3 bar hydraulic pressure due to reduced feed ECP.
Figure 3.17. Effect of membrane orientation on water flux in PAFO for BW-PA and FO-CTA-2 membranes (0.5 M NaCl draw solution, DI water feed).

Figure 3.18. Effect of hydraulic pressure on osmosis driving force in PAFO in SL-FS orientation according to the SDWD model (0.5 M NaCl draw solution, DI water feed).
3.4.3. Implications for future process and membrane development

ICP is generally regarded as the controlling resistance to water flux in FO and PRO [24, 33, 40]. Efforts to reduce ICP focus on porous support layer modification [41-45]. PAFO can also increase water flux by reducing ICP. Without addressing any possible fouling issues in the SL-DS orientation, this section focuses on potential directions to optimize PAFO based on modeling.

Parameters which can be tailored to enhance PAFO performance include: hydraulic pressure $p$, $A$, $B$, $K$ and $L_d$. Higher pressure requires higher membrane mechanical strength. $A$, $B$ and $L_d$ are selective layer properties and $K$ is mainly a porous support layer property. In this section, BW-PA is used as a base case to investigate the influence of the above-mentioned parameters on PAFO, using the SDWD model. The results are shown in Figure 3.19.

Water flux in PAFO increases with increasing hydraulic pressure; however, after pressure reaches about 1 bar, the slope decreases (Figure 3.19a) because ECP becomes the controlling resistance. High $A$, low $B$ and high $L_d$ increase PAFO water flux (Figure 3.19b, c, e). Notably, water flux barely changes with $A$, $B$ or $L_d$ at zero hydraulic pressure, because the controlling resistance at this $K$ is ICP (Figure 3.12). With increasing hydraulic pressure, convection through defects mitigates ICP and increases osmotic driving force. This increase is higher if convection through defects ($L_d$) is higher. However, diffusion through these same defects increases $B$. Therefore, high $L_d$ and low $B$ are restraints for each other.
In Figure 3.19d, lower $K$ generates higher water flux at low hydraulic pressures; at higher hydraulic pressures, the influence of $K$ diminishes. At lower $K$, more solute diffuses from the support to the feed solution, reducing ICP. At higher hydraulic pressures, more solute convects from the support to the draw solution, reducing ICP. PAFO and low $K$ provide similar water flux benefits.
Figure 3.19. Effects of pressure, $A$, $B$, $K$ and $L_d$ on water flux in PAFO using SDWD model (values of $A$, $B$, $K$ and $L_d$ of BW-PA were used as the base case; in (a), all four parameters were unchanged; in (b)-(e), only the parameter stated in the figure was...
changed, e.g. in (b), $A$ was changed by the indicated factor with the other three unchanged. 1.5 M NaCl Draw solution, DI water feed, SL-DS).

### 3.5. Conclusions

This work systematically investigated the effects of hydraulic pressure, membrane properties and orientations on PAFO performance by experimental and modeling methods. It is concluded that defects exist in the selective layer of PA-TFC membranes under aqueous conditions. This is verified by the dramatically different PAFO flux behavior of PA-TFC membranes compared to CTA and PEBAX-coated PA-TFC membranes. Hydraulic-driven convection through defects influences concentration polarization in PAFO. In SL-DS orientation, osmosis driving force increases with increasing hydraulic pressure; while in SL-FS orientation, it decreases. The SDWD model developed shows better agreement with experimental results than the SD model. It is hypothesized that in PRO, convection through defects may increase ICP, reducing power density.

### Acknowledgments

Research reported in this publication was supported by the King Abdullah University of Science and Technology (KAUST). The authors acknowledge HTI for providing FO membranes for this research. The authors also acknowledge Dr. Federico Pacheco for valuable discussions and Dr. Ali Behzad from KAUST Advanced Nanofabrication Imaging and Characterization Core Lab for assistance.
### Nomenclature

- $A$: pure water permeability coefficient ($L/m^2 \cdot h \cdot \text{bar}$)
- $B$: solute permeability coefficient ($L/m^2 \cdot h$)
- $C_b$: solute concentration in bulk solution (g/L)
- $C_m$: solute concentration at membrane outer surface (g/L)
- $C_{\text{draw},b}$: solute concentration in bulk draw solution (g/L)
- $C_{\text{draw},m}$: solute concentration at membrane outer surface on draw side (g/L)
- $C_{\text{draw},s}$: solute concentration at selective layer on draw side (g/L)
- $C_{\text{feed},b}$: solute concentration in bulk feed solution (g/L)
- $C_{\text{feed},m}$: solute concentration at membrane outer surface on feed side (g/L)
- $C_{\text{feed},s}$: solute concentration at selective layer on feed side (g/L)
- $C_{\text{permeate},s}$: solute concentration at selective layer on permeate side (g/L)
- $d_h$: hydraulic diameter (m)
- $D_s$: diffusion coefficient of solute in support layer ($m^2/s$)
- $i$: dimensionless van’t Hoff factor (-)
- $J_s$: solute flux (g/m$^2 \cdot h$)
- $J_w$: water flux ($L/m^2 \cdot h$)
- $J_{w,\pi}$: osmosis-driven water flux ($L/m^2 \cdot h$)
- $J_{w,\pi,p=0}$: osmosis-driven water flux with no hydraulic pressure ($L/m^2 \cdot h$)
- $J_{w,p}$: pressure-driven water flux ($L/m^2 \cdot h$)
- $k$: mass transfer coefficient ($L/m^2 \cdot h$)
- $K$: solute resistance to diffusion in support layer ($m^2 \cdot h / \text{L}$)
- $l$: length of channel (m)
- $L_d$: convective flow permeability coefficient ($L/m^2 \cdot h \cdot \text{bar}$)
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<td>( \Delta p )</td>
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<tr>
<td>( R )</td>
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<tr>
<td>( t )</td>
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<td>m</td>
</tr>
<tr>
<td>( T )</td>
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<td>K</td>
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**Greek letters**

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<tr>
<td>( \tau )</td>
<td>tortuosity of support layer</td>
<td>-</td>
</tr>
<tr>
<td>( \Psi )</td>
<td>osmosis-driven water flux ratio</td>
<td>( J_{w,\pi_1}/J_{w,\pi_1,\pi_0} )</td>
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<tr>
<td>( \pi_{\text{feed,m}} )</td>
<td>osmotic pressure of feed solution at membrane outer surface</td>
<td>bar</td>
</tr>
<tr>
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4. Microporosity of Polyamide and Gas Permeation Properties of Polyamide Thin-Film Composite Membranes

Abstract

Crosslinked aromatic polyamide (PA) synthesized from \(m\)-phenylene diamine and trimesoyl chloride is the most common selective layer material in water desalination membranes. This work systematically investigated the intrinsic structures of the PA material and the substructures of the PA selective layer by gas adsorption measurements and gas permeation tests. Two different adsorption isotherms (\(N_2\) at 77 K and \(CO_2\) at 273 K) showed higher gas uptake in PA than that in cellulose triacetate (CTA) and polysulfone (PSF). Calculated BET surface areas of PA based on \(N_2\) and \(CO_2\) isotherms are 33 and 92 m\(^2\)/g, respectively, much higher than those of CTA and PSF. The sharp gas uptake of PA at low relative pressures suggests the existence of micropores. A micropore distribution in the range of 4.5-8.5 Å was obtained for PA based on \(CO_2\)@273 K isotherm and the NLDFT model. Gas permeation of the pristine PA-TFC membranes showed close to Knudsen selectivity for various gas pairs, which confirmed the existence of defects in the dry PA selective layer. After coating with Nafion\textsuperscript{®}, gas permeance significantly decreased and gas selectivity sharply increased for small gases/large gases, \(CO_2/CH_4\) and \(O_2/N_2\), which demonstrates the separation properties of the dense PA
matrix. Potential applications of this membrane type are He recovery and H₂/CO₂ separation in pre-combustion CO₂ capture.

4.1. Introduction

Polyamides (PA) have been proposed as high-performance gas separation materials because of their excellent thermal and mechanical stability and good chemical resistance [1]. However, linear aromatic polyamides generally exhibit low gas permeability which is related to their high cohesive energy density and efficient polymer chain packing [1]. One technique to increase gas permeability is to introduce bulky substituents into polymer chains to disrupt polymer chain packing and increase free volume [2, 3]; another is introduction of specific functional groups or crosslinking [4-7] into polymer chains by interfacial polymerization (IP). By reacting an amine in an aqueous solution with an acyl chloride in an organic solution, an ultrathin PA selective layer can be efficiently deposited on a porous support, forming the favorable thin-film composite (TFC) membrane structure. This IP technique minimizes the formation of macrovoid defects [8] and allows easy control of functional groups; in addition, insoluble crosslinked PA can be easily formed into a selective layer. Technical and economic feasibility of the IP technique has been successfully demonstrated in commercial PA-TFC reverse osmosis (RO) and nanofiltration (NF) membrane production for water desalination.

Previous studies of IP-based PA-TFC gas separation membranes [4-7] primarily focused on CO₂ separations from N₂ and CH₄. Two mechanisms have been employed to increase CO₂ permeability and selectivity: i) increase the CO₂ solubility in the membrane by introducing ether oxygen groups in the PA chains [6]; and ii) facilitated CO₂ transport by
introducing primary and secondary amine groups as fixed carriers [4, 5, 7]. Facilitated CO₂ transport was reported with a commercial piperazine-based NF membrane with humidified feed where piperazine was considered as a fixed carrier [9].

Aromatic PA-TFC membranes synthesized from m-phenylene diamine (MPD) and trimesoyl chloride (TMC) are the most common water desalination membranes. Gas permeation properties of these membranes are of particular interest for two main reasons: (i) Gas permeation studies can probe the substructure of the PA selective layer. These PA-TFC membranes account for approximately 90% of the RO market; however, the substructure of the PA layer is not fully characterized because of their ultrathin and heterogeneous morphology. In addition, the substructure characteristics can be valuable in studying the membrane formation mechanism and water and solute separation mechanism, which can potentially lead to further improvement in water desalination performance and surface morphology control. (ii) Technical and economic feasibility has been demonstrated in manufacturing these PA-TFC membranes and, therefore, ease in scale-up and application of these membranes in commercial gas separation markets can be expected if good gas separation properties can be achieved using pristine or slightly modified membranes.

However, the pristine lab-made and commercial PA-TFC membranes (MPD/TMC) have shown Knudsen selectivity for different gas pairs at room temperature [4, 10, 11]. This supports the existence of mesopores in the dry PA layer (2-50 nm pores, referred as defects in ref. [11]; referred as highly permeable regions in ref. [10]). When hydrated, this PA layer contains defects, allowing non-selective convection under relatively low hydraulic pressures, as explained in Chapter 3. This convection can be beneficial under
pressure-assisted forward osmosis conditions. In RO, under high hydraulic pressure, compaction of the swollen polymer may decrease the size and numbers of defects, minimizing their detrimental effects on desalination. In the dry state in gas tests, gas permeation through these defective sites needs to be minimized to achieve effective gas separation.

Louie et al. [11] applied a polyether-polyamide block copolymer PEBAX® 1657 on commercial PA-TFC RO membranes to seal their defects. Selectivity more than doubled for several gas pairs, generally exceeding the selectivity of the PEBAX® material itself. A H₂/CO₂ selectivity of 13 was reported with coated RO membrane which is interesting because PEBAX® is more CO₂ selective against H₂. Albo et al. [10] observed a 6-fold increase in He permeance and He/N₂ selectivity at 150 °C and concluded that the increase was from activated diffusion of He through the dense PA matrix at high temperature.

The diffusivity selectivity of the PA material is probably related to its highly crosslinked structures or the intrinsic network pores depicted in Figure 2.1 [12]. Kim et al. characterized the PA material by positron annihilation lifetime spectroscopy (PALS) and concluded that it was comprised of network pores with diameters of 4.2 - 4.8 Å and aggregate pores with diameters of 7.0 - 9.0 Å [12]. Crosslinking restrains the polymer chains under hydrated conditions, allowing them to effectively separate water molecules (2.8 Å) from hydrated Na⁺ ions (7 Å). This can be verified from the increased water permeance and decreased NaCl rejection when TMC is replaced by isophthaloyl chloride and a linear aromatic PA is formed. Crosslinking also restrains the polymer chains from efficient packing and creates network pores in the dry state, similar to the structures of
PAF-6 [13] (Figure 2.3). Qian et al. [14] reported the microporous structure of crosslinked PA synthesized from TMC and piperazine (PIP).

This chapter focuses on the intrinsic properties of the PA dense matrix regions and potential applications of PA in gas separations. First, synthesized PA powders are characterized with N$_2$ and CO$_2$ adsorption measurements, and the results are compared with those from the conventional dense polymers polysulfone and cellulose triacetate. Second, gas permeation properties of the pristine and modified PA-TFC membranes are reported. The material used to coat the PA-TFC membranes is a perfluoropolymer – Nafion®. The chemical structure of Nafion® is shown in Figure 4.1, and its general properties have been reported in [15].

![Chemical structure of Nafion®.](image)
4.2. *Experimental*

4.2.1. Materials and membranes

MPD (≥ 99 %), TMC (≥ 98 %), hexane (anhydrous, 95 %), and Nafion® perfluorinated resin solution (~ 5 % in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich Co. All materials were used as received. Polysulfone pellets (PSF, Udel® 3500) were purchased from Solvay Advanced Polymers (Alpharetta, GA, USA). Cellulose triacetate (CTA, CA-436-80S) was purchased from Eastman Chemical Company (Kingsport, TN, USA). Commercial RO membranes SW30HR and BW30 were purchased from Dow Filmtec (Minneapolis, MN, USA); RO4 and RO1 from Sepro Membranes, Inc. (Oceanside, CA, USA); CE, a cellulose acetate-based (CA) membrane from GE Osmonics (Minnetonka, MN, USA). Their general properties are shown in Table 4.1.

Table 4.1. Commercial membranes used in this study.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Label</th>
<th>Material</th>
<th>Manufacturer</th>
<th>Performance *</th>
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<tr>
<td>Seawater RO</td>
<td>SW30HR</td>
<td>PA TFC</td>
<td>Dow</td>
<td>$J_w = 17.4 \pm 0.1 \text{ L/m}^2\text{-h}$, Rejection = 99.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>RO4</td>
<td>PA TFC</td>
<td>Sepro</td>
<td>15.1 ± 0.3, 98.8 ± 0.1</td>
</tr>
<tr>
<td>Brackish water</td>
<td>BW30</td>
<td>PA TFC</td>
<td>Dow</td>
<td>33.3 ± 1.9, 98.6 ± 0.1</td>
</tr>
<tr>
<td>RO</td>
<td>RO1</td>
<td>PA TFC</td>
<td>Sepro</td>
<td>76.0 ± 1.7, 99.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>CE</td>
<td>CA</td>
<td>GE</td>
<td>14.5 ± 5.7, 96.1 ± 0.4</td>
</tr>
</tbody>
</table>

* Test conditions: 2000 ppm NaCl solution as feed; pressure = 15.5 bar; temperature = 23 °C; membrane area = 33.5 cm²; cross-flow mode with a velocity of 0.37 m/s.
4.2.2. Preparation of polyamide powder and coated membranes

PA powders were prepared by IP between 1 w/v % MPD in the aqueous phase and 1 w/v % TMC in hexane in a rotating vial. After 30 min reaction time, the polymer was collected and thoroughly rinsed with hexane, DI water, and methanol, respectively, then dried under vacuum at 60 °C for 20 h.

Pristine RO membranes were dip coated using a 5 % Nafion® solution with an immersion time of 10 s. Then the membranes were dried at 60 °C for 10 h.

4.2.3. Characterization and performance assessment

N₂ adsorption isotherms of PA, CTA and PSF at 77 K were collected using a Micromeritics ASAP 2420. CO₂ adsorption isotherms at 273 K were collected using a Micromeritics ASAP 2050. Samples were dried at 110 °C for 16 h. Cross-section scanning electron microscopy (SEM) images were captured using an FEI-Nova Nano 630 with an iridium coating (25 mA, 20 s). Samples were prepared by first peeling off the polyester backing fabric and then fracturing the remaining membranes in liquid nitrogen. Gas permeation properties of the pristine membranes were measured with He, H₂, N₂ and CO₂ using a Millipore gas permeation cell (membrane area \( A \): 12.6 cm²) at 35 °C with a 3.4 bar (50 psi) feed pressure and atmospheric permeate pressure. The permeate flow rate \( Q \) was measured with a bubble flow meter. The membrane permeance \( J \) was calculated by:

\[
J = \frac{Q}{pA} \tag{4.1}
\]

The pure gas selectivity \( \alpha \) of a gas pair is the gas permeance ratio:
\[ \alpha_{ij} = \frac{J_i}{J_j} \quad (4.2) \]

Gas permeation properties of the Nafion®-coated membranes were measured using the constant-volume/variable-pressure method with a 2 bar feed pressure at 35 °C. The permeate pressure change was measured with an MKS Baratron transducer (0.1 bar). Gases tested were He, H₂, N₂, CO₂ and CH₄. Gas permeance was calculated by:

\[ J = \frac{V}{(pART)} \cdot \frac{dp}{dt} \quad (4.3) \]

where \( V \) is the permeate volume, \( R \) is the gas constant, \( T \) is the absolute temperature, and \( \frac{dp}{dt} \) is the permeate pressure increase rate.

### 4.3. Results and discussion

#### 4.3.1. Gas adsorption of crosslinked aromatic PA

Gas adsorption is an established technique to characterize the pore properties of a material. As shown in Figure 4.2a, the CO₂ adsorption isotherm at 273 K for PA showed a steep gas uptake at low relative pressure, indicating the presence of accessible micropores in the material. In contrast, CTA and PSF showed much less CO₂ uptake. Calculated Brunauer-Emmett-Teller (BET) surface areas of PA, CTA and PSF are 92, 16 and 7 m²/g, respectively, based on the CO₂ adsorption data in the 0.10-0.25 relative pressure range (Table 4.2). The BET surface area of PA in this study is very close to that of PA synthesized by IP between PIP/TMC [14].

The pore size distributions of PA, CTA and PSF were calculated based on the CO₂ adsorption isotherms determined at 273 K using the non-local density function theory (NL-DFT) method (model - carbon, slit pore). PA showed a distribution of micropores in
the range of 4.5-8.5 Å (Figure 4.2b), which is similar to that of PIP/TMC PA [14]. This result is consistent with the PALS measurements showing the 4.2 - 4.8 Å network pores and 7.0 - 9.0 Å aggregate pores [12]. For CTA and PSF, only negligible microporosity was detected.

N₂ adsorption isotherms for PA at 77 K showed a similar trend of quantity adsorbed vs. relative pressure (Figure 4.2c). A relatively sharp increase in N₂ uptake was observed at low relative pressure (< 0.05) followed by multi-layer adsorption at medium relative pressures. The BET surface area of PA calculated based on the N₂ adsorption isotherm at 77 K is 33 m²/g, much lower than that based on the CO₂ adsorption isotherm at 273 K. There are two main reasons for this difference [16, 17]: (i) the kinetic diameter of CO₂ (3.3 Å) is smaller than that of N₂ (3.64 Å) so CO₂ has more access to narrow micropores than N₂; (ii) the temperature of CO₂ adsorption (273 K) is much higher than that of N₂ adsorption (77 K) and CO₂ has a much higher kinetic energy to enter the narrow micropores than N₂. CTA and PSF showed little adsorption of N₂ and the calculated BET surface areas were smaller than 1 m²/g. The intrinsic difference between the microporous PA and the dense CTA probably accounts for the much faster water diffusion through PA than through CTA.
Figure 4.2. (a) CO$_2$ adsorption isotherms at 273 K of PA, CTA and PSF, (b) pore size distributions of PA, CTA and PSF based on their CO$_2$ adsorption isotherms at 273 K using the NLDFT method, and (c) N$_2$ adsorption isotherms at 77 K of PA, CTA and PSF.

Table 4.2. BET surface area and micropore volume of PA, CTA and PSF based on adsorption isotherms.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ at 273 K</th>
<th></th>
<th>N$_2$ at 77 K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_{BET}^a$ (m$^2$/g)</td>
<td>Memopore volume $b$ (cm$^3$/g)</td>
<td>$S_{BET}^a$ (m$^2$/g)</td>
<td>Memopore volume $c$ (cm$^3$/g)</td>
</tr>
<tr>
<td>PA</td>
<td>92</td>
<td>0.011</td>
<td>33</td>
<td>0.013</td>
</tr>
<tr>
<td>CTA</td>
<td>16</td>
<td>0.001</td>
<td>&lt;1</td>
<td>-$^d$</td>
</tr>
<tr>
<td>PSF</td>
<td>7</td>
<td>-$^d$</td>
<td>&lt;1</td>
<td>-$^d$</td>
</tr>
</tbody>
</table>

$^a$ BET surface area was calculated with adsorption data in the P/P$_o$ range 0.10-0.25.

$^b$ Total volume in pores smaller than 11.7 Å.

$^c$ Total volume in pores smaller than 25.2 Å.

$^d$ Not measurable.
4.3.2. Gas permeation properties of unmodified PA-TFC membranes

Gas permeance and selectivity values for dry, unmodified commercial PA-TFC membranes are listed in Table 4.3. Relatively large standard deviations in the permeance of the same membrane type were observed. This is typical for pore-flow-based transport, mostly resulting from the uneven defect distributions within the PA layer. Under RO test conditions, hydraulic pressure compacts the hydrated polymer, thereby reducing the sizes and numbers of defects; hence, water flux primarily occurs by diffusion in the dense polymer matrix reducing the variation in RO water flux measurements (Table 4.1). Gas selectivity values for H₂/N₂ and He/N₂ for PA-TFC membranes are slightly lower than the ideal Knudsen selectivity and the values reported by Louie et al. [11] and Albo et al. [10], whereas gas selectivity values for CO₂/N₂ are close to Knudsen selectivity. Thus it can be concluded that gas permeation occurs primarily through the defects of PA-TFC membranes.

The gas permeation properties of a CA-based CE membrane were studied as a reference. The CE coupons were pre-soaked in ethanol to remove glycerin, and then dried in air before the gas permeation tests. The same pretreatment procedure was found to have no influence on gas selectivity of PA-TFC membranes [10, 11]. CE showed much higher gas selectivity values for all the gas pairs than PA-TFC membranes, which clearly demonstrated the differences between the selective layers of these two membrane types. CE is produced by the Loeb-Sourirajan method involving casting, evaporation, precipitation and drying steps, known for producing defect-free selective membranes [18]. On the other hand, the PA layer is deposited in-situ onto the porous support during the IP reaction. These differences influence the gas permeation properties of these membranes.
Gas permeation through the CE membranes is primarily by the solution-diffusion mechanism through the defect-free selective layer.

**Table 4.3.** Gas permeation properties of commercial PA-TFC and CA membranes.

<table>
<thead>
<tr>
<th></th>
<th>Gas permeance&lt;sup&gt;a&lt;/sup&gt; (GPU)</th>
<th>Gas selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>H₂</td>
</tr>
<tr>
<td>SW30</td>
<td>240±70</td>
<td>345±99</td>
</tr>
<tr>
<td>RO4</td>
<td>204±40</td>
<td>295±70</td>
</tr>
<tr>
<td>BW30</td>
<td>67±31</td>
<td>96±45</td>
</tr>
<tr>
<td>RO1</td>
<td>27±5</td>
<td>37±8</td>
</tr>
<tr>
<td>CE&lt;sup&gt;b&lt;/sup&gt;</td>
<td>91±13</td>
<td>74±16</td>
</tr>
<tr>
<td>Knudsen&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> 3.4 bar feed pressure; 35 ± 1 °C; values reported based on three samples per membrane type; 1 GPU = 10⁻⁶ cm³ cm⁻² s⁻¹ cmHg⁻¹.

<sup>b</sup> Soaked in ethanol for 30 min and then dried in air.

<sup>c</sup> Knudsen selectivity.

Figure 4.3 shows the correlations between N₂ permeance of membranes in gas measurements and water permeance and NaCl flux in RO measurements. For PA-TFCs, the membranes with higher N₂ permeance generally exhibited lower water permeance and lower NaCl flux. This inverse relationship probably relates to the rough surfaces of PA-TFCs and different permeation paths of gas, water and solute in dry and hydrated states. N₂ permeation occurs primarily through the defective regions in the dry state; water and NaCl permeate primarily through the dense region in the hydrated state. The larger surface area of seawater RO membranes than brackish water RO membranes [19]
probably results in more defective regions along the surface in the dry state, contributing to the higher N₂ permeance. Under RO test conditions, a more compact PA layer would be formed in seawater RO membranes than brackish water RO membranes, resulting in decreased water permeance and NaCl flux.
Figure 4.3. Correlation of N₂ permeance of commercial membranes in gas tests with (a) water permeance and (b) NaCl flux in RO tests (gas test conditions: 3.4 bar feed pressure, 35 °C; RO test conditions: 2000 ppm NaCl feed, 15.5 bar pressure, 23 °C, cross-flow rate 0.37 m/s; error bars represent one standard deviation based on three coupons).
4.3.3. Gas permeation properties of Nafion®-coated PA-TFC membranes

Gas permeance of Nafion®-coated BW30 membranes decreased significantly compared to that of pristine BW30; for example, He permeance of coated membranes was only ~3 % of the pristine. This result is similar to the effect of PEBAX® coatings on the gas permeance of a seawater RO membrane SWC4 reported by Louie et al. [11]. As discussed earlier, gas diffusion through pristine PA-TFC occurs primarily through the defective regions of the membrane. After plugging the defects with a coating layer, gas permeance decreases significantly. This also indicates that the gas permeance obtained for the pristine BW30 membrane does not represent the material’s intrinsic gas permeation properties. A 23 μm thick Nafion® coating layer would be required to produce the measured He permeance for the coated membranes if using the BW30 gas permeance value in the series-resistance model [20] (Eq. 2.13). However, the actual Nafion® coating layer is only ~70-100 nm thick based on the cross-section SEM image in Figure 4.4. This result indicates that the main resistance to gas permeation in the coated membranes is in the dense PA matrix regions.
Table 4.4. Gas permeance of Nafion®-coated BW30 membranes.

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>H₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®b</td>
<td>40.9</td>
<td>9.3</td>
<td>0.26</td>
<td>2.43</td>
<td>0.102</td>
</tr>
<tr>
<td>BW30c</td>
<td>67±31</td>
<td>96±45</td>
<td>23±3</td>
<td>27±13</td>
<td>-d</td>
</tr>
<tr>
<td>Nafion®-coated BW30e</td>
<td>1.7(0.4)</td>
<td>0.5(0.1)</td>
<td>1.3(0.4)×10⁻³</td>
<td>0.03(0.01)</td>
<td>5.9(0.6)×10⁻⁴</td>
</tr>
<tr>
<td>PEBAX®-coated SWC4f</td>
<td>8.1(0.4)</td>
<td>7.5±0.5</td>
<td>0.7(0.3)</td>
<td>0.7(0.2)</td>
<td>-</td>
</tr>
</tbody>
</table>

a 1 GPU = 10⁻⁶ cm³·cm⁻²·s⁻¹·cmHg⁻¹.

b Ref. [21], dry Nafion® 117 membrane tested at 35 °C and 1.01 bar feed pressure; listed permeance values are for Nafion® with 1 µm thickness.

c Pristine BW30 membranes measured at 35 °C and 3.4 bar feed pressure; values reported based on three samples.

d Not measured.

e Samples were dip-coated with 5 w/v % Nafion® solution, and then dried at 60 °C; tested at 35 °C and 1.0 bar feed pressure; values reported are average of two samples; values in parentheses are the differences between two samples.

f Ref. [11], SWC4 seawater RO membrane coated with 1 wt. % PEBAX in n-butanol, and then dried at 60 °C; tested at 22 °C and 4.5 bar feed pressure.
Nafion®-coated BW30 showed slightly decreased He/H₂ selectivity compared to pure Nafion® film (Table 4.5). However, for the other gas pairs (small gases/large gases, CO₂/CH₄, O₂/N₂), the selectivity values of coated BW30 are much higher than those of Nafion®. This demonstrates the high intrinsic gas separation properties of the dense PA matrix. Ultrahigh He/CH₄ selectivity, similar to that of poly (methyl methacrylate), was obtained [22]. Relatively high selectivity values were obtained for CO₂/CH₄ and O₂/N₂. However, the extremely low permeance generally makes these separation processes impractical. Compared with PEBAX®-coated SWC4 [11], Nafion®-coated BW30 exhibits higher He/CO₂ and H₂/CO₂ selectivity, which is related to the separation property differences between PEBAX® and Nafion®. PEBAX® is more CO₂-selective against He and H₂, whereas Nafion® is more He- and H₂-selective. This makes the Nafion®-coated PA-TFC membranes potential candidates for He recovery and H₂/CO₂ separation. Especially in the latter case, for CO₂ capture in pre-combustion applications [23], increased H₂ permeance and selectivity against CO₂ can be expected, because H₂
would have more activated diffusion than CO₂ at the high feed stream temperature (~ 160 °C) [10].

**Table 4.5. Gas selectivity of Nafion®-coated BW30 membranes.**

<table>
<thead>
<tr>
<th>Gas selectivity</th>
<th>He/H₂</th>
<th>He/CO₂</th>
<th>H₂/CO₂</th>
<th>He/CH₄</th>
<th>CO₂/CH₄</th>
<th>O₂/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knudsen gas selectivity</td>
<td>0.7</td>
<td>3.3</td>
<td>4.7</td>
<td>2</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Nafion® 117 film</td>
<td>4.4</td>
<td>17</td>
<td>3.9</td>
<td>401</td>
<td>24</td>
<td>4.2</td>
</tr>
<tr>
<td>BW30</td>
<td>0.7</td>
<td>2.5</td>
<td>3.6</td>
<td>-ᵇ</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Nafion®-coated BW30</td>
<td>3.5</td>
<td>57</td>
<td>17</td>
<td>2880</td>
<td>51</td>
<td>7</td>
</tr>
<tr>
<td>PEBAX®-coated SWC4ᶜ</td>
<td>1.1</td>
<td>14</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
</tr>
</tbody>
</table>

ᵃ Ref. [21].  
b Not measured.  

### 4.4. Conclusions

In this chapter, the intrinsic structures of the PA material (MPD/TMC) and the PA selective layer in commercial PA-TFC membranes were investigated by gas adsorption measurements and gas permeation tests. Both N₂ (77 K) and CO₂ (273 K) adsorption isotherms showed higher gas uptake of PA than CTA and PSF. Calculated BET surface areas of PA was much higher than those of CTA and PSF. A distribution of micropores in the range of 4.5-8.5 Å was obtained for PA-based CO₂ adsorption using the NLDFT.
model. Gas permeation of the pristine PA-TFC membranes showed close to Knudsen selectivity for various gas pairs, which confirmed the existence of defects in the dry PA selective layer. After coating with Nafion®, gas permeance significantly decreased with a sharp increase in gas selectivity for small gases/large gases, CO₂/CH₄ and O₂/N₂, which demonstrates the gas separation properties of the dense PA matrix. These coated membranes may have applications in He recovery and H₂/CO₂ separation in pre-combustion CO₂ capture.
References


5. Preparation and Water Desalination

Properties of POSS-PA Nanocomposite Reverse Osmosis Membranes

Abstract

The application of nanotechnology to thin-film nanocomposites (TFN) is a new route to enhance membrane performance in water desalination. Here, the potential of polyhedral oligomeric silsesquioxane (POSS) as the nanofiller in polyamide (PA) reverse osmosis membranes was systematically investigated. Four POSS materials (P-8Phenyl, P-8NH3Cl, P-8NH2 and P-1NH2) were introduced into the selective layer by physical blending or chemical fixation during standard interfacial polymerization. Water flux and NaCl rejection were measured with 2000 ppm NaCl solution under 15.5 bar pressure, and SEM and TEM images of membrane selective layers were obtained. Membranes prepared without POSS had water flux of $20.0 \pm 0.5$ L/m²·h and salt rejection of $98.0 \pm 0.2\%$. TFN membranes prepared with 0.4 % (w/v) P-8Phenyl in the organic phase showed a 65 % increase in water flux compared to the pristine PA membrane while maintaining high salt rejection. The selective layer of this membrane maintained the typical ridge-and-valley structure of aromatic PA. Results with P-8NH3Cl and P-8NH2 added to the organic phase were similar. TFN membranes prepared with monoamine P-1NH2 in the organic phase had poor water flux of $3.2$ L/m²·h, a smooth and more hydrophobic surface, and a much
thicker (~ 400 nm) selective layer. One of the four POSS compounds studied, P-8NH₃Cl, is sufficiently soluble in water for incorporation into the selective layer via the aqueous phase. Membranes were prepared with P-8NH₃Cl in the aqueous phase at varying reaction time, loading, and additive (triethylamine) concentration. With these parameters optimized, water flux increased to 35.4 L/m²⋅h.

5.1. Introduction

Desalination technologies address global water scarcity by increasing water supply [1]. In 2012, 66 million m³/d of potable water was produced through desalination; this is expected to reach 100 million m³/d in 2015 [2]. Reverse osmosis (RO) accounts for around 60% of world desalination capacity [2]. Membranes, as the central component of RO, determine overall technical feasibility and economic efficiency. Most commercial RO membranes consist of an ultrathin polyamide (PA) selective layer on top of a porous support; the PA layer is formed by interfacial polymerization, most commonly between m-phenylene diamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase [3, 4]. Commercial membranes from different manufacturers offer similar salt rejections and water fluxes because of their similar chemistry and thin-film-composite (TFC) structure [5].

Nanotechnology provides a new route to improve membrane performance by incorporating nano-sized materials into the PA selective layer. Jeong et al. first reported a thin-film-nanocomposite (TFN) PA membrane containing zeolite 4A, yielding increased water flux while maintaining salt rejection [6]. Thereafter, many other nanomaterials,
including carbon nanotubes [7], silica [8, 9], TiO$_2$ [10], silver [11], and metal-organic frameworks [12], were tested; most TFN membranes showed higher water flux without decreasing salt rejection. The proposed mechanisms of the enhanced desalination performance of TFN membranes include: (i) faster water transport within the porous nanomaterials [6, 7, 9]; (ii) increased membrane affinity to water [6, 10]; (iii) PA structure change [6, 8, 13, 14]. Nanomaterials may also improve some physical membrane properties, such as thermal stability, mechanical strength [8] or fouling resistance [11].

In this work, the potential of polyhedral oligomeric silsesquioxane (POSS) in TFN membranes was investigated. POSS is comprised of an inorganic cage-shaped core and organic substituents, as shown in Figure 5.1. The length of POSS is around 1-3 nm. Major applications are property improvements of bulk polymer materials through physical blending or chemical crosslinking [15]. POSS has previously been proposed for use in membrane-based separations, e.g., gas separation [16-19] and pervaporation [20]. In water treatment applications, Kim et al. proposed using POSS as the crosslink center of polyethylene glycol (PEG) to improve membrane antifouling properties [21]; Dalwani et al. prepared a POSS-PA membrane by interfacial polymerization between a POSS ammonium salt (P-8NH$_3$Cl in Fig. 1) in the aqueous phase and TMC in the organic phase, which exhibited selectivity in liquid permeation experiments [22]. Recently, POSS was incorporated into the RO membrane selective layer by adding POSS ammonium salts into the MPD aqueous phase, yielding higher water flux and higher salt rejection than pristine membranes [23, 24]. Here, four POSS materials with different functional groups (Figure 5.1) were systematically investigated as nanofillers in the selective PA layer,
incorporated by physical blending or chemical fixation. The RO performance of these TFN membranes is reported.

![Diagram of POSS nanomaterials](image)

**Figure 5.1.** The four POSS nanomaterials used in this study.

### 5.2. Experimental

#### 5.2.1. Materials

Octaphenyl POSS (P-8Phenyl, C\textsubscript{48}H\textsubscript{40}O\textsubscript{12}Si\textsubscript{8}), octaammonium POSS (P-8NH\textsubscript{3}Cl, C\textsubscript{24}H\textsubscript{72}Cl\textsubscript{8}N\textsubscript{8}O\textsubscript{12}Si\textsubscript{8}), octaaminophenyl POSS (P-8NH\textsubscript{2}, C\textsubscript{48}H\textsubscript{48}N\textsubscript{8}O\textsubscript{12}Si\textsubscript{8}), and aminopropylisobutyl POSS (P-1NH\textsubscript{2}, C\textsubscript{31}H\textsubscript{71}NO\textsubscript{12}Si\textsubscript{8}) were obtained from Hybrid Plastics Inc. (Hattiesburg, MS, USA). MPD (≥ 99 %), TMC (≥ 98 %), hexane (anhydrous, 95 %), and triethylamine (TEA, ≥ 99 %) were purchased from Sigma-Aldrich Co. NaCl (≥ 99.5%) was from Fisher Scientific Inc. All materials were used as received. Deionized (DI) water was used throughout the experiments. The porous polysulfone support used (PS20) was obtained from Sepro Membranes, Inc. (Oceanside,
CA, USA); surface and cross-section SEM images are shown in Figure 5.2. Before use, the support was immersed in iso-propanol for 1 h and then washed with water for 24 h to remove any glycerin.

**Figure 5.2.** (a) Top and (b) cross-section SEM images of commercial PS20 ultrafiltration support.
5.2.2. Preparation of TFC and TFN membranes

TFC and TFN membranes were prepared by interfacial polymerization on PS20 support. For the TFC membranes, the support was first immersed in a 2.0 % (w/v) MPD aqueous solution for 2 min, then placed between two automatic rubber rollers to remove the excess solution. Next, it was mounted into a frame and a 0.15 % (w/v) TMC/hexane solution was poured onto the surface to react for 20 s. Finally, the hexane solution was poured off and the resulting membrane was stored in DI water before testing.

The procedure for preparing TFN membranes was identical with the exception of POSS addition. POSS were introduced into the selective layer by two routes: (i) POSS in the organic phase, and (ii) POSS in the aqueous phase. For route (i), a POSS compound (P-8Phenyl, P-8NH3Cl, P-8NH2, or P-1NH2) was dispersed in TMC/hexane solution by ultrasonication for 1 h at 23 °C, then the hexane solution was immediately poured onto the support to react for 20 s. For route (ii), P-8NH3Cl was dissolved in MPD aqueous solution before contact with TMC/hexane solution; here, different concentrations of TEA were added in the aqueous phase, and the reaction time was varied.

5.2.3. Characterization and performance assessment

SEM (FEI-Magellan) was used to characterize the surfaces of the membranes. Cross-section images were captured by transmission electron microscopy (TEM, FEI-Titan) at an accelerating voltage of 80 kV. TEM samples were prepared as follows: (i) the nonwoven fabric was gently peeled away from the polysulfone support; (ii) the remaining membrane was rinsed with ethanol thoroughly, then potted in epoxy resin; (iii) after the sample was embedded in the resin capsule by heating to 62 °C for 24 h, approximately
70-90 nm thick sections were cut on a Leica EM UC6 ultramicrotome with a diamond knife and mounted onto grids for the TEM test. The surface roughness of the membranes was measured by atomic force microscopy (AFM, ICON Veeco) in the tapping mode under ambient conditions, using commercial silicon TM AFM tips (model MPP 12100). Sessile drop contact angles of DI water were measured on the air-dried membrane samples with a contact angle goniometer (Kruss DSA25); the time between drop and measurement was ~ 10-20 s. X-ray photoelectron spectroscopy (XPS, Kratos Analytical - Axis Ultra) was used to measure the membrane surface element composition on a 700 × 200 µm area with 10 nm depth. The isolated selective layer was used for XPS characterization on the bottom surface. The sample was prepared with the procedure reported in [25].

RO performance was evaluated in a cross-flow cell (Sterlitech Corp.) with a membrane area of 33.5 cm² under brackish water testing conditions (15.5 bar, 2000 ppm NaCl feed solution) at a feed flow velocity of 0.37 m/s. Spacers were used in the feed channel to increase mixing. The feed temperature was controlled at 23 °C by a heat exchanger. The permeate and retentate were recirculated back to the feed. After 24 h of equilibration under continuous test conditions, water flux and salt rejection were measured for three coupons of each membrane.
5.3. **Results and discussion**

5.3.1. **POSS in the organic phase**

TFN membranes were prepared with POSS in the organic phase (hexane). Figure 5.3 shows the effects of POSS type and POSS concentration on RO water flux and NaCl rejection of as-prepared membranes. P-8Phenyl, P-8NH\textsubscript{3}Cl and P-8NH\textsubscript{2} increased the water flux and NaCl rejection of TFN membranes. Up to 0.4 %, higher POSS concentration resulted in higher water flux. At 0.4 %, the water fluxes of membranes with P-8Phenyl, P-8NH\textsubscript{3}Cl and P-8NH\textsubscript{2} were 65 %, 36 % and 67 % higher, respectively, compared to the pristine membrane. Addition of P-1NH\textsubscript{2} reduced water flux by 85 % at 0.05 % concentration in hexane; salt rejection also decreased.
Figure 5.3. Effects of POSS type and concentrations in hexane on (a) water flux and (b) NaCl rejection of TFN membranes (Test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm$^2$ membrane area; cross-flow velocity 0.37 m/s; error bars represent one standard deviation based on measurements of three coupons).
TFN membranes prepared with 0.4 % P-8Phenyl, P-8NH3Cl and P-8NH2, and with 0.2 % P-1NH2 were studied in more detail. RO water fluxes and NaCl rejections are listed in Table 5.1. SEM images of pristine TFC (Figure 5.4a) and TFN membranes with P-8Phenyl, P-8NH3Cl and P-8NH2 (Figure 5.4b-d) showed the typical ridge-and-valley structure found in aromatic PA RO membranes [25]. These three TFN membrane surfaces appear slightly rougher than the pristine PA membrane. This observation was confirmed with AFM results (Table 5.1, Figure 5.5) and differs from those of zeolite- [6] or silica-based [9] TFN membranes, which showed smoother surfaces than the pristine membrane. The smaller size of POSS (1-3 nm) may affect PA layer formation differently than the zeolite or silica (~ 100 nm). Lind et al. [13] proposed the “template” effect of large fillers on PA growth; smaller POSS, on the other hand, could be easily covered with the growing PA. The TFN membrane with P-1NH2 (Figure 5.4e) showed a smoother surface compared with the other types. A single site of -NH2 may react with TMC in hexane, thereby reducing the extent of crosslinking during interfacial polymerization. Subsequent interfacial polymerization would be similar to that between MPD and isophthaloyl chloride (IPC), forming a smooth membrane surface [26].

For water desalination membranes, hydrophilic materials are preferred because high affinity to water is associated with higher water solubility and, therefore, higher water flux [27]. However, POSS materials are generally hydrophobic [28], and blending with POSS normally increases the hydrophobicity of the composite [29]. Table 5.1 lists the apparent and corrected water contact angles $\theta$ and $\theta^*$ of the pristine and TFN membranes. $\theta$ is the measured water contact angle; $\theta^*$ is corrected with roughness area ratio $r$ obtained from AFM measurements by $\cos\theta^* = \cos\theta / r$ [30, 31]. Both parameters show that
membranes with P-8Phenyl, P-8NH$_3$Cl and P-8NH$_2$ have more hydrophilic surfaces than the pristine PA, whereas membranes with P-1NH$_2$ have more hydrophobic surfaces. This agrees with the water fluxes in RO tests: membranes with more hydrophilic surfaces produce higher water fluxes. The surface hydrophilicity change with different POSS materials may be related to the surface composition, e.g. whether POSS is directly exposed to water on the surface. If POSS is located below the PA surface, or serves as a crosslinking center, the surface hydrophilicity may not be affected significantly by the POSS. The hydrophilic POSS-PEG coating used for anti-fouling is an example [32]. On the other hand, POSS on the surface would increase average surface hydrophobicity. This may be the case with P-1NH$_2$ – chemically fixed at the surface through one linkage and in direct contact with water.
Table 5.1. RO performance, surface roughness, apparent and corrected water contact angle of TFC (pristine) and TFN (P-8Phenyl, P-8NH3Cl, P-8NH2 and P-1NH2) membranes (TFN membranes prepared with POSS in hexane).

<table>
<thead>
<tr>
<th>POSS type</th>
<th>Concentration (w/v %)</th>
<th>Water fluxa (L/m²·h)</th>
<th>Rejectiona (%)</th>
<th>Roughnessb (nm)</th>
<th>θc (°)</th>
<th>θ*d (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0</td>
<td>20.0 ± 0.5</td>
<td>98.0 ± 0.2</td>
<td>46 ± 5</td>
<td>60 ± 4</td>
<td>65</td>
</tr>
<tr>
<td>P-8Phenyl</td>
<td>0.40</td>
<td>33.0 ± 3.0</td>
<td>98.2 ± 0.3</td>
<td>64 ± 5</td>
<td>51 ± 4</td>
<td>62</td>
</tr>
<tr>
<td>P-8NH3Cl</td>
<td>0.40</td>
<td>27.1 ± 1.1</td>
<td>98.9 ± 0.2</td>
<td>73 ± 8</td>
<td>42 ± 3</td>
<td>57</td>
</tr>
<tr>
<td>P-8NH2</td>
<td>0.40</td>
<td>33.4 ± 1.1</td>
<td>98.6 ± 0.3</td>
<td>55 ± 9</td>
<td>35 ± 3</td>
<td>53</td>
</tr>
<tr>
<td>P-1NH2</td>
<td>0.20</td>
<td>3.2 ± 0.7</td>
<td>95.9 ± 0.6</td>
<td>29 ± 2</td>
<td>73 ± 5</td>
<td>75</td>
</tr>
</tbody>
</table>

a RO test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm² membrane area; cross-flow velocity 0.37 m/s; error bars based on measurements of three coupons.

b Root-mean-square surface roughness obtained from AFM; error bars based on at least three measurements.

c Apparent water contact angle measured directly; error bars based on three measurements.

d Corrected water contact angle by cosθ*=cosθ/r, where r is roughness area ratio measured by AFM [30, 31].
Figure 5.4. Surface SEM images of (a) pristine TFC membrane, and (b-e) TFN membranes prepared with P-8Phenyl, P-8NH$_3$Cl, P-8NH$_2$ and P-1NH$_2$ in hexane, respectively.
Figure 5.5. Surface AFM images of membranes of (a) pristine TFC membrane, and (b-e) TFN membranes prepared with P-8Phenyl, P-8NH3Cl, P-8NH2 and P-1NH2 in hexane, respectively.

Cross-section TEM images (Figure 5.6) show the PA selective layer thickness and substructure. Compared with the pristine PA membrane, P-8Phenyl (Figure 5.6b), P-8NH3Cl and P-8NH2 (Figure 5.6d) membranes have slightly thicker selective layers, and
P-1NH₂ (Figure 5.6e) shows a much thicker layer (~ 400 nm). Similar thickness increase is observed in the cross-section SEM or TEM images of TFN membranes with zeolite [6, 14], carbon nanotubes [33, 34] and silica [9]. Lind et al. [13] also reported increased selective layer thickness (derived from AFM) with increasing zeolite size in TFN membranes. The pristine interfacial polymerization of MPD and TMC is generally believed to comprise two stages: (i) an initial fast stage, forming a dense barrier layer and (ii) a following slow growth stage, limited by monomer diffusion through the barrier layer [35-37]. Nanomaterials, either physically trapped or chemically bonded in the initial formation stage, could reduce the density of the barrier layer either by: (i) their intrinsic porous structures (e.g. zeolite, carbon nanotubes etc.), (ii) creating gaps between the PA and nanomaterials, or (iii) changing extent of crosslinking. Reduced density would allow more monomers to cross the barrier layer during the slow growth stage, resulting in increased thickness for given monomer concentrations and reaction time. The resulting selective layer may be less permeable to water because it is thicker, or more permeable because it is less dense.

P-8Phenyl resembles unmodified zeolite and carbon nanotubes in that it contains no reactive moieties, so will be incorporated into the selective layer only if physically trapped. P-8NH₂ and P-8NH₂Cl introduce POSS as cross-linkers in the final PA layer. This could result in higher free volume, though simulation results from Moon et al. [24] indicate that the crosslinking extent of the final matrix is not affected significantly. P-1NH₂ converts TMC into POSS-grafted-TMC through amide linkages, which could dramatically reduce the crosslinking extent in the initial barrier layer, thus allowing much more MPD to pass through, forming a thicker layer and reducing water flux.
POSS could not be directly observed in SEM or TEM images. Fourier transform infrared spectroscopy and energy-dispersive x-ray spectroscopy also did not show evidence of POSS. This is probably because of the small sizes of POSS fillers (1-3 nm) and low concentration in the selective layers. On the other hand, XPS has a higher resolution and it was possible to detect Si concentrations of ~ 2-3 % in the TFN selective layers (Figure 5.7, binding energy peaks 102 eV for Si 2p and 153 eV for Si 2s). The XPS results are listed in Table 5.2. The element ratios O/N and C/N reflect the crosslinking extent in the PA layer. When the element contributions from POSS are subtracted, P-8NH₃Cl and P-8NH₂ show increased element ratios (denoted O/N* and C/N*) compared with the pristine PA membrane, indicating less crosslinking; P-Phenyl and P-1NH₂ show essentially no influence on PA crosslinking. For P-NH₃Cl (C₂₄H₇₂Cl₈N₈O₁₂Si₈), if it were physically incorporated in the selective layer, Cl concentration would be equal to Si concentration; however, XPS results showed a much lower Cl/Si ratio (1/18), thereby verifying the reaction between P-NH₃Cl and TMC. The POSS crosslinking center from P-8NH₃Cl and P-8NH₂ imposes steric effects on further reaction between MPD and TMC,
reducing the crosslinking extent. This could expose more carboxylic acid groups on the surfaces, making them more hydrophilic.

**Figure 5.7.** Normalized XPS spectra obtained from top surfaces of the selective layers of (pristine) and TFN (P-8Phenyl, P-8NH₃Cl, P-8NH₂ and P-1NH₂) membranes (TFN membranes prepared with POSS in hexane; XPS spectra normalized against the carbon 1s peak at ~ 284 eV).

**Table 5.2.** XPS results of TFC and TFN membranes (TFN membranes prepared with POSS in hexane).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>Si (%)</th>
<th>Cl (%)</th>
<th>C/N⁰</th>
<th>C/N⁰ᵇ</th>
<th>O/N⁰</th>
<th>O/N⁰ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>77.0</td>
<td>13.8</td>
<td>9.2</td>
<td>-</td>
<td>-</td>
<td>8.4</td>
<td>8.4</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>P-8Phenyl</td>
<td>75.2</td>
<td>15.0</td>
<td>7.9</td>
<td>1.9</td>
<td>-</td>
<td>9.5</td>
<td>8.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>P-8NH₃Cl</td>
<td>75.4</td>
<td>14.4</td>
<td>8.3</td>
<td>1.8</td>
<td>0.1</td>
<td>9.1</td>
<td>10.8</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>P-8NH₂</td>
<td>74.4</td>
<td>14.5</td>
<td>8.6</td>
<td>2.5</td>
<td>-</td>
<td>8.7</td>
<td>9.8</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>P-1NH₂</td>
<td>75.7</td>
<td>13.4</td>
<td>8.0</td>
<td>2.9</td>
<td>-</td>
<td>9.4</td>
<td>8.4</td>
<td>1.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>
5.3.2. POSS in the aqueous phase

P-8NH₃Cl, as an ammonium salt, is soluble in water. Figure 5.8 illustrates a route to incorporate POSS into the selective layer of TFN membranes from the aqueous phase. Dalwani et al. first proposed the interfacial polymerization between P-8NH₃Cl in water and TMC in the organic phase, forming a POSS-PA membrane by converting -NH₃Cl into -NH₂ with the addition of NaOH or TEA [22]. However, the as-made POSS-PA membrane showed poor NaCl rejection (~ 20-80 %) [22]. Moon et al. prepared POSS-TFN membranes using a similar procedure but used MPD together with POSS ammonium salt in the aqueous solution; this method resulted in improved water flux and salt rejection [24]. However, the experimental section was not explicit and the mechanism of reaction between TMC and MPD/POSS ammonium salt was not explained. In this section, the effects of reaction time, additive and POSS concentration on desalination performance are systematically investigated, and a possible mechanism is discussed.
Figure 5.8. Scheme for the preparation of a POSS-TFN membrane by interfacial polymerization between P-8NH$_3$Cl/MPD in the aqueous phase and TMC in the organic phase.

Figure 5.9 shows the effects of reaction time on water flux and NaCl rejection. P-8NH$_3$Cl and TEA concentrations in the aqueous phase were fixed at 0.6 % and 1 %, respectively. With increasing reaction time, salt rejection increased whereas water flux initially increased and then decreased. A reaction time of 40-60 s gave optimum results. This is different from membranes prepared with traditional MPD/TMC [35] or other novel amine or acid chloride chemistries [38, 39], where water flux and salt rejection generally level off after 20 s of reaction time. For P-8NH$_3$Cl TFN membranes, the increase and then decrease of water flux could result from the slower diffusion of POSS molecules into the organic phase, creating a time lag before POSS is fixed in the selective layer. This slower incorporation of POSS through amide linkage is consistent with the pure POSS-PA layer formation rate (~5 min) observed by Dalwani et al. [22]. The water flux decline after 60 s probably results from increased selective layer thickness.
Figure 5.9. Effects of interfacial polymerization time on water flux and NaCl rejection of TFN membranes prepared with P-8NH₃Cl in aqueous phase (0.6 % P-8NH₃Cl and 1 % TEA in aqueous phase; test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm² membrane area; cross-flow velocity 0.37 m/s; error bars represent one standard deviation based on measurements of three coupons).

Figure 5.10 shows the effects of P-8NH₃Cl concentration on water flux and NaCl rejection. TEA concentration in the aqueous solution was fixed at 1.0 % and the reaction time was 60 s. The resulting NaCl rejections were roughly the same, ~ 98 % for all P-8NH₃Cl concentrations. As P-8NH₃Cl concentration increased, water flux first increased by 43 % from 24.8±1.6 L/m²·h (at 0 %) to 35.4±1.0 L/m²·h (at 0.6 %). It then declined slightly at higher P-8NH₃Cl concentrations. In the initial stage, with increasing POSS concentration, more POSS crosslinking sites could be introduced into the matrix, producing higher free volume and increasing water flux [24]. However, more POSS in the barrier layer could lead to a thicker selective layer in the following growth stage, which would then reduce the water flux.
Figure 5.10. Effects of P-8NH₃Cl concentration on water flux and NaCl rejection of TFN membranes prepared with P-8NH₃Cl in aqueous phase (1 % TEA in aqueous phase, interfacial polymerization time 60 s; test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm² membrane area; cross-flow velocity 0.37 m/s; error bars represent one standard deviation based on measurements of three coupons).

Figure 5.11 shows the effects of the TEA concentration on water flux and NaCl rejection. P-8NH₃Cl concentration in the aqueous solution was 0.6 % and the reaction time was 60 s. As the TEA concentration increased to 1 %, the water flux initially increased and then decreased. The water flux of the TFN membrane prepared without TEA was 28.8±4.8 L/m²·h, surpassing the 20.0±0.5 L/m²·h of the pristine TMC/MPD membrane. This could be because of the conversion of -NH₃Cl to -NH₂ groups by MPD, a weak alkaline. By addition of 1 % TEA, the water flux increased to 35.4±1.0 L/m²·h because of the increased conversion of the -NH₃Cl groups. Higher TEA concentration could convert more -NH₃Cl to incorporate POSS in the selective layer, possibly leading to a thicker layer and lower water flux. Alternatively, excess acid acceptors could accelerate the reaction by neutralizing HCl, thus increasing the selective layer density. The influence of
TEA shown in Figure 5.11 agrees with experimental results by Liu et al. [39] and Yu et al. [40].

![Figure 5.11](image)

**Figure 5.11.** Effects of TEA concentration on water flux and NaCl rejection of TFN membranes prepared with P-8NH₃Cl in the aqueous phase (0.6 % P-8NH₃Cl in aqueous phase, interfacial polymerization time 60 s; test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm² membrane area; cross-flow velocity 0.37 m/s; error bars represent one standard deviation based on measurements of three coupons).

All TFN membranes prepared with P-8NH₃Cl in the aqueous phase exhibited the typical ridge-and-valley surface morphology. Figure 5.12a shows the surface SEM image of the optimized TFN membrane prepared with 0.6 % P-8NH₃Cl and 1 % TEA in the aqueous phase and 60 s reaction time. It resembles the surface of the pristine TFC membrane in Figure 5.4a. From AFM and contact angle measurement, it is approximately as smooth and hydrophilic as the pristine membrane (surface roughness 41±3 nm vs. 46±5 nm, corrected water contact angle 57° vs. 65°). The cross-section TEM image in Figure 5.12b confirms a thicker selective layer than the pristine PA membrane. XPS results (Figure
5.13) showed little Si on the top surface of the selective layer and high Si concentration on the bottom surface. This observation contradicts the modeling results from Moon et al. [24] that predicted uniform distribution of POSS throughout the selective layer. In their study, a fixed number of MPD, TMC and POSS molecules were introduced in the simulation cell, assuming that all monomers move without constraints during polymerization. However, under real circumstances, the interfacial polymerization between amine and TMC is a diffusion-limited reaction in which amine molecules diffuse into the organic phase to react with TMC, and the nascent film imposes resistance to further amine diffusion [41]. The large POSS molecules diffuse more slowly than MPD and are more easily blocked by the nascent PA film, resulting in more POSS trapped at the bottom layer. The corrected C/N* and O/N* ratio suggests that the PA matrix is more crosslinked at the bottom than at the top (Table 5.3).
Figure 5.12. (a) Surface SEM image, (b) cross-section TEM image and (c) surface AFM image of a POSS-TFN membrane (P-8NH₃Cl in the aqueous phase; 0.6 % P-8NH₃Cl and 1 % TEA in aqueous solution; reaction time 60 s).
Figure 5.13. Normalized XPS spectra obtained from top (P-8NH₃Cl(H₂O)-top) and bottom (P-8NH₃Cl(H₂O)-bottom) surfaces of the selective layers of as-prepared TFN membrane with P-8NH₃Cl in aqueous phase (0.6 % P-8NH₃Cl and 1 % TEA in aqueous solution; reaction time 60 s; sulfur signal is from residual polysulfone)

Table 5.3. XPS results obtained from the top and bottom surface of selective layers of TFN membranes* prepared with P-8NH₃Cl in aqueous solution.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>Si (%)</th>
<th>Cl (%)</th>
<th>S (%)</th>
<th>C/Nb</th>
<th>C/N*</th>
<th>O/Nb</th>
<th>O/N*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>79.3</td>
<td>12.7</td>
<td>8.0</td>
<td>&lt; 0.1</td>
<td>-</td>
<td>-</td>
<td>9.9</td>
<td>9.9</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Bottom</td>
<td>79.7</td>
<td>10.0</td>
<td>9.0</td>
<td>0.4</td>
<td>0.3</td>
<td>0.6</td>
<td>8.9</td>
<td>7.2</td>
<td>1.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*a 0.6 % P-8NH₃Cl and 1 % TEA in aqueous solution, reaction time 60 s.
*b Element overall atomic ratio obtained directly with values from XPS.
*c Corrected C/N ratio, excluding C and N from P-8NH₃Cl molecule and residual polysulfone (repeating unit assumed as C₂₇H₃₉O₄S).
*d Corrected O/N ratio, excluding O and N from P-8NH₃Cl molecule and residual polysulfone.
5.4. Conclusions

The potential of incorporating POSS into thin-film-composite RO membranes was systematically investigated. POSS can be introduced into the selective layer by physical blending and/or chemical crosslinking, from either the organic phase or the aqueous phase depending on the functional groups of the POSS compound. Physical blending of P-8Phenyl into the selective layer increased water flux by 65 % while maintaining NaCl rejection of 98 %. Chemical fixation of monoamine P-1NH₂ yielded poor water flux, whereas chemical crosslinking of multi-functional groups P-8NH₂ and P-8NH₃Cl yielded increased water flux. The use of POSS in TFN membranes may provide more freedom to tailor the chemistry of advanced RO membranes for water purification.

Acknowledgments

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Abstract

A hydrophobic, hydrothermally stable metal-organic framework (MOF) – zeolitic imidazolate framework-8 (ZIF-8) – was successfully incorporated into the selective polyamide (PA) layer of thin-film nanocomposite (TFN) membranes for water desalination. The potential advantages of ZIF-8 over classic hydrophilic zeolite used in TFNs include: i) theoretically faster water transport within the framework and ii) better compatibility with the PA matrix. The TFN membranes were characterized with SEM, TEM, AFM, XPS, water contact angle measurements and reverse osmosis tests under 15.5 bar hydraulic pressure with 2000 ppm NaCl solution. Lab-made, nano-sized (~200 nm) ZIF-8 increased water permeance to 3.35±0.08 L/m²·h·bar at 0.4 % (w/v) loading, 162 % higher than the pristine PA membranes; meanwhile, high NaCl rejection was maintained. The TFN surface was less crosslinked and more hydrophilic than that of the pristine PA. A filler encapsulation mechanism was proposed for the effects of filler on TFN membrane surface morphology and properties. This study experimentally verified the potential use of ZIF-8 in advanced TFN RO membranes.
6.1. Introduction

Global water scarcity drives the demand for more energy-efficient desalination technology [1]. Reverse osmosis (RO) can produce drinking water at less cost than conventional thermal-based desalination technologies [1]. Early research on RO dates back to the 1950s [2]; now RO produces around 42 million m$^3$ of potable water per day, accounting for 60% of world desalination capacity [3]. It is expected to play a pivotal role in addressing water shortages in the coming decades [1, 3]. Highly optimized commercial RO membranes provide high water flux with excellent solute rejection. Most membranes have a thin-film-composite (TFC) structure with an ultrathin polyamide (PA) selective layer, prepared based on the classic m-phenylene diamine (MPD)/trimesoyl chloride (TMC) interfacial polymerization process invented by Cadotte [4]. PA formation protocols between different commercial membrane manufacturers use optimized combinations of monomers, additives, co-solvents, post-treatment, etc. [5]; however, there is still an opportunity to improve the performance of interfacially-polymerized TFCs to further enhance the efficiency of RO [6-8].

A new recent concept for preparation of advanced RO membranes is integration of nanoparticles within the PA layer to produce a thin-film-nanocomposite (TFN) structure [9]. It was demonstrated that TFNs based on zeolite 4A exhibited higher water flux at comparable NaCl rejection relative to pristine PA TFCs [10-12]. Hypothesized mechanisms for the increased water flux with zeolite/PA TFN membrane include: (i) fast water transport through the hydrophilic zeolite pores [10]; (ii) increased membrane affinity to water [10]; (iii) PA structure change because of heat release from zeolite hydration [11, 12]; (iv) fast water transport through the voids between zeolite and PA
The first three mechanisms are directly related to the hydrophilicity of zeolite 4A. Consequently, alternative hydrophilic porous and nonporous fillers listed in Table 6.1 were selected in previous work to enhance TFN membrane performance [13-21].

In contrast to the results above, molecular dynamic (MD) simulations [22] and other experimental [23-25] results have shown much lower than expected water flux through hydrophilic zeolite pores. Water permeability of zeolite is 10-fold lower than commercial PA membranes [22, 23] (PA permeability was obtained by assuming a dense selective layer [9]). More surprisingly, water permeates faster in relatively more hydrophobic zeolite pores (higher Si/Al ratio) because of less affinity between water and the pore wall [22]. Huang et al. [26] compared RO TFN membranes prepared with silicalite-1 and zeolite 4A, and observed much higher flux increase with silicalite-1 (233 %) than with zeolite 4A (70 %) while maintaining high NaCl rejection. The hydrophobicity differences of these two zeolites were not explicitly highlighted; however, the weaker interaction between water molecules and silicalite-1 framework atoms was proposed as one possible reason for the higher diffusion rate of water through silicalite-1 [26].
Table 6.1. Summary of fillers in TFN membrane preparation.

<table>
<thead>
<tr>
<th>Filler type</th>
<th>Filler size (nm)</th>
<th>Pore size (Å)</th>
<th>Route&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Results&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>~ 50-100</td>
<td>Dense</td>
<td>Organic</td>
<td>$J_w$ and $R_{MgSO_4}$ essentially unchanged; reduced fouling against bacteria</td>
<td>[13]</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>~ 30</td>
<td>Dense</td>
<td>Organic</td>
<td>$J_w$ slightly decreased and $R_{MgSO_4}$ increased with up to 5 % TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>[14]</td>
</tr>
<tr>
<td>Silica</td>
<td>~ 3, 16</td>
<td>Dense</td>
<td>Aqueous</td>
<td>$J_w$ increased up to 134 % with maintaining $R_{NaCl}$; increased thermal stability</td>
<td>[15]</td>
</tr>
<tr>
<td>POSS salt</td>
<td>~ 1-3</td>
<td>Dense</td>
<td>Aqueous</td>
<td>$J_w$ increased up to 35 % with maintaining $R_{NaCl}$</td>
<td>[16]</td>
</tr>
<tr>
<td>Zeolite</td>
<td>~ 50-150</td>
<td>4</td>
<td>Organic</td>
<td>$J_w$ increased up to 81 % with maintaining $R_{NaCl}$</td>
<td>[10]</td>
</tr>
<tr>
<td>Silica</td>
<td>~ 100</td>
<td>~ 30</td>
<td>Organic</td>
<td>$J_w$ increased up to 65 % with maintaining $R_{NaCl}$</td>
<td>[17]</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>~ 1000</td>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Organic</td>
<td>$J_w$ increased up to 233 % and $R_{NaCl}$ increased</td>
<td>[18]</td>
</tr>
<tr>
<td>Metal-organic framework&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Not specified</td>
<td>9</td>
<td>Organic</td>
<td>$J_w$ increased up to 51 % with maintaining $R_{NaCl}$</td>
<td>[19]</td>
</tr>
<tr>
<td>Zeolite</td>
<td>~ 100</td>
<td>4</td>
<td>Aqueous</td>
<td>$J_w$ increased up to 29 % and $R_{NaCl}$ decreased</td>
<td>[12]</td>
</tr>
<tr>
<td>Ordered mesoporous carbon</td>
<td>~ 1000</td>
<td>~ 10-30</td>
<td>Aqueous</td>
<td>$J_w$ increased up to 26 % and $R_{NaCl}$ decreased</td>
<td>[20]</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>~ 50</td>
<td>5.6</td>
<td>Organic</td>
<td>$J_w$ increased up to 233 % and $R_{NaCl}$ increased</td>
<td>[26]</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>~ 1000-5000</td>
<td>~ 50</td>
<td>Aqueous</td>
<td>$J_w$ increased up to 80 % and $R_{NaCl}$ decreased; reduced fouling against BSA and Ca(HCO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;; increased chlorine resistance</td>
<td>[21]</td>
</tr>
</tbody>
</table>

<sup>a</sup> Route refers to the aqueous or organic phase in which the filler is added.

<sup>b</sup> $J_w$ - water flux, $R$ - rejection.

<sup>c</sup> Outer diameter.

<sup>d</sup> Cu-BTC.
Recently, various POSS types were incorporated into TFN membranes as hydrophobic dense fillers [16, 27]. As discussed in the previous chapter, physical incorporation of POSS and chemical fixation of POSS as crosslinking center into the PA layer can increase free volume and, therefore, increase water flux. Carbon nanotubes (CNT), in contrast, are hydrophobic porous fillers for TFNs [18, 21, 28-30]. MD simulations suggested and experimental results confirmed ultra-fast water transport through hydrophobic CNT pores [31, 32]. Water is not in direct contact with the CNT pore walls eliminating the influence of friction on water permeation [31, 32].

In this study, for the first time, a hydrophobic, porous metal-organic framework (MOF) material – zeolitic imidazolate framework-8 (ZIF-8) – was applied as nanofiller in TFN membranes for water desalination. So far the only MOF investigated, the hydrophilic Cu-BTC (Table 6.1) [19] is unstable in water [33]. In contrast, ZIF-8 is a stable MOF under thermal, hydrothermal and chemical conditions [34]. ZIF-8 is similar to zeolite in crystal structure and pore configuration: 11.6 Å cavity cages are connected with 3.4 Å pore apertures, which is effective for water (2.8 Å) and hydrated sodium ion (7 Å) separation. MD simulations showed fast water transport through ZIF-8 and high NaCl rejection under RO conditions [35]. Calculated water permeability of ZIF-8 is 0.47 L·µm/m²·h·bar [35], which is much higher than that of zeolite at 0.06 L·µm/m²·h·bar [22]. Moreover, the imidazolate linker increases compatibility between the hybrid inorganic-organic ZIF-8 and PA matrix. According to Sorribas et al. [36], nonselective voids between MOF and PA can be eliminated because of high affinity between these two materials. Differences between ZIF-8 and zeolite in hydrophilicity, water permeability and compatibility with
PA may shed light on the mechanisms responsible for the increased desalination performance of TFN membranes.

6.2. Experimental

6.2.1. Materials

Zn(NO$_3$)$_2$·6H$_2$O ($\geq 99\%$), 2-methylimidazole ($99\%$), MPD ($\geq 99\%$), TMC ($\geq 98\%$), and hexane (anhydrous, 95\%) were purchased from Sigma-Aldrich Co. NaCl ($\geq 99.5\%$) was obtained from Fisher Scientific Inc. All materials were used as received. Deionized (DI) water was used throughout the experiments. The porous polysulfone support used (PS20) was obtained from Sepro Membranes, Inc. (Oceanside, CA, USA); surface and cross-section SEM images were previously reported in [37]. Before use, the support was immersed in iso-propanol for 1 h and then washed with water for 24 h to remove any glycerin.

6.2.2. Preparation of nano-sized ZIF-8

ZIF-8 nanoparticles were prepared by a previously reported procedure [38]. Zn(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole were first separately dissolved in DI water at room temperature (\(~23\,^\circ C\)); then the two solutions were mixed under vigorous stirring. The molar ratio of Zn\(^{2+}\):2-methylimidazole:H$_2$O was 1:70:1238. After 5 min, ZIF-8 was collected by centrifugation, followed by thorough rising with DI water, then drying at 65\(^\circ C\) for 20 h.
6.2.3. Preparation of TFC and TFN membranes

TFC and TFN membranes were prepared by interfacial polymerization on polysulfone PS20 support (SEM images shown in Figure 5.2). The support was first immersed in a 2.0 % (w/v) MPD aqueous solution for 2 min, then placed between two automatic rubber rollers to remove any excess solution. Next, the membrane was mounted into a frame and a 0.15 % (w/v) TMC/hexane solution was poured onto the surface to react for 1 min and then poured off. The resulting membrane was dried and subsequently stored in DI water before testing. For TFN membranes, ZIF-8 was dispersed in TMC/hexane solution by ultrasonication for 1 h at 23 °C; then the hexane solution was immediately poured onto the porous support and reacted for 1 min. The concentration of ZIF-8 particles was varied between 0.05 and 0.40 w/v % based on previously used protocols for optimum preparation of zeolite TFNs [10].

6.2.4. Characterization and performance assessment

N₂ adsorption isotherms of ZIF-8 nanoparticles at 77 K were collected using a Micromeritics ASAP 2420 to calculate the BET surface area. Water vapor adsorption of ZIF-8 nanoparticles was measured with a vapor sorption analyzer (TA instruments, VTI-SA) at 35 °C. Particle sizes and size distributions were obtained by dynamic light scattering (DLS) with a Delsa™ Nano C system (Beckman Coulter). ZIF-8 particle morphology and membrane surfaces were characterized with a FEI-Nova Nano 630 SEM. Membrane cross-section images were captured by TEM (FEI-Titan) at an accelerating voltage of 80 kV. TEM samples were prepared by a previously reported procedure [37]. Isolated selective layers were imaged with projected area TEM (FEI-T12) using a
previously reported sample preparation technique [39]. Membrane surface roughness was measured by atomic force microscopy (AFM, ICON Veeco) in the tapping mode under ambient conditions. Sessile drop contact angles of DI water were measured on air-dried membrane samples with a contact angle goniometer (Kruss DSA25); the time between drop and measurement was ~ 10-20 s. X-ray photoelectron spectroscopy (XPS, Kratos Analytical - Axis Ultra) was used to measure membrane surface element composition on a 700 × 200 µm area.

RO performance was evaluated in a cross-flow cell (Sterlitech Corp., inner cell dimension 8.6 cm × 4.0 cm × 0.2 cm) with a membrane area of 33.5 cm² under brackish water testing conditions (15.5 bar, 2000 ppm NaCl feed solution) at a feed flow velocity of 0.37 m/s. Spacers were used in the feed channel to increase mixing and mitigate concentration polarization effects. The feed temperature was controlled at 23 °C. The permeate and retentate were recirculated to the feed. After 24 h of equilibration under continuous test conditions, water permeance, NaCl flux and NaCl rejection were measured. Water permeance $J_w$ was calculated by $J_w=V/(A\cdot t\cdot p)$, where $V$ is the volume (L) of permeate collected in a period of time $t$ (h), $A$ is the membrane area (m²) and $p$ is the hydraulic pressure (bar). NaCl permeance was calculated by $J_{NaCl}=J_w\cdot C_{permeate}$, where $C_{permeate}$ is measured NaCl concentration in the permeate solution. Apparent NaCl rejection was calculated by $R_{NaCl}=(1-C_{permeate}/C_{feed})\times 100\%$, where $C_{feed}$ is measured NaCl concentration in the bulk feed solution. Corrected NaCl rejection was calculated by $R_{NaCl}^*=(1-C_{permeate}/C_{feed}^*)\times 100\%$, where $C_{feed}^*$ is the NaCl concentration at the membrane surface in the feed. Concentrative concentration polarization was calculated using the method described in Section 3.2.3.
6.3. Results and discussion

6.3.1. Characterization of ZIF-8 nanoparticles

SEM images of lab-made ZIF-8 nanoparticles (Figure 6.1a) showed the typical rhombic dodecahedron shapes of ZIF-8 crystals [40]. High uniformity in nanoparticles size was observed (100-200 nm). DLS measurements (Figure 6.1b) confirmed the narrow size distribution. 50 % of nanoparticles (by volume) fall in the range of 120-200 nm; 90 % (by volume) are below 300 nm. Particles larger than 400 nm probably result from agglomeration because no large single crystals were seen in SEM images. The calculated median particle size by volume (D50) is ~ 195 nm according to the DLS measurements.

N$_2$ adsorption measurements of lab-made ZIF-8 at 77 K showed a type I isotherm (Figure 6.2a). The steep increase in the adsorbed volume of N$_2$ at low relative pressures (P/P$_0$ < 0.02) confirmed the microporous structure of ZIF-8. The BET surface area (1304 m$^2$/g) was calculated by using P/P$_0$ data points in the 0.10-0.30 range. It is very close to previously reported values from other groups [38, 41]. The water vapor adsorption isotherm at 308 K (35 °C, Figure 6.2b) showed very low water uptake (< 0.25 %) even at 95 % relative humidity, indicating the framework’s hydrophobicity. Low water uptake was also reported for commercial ZIF-8 particles [42].
Figure 6.1. (a) SEM image and (b) size distribution by volume of lab-made ZIF-8 nanoparticles.
Figure 6.2. (a) N$_2$ adsorption isotherm at 77 K and (b) water vapor adsorption isotherm at 308 K (35 °C) of lab-made ZIF-8 nanoparticles.
6.3.2. TFN membranes

Figure 6.3a shows the effects of ZIF-8 loadings on RO water permeance and NaCl flux of TFN membranes. Adding a very small amount of ZIF-8 (0.05 %) increased water permeance by 88 %. Similar sharp increases in water fluxes at low filler loadings were observed with hydrophobic carbon nanotubes [18, 43] and silicalite-1 [26]. With higher ZIF-8 loadings up to 0.4 %, water permeance continued to increase. At 0.4 %, the water permeance of TFN membrane was 2.6 times as high as that of the pristine PA membrane. Compared with the fillers previously investigated (Table 6.1), ZIF-8 yields the third highest water permeance increase ratio, following the 8 Å hydrophobic CNT [18] and silicalite-1 [26]. The larger effect on water permeance of ZIF-8, silicalite-1 and CNT over zeolite is most likely related to faster water transport through these three hydrophobic porous materials than the hydrophilic zeolite 4A pores. This “inverse” relationship between affinity of solvent to pore wall and solvent transport through the pore is also observed in organic separation between methanol and tetrahydrofuran through MIL-101(Cr) MOF: tetrahydrofuran transports faster through MIL-101(Cr) because of weaker affinity [36]. In Table 6.1, non-porous silica is reported to increase water permeance up to 134 %. However, the prepared TFN membranes exhibited relatively low NaCl rejection of only 90-95 % [15]. In this study, all membranes gave higher than 98 % NaCl rejection.

NaCl permeance also increased with increasing ZIF-8 loadings. Theoretically, the 3.4 Å ZIF-8 pores can exclude 100 % of the much larger hydrated Na⁺ and Cl⁻ ions, which should decrease overall NaCl permeance. This contradictory experimental result is probably related to changes in the PA structure and the possible introduction of voids.
between ZIF-8 and PA. PA structures exhibit various degrees of crosslinking, which can be measured by the element ratios of C/N and O/N. Surface element composition (up to 10 nm depth) was obtained by XPS (Table 6.2). When the element contributions from ZIF-8 are subtracted, both C/N* and O/N* increase with higher ZIF-8 loadings, indicating less crosslinking. It is generally accepted that high crosslinking of MPD/TMC is associated with low NaCl permeance and high NaCl rejection. Lind et al. [11] reported a similar decreased crosslinking extent of the PA layer and an increase in solute flux following addition of zeolite 4A. Meanwhile, the existence of possible voids between ZIF-8 and PA cannot be ruled out; such voids could contribute to the increased NaCl permeance observed. ZIF-8 is reported to have good compatibility with polymers because of its inorganic/organic hybrid nature [44]. Sorribas et al. [36] prepared ZIF-8/PA TFN membranes for organic nanofiltration, and assumed that no voids existed between the filler and PA matrix. Although better compatibility of ZIF-8/PA than zeolite 4A/PA is acknowledged, total elimination of voids between ZIF-8 and the surrounding PA film still needs to be verified considering the heterogeneous morphology [39] of the selective layer.

On the other hand, the NaCl permeance increase ratio is lower than the water permeance increase ratio. This proves the contribution of ZIF-8 to desalination. If water permeated through the polymer phase only, then the reduction in crosslinking of PA and the potential voids between ZIF-8 and PA would lead to a higher NaCl permeance increase ratio than a water permeance increase ratio (i.e., lower NaCl rejection).

NaCl rejection is a practical way to evaluate the performance of RO membranes. As shown in Figure 6.3b, apparent NaCl rejection first increased, then decreased with increasing ZIF-8 loadings. The trend is not very clear given the relatively large error bars.
Rejection is known to be closely related to operating conditions (e.g., flow rates) because concentration polarization can be a significant factor at high water fluxes. Based on the cell dimensions and the 0.37 m/s cross-flow rate (Re = 1408), the calculated feed concentration at the membrane surface was 2480 ppm at 19.8 L/m²·h water flux, and 3560 ppm at 53.0 L/m²·h water flux. This explains part of the increase in NaCl permeance at higher ZIF-8 loadings, because the driving force for solute diffusion in the solution-diffusion model is the concentration difference between the surfaces of the PA layer. At higher ZIF-8 loadings, the solute concentration difference is larger because of the higher water flux, which leads to a higher NaCl permeance. After factoring out this concentration polarization effect, the corrected NaCl rejection first increases with ZIF-8 loadings, then stabilizes (Figure 6.3b).
**Figure 6.3.** Effects of ZIF-8 loadings on (a) water and NaCl permeance and (b) apparent and corrected NaCl rejection of TFN membranes (Test conditions: 2000 ppm NaCl feed; 15.5 bar; 23 °C; 33.5 cm² membrane area; cross-flow velocity 0.37 m/s).
Table 6.2. XPS results, surface roughness, apparent and corrected water contact angle of TFC (0 % ZIF-8) and TFN membranes prepared with lab-made, nano-sized ZIF-8 at different loadings.

<table>
<thead>
<tr>
<th>$C_{\text{ZIF-8}}$ (w/v %)</th>
<th>Zn$^a$ (%)</th>
<th>C/N$^b$ (-)</th>
<th>C/N*$^c$ (-)</th>
<th>O/N$^b$ (-)</th>
<th>O/N*$^c$ (-)</th>
<th>R$q^d$ (nm)</th>
<th>$\theta$$^e$ (°)</th>
<th>$\theta^*$$^f$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>8.37</td>
<td>8.37</td>
<td>1.49</td>
<td>1.49</td>
<td>46 ± 5</td>
<td>60 ± 4</td>
<td>65</td>
</tr>
<tr>
<td>0.05</td>
<td>0.07</td>
<td>8.05</td>
<td>8.24</td>
<td>1.61</td>
<td>1.74</td>
<td>39 ± 1</td>
<td>57 ± 3</td>
<td>64</td>
</tr>
<tr>
<td>0.10</td>
<td>0.04</td>
<td>8.55</td>
<td>8.67</td>
<td>1.76</td>
<td>1.84</td>
<td>39 ± 2</td>
<td>39 ± 3</td>
<td>51</td>
</tr>
<tr>
<td>0.20</td>
<td>0.04</td>
<td>8.82</td>
<td>8.96</td>
<td>1.90</td>
<td>1.99</td>
<td>46 ± 2</td>
<td>36 ± 4</td>
<td>51</td>
</tr>
<tr>
<td>0.40</td>
<td>0.18</td>
<td>9.03</td>
<td>9.69</td>
<td>2.09</td>
<td>2.51</td>
<td>45 ± 4</td>
<td>39 ± 2</td>
<td>52</td>
</tr>
</tbody>
</table>

$^a$ Zn element atomic concentration obtained from XPS;

$^b$ Element overall atomic ratio obtained directly with values from XPS;

$^c$ Corrected C/N and O/N ratio, excluding element concentration from ZIF-8, based on chemical structure of ZIF-8 ($C_8H_{12}N_4Zn)_n$ and Zn concentration from XPS;

$^d$ Root-mean-square surface roughness obtained from AFM; error bars based on at least three measurements;

$^e$ Apparent water contact angle measured directly; error bars based on three measurements;

$^f$ Corrected water contact angle by $\cos\theta^* = \cos\theta/r$, where $r$ is roughness area ratio measured by AFM [45, 46].
Surface morphologies of the TFN membranes changed with addition of ZIF-8 nanoparticles. The SEM image of a pristine TFC (Figure 6.4a) shows the typical ridge-and-valley structure found in aromatic PA RO membranes [39]. With ZIF-8 loadings up to 0.10 % (Figure 6.4b and Figure 6.4c), less pronounced ridge-and-valley structures with smoother surfaces were observed. This was confirmed with AFM results (Table 6.2 and Figure 6.5b and Figure 6.5c). At higher ZIF-8 loadings (0.40 % in Figure 6.4d), more “cubic” features appear on the surface, which are most likely ZIF-8 nanoparticles covered with PA. These surface morphology changes resemble those observed in zeolite-TFN membranes [10]. Notably, none of the distinctive ZIF-8 crystal features shown in Fig. 1a were observed in the SEM images, suggesting that all nanoparticles in the PA layer were completely embedded inside the PA thin film. The pristine interfacial polymerization between MPD and TMC is generally believed to be diffusion-limited: MPD diffuses into the organic phase to react with TMC [47-49]. The reaction only stops when no MPD is able to further penetrate across the barrier layer formed in the reaction zone. For TFN membranes prepared with fillers in the aqueous solution, fillers were pre-deposited on the support; most of the fillers incorporated reside at the bottom region of the selective layer [12, 37, 50], showing no features induced by filler morphologies on the membrane top surface. For TFN membranes prepared with fillers in the organic solution, fillers were mostly incorporated in situ during the interfacial polymerization; more fillers reside in the middle and top regions of the selective layer [10, 12, 17], resulting in the more visible “cubic” features on the surfaces. For porous zeolite 4A and ZIF-8, MPD molecules (kinetic diameter > 5.9 Å) cannot diffuse through the pores. If the interface between the nascent PA film and the filler allowed no diffusion of MPD, the film formation would be
the same as that of the pristine. Relatively large particles would then be partially embedded within the PA matrix. If the interface between the PA film and the filler allowed diffusion of MPD, the film growth would only be terminated when the filler was fully encapsulated by the PA film. This is similar to the “template” effect proposed by Lind et al. [11] for zeolite 4A TFN membrane preparation. Further proof of filler encapsulation can be seen in Figure 6.6 where a micron-sized commercial ZIF-8 particle (Basolite® Z1200) was fully covered with PA film.

It should be noted that the filler encapsulation also changed the surface properties by changing the rate and the pathway of MPD diffusion. During the interfacial polymerization, lower MPD concentration would be expected at the top surface of the filler particles, which would result in reduced crosslinking extent, as the XPS results show in Table 6.2. Water contact angle measurements also verified the encapsulation and its effects on surface properties. If hydrophobic ZIF-8 nanoparticles were exposed on the surface, the apparent water contact angles would increase. However, decreased water contact angles θ were measured with increasing ZIF-8 loadings (Table 6.2). θ is closely related to surface roughness and material properties [45, 46]. After correcting with roughness area ratio r obtained from AFM measurements by \( \cos \theta^* = \cos \theta / r \) [45, 46], corrected water contact angles \( \theta^* \) decreased with increasing ZIF-8 loadings. This is related to the reduced crosslinking extent of the PA surface structure; more carboxylic acid groups exposed on the surface result in reduced water contact angle of TFN membranes. More hydrophilic surfaces could potentially reduce the organic fouling propensity of these membranes [51].
Figure 6.4. Surface SEM images of (a) pristine TFC membrane and (b-e) TFN membrane prepared with 0.05, 0.10, 0.20 and 0.40 % lab-made ZIF-8, respectively.
Figure 6.5. Surface AFM images of (a) pristine TFC membrane and (b-e) TFN membrane prepared with 0.05, 0.10, 0.20 and 0.40 % ZIF-8 nanoparticles, respectively.
Figure 6.6. Surface SEM image of a TFN membrane prepared with 0.10 % commercial ZIF-8 in the organic phase (after use in RO test; ZIF-8 purchased from Sigma-Aldrich, median particle size by volume D50 ~ 4.9 µm according to specification sheet; no delamination or physical failure of the embedded micron-sized ZIF-8 under the hydraulic pressure and shear force in RO test).

Cross-section TEM images (Figure 6.7) showed little change between the TFC and TFN membranes in selective layer thickness (~ 100 nm in all cases). The projected area TEM image in Figure 6.8 shows the embedded ZIF-8 particles (marked with an arrow) in the PA layer. The contrast between ZIF-8 and PA is not significant because of the inorganic-organic hybrid nature of ZIF-8. However, the sharp edges and cubic features of ZIF-8 [38] helped to identify the embedded particles in the selective layer, most of which reside under the PA ridges.
Figure 6.7. Cross-section TEM images of (a) pristine TFC membrane and (b-e) TFN membrane prepared with 0.05 %, 0.10 %, 0.20 % and 0.40 % ZIF-8, respectively.
Figure 6.8. Projected area TEM image of TFN membrane prepared with 0.40 % ZIF-8 (backing fabric and PSF support were removed; ZIF-8 particle edges marked with arrows).

Table 6.3 compares the desalination performance of membranes prepared in this work with commercial seawater and brackish water RO membranes, and with other high flux TFN membranes reported. The pristine TFC membranes in this study exhibited slightly higher water permeance and slightly lower NaCl rejection than commercial SW30HR and RO4. Adding 0.4 % ZIF-8 in the organic phase increased water permeance to 3.35±0.08 L/m²·h·bar, higher than BW30. This number is similar to the high water permeances of CNT-embedded TFN membranes [18, 29]. Silicalite-1 TFN membranes gave higher water permeance, but had inferior NaCl rejection [26]. Note that the membranes in this study were prepared using the most basic recipe of MPD/TMC. No additives or post-treatment were applied to improve membrane properties. Optimization in monomer
concentration and ratio, reaction time, and support properties could potentially further enhance desalination performance; additives, co-solvents, post-treatments etc. also help tailor the membrane properties to satisfy different applications.

**Table 6.3.** Desalination performance of commercial RO membranes, TFN membranes prepared with ZIF-8 and other high flux TFN membranes.

<table>
<thead>
<tr>
<th>Membrane designationa</th>
<th>Filler loadingb</th>
<th>Water permeance (L/m²·h·bar)</th>
<th>Apparent R\textsubscript{NaCl} (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow-SW30HR</td>
<td>-</td>
<td>1.12±0.01</td>
<td>99.4±0.3</td>
<td>This work</td>
</tr>
<tr>
<td>Dow-BW30</td>
<td>-</td>
<td>2.15±0.12</td>
<td>98.6±0.1</td>
<td>This work</td>
</tr>
<tr>
<td>Sepro-RO4</td>
<td>-</td>
<td>0.97±0.02</td>
<td>98.8±0.1</td>
<td>This work</td>
</tr>
<tr>
<td>Sepro-RO1</td>
<td>-</td>
<td>4.90±0.11</td>
<td>99.1±0.1</td>
<td>This work</td>
</tr>
<tr>
<td>Pristine TFC</td>
<td>-</td>
<td>1.28±0.03</td>
<td>98.1±0.2</td>
<td>This work</td>
</tr>
<tr>
<td>TFN-ZIF-8</td>
<td>0.40 w/v % (O)</td>
<td>3.35±0.08</td>
<td>98.5±0.5</td>
<td>This work</td>
</tr>
<tr>
<td>TFN-CNT\textsuperscript{c}</td>
<td>0.01 wt % (O)</td>
<td>3.57±0.54</td>
<td>99.3±0.2</td>
<td>[18]</td>
</tr>
<tr>
<td>TFN-CNT\textsuperscript{d}</td>
<td>0.375 wt % (A)</td>
<td>~ 3.31</td>
<td>~ 98.5</td>
<td>[29]</td>
</tr>
<tr>
<td>TFN-Silicalite-1\textsuperscript{d}</td>
<td>0.05 w/v % (O)</td>
<td>4.16</td>
<td>96.4</td>
<td>[26]</td>
</tr>
</tbody>
</table>
a SW30HR and RO4 - commercial seawater RO membranes; BW30 and RO1 - commercial brackish water RO membranes; all membranes were tested under 15.5 bar hydraulic pressure with 2000 ppm NaCl feed unless otherwise noted.

b “O” represents filler in organic phase; “A” represents filler in aqueous phase.

c Tested under 13.8 bar hydraulic pressure with 2000 ppm NaCl feed.

d Tested under 16.0 bar hydraulic pressure with 2000 ppm NaCl feed.

### 6.4. Conclusions

A hydrophobic, microporous, hybrid material ZIF-8 was systematically investigated as filler in thin-film-nanocomposite RO membranes. Nano-sized lab-made ZIF-8 increased water flux up to 162 % while maintaining NaCl rejection of 98 % under brackish water RO conditions. The surface of the selective layer with ZIF-8 is less crosslinked and more hydrophilic than that of the pristine PA membrane. Compared with the hydrophilic zeolite used in previous TFN studies, ZIF-8 theoretically has faster water transport within the framework and better compatibility with the polyamide matrix. This study demonstrates that MOFs offer novel approach in developing advanced TFN RO membranes for water purification.

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References


7. Conclusions and Suggested Future Work

7.1. Conclusions

The structure-property-performance relationships of the PA selective layer in TFC membranes were systematically investigated using novel characterization and membrane preparation methods. The PA layer was found to be heterogeneous, containing both dense polymer matrix regions and defective regions in dry and hydrated states. Process design and membrane preparation were tailored to improve separation performance. Specifically, the following conclusions can be drawn from the results of this research:

Convection through defective regions in the hydrated PA selective layer influences concentration polarization in osmotic processes and affects water transport through dense polymer matrix regions. When tested with pure water on the porous support side and 1.5 M (\(\pi = 72.7\) bar) sodium chloride solution on the selective layer side, applying 1.25 bar of hydraulic pressure to the porous support side increased water flux by an order of magnitude for PA-TFC membranes, but had negligible effect on CTA membrane flux. A solution-diffusion with defects model was established to describe this process and showed good agreement with experimental results. To confirm the existence of defects, a PA-TFC membrane was coated with a uniform, highly water-permeable, nonselective polymer. After applying the coating to block convection through defects, the influence of hydraulic pressure on water flux through this membrane essentially disappeared. Water flux through these defects was low (< 1% of total water flux for PA-TFC membranes) and of little consequence in practical FO or reverse osmosis (RO) applications. But in
pressure-assisted forward osmosis (PAFO) or pressure-retarded osmosis (PRO), convective transport through defects affected the solute concentration difference across the membrane selective layer, increasing or decreasing water flux through defect-free regions.

The PA material formed by MPD and TMC was confirmed to contain microporosity by gas adsorption measurements. Both N$_2$ and CO$_2$ adsorption isotherms, measured at 77 and 273 K, respectively, showed higher gas uptake in PA than in CTA or PSF. Calculated BET surface areas of PA based on N$_2$ adsorption and CO$_2$ adsorption were 33 and 92 m$^2$/g, respectively, much higher than those of CTA and PSF. The sharp gas uptake of PA at low relative pressures suggests the existence of micropores. A micropore size distribution in the range of 4.5-8.5 Å was obtained for PA based CO$_2$ adsorption using the NLDFT model.

Gas permeation in pristine PA-TFC membranes primarily occurs in defective regions; the dense polymer matrix shows high selectivity for various gas pairs when defective regions are plugged. Gas permeation of the pristine membranes showed close to Knudsen selectivity, which confirmed the existence of defects in the dry PA selective layer. After coating with Nafton®, gas permeance significantly decreased and gas selectivity sharply increased for small gases/large gases, CO$_2$/CH$_4$ and O$_2$/N$_2$, which demonstrates the separation properties of the dense PA matrix.

Incorporation of POSS nanomaterial in the PA selective layer increases the free volume of the dense PA matrix and increases water diffusion rate in RO. Main advantages of POSS include (i) small sizes (1-3 nm) which can efficiently disrupt chain
packing, (ii) functionality of the POSS cages to serve as crosslinking centers and (iii) good compatibility with PA because of the inorganic-organic hybrid nature of POSS. The effects of POSS incursion into the PA layer on the properties and desalination performance were systematically investigated by varying the functional groups of POSS, concentrations, routes, additives and reaction time. By physical blending a POSS with octaphenyl groups increased the water flux by 65% compared to the pristine PA membrane while maintaining high salt rejection. The selective layer of this membrane maintained the typical ridge-and-valley structure of aromatic PA thin films. Results with chemical fixation of POSS with octaammonium and octaamine groups were similar. Incursion of POSS with monoamine groups resulted in poor water flux, a smooth and more hydrophobic surface, and a much thicker (~400 nm) selective layer. POSS with octaammonium was also introduced through the aqueous route. With parameters optimized, water flux increased by 77%.

**Incorporation of ZIF-8 nanoparticles in the PA selective layer changes the structures of dense PA matrix regions and significantly increases the water diffusion rate of membranes in RO.** The TFN membranes were characterized with SEM, TEM, AFM, XPS, water contact angle measurements and reverse osmosis tests. Lab-made, nano-sized ZIF-8 nanoparticles (~200 nm) increased water permeance by 162% (3.35±0.08 L/m²·h·bar at 0.4% w/v loading) compared to the pristine PA membranes while maintaining high NaCl rejection. The TFN surfaces were less crosslinked and more hydrophilic than that of the pristine PA membrane. A filler encapsulation mechanism was proposed for the effects of filler on TFN membrane surface morphology and properties. Compared with the hydrophilic zeolite used in TFNs, ZIF-8 exhibits theoretically faster
water transport within the particle framework and better compatibility with the PA matrix. This study experimentally verified the potential use of ZIF-8 in advanced TFN RO membranes.

### 7.2. Suggestions for future work

The following topics are identified as areas for future work based on the findings of this dissertation:

**Optimization of coating layer formation on PA-TFC membranes.** A systematic investigation of coating conditions (e.g. polymer concentration, post-treatment) on coating layer formation would be beneficial to improve the separation properties of composite membranes in liquid and gas separations. In addition, the effects of the coating layer on the overall performance can be of interest in other emerging processes.

**Optimization of preparation conditions for PA-TFN membranes.** This study focused on evaluating the effects of nanofillers on properties of TFN membranes. Further improvement in desalination performance can be expected by varying additives, monomer concentrations, co-solvents and post-treatments. The changes of TFN membrane morphology and substructure would be of interest to correlate with desalination performance. These TFN membranes potentially exhibit superior gas separation properties compared to pristine membranes.