Pressure retarded osmosis – a multi-functional osmotic energy membrane-based harvest technology

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Abstract. Pressure retarded osmosis (PRO) is a re-emerging membrane-based technology to harvest salinity gradient energy (SGE). Membrane is the key factor to further PRO development. Polymer blend is an effective method to enhance membrane properties. In this work, conventional polysulfone (PSf) and polyethersulfone (PES) were blended in 1:1 ratio to fabricate the support membrane. The intrinsic water and salt permeabilities of PSf:PES membrane were enhanced to 1.90 ± 0.42 LMH/bar and 0.46 ± 0.10 gMH, respectively compared to the pristine PSf and PES with only slight drop (1.2 %) in salt rejection of 97.7 %. PSf:PES membrane gave the highest water fluxes of 26.19 and 22.62 LMH at applied hydraulic pressure of 2 and 4 bar, respectively. The resultant power density obtained was 1.46 and 2.51 W/m\(^2\) with the respective hydraulic pressure. The PSf:PES membrane substrate was found to bring a positive impact on the IP reaction with resultant fully cross-linked, leaf-like PA structure which ultimately gives a greater surface/volume ratio on its respective TFC PRO membrane performance.

1. Introduction
Salinity gradient energy (SGE) is released from the spontaneous mixing process of water streams with different salinities [1]. Pressure retarded osmosis (PRO) is one of the re-emerging membrane technologies to harvest SGE in recent decades. In PRO process, water is “retarded” from a low concentration feed solution (FS) into a pressurized high concentration draw solution (DS) across a semi-permeable membrane down osmotic pressure gradient [2]. Consequently, the diluted DS by water is depressurized through a hydro-turbine, converting mechanical energy into electric power generation in which it is the product of hydraulic pressure and water flux. The global osmotic power generation is estimated to be 1600-2600 TWh/year for natural SGE, typically arising from RW to SW [3]. The target power density of 5 W/m\(^2\) is necessary to make PRO economically viable [4]. PRO could be working as an independent power generation system and be a supplementary technology to recover SGE from concentrated brine from desalination plants for water conservation. Its multifunctionality and sustainability at nearly zero greenhouse gases emission attract membrane technologists’ interest to develop the design of PRO operations to the fullest in the purpose of decarbonization [2].

Membrane is one of the key factors in optimizing PRO process [5]. The lack of suitable PRO membranes capable of allowing enough water flow hindered the development of PRO in harvesting SGE since 1970s [4]. The current PRO applications are mostly employing FO membranes in opposite
The orientation of FO mode that is active layer facing DS (AL-DS) [6]. The most FO/PRO membranes are thin film composite (TFC) membranes using polymeric membrane substrate as a support for selective layer (active layer) on its top. An ideal TFC PRO membrane should exhibit high water permeability (A), low salt permeability (B), low structural parameter (S) and excellent salt rejection (R) [5]. The common conventional polymers used for synthesis of membrane substrates are intrinsic hydrophobic such as polysulfone (PSf) and polyethersulfone (PES) which are usually cannot fulfil the requirements [7]. Hence, some modifications were used to synthesize a more hydrophilic membrane substrates and one of them is polymer blend [8, 9]. PES is well-known less polar and hydrophilic with a higher content of sulfone groups than PSf [10, 11]. Therefore, in this work, PSf blended with PES (1:1) was investigated.

The main objective of this work is to investigate the TFC PRO membranes with the PSf:PES blend substrate, the pristine PSf and PES in term of surface morphology, intrinsic coefficients, and power density.

2. Materials and methods

2.1. Chemicals
Polysulfone (PSf, Udel® P-1700, Mw = 67,000, Solvay) and Polyethersulfone (PES, 3000P, Mw = 58,000, Merck) were used as membrane supports. N-methyl-2-pyrrolidone (NMP, ≥99.5%, Mw = 99.13 g/mol, Merck) was used to dissolve polymers and polyethylene glycol 600 (PEG 600, MW = 570 g/mol, Merck) was used as pore-former additive. 1,3-phenylenediamine (MPD, ≥99%, Mw = 108.14 g/mol, Merck); 1,3,5-benzenetricarbonyl trichloride (TMC, 98%, Mw = 265.47 g/mol, Merck) and n-hexane (ACS grade, ≥96%, Mw = 86.18 g/mol, Merck) were used in interfacial polymerization process. Sodium chloride (NaCl, Mw = 58.44 g/mol, Hamburg) was used to make synthetic salt water.

2.2 Fabrication of support membrane
Dope solutions were mixed in 18 wt.% polymers containing weight ratios of 3PSf:0PES, 1PSf:1PES, and 0PSf:3PES with 72 wt.% NMP as solvent and 10 wt.% PEG 600 as pore former. They were labelled as PSf, PSf:PES and PES in order. The support membranes were fabricated by non-solvent induced phase separation method as established elsewhere [8]. The dope solution was casted on a glass plate by using casting knife at thickness of 200 μm. The glass plate was then immediately immersed in the deionized water bath at ambient temperature until the precipitation of support membrane completed. It was then kept in new deionized water for complete solvent removal.

2.3 Synthesis of TFC PRO membrane
The interfacial polymerization technique was adapted from Sun et al. [9]. The support membrane was immersed in an aqueous solution containing 2 wt.% MPD for 2 min, followed by 0.1 wt.% of TMC in n-hexane for 1 min to form a polyamide (PA) active layer on the support membrane. Then, the membrane was dried in the oven at 60 °C for 5 min, followed by cooling for 2 min at room temperature prior immersion in DI water.

2.4 Determination of intrinsic coefficients of TFC PRO membrane
The intrinsic coefficients of TFC PRO membranes were determined by using a dead-end filtration method to determine the water permeability coefficient, A (LMH/bar); salt rejection, R (%) and salt permeability coefficient, B (gMH) of TFC PRO membranes using DI water and 2 g/L NaCl solution, respectively. The water permeability coefficient, A; salt permeability coefficient, B and salt rejection, R were described in Eq. 1, 2 and 3, respectively [12].

\[
A = \frac{J_w}{\Delta P} = \frac{\Delta V}{A \times \Delta t \times \Delta P}
\]  

(1)
\[ B = A \left( \frac{1-R}{R} \right) \frac{(\Delta P - \Delta \pi)}{R} \]  \hspace{1cm} (2)

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \]  \hspace{1cm} (3)

where \( \Delta V \) is the permeate volume (L), \( A \) is the effective membrane area (m²), \( \Delta t \) is the time permeate collected (h), \( \Delta P \) is applied pressure difference (bar), \( \Delta \pi \) is osmotic pressure difference (bar), \( C_p \) is the permeate concentration (g/L) and \( C_f \) is the feed concentration (g/L).

### 2.5 PRO bench scale

A flat-sheet module bench-scale PRO system (CF016, Sterlitech) was used to evaluate the PRO performances of TFC membranes. Both FS and DS streams were designed to cross flow counter-currently on both sides of TFC PRO membrane. The volume of both FS (DI water) and DS (35 g/L NaCl) were prepared in volume of 10.0 ± 0.1 L in two tanks respectively at the beginning of the experiment and circulated at 1.5 L/min. The tanks were placed on electronic weighing balances that are connected to a controller for continuous data recording. The DS’s applied pressure was monitored at 2 and 4 bar. Water flux (LMH) was calculated by Eq. 4 based on the weight change in the DS tank and salt flux (gMH) was obtained by Eq. 5 based on the concentration change in the FS tank [13]. The power density (W) of the TFC PRO membrane was determined by Eq. 6 [2] and the structural parameter (\( \mu m \)) of the membrane was obtained according to Eq. 7 [12].

\[ J_w = \frac{\Delta V}{A \times \Delta t} \]  \hspace{1cm} (4)

\[ J_s = \frac{\Delta (C_t V_t)}{A \times \Delta t} \]  \hspace{1cm} (5)

\[ W = J_w \Delta P \]  \hspace{1cm} (6)

\[ S = \frac{D_s}{J_w} \ln \ln\left( \frac{A \pi_D + B - J_w}{A \pi_F + B + B} \right) \]  \hspace{1cm} (7)

where \( \Delta V \) (L) is the volume changes in the tank, \( A \) (m²) is the effective membrane area, \( \Delta t \) (h) is the time permeate collected, \( C_t \) (g/L) and \( V_t \) (L) are the concentration and volume of the FS at the end of PRO experiments, \( \Delta P \) (bar) is the hydraulic pressure difference, \( J_w \) (LMH) is the water flux, \( D_s \) is the draw solute diffusion coefficient which is assumed to be 1.48×10⁻⁹ m²/s [14] (Straub et al., 2014), \( \pi_D \) (bar) and \( \pi_F \) (bar) are the osmotic pressure of bulk DS and bulk FS, respectively.

### 2.6 Characterizations of TFC PRO membranes

The top surfaces of the synthesized support and TFC PRO membranes were observed by scanning electron microscopy (JEOL JSM-6010LV) with 1000-3000× magnifications. All the membrane samples were sputtered with platinum before SEM analyses.

### 3. Results and Discussion

#### 3.1. Intrinsic coefficients of TFC PRO membranes overview

Figure 1 shows the water permeability, salt permeability coefficients and salt rejection of the TFC PRO membranes on the support PSf, PSEPES and PES. From the figure, the water permeability coefficient
of PSf:PES membrane was further enhanced without any significant negative effect in salt permeability coefficient and rejection compared to the pristine PSf and PES. PSf:PES membrane achieved the highest A of 1.90 ± 0.42 LMH/bar and B of 0.46 ± 0.10 gMH. However, the pristine PSf has a slightly lower A of 1.77 ± 0.02 LMH/bar with the lowest B of 0.2 gMH. The pristine PES has the lowest A of 1.01 ± 0.38 LMH/bar and similar B of 0.22 ± 0.08 gMH to PSf. The pristine PSf has the highest salt rejection of 98.90 %, followed by pristine PES (97.93 %) and PSf:PES (97.70 %). The highest water permeability of PSf:PES brought a slight drop in rejection by only 1.2 %, showing its success by this kind of polymers blending. In PRO process, a membrane with high water flux and moderate salt rejection would be considered because its performance benchmark in terms of power density is the product of water flux.

3.2 PRO performances of TFC PRO membranes

Figure 2 shows the PRO performances of TFC PRO membranes in terms of water and salt fluxes in the membrane orientation of AL-DS using 35 g/L NaCl as DS. In PRO processes, the salt flux in reverse direction occurs simultaneously with water permeation [15]. The pristine PSf and PES have lower water flux with 21.43 LMH and 18.45 LMH, respectively at lower applied hydraulic pressure of 2 and 4 bar. Their salt fluxes are correspondingly lower with 3.60 gMH and 4.19 gMH, as compared to the PSf:PES membrane. After the less polar PES added into PSf, the PRO performances were significantly improved. The polymer blend of PSf:PES has the highest water flux of 26.19 LMH and relatively highest salt flux of 6.57 gMH. At increased applied hydraulic pressure of 4 bar, the water fluxes of all membranes decreased. The water fluxes of pristine PSf and PES are 17.86 LMH and 15.48 LMH which is lower than at 2 bar due to the higher pressure resistance from DS to the water passage (as in RO mode). Their salt flux also increased to 4.79 gMH (PSf) and 5.98 gMH, respectively. The PSf:PES exhibits the highest water and salt flux of 22.62 LMH and 7.76 gMH. This can be attributed to that less cross-linked PA layer on PSf:PES membrane substrate would consequently reduce salt rejection and increase reverse salt flux from DS [16]. More salt diffuses in opposite direction of water with the aid of higher hydraulic pressure in PRO experiments, thus accumulates inside the porous structures and induces significant drop in water flux. The trend of PRO performances is consistent with that intrinsic coefficient (A, B and R) tests.
Figure 2: PRO performances of TFC PRO membranes.

An efficient quantity describes the amount of salt diffuses across membranes normalized by water flux was measured by specific salt flux \((J_s / J_w)\). In Table 1, the specific salt flux and structural parameter of three membranes are shown. It reveals that they are pressure-dependent and increase with applied pressure. The structural parameter is a medium to measure the effect of internal concentration polarization (ICP) which occurs in osmotically driven membrane processes. Due to accumulation of reverse salt flux which form "salt wall" in porous structures, leading to increase in internal concentration polarization, hence the structural parameter of each membrane increases.

| Membrane | 2 bar | 4 bar |
|----------|-------|-------|
|          | \(J_s / J_w\) | \(S\) (\(\mu m\)) | \(J_s / J_w\) | \(S\) (\(\mu m\)) |
| PSf      | 0.17  | 324   | 0.27  | 398   |
| PSf:PES  | 0.25  | 227   | 0.34  | 270   |
| PES      | 0.23  | 303   | 0.39  | 383   |

The ultimate PRO performance of a membrane is evaluated in terms of power density harvested by a PRO membrane. The multifunctional PRO system may require the PRO membrane with high water flux and moderate salt rejection to give high power density and recover SGE before discharge. In PRO experiments, water flux and hydraulic pressure is the main contributor of power density. The TFC PRO membrane exhibits the highest water flux produces the highest power density like PSf:PES, followed by pristine PSf and the last, pristine PES. The PSf:PES membrane produced 1.46 W/m² and 2.51 W/m²; the pristine PSf produced 1.19 W/m² and 1.98 W/m² and the pristine PES produced only 1.03 W/m² and 1.72 W/m² at 2 and 4 bar, respectively. The PSf:PES membrane could produce 22.69 % and 41.75 % higher power density compared to the pristine PSf and PES at 2 bar. However, at higher applied pressure of 4 bar, greater increment was found between them. The power density of PSf:PES membrane was 26.77 % and 45.93 % higher at this pressure, as compared to the pristine PSf and the pristine PES, respectively.

The peak power density is reached when the hydraulic pressure is approximately half of the osmotic pressure [17]. The peak power density of PSf:PES membrane was estimated to be 3.38 W/m² when the hydraulic pressure applied at 8 bar. For pristine PSf, the estimated peak power density would be 2.4 W/m² at 7 bar. Meanwhile, the pristine PES is able to achieve only 2.1 W/m² at 7 bar which is the lowest among all membranes. The reversal power density also begins at the same hydraulic pressure and reaches zero at different hydraulic pressures due to each membrane has different water permeability.
3.3 Characterization of TFC PRO membranes

Representative SEM micrographs on the top surface of the supports and their respective TFC PRO membranes at magnification of ×5000 are presented in Figure 4. Figure 4a and 4b shows the top surface micrographs of the pristine PSf and PSf:PES support membranes, illustrating some leftover unreacted polymer whereas Figure 4c shows a top surface of the pristine PES with homogenous and large surface pores. They exhibit different top surface morphology as their dope solutions have different physicochemical properties. With similar surface morphology of the PSf and PSf:PES support membranes, they may give similar impact during interfacial polymerization under constant conditions. Figure 4d and 4e shows the top surface micrographs of the TFC PRO membrane on pristine PSf and PSf:PES support with homogenous, fully cross-linked polyamide (PA) layer in leaf-like shape. This gives a better surface/volume ratio to the water permeation, resulting in a higher water permeability. Figure 4f shows the top surface of the TFC PRO membrane on the pristine PES support. The fully cross-linked PA structure in globular shape was formed due to its large surface pores on support [18]. It gives a lower surface/volume ratio to water permeation, but the salt rejection performance remained constant. The blend of PSf and PES has successfully shared their characteristics which give a better performance.

Figure 3: Experimental and modeled power density of TFC PRO membranes.

Figure 4: (a) PSf support; (b) PSf:PES support; (c) PES support; (d) TFC PRO membrane on PSf support; (e) TFC PRO membrane on PSf:PES support and (f) TFC PRO membrane on PES support.
4. Conclusion

The effect of polymer blend by PSf and PES was systematically investigated in this work. The PSf:PES membrane substrate has led to an increase in intrinsic water and salt permeability with $1.90 \pm 0.42$ LMH/bar and $0.46 \pm 0.10$ gMH, respectively but without an obvious drop in salt rejection of 97.7% in comparison to the pristine PSf and PES. This polymer blend also gave the highest PRO water flux with 26.19 LMH and 22.62 LMH at applied hydraulic pressure of 2 and 4 bar in PRO experiments. In respect of the highest water flux, it could generate the highest resultant power density with 1.46 and 2.51 W/m² at 2 and 4 bar, respectively and then reach the peak with 3.38 W/m² at 8 bar in modeling. The PSf:PES membrane substrate also brings a positive impact on the IP reaction with resultant fully cross-linked, leaf-like PA structures which give a greater surface/volume ratio on its respective TFC PRO membrane.

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