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Fabrication and Characterization of Fabric-reinforced Pressure Retarded Osmosis Membranes for Osmotic Power Harvesting

by

Qianhong She\textsuperscript{a,1}, Jing Wei\textsuperscript{a,1}, Ning Ma\textsuperscript{a,†}, Victor Sim\textsuperscript{a}, Anthony G. Fane\textsuperscript{a,b}, Rong Wang\textsuperscript{a,b,*}, Chuyang Y. Tang\textsuperscript{c,**}

\textsuperscript{a} Singapore Membrane Technology Centre, Nanyang Environment & Water Research Institute, Nanyang Technological University, Singapore 637141
\textsuperscript{b} School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798
\textsuperscript{c} Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong

* Corresponding author address: Nanyang Technological University, N1-01a-16/N1-01a-22, 50 Nanyang Avenue, Singapore, 639798; Tel.: +65 6790 5327; fax: +65 6791 0676; E-mail: rwang@ntu.edu.sg

** Co-corresponding author address: The University of Hong Kong, HW6-19B, Haking Wong Building, Pokfulam, Hong Kong; Tel: +852 2859 1976; Fax: +852 2559 5337; Email: tangc@hku.hk

\textsuperscript{1} These authors contributed equally to this study.

† present address: Beijing Key Laboratory of Water Environmental and Ecological Technology for River Basins, Beijing Water Science and Technology Institute, Beijing 100048, China
Abstract

In recent years, pressure retarded osmosis (PRO) has attracted increasing interest in the harvesting of the renewable osmotic power. However, its performance can be significantly influenced by the membrane deformation in the operation when the PRO membrane is lack of sufficient mechanical strength. In this study, we fabricated three different fabric-reinforced thin-film composite (TFC) flat-sheet PRO membranes for osmotic power harvesting. These membranes were prepared through integrating three different types of fabric reinforcement (i.e., tricot fabric, woven fabric and nonwoven fabric) in the membrane substrate layer. It was found that the fabric reinforcement plays an important role in the membrane structural property and mechanical property, both of which can significantly influence the PRO performance. The nonwoven-fabric-reinforced membrane had the greatest structural parameter and thus exhibited the lowest performance. Although the tricot-fabric-reinforced membrane and the woven-fabric-reinforced membrane had similar performance in the forward osmosis (FO) condition ($\Delta P=0$), the former showed superior performance in the PRO condition ($\Delta P>0$). This is mainly because the tricot-fabric-reinforced membrane had better mechanical resistance to the multi-directional tensile stretching, which rendered it less prone to changes in structural and separation properties in the PRO operation. This further suggests that the tricot fabric has high potential for future PRO membrane fabrication. The current study also elaborates the coupled effects of compression and stretching on PRO membrane deformation and performance. The results obtained in this study may provide important insights into reinforced PRO membrane design.

Keywords: pressure retarded osmosis (PRO); fabric-reinforced membrane; tricot fabric; membrane deformation; stretching; osmotic power.
1. Introduction

Pressure retarded osmosis (PRO) is one of the most promising technologies for harvesting the renewable osmotic power from the mixing of two solutions with different salinities [1-5]. In PRO, water in a low salinity feed solution (FS) permeates through a selective membrane into a high salinity draw solution (DS) where a hydraulic pressure lower than the osmotic pressure difference across the membrane is applied [6]. In this controlled mixing process, the osmotic power can be eventually harvested in terms of electricity by running the pressurized DS through a hydroturbine.

Although PRO has been proposed for around 40 years [7], its development was retarded primarily due to the lack of suitable PRO membranes from the technical point of view. Early studies revealed that the membranes used for PRO could suffer severe internal concentration polarization (ICP) within the support layer and thus delivered extremely low performance [8-12]. While the ICP can be reduced by tailoring the membrane support layer [13-17], recent studies found that membrane deformation in the operation can also significantly reduce the PRO performance [18-20]. Membrane deformation gives rise to a substantially increased reverse solute diffusion (RSD, i.e., solute leakage from DS into FS) that can further enhance ICP [18, 19]. As such, the mechanical strength has been generally regarded as one of the critical criteria for PRO membranes [18-23]. Recently, it was reported that robust hollow-fibre membranes can be fabricated for PRO with appreciable power density [24-26]. The improved mechanical strength of those hollow-fibre membranes was achieved by using new types of materials as well as optimizing the substrate structure and/or hollow-fibre dimension [24-26].
In the context of flat-sheet membrane, the mechanical strength can be significantly reinforced by integrating a suitable fabric in the support layer in addition to using above-mentioned strategies for reinforcing hollow-fibre membrane. For example, commercial RO membranes are typically reinforced with a nonwoven fabric at the back of substrate layer. However, a fabric reinforcement integrated in the support layer could result in an increased membrane structural parameter [14] and thereby an increased ICP effect in the PRO process. Thus, many flat-sheet PRO membranes reported in the literature only consisted of a polymeric substrate layer and a rejection layer without using a fabric reinforcement [27-30]. This, in turn, could result in a remarkably reduced membrane mechanical strength [23], which is likely to reduce the PRO performance and limit the large-scale membrane production. Although some membranes integrated a nonwoven fabric or a woven fabric in the support layer [18, 22, 23, 31], relatively low PRO performance was obtained in the testing. Therefore, it is necessary to select new types of fabric for PRO membrane fabrication and further study the effect of fabric on the PRO membrane performance.

In the PRO operation, She et al. revealed that the membrane mechanical stability of a flat-sheet membrane is not only influenced by the membrane intrinsic mechanical strength but also strongly dependent on the spacer geometry in the feed flow channel [19]. A feed spacer with greater opening size could result in more severe membrane deformation and thus lower PRO performance [19]. Therefore, many studies selected the feed spacer with very small openings to sufficiently support the membranes against tensile deformation in the PRO testing (e.g., using fine mesh [27-29, 32] or RO permeate carrier [19, 30, 33]). However, using this type of spacer could result in several adverse effects: (1) increase feed flow resistance due to confined space in
the feed channel [19, 34]; (2) reduce effective membrane filtration area due to “shadow effect” [19, 20]; (3) potentially exacerbate external fouling on membrane surface due to accumulation of foulants within the voids of the spacer [35-37]. Therefore, it should be more practical to use a typical net-type feed spacer (as the one used in RO/NF/UF spiral wound modules) in the PRO testing. In addition, there is an urgent need to develop stronger PRO membranes that can use typical net-type spacers in the PRO process without loss of membrane mechanical stability.

The objectives of this study are to (1) fabricate and characterize fabric-reinforced TFC PRO membranes for osmotic power harvesting, and (2) explore the underlying mechanisms on PRO membrane deformation and performance when using a typical net-type feed spacer in the testing. For the first time, tricot fabric, which allows isotropic transfer of multi-directional tensile forces, is selected to reinforce the PRO membrane in this study. Woven fabric and nonwoven fabric are also selected for comparison. The implications for reinforced-PRO membrane design are elaborated.

2. Materials and Methods

2.1. Chemicals and materials

Unless otherwise specified, all chemicals used in current study were ACS grade. Polysulfone beads (PSf, molecular weight 75,000 – 81,000 Da, Solvay Advanced Polymers, LLC, GA) were used for casting membrane substrates. N-methyl-2-pyrrolidone (NMP, Merck Schuchardt OHG, Hohenbrunn) was used as the solvent for preparing casting solution. Polyvinyl pyrrolidone (PVP, average molecular weight 1,300,000 Da, Alfa Aesar, MA) were used as pore former in the casting solution. Chemicals used for interfacial polymerization included m-phenylenediamine.
(MPD, Sigma – Aldrich Pte. Ltd, Singapore), trimesoyl chloride (TMC, Sigma-Aldrich), and n-
hexane (Merck). Sodium chloride (NaCl, Merck, PH EUR) was dissolved in ultrapure water to
prepare both draw solutions and feed solutions. The Ultrapure water with a resistivity of 18.22
MΩ.cm was supplied from a Milli-Q system (Millipore Singapore Pte Ltd). Three types of
polyester (PET) fabric reinforcement (Figure 1) were selected to fabricate the reinforced PRO
membrane. They were non-woven fabric, woven fabric and tricot fabric. Detailed
characterization of the morphology and properties of these fabrics are described in Section 3.1.

2.2. Preparation of fabric-reinforced TFC membranes

2.2.1. Preparation of fabric-reinforced support layer

The fabric-reinforced support layer was casted via phase inversion method, following the
procedure described previously [14]. Briefly, the dope solution for casting the support layer was
prepared by dissolving PSf (18.0 wt. %) and PVP (10.0 wt. %) in NMP and stirred by a magnetic
stirrer at 70 °C until a homogeneous and transparent solution was obtained. The dope solution
was then cooled down to room temperature (23 °C) and degassed statically. The selected fabric
reinforcement was smoothly attached on a glass plate. The casting solution was spread onto the
fabric using a casting knife with a fix height of 250 µm. The glass plate together with the fabric
and whole polymer film were then quickly and smoothly immersed into a coagulant bath
containing room temperature tap water for phase inversion. The nascent fabric-reinforced
support layer was transferred into a flowing water bath to remove residual solvent overnight and
then stored in ultrapure water before use. The three types of fabric-reinforced support layers
were prepared using the identical dope solution and casting conditions.
2.2.2. Preparation of polyamide active layer

A dense polyamide active layer was formed on the top of the support layer through interfacial polymerization using the similar method reported previously [14]. Briefly, the aqueous phase was prepared by dissolving 1.5 wt. % MPD in water, while the organic phase was prepared by dissolving 0.1 wt./v % TMC in n-hexane. The support layer was heated in 70 °C ultrapure water for 2 min and then cooled down to room temperature (23 °C) in ultrapure water, in order to form a defect-free and stable structure of support layer [14, 38]. The pretreated support layer was soaked into the MPD solution for 5 minutes. Then, the excess MPD solution on the top surface of the support layer was removed by compressed nitrogen gas using an air knife. Next, the TMC solution was poured onto the MPD-soaked support layer surface and was allowed to react with the residual MPD for 1 min to form the polyamide rejection layer. The resultant TFC composite membrane was rinsed thoroughly using tap water to remove the residual reactants and was stored in ultrapure water prior to characterization.

2.3. Membrane characterization

2.3.1. Membrane morphology and mechanical strength

The morphologies of the fabrics and reinforced TFC PRO membranes were observed using a Joel JSM 7600F thermal field emission scanning electron microscopy (FESEM). Samples were first fractured in liquid nitrogen before drying in vacuum in a freeze drier (Christ Alphr 1-4 LD, Germany) overnight. Then, they were coated with a thin layer (~5 nm) of platinum in an EMITECH SC7620 sputter coater (Quorum Technologies Ltd, UK). All samples were scanned at an accelerating voltage of 2 kV or 5 kV. The tensile properties of fabrics and membranes were measured using an Instron 5567 tensile machine at a constant crosshead speed of 50 mm/min.
with a 500 N load cell. Samples were cut with a dumbbell die (3.18 mm in width of narrow section and 9.53 mm in length of narrow section) in accordance to the standard ASTM D638-V [39]. At least three replicates of each sample were measured.

2.3.2. Membrane separation properties

It was reported that the membrane separation properties could change with the applied pressure in PRO testing due to membrane deformation [19, 20]. In this study, the actual separation properties of the reinforced PRO membrane at different applied pressures were measured following the modified RO method as reported elsewhere [19]. Briefly, the modified RO test was performed in the same PRO membrane testing cell, where the RO feed solution was circulated and pressurized in the PRO DS channel while the RO permeate was collected from the PRO FS channel. In RO testing, the same PRO feed spacer was placed in the RO permeate channel to simulate the actual membrane state at applied pressures. 10 mM NaCl was used as feed solution and the cross-flow velocity was maintained at 11.1 cm/s. At each applied pressure, the membrane was tested at least for ~45 min to reach a stable permeate flux. The RO permeate water was collected at predetermined time interval to determine the water flux and solute rejection, whereby the membrane water permeability \( A \) and solute permeability \( B \) were determined [19].

2.3.3. PRO performance evaluation

PRO performance of the reinforced PRO membranes was evaluated in a cross-flow PRO experimental setup that has been reported elsewhere [19, 40]. The PRO test cell was comprised of two symmetric Delrin half-cells with identical dimension of flow channel (85 mm length \( \times \) 39
mm width). Identical net-type spacers were placed in both DS and FS flow channels. This spacer has also been used in our previous study [19] and has a thickness of 1.55 mm, filament diameter of 0.90 mm, opening size of 2.6 mm and opening ratio (i.e., the ratio of opening area over total spacer area) of 55%. The membrane was placed in the cell with its active layer facing the draw solution (AL-DS).

In each PRO testing, the membrane was initially operated at zero pressure (i.e., a FO process). Then, the pressure applied in the DS was gradually increased to a predetermined value. At each applied pressure, the membrane was tested for at least ~45 minutes to reach a stable flux. The hydraulic pressure in the DS flow channel and the back pressure in FS flow channel were recorded with digital pressure transducers. The effective applied pressure on the membrane is the difference between the applied pressures in DS and FS flow channels. During the PRO process, the DS tank was dosed with a concentrated NaCl solution to maintain the concentration of DS constant. In addition, the FS tank was continuously topped up with stocked ultrapure water to maintain the FS volume constant. The weight change of the stocked ultrapure water with time was used to determine the water flux ($J_w$). The conductivity in FS tank was also monitored at predetermined time intervals to determine the reverse solute flux ($J_s$) following the method reported previously [19]. The testing conditions include draw solution of 1 M NaCl, feed solution of 10 mM NaCl, temperature of $25 \pm 0.5$ °C in both the DS and the FS, and cross-flow velocity of 11.1 cm/s.
3. Results and discussion

3.1. Morphology and mechanical properties of fabric reinforcements and reinforced PRO membranes

Figure 1 shows the SEM images of nonwoven (Figure 1a), woven (Figure 1b) and tricot fabric reinforcement (Figure 1c) used for the reinforced PRO membranes in this study. For nonwoven fabric, the PET fibres are randomly bonded together into a flat sheet. This type of fabric is typically used to reinforce the RO membrane mechanical strength [41]. Nevertheless, it is much less porous compared to woven fabric and tricot fabric. This suggests that the nonwoven fabric may have greater resistance to mass transfer and induce more severe ICP when used in FO/PRO membranes. In contrast, woven fabric and tricot fabric are much more porous. For woven fabric, the opening size between adjacent fibres is ~170 µm and the opening ratio is ~0.40, and corresponding parameters for tricot fabric are < 250 µm and ~0.35, respectively. Thus, compared to nonwoven fabric, the woven fabric and tricot fabric may be better candidates acting as support for fabricating osmotic membranes with a smaller structural parameter.

FIGURE 1

Unlike the nonwoven fabric with an irregular pattern, woven fabric and tricot fabric are regularly structured. Woven fabric has a mesh structure, which is formed in a weaving method by interlacing warp (0°) fibres and weft (90°) fibres in a plain weave style according to the textile manufacturing industry [42]. However, this mesh structure results in significantly varied resistances to the stretching of the fabric along different directions. As indicated by the tensile properties in Table 1, the woven fabric is much more stretchable (with weaker tensile resistance) in diagonal directions than that along the fiber directions. In comparison, tricot fabric has double-
layered structure and asymmetric surfaces viewed from both sides. It has a close-knit design, whereby fibres run in a crosswise direction in the top layer (Figure 1c1) while fibres run in a lengthwise direction in the bottom layer (Figure 1c2). The two layers are interlooped with fibres following a yarn pattern, which gives the tricot fabric a sturdy appearance. The tensile stretching measurements (Table 1) reveal that the tricot fabric exhibits very similar resistances to stretching in different directions. This indicates that the multi-layered tricot fabric produced by the knitting method ensures a more uniform and isotropic transfer of mechanical force upon stretching.

TABLE 1

Figure 2 shows the SEM images of the TFC PRO membranes reinforced with using the fabrics in Figure 1. For all the three fabric-reinforced membranes, their active layers had similar valley-and-ridge surfaces (Figure 2 a1-c1) as typical polyamide layer formed by MPD and TMC [14]. In addition, their substrate layers had sponge-like structures without macrovoids. The pores in the top region of the substrate layer were generally smaller than those in the bottom region of the substrate layer. For nonwoven-fabric-reinforced TFC membrane (TFC-N), the whole PSf substrate layer was formed on the surface of the fabric, while for woven-fabric-reinforced TFC membrane (TFC-W) and tricot-fabric-reinforced TFC membrane (TFC-T), the fabric was partially imbedded into the PSf substrate layer. The tensile properties of these fabric-reinforced membranes are shown in Table 1. The results revealed that the tensile behavior of the fabric-reinforced membrane was consistent with that of the corresponding fabric. For example, the TFC-W membrane exhibited a much more remarkable variation in the tensile strength upon stretching in different directions, while the TFC-T membrane was more stable against multi-directional stretching. This indicates that the tensile properties of the fabric reinforcement can
play a dominant role in those of the fabric-reinforced membrane. The results of tensile
measurement also suggest that the TFC-T membrane may have better mechanical stability and
performance in the PRO testing, which will be demonstrated in the subsequent sections.

FIGURE 2

3.2. Separation parameters of fabric-reinforced TFC membranes

Figure 3 shows the water permeability ($A$) and solute/water selectivity (i.e., $B/A$ that is inversely
proportional to rejection) of the fabric-reinforced TFC membranes at different applied pressures
measured in the modified RO mode. For all the membranes, $A$ values were relatively more stable
than $B/A$ values against the applied pressure. The $A$ values of TFC-T and TFC-W were nearly
unchanged with increasing pressures, while $A$ values of TFC-N only slightly increased with
increasing pressures. Since the membrane in the testing would undergo both hydraulic
compaction and tensile stretching, the results indicate that the coupled effects could not result in
significant differences on the $A$ values for these fabric-reinforced TFC membranes. The slight
increase of $A$ value of TFC-N membrane at high applied pressures is probably caused by the severe stretching effect, which results from the
irregular structure (and thus varied mechanical resistance to multi-directional stretching) of the
nonwoven fabric as well as the relatively small membrane mechanical resistance (i.e., small $E \times t$). In existing literature of PRO and pressure assisted osmosis, significant changes of $A$ value
have been reported for membranes under severe mechanical stretching [19, 43]. More
systematic study will be performed in the future to identify all the possible reasons. Above
observation is different from that of support layers. As shown in Figure B1 in Appendix B, the $A$
values of the support layer decreased with pressures, where hydraulic compaction might play a dominate role.

Figure 3

Interestingly, $B/A$ values for these fabric-reinforced TFC membranes increased with the initial increase of pressures but then decreased with further increasing the pressures. The strong pressure-dependent $B/A$ might be caused by the structural change of the polyamide chains in the selective active layer due to the coupled effects of hydraulic compression and tensile stretching in the modified RO operation. The initial increase of $B/A$ may be dominated by the stretching of polyamide layer, where the hydraulic compaction may be less significant at relatively lower applied pressures (< 15 bar). This is consistent with previous observations of increased $B/A$ for CTA FO membrane at elevated pressures [19]. When the applied pressures were further increased to a certain level (> 15 bar), the effect of hydraulic compaction may suppress the effect of tensile stretching and become dominant over the membrane selectivity, which resulted in the reduced $B/A$ values. The reduced $B/A$ at high applied pressures has been extensively observed in RO/NF membranes [44-48].

While the $B/A$ for all the fabric-reinforced TFC membranes responded similarly to the applied pressures, the specific $B/A$ value at the same pressure for each membrane was different and followed the trend of TFC-T < TFC-N < TFC-W. This can be attributed to the different tensile properties of these fabric-reinforced membranes. As discussed in Section 3.1, the TFC-W membrane is much more vulnerable to the multi-directional stretching. Thus, its active layer may undergo greater stretching and more structural change upon pressurized, which results in greater
change of selectivity. In contrast, TFC-T allows more uniform distribution of tensile force and exhibits greater resistance to the stretching in different directions, which may lead to less change in its active layer’s structure and membrane selectivity.

3.3. PRO performance

Figure 4 shows the PRO performance (water flux, power density, and specific reverse solute flux) of the fabric-reinforced TFC membranes tested using a typical net-type feed spacer. Clearly, different types of fabric-reinforced membranes showed different performances in the PRO testing. When the applied pressure was zero (i.e., in FO operation), water fluxes for the TFC-T and TFC-W membranes were similar (~23 L/m².hr) but greater than that of the TFC-N membrane (~15 L/m².hr). This is attributed to the greater structural parameter (S value) of the TFC-N membrane resulting from the nonwoven fabric structure (Figure 1 and 2 in Section 3.1). Noting that the membrane separation parameters of these three pristine membranes were comparable, the S values were ~785 µm for TFC-T, ~723 µm for TFC-W and ~1380 µm for TFC-N respectively. As such, the TFC-N membrane suffered more severe ICP and delivered lower performance. Consistent with the observation in the current study, inferior FO/PRO performance was also observed for commercial membranes with nonwoven fabric in the support layer previously [14, 18, 49]. These observations suggest that the nonwoven fabric may not be suitable for FO/PRO membranes although it is extensively used for reinforcing RO membranes.

Figure 4

Despite similar water fluxes for the TFC-T and TFC-W membranes when ΔP=0, higher water fluxes and power densities were observed for the TFC-T membrane when the membranes were
tested in the PRO condition ($\Delta P > 0$) (Figures 4a and 4b). The measured peak power density for TFC-T was ~7.1 W/m$^2$ at $\Delta P$ of 18.4 bar and for TFC-W was ~4.7 W/m$^2$ at $\Delta P$ of 16.6 bar, respectively. The higher PRO water flux and power density for the TFC-T membrane are thanks to the less severe reverse solute diffusion (RSD). As shown in Figure 4c, the specific reverse solute flux ($J_s/J_w$) for TFC-T membrane was much smaller than that for TFC-W membrane at higher pressures. Consequently, the effect of RSD-enhanced ICP for the TFC-T membrane is less pronounced [18, 19, 37], which results in its better PRO performance. The superior PRO performance of the TFC-T membrane is consistent with its superior separation properties measured in the modified RO mode (Section 3.2). Again, this could be attributed to the superior mechanical properties of the tricot-fabric-reinforced membrane (Section 3.1).

Table 2 compares the PRO performance of the fabric-reinforced membranes in the current study and other membranes in the literature. The type of feed spacer used in the PRO testing is specifically summarized in the table, since the feed spacer can strongly influence the PRO membrane deformation and performance [19]. From the table, most of the high performance PRO membranes were tested using a RO permeate carrier or porous mesh (with very small openings) as feed spacer. This type of feed spacer can sufficiently support the membrane against the applied pressures, whereby the tensile stretching of membrane is minimized and the membrane mainly undergoes hydraulic compaction. In such testing condition, the mechanical strength of the PRO membranes becomes much less important compared to that using a typical net-type spacer (with larger openings). Therefore, the membranes even without a back reinforcement [14, 27-30] or only weakly reinforced with a very thin and porous nonwoven fabric (different from the typical one used in typical RO membranes) [22, 32, 50, 51] are able to
be efficiently tested in the PRO operation. However, such testing condition could not sufficiently demonstrate those types of membranes are able to resist the strong tensile stretching induced by using a typical net-type feed spacer in the PRO testing. For example, in the current study, we also observed that the membranes without fabric reinforcement was immediately damaged upon pressurized in the PRO testing when using the net-type feed spacer. Moreover, using RO permeate carrier or porous mesh as feed spacer could result in increased flow resistance in the feed channel [19, 34, 52], enhanced “spacer shadow effect” [19, 20] as well as increased fouling potential [35-37] in real applications. As such, the current study selected a typical net-type feed spacer to simulate a more practical scenario. By comparing with the PRO performance tested using RO permeate carrier as feed spacer (Figure C1 and Figure C2 in Appendix C), the results further reveal that the tricot fabric-reinforced TFC membrane was able to maintain its mechanical stability and high PRO performance at high applied pressures in such testing condition with the net-type feed spacer. The results in the current study suggest that a better reinforced membrane (e.g., TFC-T) allows a more open type of spacer to be adopted in the PRO test, which provides more freedom in spacer selection/optimization to minimize the potential adverse effects associated with the confined spacers such as RO permeate carrier.

Table 2

3.4. Coupled effects of hydraulic compaction and tensile stretching on PRO membrane deformation: implications for PRO membrane design

As schematically illustrated in Figure 5, membrane deformation can be induced by the coupled stresses in the PRO operation: (1) compressive stress perpendicular to the membrane surface exerted by the applied hydraulic pressure, and (2) tensile stress tangential to the membrane
surface resulting from the insufficient support of the membrane (e.g., using a net-type spacer with large openings) under the applied pressure. Compressive stress leads to the compaction of the membrane and thereby the compressive membrane deformation. Tensile stress leads to the stretching of the membrane and thus the tensile membrane deformation.

**Figure 5**

The coupled effects of hydraulic compaction and tensile stretching could result in the change of membrane separation and structural properties (refer to Section 3.2, Appendix D, and refs. [19, 20, 24, 30]). Compaction of the membrane could reduce the membrane thickness and void volume, and increase the effective diffusion path length [46], which may result in the reduced $A$ value for typical TFC membranes. In addition, compaction may also change the membrane $S$ value due to the compressed substrate pore radii and/or the reduced substrate thickness (Figure D1 in Appendix D). In comparison, stretching of the membrane could lead to the rearrangement and even the breakage of polymer chains in the rejection layer, which may result in the increased $A$ value and reduced rejection (increased $B/A$ value) [19, 20]. In addition, stretching of the membrane could enlarge the pores along the tensile direction in the substrate layer, which may result in the reduced $S$ value (Figure D2 in Appendix D and refs. [19, 24]).

Although both compaction and stretching of the membrane could influence the PRO membrane performance, stretching may play a more important role. This is primarily because severe tensile membrane deformation induced by stretching could result in significant loss of membrane selectivity and even damage of the membrane. For example, it has been extensively observed that the weekly reinforced membranes could be damaged when an open net-type feed spacer was
used in PRO testing where the membrane underwent severe stretching at high applied pressures [19, 20, 50]. On the other hand, even the weekly reinforced membranes could perform well even at severe compaction when permeate carrier was used as feed spacer where stretching was minimized [19, 30, 53]. Based on the experimental observations, Figure 6 illustrates the two possible scenarios on the change of membrane selectivity (i.e., $B/A$) as a function of applied pressures when membrane undergoes both hydraulic compaction and tensile stretching using a typical net-type feed spacer in the PRO operation. In scenario 1, $B/A$ is dominated by the stretching effect and keeps increasing significantly with increasing applied pressure. This is possible for those membranes with very poor mechanical strength that cannot resist tensile stretching (e.g., the commercial CTA membranes [19] and the membranes without fabric reinforcement [14, 23, 30]). Scenario 2 is possible for strongly reinforced PRO membranes. In scenario 2, $B/A$ may experience different stages: (I) tensile stretching dominated stage where $B/A$ increases substantially with pressure; (II) hydraulic compaction dominated stage where the increase of $B/A$ with pressure becomes much less significant or $B/A$ even slightly decreases with pressure; (III) stretching dominated stage where $B/A$ increases dramatically with pressure. The change of $B/A$ in the first two stages was observed in the current study for the fabric-reinforced TFC membranes (Figure 3 and Section 3.2), while that in the third stage is likely to occur if the applied pressure is sufficiently large to rupture the membrane reinforcement.

**Figure 6**

The current study implies that the selection of a suitable fabric is of paramount importance to design a reinforced membrane, since the fabric reinforcement at the bottom layer plays a
dominant role in its mechanical strength for resisting the tensile stretching (Figure 5). In the current study, the tricot fabric-reinforced membrane exhibited better resistance to multidirectional tensile stretching, which allowed it to perform better in the PRO testing where the membrane underwent tensile stretching (Section 3.3). In addition, the performance of this membrane showed better structural stability (Figure D2 in Appendix D) as well as better reversibility when it was tested in a repeat cycle (Appendix E). This implies that tricot fabric could be a new type of fabric reinforcement for fabricating the future PRO membranes. Besides this, other types of reinforcement with enhanced resistance to tensile stretching may also be considered in the future studies to enhance the PRO membrane mechanical strength.

4. Conclusions

In the current study, fabric-reinforced TFC PRO membranes were fabricated for osmotic power harvesting. Three different types of fabrics (i.e., tricot fabric, woven fabric and nonwoven fabric) were selected to reinforce the membrane mechanical strength through integrating them in the membrane substrate layer. The performance of these fabric-reinforced membranes was evaluated using a typical net-type feed spacer in the PRO testing. It was observed that the nonwoven fabric-reinforced membrane exhibited the lowest performance due to the greatest membrane structural parameter. In contrast, the tricot fabric-reinforced membrane had the best PRO performance. The tensile measurement revealed that the tricot fabric-reinforced membrane allows better isotropic transfer of tensile force induced in the PRO operation. Therefore this membrane exhibited a better structural stability and less change of separation properties compared to the woven fabric-reinforced membrane. The current study further elaborates that the membrane deformation in the PRO operation results from the coupled effects of hydraulic
compaction and tensile stretching. In addition, the tensile stretching plays a dominant role in the PRO membrane deformation and performance. The current study suggests that the tricot fabric with higher resistance to multi-directional tensile stretching could be an excellent candidate for fabricating the reinforced PRO membranes. The future studies may also consider the selection of tricot fabric with systematically optimized geometry and mechanical properties, with the aid of both theoretical analysis and experimental investigation. The role of fabric reinforcement on mechanical stress transfer in the polymeric substrate and its effect on the separation properties of PRO membranes requires further research.

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Appendix A. Measurement of tensile properties of the fabric reinforcements and reinforced PRO membranes

In the tensile measurement, samples for the nonwoven fabric and corresponding reinforced membrane were stretched randomly due to the irregular structure of this fabric. Samples for the woven fabric and tricot fabric and their corresponding reinforced membranes were stretched along the directions shown in Figure A1.

Figure A1

Figure A2 shows the stress-strain (S-S) curves for all the fabrics and corresponding reinforced membranes obtained in the tensile measurement. The slope of the S-S curve in the linear elastic region is used to determine the Young’s modulus. Clearly, the S-S curve of the fabric-reinforced membrane follows the similar trend to that of the corresponding fabric reinforcement. Upon stretching in different directions, the S-S curves for the tricot fabric (as well as the reinforced membrane) in the linear elastic region almost overlap and have similar slopes, while the curves for the woven fabric (as well as its reinforced membrane) exhibit significantly different trends and have different slopes. In addition, a large toe region is observed for the woven fabric when stretching in the diagonal direction, demonstrating that the woven fabric is very stretchable in its diagonal direction.

Figure A2

The tensile properties of the TFC polymeric membrane without fabric reinforcement were also measured with the Young’s modulus value of ~49.1±11.9 MPa. Apparently, this value was significantly lower compared to that of the fabric reinforcement, which could explain the reduced Young’s modulus value for the composite fabric reinforced membranes compared to the
respectively values of the fabric reinforcement (Table 1). Alternatively, the volumetric shrinkage of the casted polymer film during phase inversion may create some internal stress to the fabric reinforcement [54, 55], which could lead to a reduced ability to withstand the tensile action upon the application of external force. In addition, the interactions between the fabric reinforcement and the solvent might also result in the reduced mechanical properties of the composite fabric-reinforced membrane. Further studies are still needed to determine the exact causes.

It is worthwhile to note that Young’s modulus ($E$) is an intrinsic property of the material. To fully describe the membrane’s ability to resist tensile stretching, the cross sectional dimension is also important. According to the classical mechanics, stress ($\sigma$), strain ($\varepsilon$), and the applied force ($F$) are related by

$$\sigma = E \varepsilon$$ \hspace{1cm} (A1)

$$\sigma = F / (wt)$$ \hspace{1cm} (A2)

where $w$ and $t$ are the width and thickness of the membrane cross-section, respectively.

Following those above equations, the applied force normalized by membrane width is related to the strain via the proportionality constant $Et$:

$$F/w = (Et) \times \varepsilon$$ \hspace{1cm} (A3)

The physical meaning of $Et$ is the resistance ($Ewt$) to tensile strain ($\varepsilon$) per unit membrane width ($w$).

**Appendix B. Water permeability of fabric-reinforced support layers**

As shown in Figure B1, water permeability coefficient ($A$ value) of all the fabric-reinforced membrane support layers decreased with increasing the applied pressures and approached to
nearly identical value at higher pressures (i.e., greater than 20 bar). These phenomena are primarily attributed to the enhanced compaction of porous support layer at increased applied pressures where the void volume of the porous polysulfone layer is decreased [45, 46]. At a very high applied pressure, the polysulfone porous substrate layer for different samples (that were casted under identical conditions) might be compacted to a dense structure with comparable void volume [45], such that the water permeability declined to a similar value. It is worthwhile to note that the membrane support layers also underwent severe tensile deformation at applied pressures due to insufficient support of the net spacer in the permeate channel. While previous studies reported the tensile stretching induced by membrane deformation could lead to the increased membrane water permeability [19], the results in the current study suggests that compaction plays a more predominant role in the change of water permeability for the porous support layers.

Figure B1

Appendix C. PRO performance with RO permeate carrier as feed spacer in the testing

Figure C1 and Figure C2 compare the PRO performance using net-type spacer and RO permeate carrier in the feed side for TFC-W and TFC-T membranes, respectively. For the TFC-W membrane that has less mechanical stability with net-type feed spacer, using the RO permeate carrier could significantly improve its PRO performance due to the significantly reduced stretching effect. In contrast, using the RO permeate carrier could not improve the PRO performance of TFC-T membrane but further result in a slightly reduced peak power density, although TFC-T membrane has better mechanical resistance to multidirectional stretching. This suggests that the adverse “shadow effect” by using the RO permeate carrier would suppress the benefit of reduced stretching effect on the performance of the strongly-reinforced membranes.

Figure C1
Appendix D. Change of membrane structural property in the PRO testing

Figure D1 shows the SEM images of cross section of the pristine membranes and the membranes after the PRO testing. Clearly, after the PRO testing, the thickness of each membrane was significantly reduced, indicating that the membranes underwent severe compaction in the PRO testing.

Figure D2 shows the actual $S$ value at different applied pressures for the three fabric-reinforced membranes. The $S$ value was determined using the similar method as reported elsewhere [19]. Briefly, it was obtained by inputting the experimentally measured $A$, $J_w$ and $J_s/J_w$ at the specific pressure into Eq. (D1).

$$S = \frac{D}{J_w} \ln \left[ \left( \frac{\pi_{ds} + J_s/J_k}{J_w} \right) \exp \left( -\frac{J_w}{k_{exp}} \right) - \frac{J_w}{A} - \Delta P \right]$$  \hspace{1cm} (D1)

As shown in Figure D2, the $S$ values for all the membranes were not constant against the applied pressures. Their change with pressure followed a similar trend. That is, they initially decreased with increasing the pressures and then increased with further increasing the pressures. The initial decrease of $S$ value might be attributed to the tensile stretching of the membrane that enlarged the pores, while the subsequent increase of $S$ value might be dominated by the severe hydraulic compaction of the membrane at high applied pressures that compressed the void volume.
Appendix E. Reversibility of PRO performance

The reversibility of the PRO membrane performance was evaluated by conducting another round of PRO testing immediately after the first round. In the second round of PRO testing, the applied hydraulic pressure was again increased from zero to selected pressures stepwise. Figure E1 shows the membrane PRO performance in the two rounds of PRO testing. For all the fabric-reinforced membranes, the fluxes at FO condition ($\Delta P = 0$) were improved in the second round of testing, but declined to the values nearly identical to those in the first round when the pressure was increased to above 15 bar. This is probably because at $\Delta P = 0$ in the second round of testing, the already deformed membrane after the first round of testing had a favorable structural and separation properties for the osmotic process. Previous studies also observed the similar phenomenon that the pre-deformation of the membrane could result in an improved osmotic performance [24, 26, 50]. The later substantial decrease of flux at high applied pressures may be caused by the severe coupled compaction and stretching that resulted in the similar structural and separation properties to those in the first round of testing. It is worthwhile to note that the tricot fabric-reinforced membrane showed best reversibility compared to the other two membranes, primarily due to its best tensile capacity against the stretching resulted in the PRO operation.

Figure E1
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Table 1. Tensile properties of fabric reinforcements and fabric-reinforced PRO membranes

Table 2. Comparison between the PRO performance of the fabric-reinforced membranes in the current study and that of other flat-sheet membranes in the literature

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Figure 2. SEM images of reinforced TFC PRO membranes. (a) nonwoven fabric-reinforced TFC membrane (TFC-N), (b) woven fabric-reinforced TFC membrane (TFC-W), and (c) tricot fabric-reinforced TFC membrane (TFC-T). (a1)-(c1) surface of active layer, (a2)-(c2) surface of bottom layer, (a3)-(c3) top region of cross-section in large magnification, (a4)-(c4) whole cross section, and (a5)-(c5) bottom region of cross-section in large magnification.

Figure 3. Water permeability ($A$) and solute/water selectivity ($B/A$) of fabric-reinforced TFC membranes. The separation parameters were measured in the modified RO testing where RO permeate channel was filled with a net-type spacer that was identical to the spacer in the PRO feed channel.

Figure 4. PRO performance at different applied pressures. (a) water flux, (b) power density, and (c) specific reverse solute flux. Testing conditions: 1 M NaCl draw solution, 10 mM NaCl feed solution, net-type feed spacer, temperature of 25±0.5℃, and AL-DS membrane orientation. The power density was calculated by the product of water flux and effective applied pressure.

Figure 5. Schematic illustration of the coupled effects of hydraulic compaction and tensile stretching on the membrane deformation in the PRO operation. (a) Membrane is in the original state without deformation, (b) membrane is undergoing deformation in the PRO testing, and (c) magnified image of dotted area in (b) to illustrate the coupled compressive stress and tensile stress exerted on the active layer surface when membrane is undergoing deformation. The coupled effects of compaction and stretching could influence the overall membrane separation and structural parameters in the PRO process.

Figure 6. Illustration of possible scenarios of the change of membrane integrity in the PRO operation using a typical net-type feed spacer. Greater $B/A$ indicates lower rejection and more loss of membrane integrity.

Figure A1. Directions of stretching in the tensile measurement for different samples. The samples of fabric-reinforced membrane were stretched in the same direction as those of the corresponding fabric reinforcement.
Figure A2. Stress-strain response in the tensile measurements for the fabrics and reinforced membranes. (a1), (b1) and (c1) are stress-strain curve for nonwoven, woven, and tricot fabrics, respectively; (a2), (b2) and (c2) are stress-strain curve for nonwoven, woven, and tricot fabric-reinforced membranes, respectively. All the curves are obtained using three samples in three independent measurements.

Figure B1. Water permeability ($\mathcal{A}$) of fabric-reinforced membrane support layers. The separation parameter was measured in the modified RO testing where RO permeate channel was filled with a net-type spacer that was identical to the spacer in the PRO feed channel.

Figure C1. Comparison of PRO performance of TFC-W membrane by using net-type feed spacer and RO permeate carrier. Testing conditions: 1 M NaCl draw solution, 10 mM NaCl feed solution, temperature of 25±0.5 °C, and AL-DS membrane orientation.

Figure C2. Comparison of PRO performance of TFC-T membrane by using net-type feed spacer and RO permeate carrier. Testing conditions: 1 M NaCl draw solution, 10 mM NaCl feed solution, temperature of 25±0.5 °C, and AL-DS membrane orientation.

Figure D1. SEM images of cross sections of the fabric-reinforced PRO membranes before and after PRO testing. (a1), (b1) and (c1) are TFC-N, TFC-W and TFC-T membranes before PRO testing respectively; (a2), (b2) and (c2) are TFC-N, TFC-W and TFC-T membranes after PRO testing respectively.

Figure D2. Structural parameter ($S$ value) at different applied pressures for the three fabric-reinforced membranes. The $S$ value was calculated using all the experimental measured parameters based on Eq. (D1).

Figure E1. Reversibility of PRO performance in the testing. In the first round of PRO testing, the applied pressure was increased stepwise from zero till over 25 bar. Reversibility of PRO performance was tested after the first round of PRO testing, and the applied pressure was again increased stepwise from zero to selected pressures.
<table>
<thead>
<tr>
<th>Fabric</th>
<th>Young's modulus – $E$</th>
<th>Thickness – $t$</th>
<th>$E \times t$</th>
<th>Membrane</th>
<th>Young's modulus – $E$</th>
<th>Thickness – $t$</th>
<th>$E \times t$</th>
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</thead>
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* The wet samples of fabric reinforcement and fabric-reinforced membrane were used in the tensile measurement.
* $E$ is determined from the slope of stress-strain curve in the linear elastic region (refer to Figure A2 in Appendix A).
* The thickness was measured with a micrometer.
* $E \times t$ indicates the membrane intrinsic mechanical resistance to tensile strain per unit width membrane (also refer to Appendix A).
* Directions of stretching in the tensile measurement for different samples (also refer to Appendix A).
Table 2. Comparison between the PRO performance of the fabric-reinforced membranes in the current study and that of other flat-sheet membranes in the literature

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Fabric Reinforcement</th>
<th>Substrate Layer</th>
<th>Active Layer</th>
<th>Draw Solution</th>
<th>Feed Solution</th>
<th>Feed Spacer a</th>
<th>Effective Applied Pressure (bar)</th>
<th>Water Flux (LMH)</th>
<th>Power Density (W/m²)</th>
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<td>Active Layer</td>
<td>Draw Solution</td>
<td>Feed Solution</td>
<td>Feed Spacer a</td>
<td>Effective Applied Pressure (bar)</td>
<td>Water Flux (LMH)</td>
<td>Power Density (W/m²)</td>
<td>Ref.</td>
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<td>12.2</td>
<td>10.6</td>
<td>4.5</td>
<td>[18]</td>
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</table>

a RO permeate carriers and porous meshes have very small openings that can well support the membrane against the tensile stretching in the PRO testing. Thus, membrane mainly undergoes hydraulic compression when they are used as PRO feed spacer. Net-type spacer has large openings that cannot sufficiently support the membrane in the PRO testing. Thus, membrane undergoes both tensile stretching and hydraulic compression.

b The number is estimated from the figures in the reference.

c “n.a.” indicates the information not available from the reference.
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Figure C1. Comparison of PRO performance of TFC-W membrane by using net-type feed spacer and RO permeate carrier. Testing conditions: 1 M NaCl draw solution, 10 mM NaCl feed solution, temperature of 25±0.5 °C, and AL-DS membrane orientation.
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