Polyacrylonitrile Supported Thin Film Composite
Hollow Fiber Membranes for Forward Osmosis

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Abstract

Thin film composite (TFC) hollow fiber membranes have shown great promise as a platform for osmotic processes such as forward osmosis (FO) and pressure retarded osmosis (PRO). Previous work on asymmetric FO membranes demonstrated that employing a hydrophilic supporting structure is essential to promote wetting and mitigate concentration polarization. In this study, we have developed an intrinsically hydrophilic polyacrylonitrile (PAN) hollow fiber supported TFC membrane. A selective polyamide thin film was synthesized on the membrane shell side via interfacial polymerization. The impact of fiber pore structure was investigated during our study with some of our membranes exhibiting water flux of $36.6 \text{ L m}^{-2}\text{h}^{-1}$ using 1 M sodium chloride draw solution against deionized water in PRO mode. These results suggest the potential of utilizing intrinsically hydrophilic polymeric hollow fibers with finely tuned pore structures as support for TFC membranes for osmotic processes.

Keywords: Forward osmosis; thin film composite; hollow fiber membranes.

1. Introduction

Forward osmosis (FO), a platform technology that utilizes osmotic pressure difference to drive water across a semipermeable membrane from a dilute feed solution to a concentrated draw solution while rejecting most solutes, has been touted as a high water recovery and low cost option for seawater desalination and wastewater purification [1-5]. As an osmotically driven membrane process (ODMP), the commercial development of FO has long been hampered by membrane design [6-8]. Therefore, the developments of high performance membranes specifically for FO have been intensively studied in both academic laboratories and industry during the past decade [8-12].

As new membranes are considered for FO, specific design criteria must be met. The selective layer needs to have good permeance and selectivity. The support layer needs to be thin and have an open and interconnected pore structure. These characteristics contribute to the structural parameter, S , defined as the product of the thickness (t) and tortuosity (τ), divided by the porosity (ϵ) (i.e., $S = \tau t / \epsilon$). S must be minimized in order to minimize internal concentration polarization (ICP) [13-15].

Hollow fiber membranes are desired in many membrane applications because of their high packing densities relative to flat sheet and spiral wound

configurations. This higher packing density allows for small footprint systems and makes low flux performance more tolerable. These benefits have translated well for FO, making them a preferred platform for many academic groups [7, 16, 17]. A number of hollow fiber membranes have been developed for FO in academic laboratories, with many showing some promise of high performance [11, 18-21]. Only recently have some companies designed new hollow fiber FO membranes and manufactured on a large scale. But those membranes, with moderate performance, are still largely unavailable to academic researchers or industrial operations [22].

Amongst the first hollow fiber membranes developed for FO were integral asymmetric membranes. Polybenzimidazole (PBI) and cellulose acetate (CA) were chosen because of their excellent nanofiltration (NF) characteristics [18, 23, 24]. Thermal and chemical treatments were used to enhance their selectivity and the resultant membranes showed good rejection to divalent ions. However, the relatively low selectivity to monovalent ions limited their capabilities in desalination applications. Follow-up work was focused on enhancing the water flux for FO applications using dual-layer composite membranes comprised of polybenzimidazole/polyethersulfone/polyvinylpyrrolidone (PBI/PES/PVP) [19]. Another study utilized polyamide-imide (PAI) as hollow fiber substrate material followed by polyelectrolyte post-treatment with polyethyleneimine (PEI) to

achieve a NF-like selective layer [21]. Similarly, a dual-layer composite membrane comprised of PAI/PES was also investigated [25]. These membranes all exhibited good flux performance, but were still limited to nanofiltration selectivity.

A leap forward in composite hollow fiber membrane occurred when Wang et al first synthesized a reverse osmosis (RO)-like thin film composite (TFC) hollow fiber membrane in 2010 [11, 20]. The polyamide (PA) selective layer was formed via *in-situ* interfacial polymerization on a porous polyethersulfone (PES) hollow fiber substrate. Since then, a number of studies have been focused on investigating the structure-performance relationships of TFC hollow fiber membranes. Shi et al has investigated the effect of substrate structure on the FO performance of PES hollow fiber membranes. The substrate surface structure was proved to be essential for forming the TFC layer and it should possess a MWCO of less than 300 kDa in order to achieve a desirable performance. Cross-section structures with different proportions of needle-like pores, sponge-like pores and large macrovoids were investigated, but no significant difference were found in their FO performances [26]. Based on the same substrate material (PES), Sukitpaneemit et al designed a macrovoid-free fully sponge-like structure. This macrovoid-free TFC hollow fiber membrane showed slightly inferior FO performance but enhanced strength, which resulted in a more stable operation process [27]. Moreover, novel substrate materials were studied and aimed for a lower structural parameter and greater

hydrophilicity. Zhong et al used direct sulfonated polyphenylenesulfone (sPPSU) as substrate material for TFC hollow fiber membrane. With increased degree of sulfonation, the hydrophilicity of substrate was increased and resulted in higher FO performance [28].

A hydrophilic support layer is favored in TFC membrane design for FO as support layer wetting was found to be essential for osmotic flow. The solutes can only diffuse through the wetted porosity of the support layer and an intrinsically hydrophilic support can effectively minimize ICP [29]. A number of studies on TFC FO flat sheet membranes have shown high performance by utilizing intrinsically hydrophilic material or physically wetting membrane support [30-32]. For hollow fiber membranes, intrinsically hydrophilic materials have been only investigated as integral asymmetric membranes with NF selectivity [24].

In this study, an intrinsically hydrophilic polymer -- polyacrylonitrile (PAN) -- was selected as the support material for TFC hollow fiber membranes for FO because it is hydrophilic, inexpensive and easy to spin. Different structures were considered by altering the fabrication technique. The polyamide selective layer was formed *in-situ* on the shell side surface of hollow fiber substrates. In comparison to the lumen-selective hollow fiber membranes, the shell-selective hollow fiber membrane has more surface area per module and less propensity for serious fouling [16, 33]. However, forming a perfect PA layer on fiber shell surface is more

challenging than on lumen surface. Neither an air purge nor solvent can be applied for removing excess amine from the shell surface. Therefore, the preferred method in the literature is lumen side selective layer formation [11, 34]. Recent studies show that when interfacial polymerization is conducted on fiber shell surface in bundle, the PA tends to form between fibers and induce defects if the excess monomer solution is not sufficiently removed. In a continuous process, submerging fiber through several monomer solutions to synthesize the selective layer is troublesome since the fiber shell surface will contact multiple rollers during the process, thereby inducing defects on the PA layer [33]. In this work, we developed a batch coating method for fiber shell-selective layer synthesis. The TFC FO hollow fiber membranes exhibited reasonable osmotic fluxes in both FO and PRO modes and demonstrated the potential of PAN being a suitable substrate polymer for TFC hollow fiber membranes with shell side selective layers.

2. Experimental

2.1 Materials

Polyacrylonitrile (PAN, M_w = 150,000 g/mol), m-phenylene diamine (MPD, >99.0%), triethylamine (TEA, >99.0%), sodium dodecyl sulfate (SDS, >99.0%) and 1, 3, 5-benzenetricarbonyl trichloride (TMC, 98.0%) were purchased from Sigma Aldrich (St. Louis, MO). N, N-dimethylformamide (DMF,

anhydrous, >99.8%), glycerol (certified ACS, >99.5%), *n*-hexane (HPLC, >98.5%), 2-propanol (IPA, >99.5%) and sodium chloride (NaCl, crystalline, >99.0%) were purchased from Fisher Scientific (Pittsburgh, PA). Deionized water (DI) was obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

2.2 Fabrication of hollow fiber substrates

16 wt. % of PAN was dissolved in DMF at 60°C to obtain homogeneous solutions. The solutions were continuously stirred at room temperature for 24 h and then rested to allow air bubbles to escape. Hollow fiber membranes were prepared via dry-jet wet-spinning process. Similar method has been reported in our previous studies [35, 36]. The degassed polymer solutions and bore fluids were extruded through the spinneret. Three bore fluids: DI water, 30 and 60 wt. % DMF aqueous solutions were used and delivered by syringe pump KDS220 (KD Scientific, Holliston, MA) at a flow rate of 4 mL/min. The hollow fiber membranes formed were designated as PAN-0, PAN-30 and PAN-60, respectively. The nascent fiber went through an air gap of 2 cm before immersing into an external coagulation bath. Tap water was used as the external coagulant and circulated throughout the spinning processes. Fibers were taken up by a rotating drum at a linear speed of 2 m/min. To remove residual solvent, the hollow fiber substrates were stored in DI water for at

least two days. Afterwards, the fibers were post-treated by 50 wt.% glycerol aqueous solution for 24 h to prevent the collapse of porous structures when they were dried [35, 37].

2.3 Synthesis of polyamide selective layer

The thin film polyamide selective layer was synthesized on the shell side surface of hollow fiber substrates via *in-situ* interfacial polymerization. First, the glycerol treated PAN hollow fiber substrates were taped on a rubber frame with sufficient fiber length and space between adjacent fibers. The whole fiber frame was immersed in DI water for 1 h to remove surface glycerol. Then the fibers were sealed at both ends and immersed in a 2/2/0.1 wt. % MPD/TEA/SDS aqueous solution for 3 min. The excess MPD solution residual were removed by filter paper then dried in fume hood for 3 min. After that, a 0.1 wv. % TMC/hexane solution was brought into contact with the MPD-saturated fiber shell surface for 1 min. After the reaction, the fibers were rinsed with hexane to remove unreacted monomers and dried in air at room temperature for 1 min. Similarly, the effective part of TFC hollow fiber membranes were cut off from rubber frame and post-treated by 50 wt. % glycerol aqueous solution overnight.

After drying in air at room temperature, both hollow fiber substrates and TFC membranes were bundled and inserted into clear 6-inch PVC tubes, respectively.

Epoxy resin (Cytec Industries, Olean, NY) was employed as potting material and prepared modules for further testing.

2.4 Hollow fiber membrane characterization

All the dimensions of the fibers were obtained based on physical measurements on water saturated fibers at five different locations for each membrane sample. The fiber diameter and fiber wall thickness were measured with coolant proof digital micrometer (IP65-MX, Mitutoyo, IL) on wetted membranes. The effective fiber length in module is measured with solar digimatic caliper (Absolute 500, Mitutoyo, IL).

The morphology of the hollow fiber substrates and TFC membranes were imaged with a cold cathode field emission scanning electron microscope JSM-6335F (FESEM, JEOL Ltd., Japan). To view the cross sections of the membranes, the samples were submerged in liquid nitrogen to preserve the pore structure and cut with a razor blade. Prior to imaging, the samples were sputter coated with gold.

Dynamic contact angle (DCA) measurements were performed using a Cahn 322 dynamic contact angle analyzer (Thermo Scientific, Newington, NH) to determine the hydrophilicity of the hollow fiber membranes [11]. Each hollow fiber was tested by a single cycle-single loop method with a moving rate of $80\mu\text{m/s}$

and an immersion depth of 4mm. The values were taken as an average of four advancing contact angles. All measurements were taken at room temperature.

A bench-scale ultrafiltration testing unit was used to evaluate the pure water permeance of hollow fiber substrates at $20 \pm 1^\circ\text{C}$. DI water was circulated through the shell side of the membrane module at a transmembrane pressure of 0.07 bar with a fixed cross-flow velocity of 0.06 m/s. Similar apparatus was described in our earlier studies [35, 37].

The mechanical properties of hollow fiber substrates and TFC hollow fiber membranes were obtained from the tensile tests in air at 25°C using a Dynamic Mechanical Analyzer 2980 (DMA, TA Instruments, New Castle, DE). Hollow fibers were cut into 15 mm sample segments and stored in DI water before measurement. Tests were run at a ramp rate of 1 N/min and conducted on wet hollow fiber substrates and TFC membranes. Data acquisition and analysis was completed using Universal Analysis software from TA Instruments. Values presented are the average of four tests.

2.5 Membrane performance tests

2.5.1 Pure water permeance of TFC membranes

Pure water permeances (A , $L\ m^{-2}h^{-1}bar^{-1}$) of the TFC hollow fiber

membranes were evaluated in a lab-scale cross-flow RO test unit designed for hollow fibers. The hydraulic pressure was applied on the shell side of TFC hollow fiber membrane during the RO experiments. The A value was obtained from pure water flux with applied pressure of 1 bar at $20\pm0.5^{\circ}\text{C}$. The salt permeability coefficients (B , $\text{L m}^{-2}\text{h}^{-1}$) were determined by testing the membrane under the RO mode following a method described elsewhere [20]. A feed solution of 100 ppm NaCl and a feed pressure of 0.5 bar was used and the salt permeability B was derived using methods previously described [9, 11, 20, 27].

2.5.2 Osmotic flux tests of TFC membranes

Osmotic water flux and reverse salt flux through TFC membranes were characterized using a custom lab-scale cross-flow forward osmosis system. The similar experimental setup was described in earlier investigations [12, 30]. Osmotic flux tests were carried out with the membrane oriented in both FO mode (the membrane selective layer faces the feed solution) and PRO mode (the membrane selective layer faces the draw solution). The TFC membranes were tested under a previously provided standard method in which water and salt fluxes were measured at $20\pm0.5^{\circ}\text{C}$ using DI feed and 1 M NaCl draw solution [38]. The hydraulic pressure was equal on both sides of membrane while the Reynolds numbers of the fluid flowing in the fiber lumen and shell were 1100 and 800,

respectively [39]. The osmotic water flux, J_w , was calculated by dividing the volumetric flux by the membrane area. By measuring the conductivity of the feed solutions at certain time points during the tests, the reverse salt flux, J_s , was calculated by dividing the NaCl mass flow rate by the membrane area. The specific salt flux is simply a ratio of salt flux to water flux, J_s/J_w . The structural parameters (S , μm) were empirically determined by solving the following set of equations when membranes were oriented in FO mode [40]:

$$J_w = A \left\{ \frac{\pi_D \exp(-\frac{J_w S}{D}) - \pi_F \exp(\frac{J_w}{k})}{1 + \frac{B}{J_w} [\exp(\frac{J_w}{k}) - \exp(-\frac{J_w S}{D})]} \right\} \quad (1)$$

$$J_s = B \left\{ \frac{c_D \exp(-\frac{J_w S}{D}) - c_F \exp(\frac{J_w}{k})}{1 + \frac{B}{J_w} [\exp(\frac{J_w}{k}) - \exp(-\frac{J_w S}{D})]} \right\} \quad (2)$$

where J_w and J_s are the water and reverse salt flux in FO mode. k is the mass transfer coefficient for the feed channel (*i.e.* shell side) of hollow fiber module [41]. D is the bulk diffusion coefficient of the draw solute. The water permeance A and salt permeability coefficient B are determined from the RO tests. Other parameters: draw solution concentration c_D , feed solution concentration c_F , and the corresponding osmotic pressures, π_D and π_F , are all experimentally accessible. Once all of these known values are input into the model, S can be determined numerically.

3. Results and discussion

3.1 Morphology of hollow fiber membranes

The TFC hollow fiber membranes are designed with a shell-selective layer and three different interior structures to investigate their effects on performance. Figure 1 shows the cross-sectional structure of the three hollow fiber substrates. These fibers were designed to have a fixed outer diameter of about 1100 ± 50 μm . A sponge-like dense layer was observed underneath the fiber shell surface for each fiber. This is due to an instantaneous de-mixing induced by the non-solvent external coagulant (*i.e.* tap water) [16, 42]. Figure 2 shows the surface morphology of hollow fiber substrates and TFC membranes. A smooth and uniform shell surface morphology was observed for all three fibers. This is critical for interfacial polymerization to form a robust and defect-free PA selective layer on the shell surface of hollow fiber substrates [9].

Figure 1

As expected, the lumen surfaces and cross-section morphologies underneath the lumen surfaces of the hollow fibers were varied with different fabrication conditions. As the concentrations of solvent (DMF) in bore fluids changed from 0

to 60%, the polymer precipitation rate during phase separation was delayed and resulted in varied wall thickness. The PAN-0 had the thickest wall at $\sim 100\ \mu\text{m}$ and the PAN-60 had the thinnest at $\sim 50\ \mu\text{m}$ based on the micrometer measurement. PAN-0 and PAN-30 showed similar cross-sectional structure: a thick region of macrovoid structure adjacent to a relatively thin region of finger-like structure underneath the lumen surface of hollow fiber. This is due to the instantaneous polymer precipitation induced by the non-solvent-rich bore fluid for PAN-0 and PAN-30 (pure DI water and 70 wt. % DI water, respectively) [16, 42].

However, PAN-60 hollow fiber fabricated from a solvent-rich bore fluid (60 wt. % DMF) exhibit a porous interior structure with straight and open finger-like pores throughout the membrane (Figure 1f). Again, DMF in the bore fluid reduced the solvent/non-solvent de-mixing rate, which provided time for the nuclei and surface pore formation [43].

Figure 2

Figure 2 also shows the three TFC membranes selective layer surface morphology. The TFC membrane lumen surface showed uniform and defect-free ridge-and-valley morphology which is typical for polyamide synthesized using the interfacial polymerization method [44]. This suggests that thin polyamide selective

layers were successfully formed onto each of the PAN hollow fiber substrates.

3.2 Characterization of hollow fiber membranes

The dynamic contact angle and pure water permeability of the PAN hollow fiber substrates were tabulated in Table 1. The contact angles of three substrates were $\sim 50^\circ$, indicating their reasonably good hydrophilicity and is consistence with a flat-sheet cast PAN membrane [45]. The pure water permeabilities for PAN-0, PAN-30 and PAN-60 were 154.4, 231.6 and 304.7 $L m^{-2} h^{-1} bar^{-1}$, respectively.

Table 1

The mechanical properties of the hollow fiber substrates and TFC membranes were measured at room temperature. The stress-strain curves of representative membrane samples are presented in Figure 3. All the substrates and TFC membranes exhibited reasonable stiffness and excellent stretch resistance. It is worth noting that the PAN-60 membranes, with the thinnest wall, possess the highest tensile strength and elastic modulus among all three membranes. This is expected since the material mechanical properties were normalized as force per unit area and PAN-60 has smallest cross section area [11, 33, 46, 47]. By comparing the substrates with TFC membranes, it can be seen that the TFC

membranes exhibit comparable or better mechanical properties than their substrate bases. This suggests that the interfacial polymerization may not jeopardize the membrane mechanical properties. Instead, the strength and stiffness of TFC hollow fiber membranes could be enhanced by PA thin film [30, 31]. This is most obvious for PAN-60 TFC membrane, where the PA thin film occupies the highest proportion of the TFC membrane thickness.

Figure 3

3.3 Performance of TFC membranes

3.3.1 Permselectivity of polyamide selective layers

The intrinsic water permeance (A) and salt permeability (B) of the TFC membranes selective layer are reported in Figure 4. Based on the pure water permeance test, the PAN-0, PAN-30 and PAN-60 showed comparable A values of 2.05, 1.96 and 2.15 $L m^{-2} h^{-1} bar^{-1}$, respectively, which are also comparable with the commercial TFC FO membrane from Hydration Technology Innovations [12]. The B values were found to be 0.67 and 0.70 $L m^{-2} h^{-1}$ for PAN-0 and PAN-30 and 1.56 $L m^{-2} h^{-1}$ for PAN-60 when using 100 ppm NaCl as feed solution. Even at the low pressures, the PAN-60 membranes were observed to be collapsed during

the test. This collapse is possibly caused by its thin thickness, large radius, and greater rigidity [48, 49].

Figure 4

3.3.2 Osmotic flux performance of TFC membranes

The osmotic water fluxes and reverse salt fluxes of the TFC membranes are presented in Figure 5. The membranes with the thinnest walls exhibited the highest water flux for both FO and PRO modes. PAN-60 achieved fluxes ~ 50% higher than those of PAN-0 and PAN-30 in both FO and PRO modes. Meanwhile, the reverse salt flux of PAN-60 is $19.2 \text{ g m}^{-2}\text{h}^{-1}$ in FO mode, which is about 3 times higher than those of PAN-0 and PAN-30. This can be attributed to the thinness of PAN-60 membranes because the draw solutes can diffuse through the thin support structure rapidly.

Figure 5

Compared to the commercial HTI TFC membrane [12], our TFC membranes generally yield comparable or higher water and reverse salt flux in both modes.

Our highest water flux membrane, the PAN-60, exhibited higher reverse salt flux despite 30% higher water flux in PRO mode and 70% higher water flux in FO mode. The PAN-30 membrane has 2 times lower reverse salt flux than HTI TFC in PRO mode and about equal in FO mode. For the PAN-0, both water and reverse salt fluxes are about equal with the HTI TFC membrane in both modes.

The structural parameters of PAN-0, PAN-30 and PAN-60 membranes were empirically determined from Eq (1) and (2) as 549, 499 and 305 μm , respectively. It is not surprising to see a comparable structural parameter of PAN-0 (549 μm) with the HTI TFC (533 μm) since the osmotic flux performance is in good agreement. Also, the membrane thicknesses of these two membranes are comparable ($\sim 100 \mu m$). Meanwhile, we obtained a low S value of 305 μm for the PAN-60 which can be attributed to the thinness of hollow fiber wall ($\sim 50 \mu m$). However, the empirically calculated S value might be slightly larger than the real S value. This is because the lumen surface area is smaller than that of shell selective surface. It may result in mild dilution of the local concentration of draw solute at the interface of selective and support layer. This would be reflected as a slightly larger S than the real value.

Specific salt flux J_s/J_w is a metric that is used to determine the amount of draw solute loss per unit of water passed. It has been used to compare membrane performance when different membranes and/or draw solute are used [50]. Lower

J_s/J_w is desirable to prevent the loss of draw solutes in FO and help to minimize ICP in PRO. As shown in Figure 6, the high J_s/J_w of PAN-60 is due to its considerably high salt permeability. In this case, the improved water flux does not surpass the increase in salt flux. The PAN-30 membrane, with the specific salt fluxes of 0.34 and 0.26 g/L in FO and PRO modes, represent our best performing TFC membrane based on this metric of performance.

Figure 6

Along with comparison to commercial benchmark HTI TFC membrane, the PAN supported TFC hollow fiber membranes were also compared to other PAN based flat sheet TFC FO membranes [51], layer-by-layer membranes[45], other shell selective hollow fiber FO membranes [11], PRO membranes [33], and lumen selective FO hollow fiber membranes from academic research groups [20, 27, 28] and industrial company [22]. As shown in Table 2, our hollow fiber membranes exhibit significantly better water flux combined with a lower specific salt flux in both modes than PAN flat sheet TFC membranes. Compared to layer-by-layer assembled flat sheet membranes which were targeted for nanofiltration solute rejection, our membranes showed comparable water flux and lower specific salt

flux, especially in PRO mode [45]. It is worth noting that the draw solution in our tests (1 M NaCl) provided a lower osmotic driving force than that in the LbL work (1 M MgCl_2). Moreover, Mg^{2+} ions are more easily retained which results in lower reverse salt flux.

When compared with another shell-selective hollow fiber FO membrane based on PES, all of our membranes exhibited higher performance in both FO and PRO modes [11]. This is due to employing hydrophilic PAN as the support layer material. The supporting structure wetting was promoted, the effective porosity was increased and the internal concentration polarization was mitigated.

Meanwhile, the reverse salt flux of PAN hollow fiber membrane is slightly higher because it is relatively easy for the draw solute to diffuse through a hydrophilic supporting structure. While comparing with shell-selective hollow fiber PRO membranes fabricated via a vacuum-assisted interfacial polymerization in PRO mode, our membranes exhibited comparable water fluxes but much lower salt fluxes. However, our membranes showed inferior performance when compared with the lumen selective FO hollow fiber membranes. We attribute this to the general challenges of obtaining high quality shell side selective layers using current methods, even though our batch method shows promise. However, with the same packing density, shell-selective TFC hollow fiber membranes would yield higher water flux per module.

Table 2

4. Conclusions

In this work, we investigated polyacrylonitrile supported TFC hollow fiber membranes for use in forward osmosis. The intrinsically hydrophilic PAN substrate material was used to mitigate ICP by ensuring wetting of the supporting structure. We also described a simple way to adjust the structure of the fibers in order to elucidate the structure-performance relationships of TFC hollow fiber membranes during osmosis. While exhibiting good osmotic performance overall, our best performing membrane exhibited one of the lowest structural parameters of TFC hollow fiber membranes reported in the open literature. Our thinnest membrane had a wall thickness of $\sim 50 \mu\text{m}$ and was shown to have excellent performance when compared to the flat sheet counterparts and other shell-selective hollow fiber membranes reported in the literature.

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Tables

Table 1

Dynamic contact angles and pure water permeances of the hollow fiber substrates.

Substrates	Contact angle (degree)	Pure water permeance ($L\ m^{-2}h^{-1}bar^{-1}$)
PAN-0	52.0 ± 3.4	154.4 ± 6.8
PAN-30	54.8 ± 6.4	231.6 ± 9.4
PAN-60	56.2 ± 3.6	304.7 ± 13.3

Temperature during the measurements was $20 \pm 0.5^\circ\text{C}$.

Table 2

Comparison of osmotic flux performance with TFC FO membranes reported in literature.

Membranes	Configuration	Mode	Feed	Draw solution	Water flux	Salt flux	Specific salt flux	Reference
					$L\ m^{-2}h^{-1}$	$g\ m^{-2}h^{-1}$	g/L	
PAN-0	Shell selective hollow fiber	FO	DI	1 M NaCl	16.58	6.46	0.39	This work
PAN-30	Shell selective hollow fiber	FO	DI	1 M NaCl	17.01	6.00	0.34	This work
PAN-60	Shell selective hollow fiber	FO	DI	1 M NaCl	24.71	19.20	0.79	This work
HTI TFC	Flat sheet	FO	DI	1 M NaCl	15.10	4.40	0.29	[12]
H-PAN	Flat sheet	FO	DI	0.5 M NaCl	9.25	6.43	0.69	[51]
6#LbL-PAN	Flat sheet	FO	DI	1 M MgCl ₂	22.00	6.65	0.30	[45]
#A-FO HF	Shell selective hollow fiber	FO	DI	0.5 M NaCl	5.00	2.12	0.42	[11]

#B-FO HF	Lumen selective hollow fiber	FO	DI	0.5 M NaCl	14.00	1.75	0.13	[11]
#C-FO HF	Lumen selective hollow fiber	FO	DI	0.5 M NaCl	18.50	1.50	0.08	[20]
FO-PES _{water}	Lumen selective hollow fiber	FO	DI	1 M NaCl	26.00	4.30	0.17	[27]
1.5 mol % sPPSU	Lumen selective hollow fiber	FO	DI	0.5 M NaCl	22.51	5.49	0.24	[28]
Samsung Cheil HFFO	Lumen selective hollow fiber	FO	DI	1 M NaCl	10.00	3.60	0.36	[22]
PAN-0	Shell selective hollow fiber	PRO	DI	1 M NaCl	25.86	10.75	0.42	This work
PAN-30	Shell selective hollow fiber	PRO	DI	1 M NaCl	24.53	6.80	0.26	This work
PAN-60	Shell selective hollow fiber	PRO	DI	1 M NaCl	36.57	18.75	0.52	This work
HTI TFC	Flat sheet	PRO	DI	1 M NaCl	30.05	11.2	0.37	[12]
H-PAN	Flat sheet	PRO	DI	0.5 M NaCl	13.88	6.43	0.46	[51]
6#LbL-PAN	Flat sheet	PRO	DI	1 M MgCl ₂	25.09	14.25	0.57	[45]
#A-FO HF	Shell selective hollow fiber	PRO	DI	0.5 M NaCl	12.90	5.03	0.39	[11]

#B-FO HF	Lumen selective hollow fiber	PRO	DI	0.5 M NaCl	32.20	3.54	0.11	[11]
#C-FO HF	Lumen selective hollow fiber	PRO	DI	0.5 M NaCl	42.60	4.00	0.09	[20]
FO-PES _{water}	Lumen selective hollow fiber	PRO	DI	1 M NaCl	37.50	5.10	0.14	[27]
1.5 mol % sPPSU	Lumen selective hollow fiber	PRO	DI	0.5 M NaCl	49.39	11.00	0.22	[28]
Samsung Cheil HFFO	Lumen selective hollow fiber	PRO	DI	1 M NaCl	19.00	8.88	0.47	[22]
M1IP1 HF-PRO	Shell selective hollow fiber	PRO	DI	1 M NaCl	21.78	12.85	0.59	[32]
M1IP2 HF-PRO	Shell selective hollow fiber	PRO	DI	1 M NaCl	36.29	33.75	0.93	[32]
M2IP2 HF-PRO	Shell selective hollow fiber	PRO	DI	1 M NaCl	33.17	23.88	0.72	[32]

Figure 1: Cross-sectional FESEM images of hollow fiber substrates. (a), (b) and (c) PAN-0, PAN-30 and PAN-60 at 65×, respectively. (d) PAN-0 at 600×, (e) PAN-30 at 950×, (f) PAN-60 at 1000×.

Figure 2: Inner and outer surface FESEM images of hollow fiber substrates and selective layer surface FESEM images of TFC hollow fiber membranes at magnifications of 10,000 $\times$.

Figure 3: Representative stress-strain curve of hollow fiber substrates (HF) and TFC membranes for PAN-0, PAN-30 and PAN-60.

Figure 4: Pure water permeance (A) and salt permeability coefficients (B) for the three TFC membranes. Results are an average of three experiments with different modules. Error bars indicate standard deviation. Rejection test operating conditions: feed 100 ppm NaCl, feed pressure 0.5 bar, feed temperature 20 °C, feed flow velocity 0.08 m/s, Reynolds number 800.

Figure 5: Water and reverse salt fluxes (J_w and J_s) of FO and PRO tests for three membranes. Results are an average of three experiments with different modules. Error bars indicate standard deviation. Operating conditions: 1 M NaCl draw solution, deionized water feed, 20 °C feed and draw solution temperature. Reynolds number 1100 and 800 on lumen and shell sides, respectively.

Figure 6: Specific salt fluxes J_s/J_w of FO and PRO tests for three membranes. Results are an average of three experiments with different modules. Operating conditions: 1 M NaCl draw solution, deionized water feed, 20 °C feed and draw solution temperature. Reynolds number 1100 and 800 on lumen and shell sides, respectively.

Graphical Abstract