Tailored Multi-zoned Nylon 6,6 Supported Thin Film

Composite Membranes for Pressure Retarded Osmosis

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Abstract

Sustainable energy can be harnessed from natural or engineered salinity gradients using a process known as pressure-retarded osmosis (PRO). One major challenge is the lack of a suitable semi-permeable membrane that can withstand the pressure of the process yet still employ a support layer that is thin and compaction resistant in order to limit internal concentration polarization. In this study, we report on a full-scale produced thin film composite (TFC) PRO membrane support platform, which involves a customized, thin “multi-zone” nylon 6,6 structure integrated with a nonwoven scrim in order to enhance mechanical properties and compaction resistance. Two types of TFC membranes with different permselectivities were fabricated based on this support via in-situ interfacial polymerization and then tested under real PRO conditions. Overall our membranes exhibit higher compaction resistance than a commercial FO membrane evidenced by the less severe structural parameter increase under the ramping pressure. In addition, our TFC membranes were able to capture 65-81% of theoretical maximum power density performances in comparison to only 50% of the commercial FO membrane tested. These results demonstrate that compaction during PRO can substantially reduce power density and the effect can be lessened with appropriate membrane design.

Keywords: pressure retarded osmosis, internal concentration polarization, thin film composite, nylon 6,6, membrane compaction

1 Introduction

Osmotically driven processes are an emerging technology platform that harness the natural phenomenon of osmosis to address water and energy scarcity [1-3]. Osmotic pressure differential can be used to drive the permeation of water for applications of desalination, reuse,

and power production. For power production, pressure retarded osmosis can capture the work created when osmotic flow moves against a resistive force. The work from expanding draw solution volume may be captured through a mechanical energy recovery device such as turbine or pressure exchanger [4-6]. Pioneered by Loeb [4, 5, 7], PRO is a unique energy harvesting approach that has generated substantial interest over the last decade [6, 8-10].

One of the major obstacles to viable PRO technology is the lack of a membrane specifically designed to withstand the typical operating conditions of the process. Of the membrane platforms available, the thin film composite (TFC) has become a popular choice among academic groups and companies. These membranes are fabricated by in-situ interfacial polymerization which forms an aromatic polyamide selective layer on top of a porous supporting structure. This approach has been used to make RO membranes for decades [11-15] and should serve to provide a pressure tolerant and salt selective membrane for PRO. However, as has been determined critical for all osmotic process, the TFC support layer must be designed to be thinner, more porous, less tortuous, and hydrophilic in order to reduce the tendency for internal concentration polarization (ICP) [16-19].

Unfortunately, thin, highly porous support layers make for pressure intolerant TFC membranes. Recent studies show that although currently available FO membranes are able to achieve desirable performance in no-or low-pressure FO processes [20, 21], they are far from ideal under PRO conditions. The qualities that make the membranes good for FO (thin and porous support layers) have poor mechanical properties under pressure. These membranes can be deformed or even break under typical operating pressures of PRO[22, 23]. If they manage to maintain their integrity, the highly porous supporting layers can compact under the pressure, leading to substantial increases in mass transfer resistance and severe ICP. Overall, compaction

leads to a substantially lower power density than those predicted by conventional modeling. Some high performance FO flat sheet membranes exhibit high water flux under zero-transmembrane pressure FO while demonstrating power densities of less than 1 W/m² under hydraulic pressure in PRO[22, 24].

The challenge for PRO membrane designers is to promote good mass transfer and minimal ICP while maintaining mechanical strength. Recently, Song [25] and Bui [26] have introduced intrinsically low diffusion resistant nanofibers as a TFC PRO membrane support. While the compaction of these PRO membranes has never been studied explicitly, our previous work had found that compaction in nanofibers could be significant in pressures less than 10 psi [27]. Self-supported hollow fibers could be another potential option for PRO [10, 28, 29]. However, these membranes also are not exceptionally pressure tolerant unless they are made with extremely thick walls (high structural parameter) or small lumen sizes.

Membranes tailored for PRO must exhibit excellent pressure tolerance and compaction resistance while retaining low structural parameter, low cost, and manufacturability. In our previous work[30], we worked with 3M Purification in Meriden, CT to evaluate a commercial nylon based microfiltration membrane (the LifeASSURE™ BLA Series) as a support for a TFC membrane for FO. This membrane was mechanically robust due to an integrated nonwoven scrim, but was also very thick to the presence of thick porous layers which were needed for microfiltration applications. These membranes consisted of a supporting zone, which was in contact with the polyamide layer, a buffer zone that includes the embedded scrim, and a pre-filter zone that is normally used to prefilter solutions for larger solids during MF, but for this previous work served no purpose other than to make the membrane thicker. This was discussed as a drawback for using this type of membrane since it was simply used off-the-shelf and was not in

any way tailored for use in FO or other osmotic process.

In this study, we used this same platform to fabricate a new membrane but remove the prefilter zone entirely. The resulting membrane is a 2 zone structure with a supporting zone and a buffer zone with embedded mesh. The supporting zone was kept as thin as possible in order to ensure that the scrim would be embedded through as much of the membrane thickness as possible to create a “truss network” to resist compaction the rest of the support. The resultant membrane was half the thickness of the commercial membrane with a lower structural parameter without sacrificing strength. More importantly, this new membrane was fabricated on a roll-to-roll manufacturing line in collaboration with 3M Purification. This new support was used to support a polyamide selective layer formed through interfacial polymerization and the resulting TFC membrane was tested under FO and PRO conditions.

2 Materials and Methods

2.1 Customized Supporting Membrane

The nylon 6,6 support is manufactured at 3M Purification Inc. (Meriden CT). The process to form the “two-zone” support structure involves casting two dopes of nylon 6,6 solution onto a continuously supplied scrim using a “slot-die” casting apparatus. The scrim is pressure impregnated (pre-coat) with a nylon 6,6 dope first to reach to a desired penetration, which then allows subsequent coating of the supporting zone dope to form finer pores. This insures that the supporting zone does not intrude into the scrim layer which could lower porosity. The membrane is then formed by phase inversion and quenching, which is then rinsed and washed to form the multi-zone membrane. Details of formation methods of this support have been described elsewhere [31].

2.2 Interfacial polymerization

An aromatic polyamide thin film is formed onto the customized supporting membrane via the interfacial polymerization. A 2.0% (wt/v) m-phenylenediamine (MPD) solution in water and 0.15% (wt/v) trimesoyl chloride (TMC) in hexane were the reacting solutions. The aqueous phase also contained 2.0% (wt/v) TEA as an acid acceptor. The resulting TFC membrane was denoted as TFC-1. A second TFC membrane with lower selectivity and higher permeance was also prepared for comparison by adding 1.0% (wt/v) DMSO to the MPD solution [32]. This membrane is designated TFC-2.

To make each membrane, the customized nylon 6,6 support was taped onto a glass plate and then immersed into the aqueous MPD solution for 120s. Excess MPD solution was removed from the support membrane surface using a rubber roller. The support membranes were then dipped into TMC solution for 60 s to form an ultrathin polyamide film. The resulting composite membranes were air dried for 120 s and subsequently cured in an oven at 80 °C for 5 min. The TFC polyamide membranes were thoroughly washed with and stored in DI water at 4 °C before further use.

2.3 Support and TFC membrane characterization

Surface morphology and cross-sectional structure of the TFC membranes were imaged using a cold cathode field emission scanning electron microscope JSM-6335F (JEOL Company, USA). Cross-sectional samples were prepared for cross-sectional imaging using a freeze fracture technique involving liquid nitrogen. A razor blade was emerged into liquid nitrogen with the sample strip simultaneously and then used to quickly cut the sample in half once removed from the liquid nitrogen. Before imaging, samples were kept overnight in a desiccator and then sputter coated with a thin layer of platinum to obtain better contrast and to avoid charge accumulation. The thickness of the TFC membranes was measured using both a digital

micrometer at 5 different locations for each membrane sample and cross-sectional SEM images.

2.4 Determination of transport properties in cross-flow reverse osmosis

A bench-scale cross-flow RO testing unit was used to evaluate the pure water permeance, A , and solute permeability, B , of the TFC membranes at 20 ± 1 °C using a method described elsewhere [19, 30]. The system was operated at 150 psi with a fixed cross-flow velocity of 0.26 m/s ($Re \sim 1200$) using DI or a 2000 ppm NaCl feed solution to determine A and B , respectively. The determined transport properties were then used to derive structural parameter in FO tests. A commercial sea-water RO membrane (SW30-XLE) was provided by Dow Water and Process Solutions for structure comparison purposes.

2.5 Zero transmembrane pressure osmotic flux tests

Osmotic water flux and reverse salt flux of polyamide TFC membranes were evaluated using a custom lab-scale, cross-flow forward osmosis system described in detail elsewhere. A 0.5M, 1M and 1.5 M sodium chloride solution was used as the draw while using DI water as the feed at the temperature of 20 ± 1 °C. Osmotic flux tests were carried out with the membrane oriented in both PRO mode (the membrane active layer faces the draw solution) and FO mode (the membrane active layer faces the feed solution). The cross-flow velocities were kept at 0.18 m/s for both the feed and draw sides. Conductivity of the feed was used to measure the reverse salt flux through the membrane.

The osmotic water flux, J_w , was calculated by dividing the volumetric flux by the membrane area. By measuring the conductivity change during the test, the reverse salt flux, J_s , was calculated by dividing the NaCl mass flow rate by the membrane area. The structural parameter (S) can be determined by numerically solving the following equation where the membrane is orientated in PRO mode at zero-transmembrane pressure:

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} - \Delta P \right\} \quad (1)$$

162 In this equation, k is the external mass transfer coefficient, D is the diffusion coefficient of the
 163 draw solute, J_w is the measured water flux, B is the solute permeability, A is the pure water
 164 permeance, $\pi_{D,b}$ is the bulk osmotic pressure of the draw, and $\pi_{F,b}$ is the bulk osmotic pressure of
 165 the feed, and ΔP is the trans-membrane pressure. For our calculations, we simplified this
 166 equation for $\pi_{F,b}$ being zero (deionized water feed) to get

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w}{k}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} - \Delta P \right\} \quad (2)$$

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168 **2.5 Simulated PRO water flux, power density, and reverse salt flux**

169 The PRO water flux of TFC membranes can be numerically modeled as a function of
 170 transmembrane pressure, feed solution osmotic pressure, and draw solution osmotic pressure by
 171 specifying these parameters and solving Eq. (2) for the water flux through the membrane. To
 172 model flux, A and B were determined under RO test conditions and S was determined from the
 173 osmotic flux test in PRO mode at $\Delta P = 0$. It is important to note that the simulation was based on
 174 the assumption that the membrane permselectivity (A and B) and structural parameter (S) are not
 175 impacted by hydraulic pressure. The PRO power density (W) is equal to the product of the water
 176 flux through the membrane and the hydraulic pressure differential across the membrane (Eq. (3)).

$$W = J_w \Delta P \quad (3)$$

177 The reverse salt flux can also be predicted as a function of trans-membrane pressure using

178 the PRO specific salt flux equation derived by She [23]:

$$\frac{J_s}{J_w} = \frac{B}{A\beta R_g T} \left(1 + \frac{A\Delta P}{J_w} \right) \quad (4)$$

179 Rearranging Eq. (4), we obtained the equation to determine J_s :

$$J_s = \frac{B}{A\beta R_g T} (J_w + A\Delta P) \quad (5)$$

180 In this equation, J_s is the reverse salt flux, J_w is the simulated water flux, B is the solute
181 permeability, A is the pure water permeance, β is the Van't Hoff Coefficient, R_g is the gas
182 constant, T is the temperature, and ΔP is the trans-membrane pressure.

183 **2.6 PRO testing**

184 The TFC membranes were tested in triplicate on a bench scale pressure retarded osmosis
185 test system, which has been described elsewhere [26]. Tests were run at an operating
186 temperature of 20 °C using a 0.5 M NaCl draw solution and DI water feed with a cross-flow
187 velocity of 0.25 m/s for both draw and feed solutions. Both membranes were supported by tricot
188 RO permeate carriers packing the feed channel. The channel dimension is 3 in. long by 1 in.
189 wide by 1/8 in. deep. Note that under experimental conditions the tricot feed spacer generated a
190 large feed pressure drop with an inlet pressure of approximately 1.9 bar (27 psi) and an outlet
191 pressure of 0.2 bar (3 psi). An average feed pressure drop of 1bar was assumed. As no
192 noticeable pressure drop was observed for the draw solution and zero pressure is applied on the
193 feed side, the trans-membrane pressure is the applied pressure from the draw side minus the 1bar
194 pressure drop of the feed.

195 Tests were begun with a draw solution hydraulic pressure of 2.8 bar (40 psi) and
196 increased at 2.8 bar (40 psi) increments until reaching the flux reversal point, which is the
197 hydraulic pressure where the water flux is approximately zero. This is referred to as the

ascending pressure ramp. After data was collected at the flux reversal point, pressures were decreased in 2.8 bar (40 psi) increments to 2.8 bar (40 psi). This is referred to as the descending pressure ramp. At each pressure point, membranes were tested for 20 min after the system stabilized before moving to the next pressure. Operating the membrane through both ascending and descending pressures allows for the examination of irreversible change of membrane structure and properties.

The effective structural parameters at different transmembrane pressures were numerically solved by using PRO water flux and membrane properties obtained in RO tests in Eq. (2). Structural parameters at pressures close to the flux inversion point (i.e. 15.5 bar for TFC-1 and 12.8 bar for TFC-2) were not shown because as the flux approaches zero, Eq. (2) is no longer suitable to describe membrane transport behavior.

3 Results and Discussion

3.1 Support structure characterization

Fig. 1(a) and (b) represent the cross-sectional structures of the customized nylon 6,6 multi-zoned support and commercial nylon 6,6 phase-inversion MF support used in a previous study [30], respectively. Compared to the previously reported off-the-shelf nylon 6,6 MF membrane, this customized support retains the “supporting zone” that directly supports the polyamide thin film and “buffer zone” that is integrated with the nonwoven scrim. The customized membrane lacks the “pre-filter zone” with larger pores underneath the scrim. The lower thickness is important to keep the structure parameter low.

The fabrication approach allows for more than just the removal of a zone. In fact, each zone can be tailored for very specific structural properties. For instance, the pore size of supporting zone and buffer zone were controlled to be 0.04 and 0.1 μm , respectively. A pore size

of 0.04 μm to support the polyamide was selected based on previous study [34] shown that TFC membranes built on pores between 0.025 and 0.1 μm tend to give high selectivity and low reverse salt flux. Fig. 1(d) represents the pore morphology of the top surface of the supporting zone (i.e. the portion of support layer directly beneath the formed polyamide).

More importantly, however, is the ability to control individual zone thickness. During casting, supporting zone thickness was adjusted down to 20 μm . The thickness of the buffer zone is limited by the thickness of the scrim and remained at approximately 80 μm . The resulting support has two important features. First, the overall support layer thickness has been reduced by half when compared to the off-the-shelf membrane from our previous work. Second, the scrim is now embedded within 80% of the support material (in our previous work it was less than 50%), which is hypothesized to provide more structural support under pressure than a membrane with unsupported zones.

The structure of the new support is compared with a conventional RO TFC membrane (SW30-XLE) from Dow Water and Process Solutions (Fig. 1(c)). RO membranes are designed to operate under high pressures. As such, they are comprised of a polysulfone (PSu) mid-layer that is cast onto a relatively dense PET nonwoven. Interestingly, the PSu layer of the RO membrane contains macrovoids. The purpose of these macrovoids in RO is unknown, but they are likely to be compacted under high pressure. This compaction does not greatly impact RO performance because, relative to the selective layer, a compacted support layer still has far lower hydraulic resistance to flow. Compaction in PRO, however, will increase the structure parameter and hence the severity of ICP. It has been reported that spongy pore structure is essential for membrane robustness and high tolerance to pressure compaction, making it preferred in PRO applications [22]. Our customized support is entirely comprised of spongy pores with no

macrovoids while also having a “truss network” support in the embedded nonwoven scrim that is largely incompressible.

We illustrate this benefit in Figure 2. Under hydraulic pressure, the entire support layer of conventional TFC is prone to compaction and most of the pores are likely to experience strong deformation, especially the macrovoids. In our support, only the supporting zone is compressible. However, this comprises only 20% of the overall thickness of the membrane. The buffer zone, which contains the scrim, is resistant to compression due to the reinforcement from the integrated and rigid scrim. In addition, the buffer zone and the scrim form a composite structure, which enhances the overall membrane mechanical properties and compaction resistance, especially in the presence of open feed spacers. Studies have already demonstrated that using open spacers in the feed channel for PRO can lead to deflection of the membrane into the spacer openings. This can compromise membrane selectivity and longevity. The potential for the membrane to deform inversely proportional to the tensile strength of the membrane [33].

Figure 1 – Scanning electron micrographs (top): cross-sectional structure of (a) multi-zoned nylon 6,6 support at 250X; (b) commercial nylon 6,6 MF membrane at 200X; and (c) Dow SW30-XLE TFC membrane at 250X.

(Bottom): Surface morphology of (d) supporting zone of (a) at -10000X; (e) polyamide selective layer of TFC-1 at 5000X; and (f) polyamide selective layer of TFC-2 at 10000X.

Figure 2 – A schematic representation of a conventional TFC membrane vs. multi-zoned nylon 6,6 supported TFC membrane before and after pressure compaction.

3.2 Selective layer characterization

3.2.1 Surface morphology of polyamide thin film

Fig.1 (e) and (f) represent the surface morphology of polyamide selective layer of TFC-1 and TFC-2. Uniform and defect free films were obtained for both TFC membranes, employing different IP approaches. However, different morphologies were observed: a denser, smoother surface with few small “craters” was seen on TFC-1, whereas a rougher surface with more and larger “craters” appeared on TFC-2. The differences in roughness were relevant to this study and were not investigated further, but the images do indicate an intact and defect free polyamide layer was formed on the support using both interfacial polymerization approaches.

3.2.2 Transport properties determination under RO test conditions

TFC-1 and TFC-2 were tested in cross-flow reverse osmosis mode and their water permeability coefficient and solute permeability are shown in Table 1. Addition of DMSO results in permeability enhancement from 1.41 LMH/bar to 2.69 LMH/bar but also an increase of solute permeability from 0.22 LMH to 0.94 LMH. Addition of DMSO has been proved as an effective way to adjust the permselectivity due to the fact that DMSO has a solubility parameter between those of water and hexane. DMSO reduces the solubility difference between water and hexane, increasing miscibility between two phases, decreasing interfacial tension, and facilitating the mass transfer of MPD to the TMC organic phase [32]. The resulting TFC membrane exhibits a looser polyamide film with lower resistance to water and solute permeation.

Table 1 – Formation and transport properties of membranes considered in this study

Membranes	Aqueous phase			Organic phase (wt/v%)	A (LMH/Bar) ¹	B (LMH) ¹	S (μm) ²
	MPD	TEA	DMSO				
TFC-1	2	2	0	0.15	1.41±0.30	0.22±0.08	836±72
TFC-2	2	2	1	0.15	2.69±0.48	0.94±0.27	520±52
BLA010³	1	0	0	0.15	0.92±0.14	0.30±0.02	1940±240

¹ determined under RO test conditions: DI or 2000 ppm NaCl feed solution, 10.3 bar (150 psi), cross-flow velocity of 0.26 m/s, and temperature of 20 °C.

² determined under zero transmembrane pressure PRO test conditions: 0.5 M NaCl draw solution, DI feed solution, cross-flow velocity of 0.26 m/s, and temperature of 20 °C.

³ BLA010 data is from reference [30].

3.3 Osmotic flux performance under zero-transmembrane pressure

3.3.1 Osmotic water flux and reverse salt flux

The osmotic water flux and reverse salt flux performances at zero-transmembrane pressure are shown in Fig. 3. In PRO mode, the TFC-2 exhibited a noticeably higher water flux than the TFC-1 at low draw solution concentration (i.e. 0.5 M), but this difference became minimal at higher concentration (i.e. 1.5 M). This is because in PRO mode, using DI water as the feed, ICP can only be induced by reverse salt flux. At low draw solution concentrations, the effect of ICP induced by reverse salt flux is small (Fig. 3 bottom) and water flux is more affected by permeability of the membrane and the TFC-2 gave a greater water flux. However, at higher concentration, the ICP and osmotic pressure loss effect is amplified by increased reverse salt flux (Fig. 3 bottom), which works against the higher permeability of TFC-2. As a result, similar water fluxes were seen for the two membranes at 1.5 M NaCl. This suggests that a more permeable membrane might have a potential benefit in PRO application using low concentration draw solutions, such as open loop seawater PRO, but the benefit is lost as solute flux increases at higher draw solution concentrations. In FO mode, on the other hand, TFC-2 exhibited the same or slightly higher water flux than TFC-1 at each draw solution concentration.

When compared to the commercial MF membrane (BLA010) supported TFC at 1.5M NaCl from our previous study [30], both TFC-1 and TFC-2 showed substantially improved water flux in each mode. This can be attributed to the lower thickness and structure parameter of the customized membrane supports. However, there is also a significant increase in reverse salt flux for both membranes. In addition to the permselectivity difference, the reduction of membrane structural parameter also promotes the diffusion of draw solution into the feed. Overall, these new TFC membranes with a customized support show improved water flux performance and have potential applications where water flux rather than salt flux is the key factor of performance, as is the case with PRO.

Figure 3 – Membrane performance in zero transmembrane pressure osmotic flux tests: Top: water flux. Bottom: reverse salt flux. Experimental conditions: $20 \pm 1^\circ\text{C}$; 0.5, 1.0 and 1.5 M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 0.26 m/s on both sides of the membrane ($Re \sim 1200$). Membranes were also compared with BLA010 at 1.5 M NaCl [30].

3.3.2 Observed structural parameter

Observed structural parameter was determined by experimentally fitting the PRO mode water flux at zero transmembrane pressure as well as A and B value from RO into Eq. (2). As shown in Table 1, TFC-2 exhibited lower structural parameter than TFC-1; however, theoretically, two TFC membranes should exhibit equal structural parameter since the same support was used. One possible explanation is that the membrane transport properties used to derive structural parameter are measured in RO (A and B) but might actually be different in FO. RO places the

polyamide layer under stresses that are not present in FO. Furthermore, the structure parameter models have come under increased scrutiny in recent studies. Our previous work has shown that these models are relatively inaccurate at predicting the true structural parameter value [35]. Nevertheless, these models are the best that are available at present and the value itself still represents a generalized mass transfer resistance of the membrane support during osmotic flow. Our customized support exhibits a structural parameter that is one-third to one-half of the commercially available BLA010 MF membrane support [30].

3.4 PRO performance

3.4.1 Water flux

Experimentally observed and simulated PRO water flux is shown in Fig. 4 (top). Experimentally, both TFC membranes exhibited the expected decrease in water flux with increasing hydraulic pressure, though the decline deviated from linearity at higher pressure. Such a phenomenon has been observed elsewhere [26] and could suggest the membrane integrity is being compromised. However, upon reducing pressure, the membrane performance was unchanged, suggesting that the membrane is still intact and that this is a reversible behavior. This strongly suggests that the membrane integrity has not been compromised.

One explanation for this could be that the pressure causes some compaction (which is expected) and the corresponding increase in the structural parameter worsens ICP which decreases flux. Note that the simulated flux, which does not account for compaction, shows no indication of this deviation. While we were hoping to see none of this in our newly designed membranes, the supporting zone of the membrane is 20 μm thick and still susceptible to compaction.

It is also worthwhile to note that the feed spacer, which is a packed layer of tricot, will

experience compaction as well under higher pressure. This not only will reduce mass transfer in the channel itself by tightening the structure and reducing Reynolds number, but it will press the spacer against the membrane and block pathways for water transport. This is usually referred to as the “shadow effect” [21]. A combined blocking of the membrane for water and solute transport with the lower Reynolds number in the channel, neither of which are captured in the model, will result in some deviation.

Figure 4 – PRO performance of TFC membranes. Top: water flux. Bottom: power density. Experimental conditions: 20 ± 1 °C; 0.5 M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 0.26 m/s on both sides of the membrane ($Re \sim 1200$).

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390 For ideal conditions where a membrane is perfectly selective and no polarization effects are
391 considered, the power density curve in PRO is symmetric and parabolic. The flux reversal point
392 occurs where the trans-membrane pressure equals the osmotic pressure difference, which is
393 approximately 24 bar (350 psi) by using 0.5 M NaCl draw and DI feed. The maximum power
394 density ($W_{\max}$) should occur at a hydraulic pressure equal to one-half of the osmotic pressure
395 difference across the membrane (~12 bar or 175 psi). Using Eq. (2), the simulated model
396 corrects for ECP, ICP, and membrane selectivity, predicting that both $W_{\max}$, the pressure at $W_{\max}$,
397 and flux inversion point shift lower for both membranes. In addition, the simulation predicts that
398 the $W_{\max}$ of TFC-2 is approximately 30% higher than that of TFC-1.

399 The observed power densities of both membranes agree well with the simulation at low
400 pressure but deviate at higher pressure. This follows the same trends with the water flux
401 predictions. Both the observed $W_{\max}$ and flux inversion point occur at lower pressures than the
402 model predicts, especially for less selective TFC-2 membrane. The observed $W_{\max}$ and flux
403 inversion of TFC-1 occur at 10 and 15.5 bar, respectively, whereas for TFC-2, it is 7.5 and 12 bar,
404 respectively. In addition, TFC-1 achieved $W_{\max}$ of 2.3 W/m^2 , 80% of what the model predicts.
405 However for TFC-2, the actual performance only matched the $W_{\max}$ of TFC-1, and was 35%
406 lower than the model prediction. Interestingly enough, although both the zero-transmembrane
407 FO test (PRO mode) and the simulation suggest the more permeable and less selective TFC-2
408 would produce a higher power density due to higher water flux, this is not the case under
409 pressurized conditions. The higher salt flux from the TFC-2 membrane suppresses flux through
410 the enhance ICP effect.

3.4.3 Reverse salt flux

Both the experimentally observed and simulated reverse salt fluxes for membranes tested under different trans-membrane pressures can be seen in Fig. 5. At each pressure point, TFC-1 exhibits expectedly lower J_s than TFC-2 due to its higher selectivity. Both experimental and simulated J_s increased with increasing ΔP for both membranes. However, while the simulated data predicts only modest changes in J_s , the experimentally measured J_s increased drastically at higher ΔP . The reason why Eq. (5) underestimates J_s at higher pressure is probably due to the fact that it assumes the membrane separation properties (A and B) remain constant under the PRO testing conditions. The substantial differences between the modeled and experimental salt fluxes are evidence to the contrary. The less selective TFC-2 seems to be more susceptible to this variation as it shows an over 500% deviation from the predicted salt flux.

As discussed in section 3.4.1, the increase of salt flux is unlikely due to pressure induced defects because there is no hysteresis on the descending pressure data. It is possible that this increase in salt flux is due to “elastic” stretching of membrane. The membrane area between the feed spacer grids is unsupported and can deform under applied pressure, which may lead to the displacement and elongation of polymer chains [33]. The higher the applied pressure, the more severe the membrane deformation is. This phenomenon has already been observed on HTI’s CTA membrane [23] under PRO conditions. This would also be supported by the TFC-2 data. The TFC-2 membrane was intentionally designed with less cross-linking density and is hence less rigid and more susceptible to stretching. Nevertheless, if there is any change of the selective layer properties under pressure, this change is reversible, because any permanent change would cause dramatic deviation of the reverse salt flux between ascending and descending pressure

ramps.

Figure 5 – Reverse salt flux under PRO tests. Inset shows simulated flux zoomed in. Experimental conditions: 20 ± 1 °C; 0.5 M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 0.26 m/s on both sides of the membrane ($Re \sim 1200$).

3.4.4 Effective structural parameter

The simulation of structural parameter based on Eq. (2) assume that A and B determined in RO are the same as those in PRO and maintain constant with increasing pressure. However, a recent study using a modified RO test protocol in a spacer-filled channel to determine the membrane properties found that the obtained A and B are different than those determined using this conventional RO method [21]. Another study has also found that even when supported by a RO permeate carrier, there is still a slight increase of A and B for a commercial FO membrane when applied pressure is increased due to a deformation of membrane [33]. In this study, the water flux and reverse salt flux data in PRO tests further support this point. This evidence suggests that the assumptions used to derive structural parameter might not be valid and could bring errors to the calculation. However, there are no other models that have been demonstrated

to be more accurate at present, so this conventional method that has been widely used in the FO community was used in this study to model structure parameter.

As shown in Fig. 6, the effective structural parameter increases with increasing pressure for both membranes. This result is consistent with another study on deformation of commercial FO membrane in the presence of similar spacers under PRO [33]. Compaction will decrease the thickness of the support layer but will also block or collapse some pores, causing a reduction of porosity and an increase in tortuosity. The steadily increasing structural parameters for all these membranes implies that the loss of porosity and corresponding increase in the tortuosity prove more detrimental than the beneficial effect of thickness reduction from compaction. The small difference in structural parameter between ascending and descending pressure ramps indicates, however, that the membrane compaction effect is also largely reversible though may have small degree of permanence. Further study is warranted on the dynamic response of these membranes under varying pressure, but PRO operation at scale will likely not involve changing pressures.

Figure 6 – Effective structural parameter under PRO tests. Experimental conditions: 20 ± 1 °C; 0.5 M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 0.26 m/s on both sides of the membrane ($Re \sim 1200$). Structural parameters at flux inversion point were not included (i.e. 15.5 bar for TFC-1 and 12.8 bar for TFC-2) to avoid the possible errors brought by the model failure when membrane transit to RO regime.

3.4.5 Comparison with a commercial TFC-FO/PRO membrane

From the above discussion we know that membrane deformation due to pressure compaction is the likely culprit in causing the increase of structural parameter and deviation between the real and the theoretical power density. Although quantifying membrane compressibility under applied hydraulic pressure is beyond the scope of this study, the difference between these values can provide us with important insight into the impact of compaction. For an ideal PRO membrane with a non-compactable support and selective layer structure, structural parameters should remain constant under ramping pressure and the real PRO performance should approach the theoretical projection. Therefore we compare structural parameter and the ratio of real maximum power density over theoretical value of a commercial TFC-FO/PRO membrane from Oasys Water, which have been investigated in our previous study [36]. Note that the PRO performance data of the Oasys membrane were obtained under the identical testing conditions and the simulation was based on the same model that we used in this study.

As shown in Table 2, the TFC-1 can capture 82% of its theoretical power, whereas for TFC-2 the percentage is 65%. This suggests that a more rigid polyamide selective layer with higher cross-linking density is more tolerant to deformation and can better preserve membrane performances. In comparison to the Oasys TFC membrane, even the TFC-2 still exhibits better pressure compaction resistance, as the commercial membrane can only achieve the $W_{\max}$ 50% of its theoretical value. In addition, the structural parameter of Oasys membrane increases more sharply than our TFC membrane under the same ramping pressure. The structural parameters of the TFC-1 and TFC-2 only increase 55% and 66% as pressure increases from 1.7 to 10 bar, respectively, in comparison to 400% for the Oasys membrane [36]. We believe our unique multi-zone, macrovoid-free support design greatly improves membrane robustness under hydraulic

pressure. The commercial FO membrane exhibits compaction from a morphology incorporating macrovoids and insufficient integration between support layers and the scrim. It is important to note, however, that the Oasys membrane is not specifically designed for PRO applications.

Though this new support design can effectively prevent membrane performance loss from compaction, its power densities are still relatively low, especially when compared to some of the more novel membrane structures discussed in the literature [25]. This is probably due to the intrinsically high structural parameter of spongy pores which have higher tortuosity than dendritic pores or macrovoids. There are opportunities to improve upon this platform and others by incorporating thinner compression resistant scrims or by improving protection of the polyamide layer to deformation through the use of smaller supporting layers pores [25, 37], though these approaches might sacrifice tensile strength and permeance, respectively.

Membranes	Support Structure Descriptions	Empirical $P_{\max}$ (W/m ²)	Simulated $P_{\max}$ (W/m ²)	Ratio	References
TFC-1	Multi-zoned spongy pores, embedded scrim	2.3	2.8	0.82	This work
TFC-2	Multi-zoned spongy pores, embedded scrim	2.3	3.5	0.65	This work
Oasys TFC	Macrovoids, non-embedded scrim	~3	~6	0.5	[36]

Table 2 – Comparison of TFC-PRO membrane performance.

4 Conclusions

In this study, we report on a new thin film composite membrane based on a customizer support structure fabricated on a commercial casting line from 3M Purification, Inc. This membrane has been engineered to have a thinner, 2-zone structure than the off-the-shelf membranes currently manufactured by 3M on the same line. The membrane exhibits excellent permselective properties and compaction resistance under PRO conditions. These findings are important since these membrane can be easily fabricated at scale with tailored characteristics that have benefit to both PRO and FO.

5. Acknowledgements

The authors gratefully acknowledge funding from the National Science Foundation (CBET #1067564), U.S. Environmental Protection Agency (#R834872), and the Department of Energy (DE-EE00003226). The corresponding author also received support from the 3M Nontenured Faculty Award. Additional funding for Jason Arena was from the National Water Research Institute and American Membrane Technology Association Membrane Technology Research Fellowship and the National Science Foundation GK-12 Fellowship.

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