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PII: S0376-7388(15)30412-9
DOI: <http://dx.doi.org/10.1016/j.memsci.2015.12.060>
Reference: MEMSCI14200

To appear in: *Journal of Membrane Science*

Received date: 15 September 2015
Revised date: 11 December 2015
Accepted date: 27 December 2015

Cite this article as: Zhen Lei Cheng, Xue Li, Ying Da Liu and Tai-Shung Chung Robust outer-selective thin-film composite polyethersulfone hollow fiber membranes with low reverse salt flux for renewable salinity-gradient energy generation, *Journal of Membrane Science* <http://dx.doi.org/10.1016/j.memsci.2015.12.060>

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Robust Outer-selective Thin-film Composite Polyethersulfone Hollow Fiber Membranes with Low Reverse Salt Flux for Renewable Salinity-gradient Energy Generation

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Abstract

This study reports outer-selective thin-film composite (TFC) hollow fiber membranes with extremely low reverse salt fluxes and robustness for harvesting salinity-gradient energy from pressure retarded osmosis (PRO) processes. Almost defect-free polyamide layers with impressive low salt permeabilities were synthesized on top of robust polyethersulfone porous supports. The newly developed TFC-II membrane shows a maximum power density of 7.81 W m^{-2} using 1 M NaCl and DI water as feeds at 20 bar. Reproducible data obtained in the 2nd and 3rd runs confirm its stability under high hydraulic pressure differences. Comparing to other PRO membranes reported in the literature, the newly developed membrane exhibits not only the smallest slope between water flux decline and ΔP increase but also the lowest ratio of

reverse salt flux to water flux. Thus, the effective osmotic driving force could be well maintained even under high pressure operations. For the first time, the effect of feed pressure buildup induced by feed flowrate was evaluated towards PRO performance. A slight increment in feed pressure buildup was found to be beneficial to water flux and power density up to 10.06 W m^{-2} without comprising the reverse salt flux. We believe this study may open up new perspectives on outer-selective PRO hollow fiber membranes and provide useful insights to understand and design next-generation outer-selective TFC hollow fiber membranes for osmotic power generation.

Keywords: Outer-selective, Thin-film composite (TFC) hollow fiber membrane, Pressure retarded osmosis (PRO), Osmotic power, Inner pressure buildup

1. Introduction

Today greenhouse gas emissions and highly fluctuated oil prices are two major issues towards earth sustainability. Intensive researches have been made to explore clean and renewable energy productions as alternative energy sources. Pressure retarded osmosis (PRO) is one of the strong candidates [1-5]. By applying a semi-permeable membrane between two salinity solutions, the salinity-gradient energy is extracted by an energy transfer device when the water transports across the membrane from the low-salinity side (i.e., feed solution) to the high-salinity side (i.e., draw solution). Either a hydro turbine or a pressure exchanger could be used in PRO to generate electricity or transfer energy [6-8]. The global potential of salinity-gradient energy from discharging the rivers into the sea is estimated to be 1650 TWh yr^{-1} [1, 6], which

is about one half of the current annual hydro-power generation reported as 3551 TWh yr^{-1} [9].

Although harvesting salinity-gradient energy was proposed about 60 years ago [10], its development has been hindered for many years by the lack of effective membranes. Only until recent years, high performance PRO membranes are available in lab-scale to surpass the membrane power density of 5 W m^{-2} , set by Statkraft for PRO commercialization [3, 6, 11-17]. Good PRO membranes generally require the following characteristics: (1) a thin selective layer allowing a high water flux with a reasonably low reverse salt flux; (2) a robust support layer to sustain high pressure operations with small transport resistance; and (3) low affinity to foulants to maintain high power generation in real environments [1, 2, 11-23]. To date, both phase inversion and interfacial polymerization methods have been employed to form the selective layer of PRO membranes [12-16, 23]. The membranes fabricated by phase inversion usually suffer from a low water flux and a low salt rejection because of the thick selective layer and membrane materials available [16, 23]. Interfacial polymerization enables a higher degree of control on membrane morphology and performance by separately tuning the selective layer and the polymeric support. The resultant thin-film composite (TFC) membranes consist of an ultrathin polyamide selective layer on top of a porous and mechanically strong substrate, providing a high water flux and a low reverse salt flux [11-15, 17, 19-23]. Thus, most PRO studies are based on TFC membranes.

So far most TFC PRO membranes are in either flat sheet or inner-selective hollow fiber configurations. There are growing interests in developing the outer-selective

TFC hollow fiber membrane due to its provision of (1) more surface area per fiber and less propensity for fouling compared to the inner-selective hollow fiber membrane [21, 24, 25]; (2) larger membrane area per module [25]; and (3) possibly less external concentration polarization (ECP) [26-28]. In addition, high pressure operations like PRO prefer the outer-selective configuration as it is more mechanically resistant to pressurize from the shell side of modules [25]. However, it is challenging to form a perfect polyamide layer on the outer surface of hollow fibers, as none of the conventional approaches such as roller rolling, air purging and solvent treatment can be applied to effectively remove the excess amine solution before the interfacial polymerization [21-24, 29-31].

Ingole et al. [30] have attempted to make the outer-selective TFC PRO hollow fiber membrane. Because of unsuitable interfacial polymerization conditions and substrates, their membranes could only achieve a peak power density of 1.62 W m^{-2} at 6 bar using 0.6 M NaCl and DI water as feeds. In order to overcome it, Sun and Chung [21] developed a vacuum-assisted interfacial polymerization to synthesize a polyamide layer on top of the outer surface. A vacuum pressure of 800 mbar was employed on the lumen side of a hollow fiber bundle to remove the excess amine solution. The resultant membrane exhibited a peak power density of 7.63 W m^{-2} at 20 bar using 1 M NaCl and DI water as feeds. Nonetheless, the membrane's high water permeability (A) was achieved but with a compromised salt permeability (B). Since a large B may cause an instant drop in initial water flux and accelerate flux decline under high hydraulic pressures [31], it would reduce the optimal operating pressure and the maximum power density. Therefore, the development of outer-selective TFC PRO hollow fiber membranes with a reasonable A and a small B is attractive for real high

pressure PRO operations. On the other hand, process parameters like flowrate and pressure drop have significantly impacts on module design and system optimization in PRO applications. For the outer-selective hollow fiber configuration, these effects have been examined in some modeling works [26, 27]. However, no relevant experimental data have been reported probably due to the limited availability of robust outer-selective hollow fiber membranes for studies.

In this study, we adapt a simplified vacuum-assisted interfacial polymerization method to synthesize the outer-selective TFC hollow fiber membranes. Polyethersulfone (PES) was chosen as the substrate material because of its good mechanical properties, outstanding chemical and thermal stability, easy processability, and superior durability in water [32]. By manipulating spinning parameters, hollow fiber supports with different dimensions and morphologies are fabricated and explored for the deposition of an ultrathin polyamide layer on their outer surfaces. We aim to 1) develop robust outer-selective TFC hollow fiber membranes possessing a reasonable water permeability and an impressively low salt permeability; 2) systematically evaluate their PRO performance and investigate the effects of pressure buildup in the module lumen side on power generation; and 3) explore an effective scheme to quantify the effectiveness of a PRO membrane using “the slope of the water decline vs. pressure” as an analytical term. This study may offer useful insights to design outer-selective TFC hollow fiber membranes and optimize process parameters to maximize PRO performance of industry-scale modules in the near future.

2. Experimental

2.1 Materials

Radel[®] A polyethersulfone (PES, Solvay Advanced Polymer, L.L.C. GA), N-methyl-2-pyrrolidone (NMP, >99.5%, Merck), polyethylene glycol 400 (PEG, Mw = 400 g mol⁻¹, Acros Organics) and deionized water (DI water, ELGA MicroMEG) were used, as the polymer, solvent, pore former and non-solvent, respectively, to prepare the spinning dope solution. A 50/50 wt% mixture of glycerol (Industrial grade, Aik Moh Pains & Chemicals Pte. Ltd., Singapore) and DI water was prepared to post-treat the as-spun hollow fiber supports before drying for storage and module fabrication. Polyethylene glycol and polyethylene oxide at various molecular weights (PEG, Mw = 2,000 g mol⁻¹, 4,000 g mol⁻¹, 6,000 g mol⁻¹, 10,000 g mol⁻¹, 12,000 g mol⁻¹, 20,000 g mol⁻¹, 35,000 g mol⁻¹ and PEO, Mw = 100,000 g mol⁻¹, 200,000 g mol⁻¹, 300,000 g mol⁻¹ respectively, Sigma-Aldrich) were employed to characterize the molecular weight cut-off (MWCO), mean pore size and pore size distribution of the hollow fiber supports. Sodium dodecyl sulphate (SDS, >97%, Fluka), m-phenylenediamine (MPD, >98%, T.C.I.), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%, Sigma-Aldrich), and hexane (99.9%, Fisher Chemicals) were applied to perform interfacial polymerization. Sodium chloride (NaCl, 99.5%, Merck) was purchased for membrane transport characterizations and PRO performance tests. All chemicals were used as received.

2.2 Fabrication of PES hollow fiber supports and post-treatments

The PES polymer was first dried in a vacuum oven at 105 °C overnight to remove moisture and then added into a NMP/PEG mixture and stirred at 65 °C overnight. After complete dissolution, the dope solution was cooled down to room temperature and a small amount of DI water was slowly added. Subsequently, the dope solution

was continuously stirred for another few hours until a transparent solution was obtained. Afterwards, the prepared spinning dope solution was loaded into a 500 mL ISCO syringe pump and kept overnight for degassing before spinning.

A dry-jet wet spinning technique was performed to spin the PES hollow fiber supports [19-21, 33]. By altering the spinning conditions, such as bore fluid composition, bore fluid flowrate, air-gap distance and take-up speed, three different hollow fiber supports with various dimensions and morphologies were obtained as listed in Table 1. The addition of hydrophilic non-solvent additive PEG into the spinning dopes aims to enhance pore formation and improve pore connectivity. A small amount of water is added to increase dope viscosity and move the dope closer to the binodal curve, resulting in interconnected open-cell pores [14]. The as-spun hollow fibers were immersed in tap water for two days to remove the residual solvent and PEG 400. Part of the fibers were kept in a water bath in order to perform a series of characterizations as specified in the subsequent sections. The others were soaked in a glycerol/water mixture (50/50 wt%) for another two days, and then dried in ambient condition. The aqueous glycerol treatment aimed to prevent pore collapse during drying [34, 35].

To make hollow fiber modules, four to six pieces of membranes were carefully spaced and housed in a 1/2 inch perfluoroalkoxy (PFA) tubing with two Swagelok stainless male run tees connected to each side. Both ends were capped with cotton and potted with a slow curing epoxy resin (EP 231, Kuo Sen, Taiwan). Prior to module fabrication, the two ends of each fiber were sealed with a fast curing epoxy resin (Araldite[®] Rapid, Huntsman, Belgium) and subsequently coated with the slow curing epoxy resin to leave a clean fiber length of 3-4 cm for PRO tests. These procedures

were to (1) ensure an accurate calculation of membrane area, and (2) eliminate the formation of a defective polyamide layer on the outer surface of fiber ends contacting with cotton.

2.3 Fabrication of PES-TFC hollow fiber membranes

The TFC membranes were synthesized via interfacial polymerization on the outer surface of PES hollow fiber supports as illustrated in Figure 1. (1) the membrane module was positioned vertically and a 0.5 wt% PEG 400 aqueous solution was recirculated on the module shell side for 30 min at a flowrate of 5.35 mL min^{-1} ; (2) A 2 wt% MPD aqueous solution comprising a SDS concentration of 2 wt% was introduced to the outer surface of hollow fibers from bottom to top for 3 min at a flowrate of 5.35 mL min^{-1} ; (3) After that, the excess MPD residual was removed by vacuum at a transmembrane pressure of 800 mbar applied from the module lumen for 6 min; (4) A 0.15 wt% TMC in hexane at a flowrate of 6.11 mL min^{-1} was brought into contact with the outer surface of MPD saturated membranes for 2 min; (5) Then, a compressed air was purged on the module shell side for a few seconds. The resultant TFC membranes were left under ambient condition for 2.5 hr to stabilize the polyamide layer before being rinsed with DI water several times and stored in DI water for further tests.

2.4 Characterizations

2.4.1 Morphology, topology, porosity, MWCO, pore size and pore size distribution of PES hollow fiber supports

Membrane morphology was examined using field emission scanning electronic microscopy (FESEM, JEOL JSM-6700). Prior to FESEM characterizations, the PES

supports and TFC hollow fiber membranes were freeze dried, fractured in liquid nitrogen and platinum coated with a Jeol JFC-1100E ion sputtering device.

Membrane surface topology was studied by atomic force microscopy (AFM, Bruker). Each membrane sample was scanned at a rate of 1.0 Hz in the tapping mode. Mean roughness (R_a) was determined using NanoScope Analysis (1.40, Bruker) from the average of 10 sample measurements.

For porosity measurements, the wet PES hollow fiber supports were cut into 5 cm shorts (l , cm) and dried by a freeze dryer (Christ Alpha 2-4 LD plus) overnight before being weighted. Every three shorts were weighted together (m , g) and at least 5 measurements were taken for each short bundle. The overall porosity (ϵ , %) was determined using the follow equation

$$\epsilon = \frac{\frac{\pi}{4}(OD^2-ID^2)l - \frac{m}{\rho_p}}{\frac{\pi}{4}(OD^2-ID^2)l} \quad (1)$$

where OD and ID are the outer and inner diameters, respectively. ρ_p is the polymer density of 1.37 g cm^{-3} [14].

The MWCO, pore size and pore size distribution of PES hollow fiber supports were characterized by the solute transport method based on the procedures described elsewhere [20, 36-39]. Briefly, 200 ppm PEG or PEO aqueous solutions with various molecular weights were prepared to test the solute rejection under a trans-membrane pressure of 1 bar. The PEG or PEO concentrations of the collected permeates were analyzed by a total organic carbon analyzer (TOC ASI-5000A, Shimadzu, Japan). The

effective solute rejection (R) was calculated from the measured feed concentration (C_f) and permeate concentration (C_p) as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Since the solute diameter (d_s , nm) as a function of molecular weight M_w obeys the following equations:

$$d_s = 3.35 \times 10^{-2} \times M_w^{0.557} \quad (\text{for PEG}) \quad (3)$$

$$d_s = 2.09 \times 10^{-2} \times M_w^{0.587} \quad (\text{for PEO}) \quad (4)$$

a straight line can be employed to regress R vs. d_s on a log-normal probability graph. The MWCO was obtained at $R = 90\%$ and the mean effective pore size (μ_p) was acquired by assuming it to be the same as the solute geometric mean size (μ_s) at $R = 50\%$. While the geometric standard deviation (σ_p) is defined as the ratio between d_s at $R = 84.13\%$ and that at $R = 50\%$. Then the pore size distribution of a membrane can be expressed based on μ_p and σ_p as following

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (5)$$

2.4.2 Determination of pure water permeability and collapse pressure of PES hollow fiber supports

The pure water permeability (PWP) of PES hollow fiber supports under different pressures were tested by using a lab-scale RO setup as described elsewhere [20, 31, 39]. DI water serving as the feed solution was pumped into the module shell side at a flowrate of 0.6 mL min^{-1} with a series of pressures in an ascending order. At each pressure stage, the permeate was subsequently collected from the lumen side for 10 min to calculate PWP using the equation below

$$PWP = \frac{Q}{A_m \Delta P} \quad (6)$$

where Q is the permeate volumetric flowrate, A_m is the effective filtration membrane area and ΔP is the trans-membrane pressure.

The collapse pressure of a membrane is defined as the highest pressure which the hollow fiber support could sustain just before its structural failure.

2.4.3 Determination of water permeability and salt permeability of PES-TFC hollow fiber membranes

The water permeability (A) and salt rejection (R_s) of the TFC hollow fiber membranes were measured using the same setup for pore size characterizations [20, 31, 39]. A was obtained by recirculating DI water through the module shell side at a trans-membrane of 1 bar, while R_s was acquired by pressurizing a 1000 ppm NaCl feed solution at a trans-membrane pressure of 1 bar. The permeate conductivity was measured by a conductivity meter (Metrohm 856 conductivity module) and the salt rejection was calculated as

$$R_s = \left(1 - \frac{Cd_p}{Cd_f}\right) \times 100\% \quad (7)$$

where Cd_p and Cd_f refer to the conductivity of the permeate and feed, respectively.

The salt permeability (B) was calculated based on the equation derived from the solution-diffusion theory [40]:

$$B = A \frac{(1-R_s)(\Delta P - \Delta \pi)}{R_s} \quad (8)$$

where $\Delta \pi$ is the osmotic pressure difference across the membrane.

2.4.4 PRO performance tests of PES-TFC hollow fiber membranes

The osmotic power generation tests were conducted by using a setup described in our previous publications [19-21] under the PRO mode where the selective layer faces the draw solution. A high-pressure pump (Minneapolis, MN) was employed to recirculate the 1 M NaCl draw solution through the module shell side at 0.6 L min^{-1} (0.056 m s^{-1}) under various hydraulic pressures from zero to their corresponding highest stable pressures in series. Then the pressure gradually reduces to zero during the 2nd run followed by increasing it up again for the 3rd run. While a variable-speed peristaltic pump (Cole-Palmer, Vernon Hills, IL) was used to recirculate the feed DI water through the lumen side at 0.01 to 0.05 L min^{-1} (0.368 to 0.910 m s^{-1}) to maintain its local pressure buildup in the lumen less than 1.00 psi. In other words, the average in pressure gauge readings located at the inlet and outlet of the lumen is less than 1.00 psi. To study the effect of inner pressure buildup on PRO performance, a higher feed flowrate was purposely introduced to induce a pressure buildup of 2.45 psi. The pressure buildup could also be estimated by the Hagen-Poiseuille equation as

$$P_b = \frac{8Q\mu L}{\pi r^4} \quad (9)$$

where **Q** is the volumetric flowrate, **μ** is the dynamic viscosity, **L** is the length of hollow fiber and **r** is the radius of hollow fiber [41].

For each TFC hollow fiber membrane, at least three modules were tested and the average value was reported. The water flux (**J_w**) was calculated based on the weight loss of the feed solution within 15 min and the reverse salt flux (**J_s**) was determined by monitoring the conductivity change. The power density (**W**) can be obtained using the following equation

$$W = J_w \times \Delta P \quad (10)$$

where ΔP is the hydraulic pressure difference across the membrane.

The structural parameter (S), describing the resistance of the support layer in osmosis processes, is defined by the tortuosity (τ), thickness (t) and porosity (ε) of the membrane support as

$$S = \frac{\tau t}{\varepsilon} \quad (11)$$

It can also be obtained from the measurements of forward osmosis (FO) experiments by setting the selective layer of the membrane facing the feed DI water (i.e., the FO mode)

$$S = \frac{D}{J_w^{FO}} \ln \left(\frac{B + A\pi_{D,b}}{B + J_w^{FO}} \right) \quad (12)$$

where D is the solute diffusion coefficient, J_w^{FO} is the measured water flux, and $\pi_{D,b}$ is the osmotic pressure of the bulk draw solution [18, 22, 23, 42].

3. Results and discussion

3.1 Characteristics of PES hollow fiber supports

The morphologies of PES hollow fiber supports spun from different spinning conditions (Table 1) are shown in Figure 2. Due to the fast demixing induced by the external coagulant, all hollow fiber supports exhibit dense and smooth outer surfaces with small pores suitable for the deposition of a thin and less defective polyamide selective layer [21, 24, 31, 43]. The inner surfaces of fibers II and III possess similar morphologies comparable to their outer surfaces because water is used as both the internal and external coagulant. The inner surface of fiber I has a few large pores of 200 – 300 μm , estimated from its FESEM picture, due to the delay demixing caused by the bore fluid of 80/20 NMP/water.

These three fibers have different cross-section morphologies. Fiber I has a single layer of finger-like macrovoids, while fibers II and III have two layers of finger-like structure across the hollow fiber walls. The latter is caused by the water penetration from both inner and outer surfaces [44]. An equal depth distribution of each finger-like layer is observed for fiber II. As the air gap distance increases, it takes time for the outer coagulant to contact the outer surface and then intrude in, whereas the inner surface immediately contacts with the bore fluid once leaving the spinneret. Hence, the depth of the inner finger-like layer grows longer than that of the outer finger-like layer for fiber III. The addition of NMP into the bore fluid retards the phase inversion rate of the inner surface and results in only one finger-like layer for fiber I. In addition, the NMP mixture induces a close-cell structure in the inner edge of the cross-section, rather than the sponge-like structure of fibers II and III. This might be also due to the fact that the inner part was re-dissolved after spinning by the NMP mixture trapped inside the lumen side and re-precipitated.

Figure 3 displays the AFM images and the mean roughness of the outer surfaces of these hollow fiber supports. All supports exhibit similar surface topologies with a mean roughness of 3 – 5 nm over a $5 \times 5 \mu\text{m}^2$ area, which is in the suitable range for interfacial polymerization [20, 45]. A clear ascending trend in roughness is observed as the air gap distance increases from fiber I to III. A higher air gap distance brings a better contact of air moisture on the outer surface, it may develop larger gradients of NMP and polymer mass fraction near the dope/air interface. As a result, the NMP concentration increases while the polymer mass fraction decreases sharply [46]. This localized polymer dilution may perturb the interface and result in a rougher outer surface.

Figure 4 shows the probability density function curves of pore size characteristics for the PES hollow fiber supports, and Table 2 summarizes the mean pore diameter, MWCO as well as geometric standard deviation. The air gap distance plays an important role on membrane nanostructure. Because of rapid phase inversion without much chain relaxation, fiber I spun from the shortest air gap distance of 0.5 cm possesses a small mean pore diameter of 3.93 nm and a sharp pore size distribution with a geometric standard deviation of 1.48. As the air gap distance increases, die swell relaxation occurs [33]. The former induces a larger elongational stress along the nascent fiber, while the latter results in chain relaxation. The combined effects can either align the polymer chains with small interstitial space or relax as well as disentangle chains with large pores depending on which factor is dominant [47, 48]. As a result, fiber II has a larger mean pore diameter of 11.61 nm, a much broader pore size distribution and a geometric standard deviation of 1.86 compared to fiber I. The MWCO increases from 17.8 kDa of fiber I to 183.2 kDa of fiber II. With a further increase in air gap distance to 20 cm, fiber III shows an enhanced MWCO of 224.8 kDa and a geometric standard deviation of 2.03. Because of the elongational stretch by gravity, fiber III has smaller OD and ID, and a larger mean pore diameter than fiber II.

Figure 5 elucidates the PWP of each hollow fiber support as a function of applied hydraulic pressure. Generally, all PWPs decline near-linearly followed by accelerated decays because of membrane compaction under pressure. A further increase in pressure may result in a complete change of membrane physical properties. The collapse pressure of each hollow fiber support is defined as the highest pressure which

the hollow fiber support could tolerate without structural failure as indicated in Figure 5. It is noticed that fibers II and III have similar initial PWP's around $130 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ at 3 bar, which is much higher than that of fiber I of around $60 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. This is due to the effects of the inner close-cell structure as well as smaller and narrower pore sizes of fiber I. When increasing the hydraulic pressure, fiber III shows a rapid PWP decline and has a relatively low collapse pressure of 20 bar. While fibers I and II exhibit much slower PWP declines and have higher collapse pressures of 26 and 30 bar, respectively. Clearly, hollow fibers with a small OD (e.g. fiber I) or thicker wall (e.g. fiber II) are beneficial for higher mechanical tolerance.

3.2 Characteristics and PRO performance of PES-TFC hollow fiber membranes

Figure 6 discloses the polyamide selective layer was successfully formed on the outer surface of PES hollow fiber supports via interfacial polymerization. Three types of morphologies could be clearly distinguished. TFC-I has a smooth surface covered by small globules and few worm-like domains with a typical “ridge-and-valley” polyamide morphology [49]. In contrast, both TFC-II and III have much rougher surfaces. The ridge curls in TFC-II have been significantly enlarged and have a “flake-like” shape. The number of ridge curls in TFC-III is reduced. A relatively smooth dense layer with some protuberances can be found beneath the ridge curls in the outer cross-section of TFC-III. This kind of surface morphology has also been observed in other studies [50, 51]. In other words, the morphology of TFC-III can be treated as a combination of those of TFC-I and II.

According to Li et al. study [43], the polyamide morphology could be significantly influenced by the support's pore sizes. Since fiber I has the smallest surface pore of

3.93 nm with the sharpest pore size distribution, it tends to firmly hold the absorbed MPD solution inside the pores. This retards the diffusion of MPD towards the TMC solution for interfacial polymerization. As a consequence, a smooth polyamide layer of around 100 nm thick with small globules and few worm-like domains is formed. On the contrary, large pores with a broader pore size distribution such as fiber II and III promote the rapid migration of MPD molecules vigorously, increasing the flow turbulence and enlarging the reaction contact area. Thus, a rough polyamide layer consisting of many “flake-like” ridge curls with a larger thickness of 300 – 500 nm is formed [51]. Since fiber III has a higher percentage of pore sizes smaller than 6 nm compared to fiber II as illustrated in Figure 4, some regions of fiber III form small globules and worm-like domains, while other regions grow the “flake-like” ridge curls.

Table 3 summarizes the transport properties of the three TFC hollow fiber membranes. All TFC membranes show good salt rejections of about 80 – 90 %, with impressively low salt permeabilities of $0.022 - 0.042 \text{ L m}^{-2} \text{ h}^{-1}$. These values are found to be about one order of magnitude lower than those of other reported PRO membranes shown in Table 4. However, their water permeabilities vary from $0.609 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ of TFC-I to $1.420 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ of TFC-II. This might be explained by the larger effective membrane area provided by the “flake-like” ridge curls in TFC-II. The cavities inside the ridge curls also facilitate water transport across the polyamide layer [52]. As the morphology of TFC-III is between those of TFC-I and II, it has a moderate water permeability of $1.122 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Comparing to TFC-II and TFC-III, TFC-I possesses the largest structural parameter of $2819 \mu\text{m}$, which might be caused by its close-cell structure near the inner surface. As a result, the high S value indicates this membrane is not suitable for osmosis driven processes [1, 4].

The key performance of the TFC hollow fiber membranes in terms of water flux, reverse salt flux and power density as a function of hydraulic pressure difference in PRO tests is displayed in Figure 7. Generally, the water flux declines with increasing ΔP due to the reduction in effective driving force, while the reverse salt flux rises. TFC-I possesses a low initial water flux of 13.30 LMH because of its small A and big S values. A sudden water flux drop and reverse salt flux upturn are observed when ΔP increases to 5 bar. The performance would further be deteriorated during the 2nd and 3rd runs as the water flux even gets lower, showing no potential for PRO applications.

For TFC-II and III, the repeated data from 2nd and 3rd runs after the 1st run confirm the membrane stability. The water flux of TFC-II at $\Delta P = 0$ is slightly lower than that of TFC-III due to its larger structural parameter (Table 3). If we measure the slope of water flux decline from $\Delta P = 0$ to where the maximum power density occurs, both TFC-II and III exhibit remarkably small slopes of the water flux decline at 0.22 LMH bar⁻¹ and 0.33 LMH bar⁻¹ respectively compared to other PRO membranes as listed in Table 4. This is due to the fact that they have superior low J_s/J_w ratios even at very high hydraulic pressure differences (i.e., 0.44 g L⁻¹ of TFC-II at 20 bar and 0.40 g L⁻¹ of TFC-III at 15 bar) [14]. As a consequence, the effective osmotic driving force across the membrane is well maintained at elevated PRO pressures, leading TFC-II and III with maximum power densities of 7.81 W m⁻² at 20 bar and 7.57 W m⁻² at 15 bar, respectively. The extremely low J_s/J_w ratio and high performance stability make the TFC-II and III membranes promising for PRO applications in comparison to other PRO membranes.

3.3 Effect of inner pressure buildup on PRO performance

The TFC-II was selected to further examine the effect of inner pressure buildup on PRO performance. Besides the normal testing condition where the inner pressure buildup is about 1.00 psi, the flowrate of the feed flowing through the fiber lumen was purposely reduced or elevated to induce a lower or higher pressure buildup. Table 5 summarizes the three testing conditions of different flowrates and their corresponding inner pressure buildups. It can be seen the estimated pressure buildups from the Hagen-Poiseuille equation are in agreement with experiments. Figure 8 illustrates the variations of water flux, reverse salt flux and power density as a function of inner pressure buildup with corresponding linear velocities calculated in the bracket. Due to its low J_s/J_w ratio and high mechanical stability, TFC-II shows similar behaviors of reverse salt flux in all three conditions from 0 to 20 bar. However, the water flux is significantly influenced by different inner pressure buildups. For the inner pressure buildups of 0.35 psi and 1.00 psi, the water fluxes have similar gentle decline trends with around 19 LMH at $\Delta P = 0$ to 14 LMH at $\Delta P = 20$ bar. However, during the 2nd and 3rd runs, the inner pressure buildup of 0.35 psi remains excellent reproducibility in water flux, while 1.00 psi somewhat deviates the water flux from that of the 1st run especially at the low ΔP region. For the highest inner pressure buildup of 2.45 psi, the water flux has been enhanced to 25.21 LMH at $\Delta P = 0$ and then reduced to 18.09 LMH at $\Delta P = 20$ bar during the 1st run followed by an even greater deviation during the 2nd and 3rd runs.

Figure 9A and 9B give a closer look at PRO performance at $\Delta P = 20$ bar in terms of water flux, reverse salt flux and power density. Two possibilities are responsible for the performance change. One is the thinner boundary layer from eddy flow induced

by a higher flowrate and results in lowering transport resistance. However, according to the Reynolds numbers calculated in Table 5, the flow patterns in all three conditions are laminar. Therefore, the increment in lumen flowrate has very limited effects on the concentrative external concentration polarization (ECP) in the feed side. Thus, the variation as a function of inner pressure buildup in PRO performance is most likely caused by the micro-deformation of the polyamide layer.

Different from inner-selective PRO hollow fiber membranes, the polyamide layer in outer-selective PRO hollow fiber membranes experiences compaction rather than expansion under a high hydraulic pressure difference. In the presence of inner pressure buildup, a slight squeeze force exerted on both sides of the polyamide layer that may induce minor structural deformation and thinner the polyamide selective layer, as illustrated in Figure 9C. This type of micro-deformation may favor water flux without compromising reverse salt flux. Further investigations are required to unravel the complicated transport mechanism behind this interesting phenomenon. In addition, the micro-deformation induced by the inner pressure buildup is not only force dependent but also likely time dependent. However, a slight increment in inner pressure buildup from 1.00 psi to 2.45 psi is beneficial for boosting water flux from 14.07 LMH to 18.06 LMH at $\Delta P = 20$ bar and peak power density from 7.81 W m^{-2} to 10.06 W m^{-2} . Future studies are needed to understand the sophisticated science and relationship between membrane structural change and inner pressure buildup to ensure the sustainability of outer-selective TFC hollow fiber membranes for osmotic power generation.

4. Conclusions

We have designed a series of outer-selective PES-TFC hollow fiber membranes via a simplified vacuum-assisted interfacial polymerization method. Firstly, robust hollow fiber supports of various dimensions and morphologies with dense and smooth outer surfaces were made using a single-layer spinneret. Secondly, almost defect-free polyamide layers were synthesized on top of supports with the aid of a vacuum pressure of 800 mbar to effectively remove excess MPD residuals during interfacial polymerization. The resultant TFC hollow fiber membranes were characterized and evaluated for their potential to harvest salinity-gradient energy via PRO. The following conclusions can be drawn from this study:

- (1) The polyamide morphology is highly dependent on pore characteristics of hollow fiber supports. Supports with small or large pores tend to result in a polyamide layer with a “globules and few worm-like” or “flake-like” morphology, respectively. The water permeability of the TFC hollow fiber membranes rely on support and polyamide morphology. The newly developed membranes display impressive low salt permeabilities of $0.022 - 0.042 \text{ L m}^{-2} \text{ h}^{-1}$, indicating that the proposed interfacial polymerization scheme could produce a nearly defect-free polyamide layer.
- (2) Among the three TFC hollow fiber membranes, the TFC-II membrane has the smallest slope of the water flux decline vs. ΔP with a slope value of $0.22 \text{ LMH bar}^{-1}$. Owing to its superior low J_s/J_w ratio of 0.44 g/L even at a very high ΔP of 20 bar, a reasonably stable osmotic driving force could be maintained across the membrane at high pressure PRO tests. Thus, the TFC-II membrane displays a peak power density of 7.81 W m^{-2} at 20 bar using 1 M NaCl and DI water as feeds. Reproducible data obtained from the 2nd and 3rd runs confirm the membrane stability, suggesting its great potential to be used in real PRO applications.

- (3) With a slight increment in pressure buildup in the fiber lumen side from 1.00 psi to 2.45 psi, the TFC-II membrane exhibits a nearly 30% enhanced water flux without compromising the reverse salt flux at $\Delta P = 20$ bar when using 1 M NaCl and DI water as feeds. The maximum power density could be raised from 7.81 W m^{-2} to 10.06 W m^{-2} . However, more studies are needed to understand the mechanism behind this interesting phenomenon.

Acknowledgements

This research study is supported by the National Research Foundation, Prime Minister's Office, Republic of Singapore, under its Environmental & Water Technologies Strategic Research Programme and administered by the Environment & Water Industry Programme Office (EWI) of the PUB. It is funded under the project entitled "Membrane Development for Osmotic Power Generation, Part 1. Materials Development and Membrane Fabrication" (1102-IRIS-11-01) and NUS Grant No. R-279-000-381-279. Special thanks are due to Dr. S. Zhang, Dr. S.P. Sun, Dr. G. Han, Dr. J.Y. Xiong, Mr. C.F. Wan, Miss Y. Cui and Mr. M. Soon for their kind help and valuable suggestions.

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Highlights

1. A new simplified method to fabricate outer-selective thin-film composite membranes.
2. The membranes exhibit small slope between water flux decline and ΔP increase.
3. The membranes display impressive low salt permeabilities of $0.022 - 0.042 \text{ L m}^{-2} \text{ h}^{-1}$.
4. The effective osmotic driving force could be well maintained even under high pressure operations.

Table 1. Spinning parameters of PES hollow fiber supports.

Spinning parameter	Hollow fiber ID		
	I	II	III
Polymer solution (wt%)	PES/PEG 400/NMP/Water: 20~22/36.9~39/36.9~39/2~4.2		
Polymer solution flowrate (ml min ⁻¹)	1.8		
Bore fluid composition (wt%)	DI water/NMP (20/80)	DI water	DI water
Bore fluid flowrate (ml min ⁻¹)	0.55	0.55	0.8
Air gap (cm)	0.5	4	20
External coagulant	Tap water (room temperature)		
Take-up speed (m min ⁻¹)	4.62 (Free falling)	2.60 (Free falling)	2.78 (Free falling)
Spinneret outer dimension (mm)	1.2

Figure 1. Schematic of interfacial polymerization process for outer-selective PES-TFC hollow fiber membrane fabrication.

Figure 2. FESEM morphologies of PES hollow fiber supports as functions of bore fluid composition and other spinning parameters.

Figure 3. AFM images of outer surfaces of PES hollow fiber supports. R_a is the mean roughness.

Figure 4. Probability density function curves of PES hollow fiber supports.

Table 2. Dimensions, porosity, pore characteristics, and collapse pressures of PES hollow fiber supports.

	Hollow fiber ID		
	I	II	III
OD/ID ($\mu\text{m}/\mu\text{m}$)	700/310	1125/525	1000/540
Thickness (μm)	195	300	230
Porosity (%)	76.8 ± 0.5	74.4 ± 0.3	74.3 ± 0.3
Mean pore diameter (nm)	3.93	11.61	11.67
MWCO (kDa)	17.8	183.2	224.8
Geometric standard deviation	1.48	1.86	2.03
Collapse pressure (bar)	26	30	20

Figure 5. Pure water permeability vs. applied pressure of PES hollow fiber supports. A pure water stream pressurized under a particular pressure was running through the shell side of the hollow fiber supports. The down-stream pressure was recorded at each point.

Figure 6. FESEM morphologies of polyamide selective layers of PES-TFC hollow fiber membranes.

Table 3. Transport properties of PES-TFC hollow fiber membranes.

	Hollow fiber ID		
	TFC-I	TFC-II	TFC-III
Water permeability, A ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	0.609 ± 0.090	1.420 ± 0.096	1.122 ± 0.040
Salt permeability, B ($\text{L m}^{-2} \text{ h}^{-1}$)	0.022 ± 0.005	0.028 ± 0.010	0.042 ± 0.004
Salt rejection ^a , R_s (%)	80.4 ± 5.3	88.4 ± 3.4	80.3 ± 1.2
Structural parameter ^b , S (μm)	2819	996	674

^a 1000 ppm NaCl as the feed solution in RO tests under an applied pressure of 1 bar.

^b Structural parameter was calculated based on FO mode performance of FO experiment using 1 M NaCl and DI water as feeds.

Table 4. Comparisons of properties and performances of selected state of the art PRO membranes reported in the literature.

Membrane	Configuration	Water permeability, A ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Salt permeability, B ($\text{L m}^{-2} \text{h}^{-1}$)	Feed solution	Draw solution	Slope of the water flux decline ^b (LMH bar^{-1})	Peak J_s/J_w^c (g L^{-1})	Reference
TFC hollow fiber	outer-selective	1.42	0.03	DI water	1 M NaCl	0.22	0.44	This work
TFC hollow fiber	outer-selective	1.12	0.04	DI water	1 M NaCl	0.33	0.40	This work
TFC hollow fiber	outer-selective	3.59 ^a	1.82 ^a	DI water	1 M NaCl	0.98	-	[21]
TFC hollow fiber	outer-selective	-	-	DI water	0.6 M NaCl	0.64	-	[30]
dual-layer hollow fiber	outer-selective	1.28	-	10 mM NaCl	1 M NaCl	0.65	-	[16]
TFC hollow fiber	inner-selective	1.52	0.24	1 mM NaCl	1 M NaCl	0.34	1.75	[13]
TFC hollow fiber	inner-selective	3.30	0.31	DI water	1 M NaCl	1.34	1.00	[14]
TFC hollow fiber	inner-selective	1.90	0.48	DI water	1 M NaCl	0.69	-	[19]
TFC hollow fiber	inner-selective	0.91	0.09	DI water	1 M NaCl	0.25	1.83	[20]
TFC flat sheet		2.77	-	DI water	1 M NaCl	4.15	-	[11]
TFC flat sheet		3.82	1.19	0.9 mM NaCl	1.06 M NaCl	1.98	-	[12]
TFC flat sheet		2.09	0.87	10 mM NaCl	1 M NaCl	1.39	3.19	[15]
TFC flat sheet		2.83	0.44	DI water	0.5 M NaCl	1.27	3.43	[17]

^a Estimated from the figure plotted

^b Slope of the water flux decline obtained as the slope of the linear regression line of the data points plotted in a PRO performance figure (water flux vs. hydraulic pressure difference). The first available PRO performance data point (normally at 0 bar) was chosen as the starting point and the data point where the maximum power density occurs was chosen as the ending point of the linear regression line.

^c Peak J_s/J_w corresponds to the ratio between reverse salt flux and water flux at the point where the maximum power density occurs.

Figure 7. Membrane performance in PRO tests using DI water as the feed solution and 1 M NaCl as the draw solution. Top (A-C): Water flux and reverse salt flux, and bottom (D-F): power density as a function of hydraulic pressure difference. (The repeated data from the 2nd and 3rd runs using the same membrane after PRO tests. The flowrates of feed solutions and draw solutions are 0.01-0.05 L min⁻¹ and 0.6 L min⁻¹, respectively)

Table 5. Inner pressure buildups of feed solution in high pressure PRO operations.

	Flowrate of feed solution		
	0.015 L min ⁻¹	0.040 L min ⁻¹	0.090 L min ⁻¹
Linear velocity (m s ⁻¹)	0.29	0.77	1.73
Pressure buildup (experimental ^a , psi)	0.35 ± 0.05	1.00 ± 0.10	2.45 ± 0.23
Pressure buildup (estimated ^b , psi)	0.44	1.16	2.63
<i>Re</i> ^c	152	404	909

^a Real pressure buildup obtained as the average reading of pressure gauges located at the inlet and outlet of the lumen side.^b Pressure buildup estimated by the Hagen-Poiseuille equation.^c *Re* is the Reynolds number.^d TFC-II was employed.

Figure 8. The effects of pressure build up on PRO performance of the TFC-II membrane using DI water as the feed solution and 1 M NaCl as the draw solution. Top (A-C): Water flux and reverse salt flux, and bottom (D-F): power density as a function of hydraulic pressure difference. (The repeated data from the 2nd and 3rd runs using the same membrane after PRO tests. The feed flowrate varies while the draw flowrate is 0.6 L min⁻¹.)

Figure 9. Top: TFC-II membrane performance in PRO tests at 20 bar using DI water as the feed solution and 1 M NaCl as the draw solution. Top-left (A): Water flux and reverse salt flux, and top-right (B): power density as a function of inner pressure buildup. Bottom (C): schematic of proposed micro-deformation of the polyamide selective layer in the presence of inner pressure buildup under a high hydraulic pressure difference.