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Effect of the support on the characteristics and permselectivity of thin film composite membranes

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Abstract

How the membrane support affects the performance of thin-film composite (TFC) membranes has long been under debate. Our present study experimentally establishes that the support pore number density (number per unit area) as well as its surface porosity play pivotal roles in affecting the characteristics and permselectivity of TFC membranes. The structure of hollow fiber supports was finely tuned and characterized via a series of techniques, which provided a link to the physicochemical properties of the interfacially polymerized polyamide films. During the spinning process, decreasing the content of N-methyl-2-pyrrolidone in the bore fluid drastically reduced the pore size and surface porosity of the support. The resultant TFC membranes showed a lower water permeability (tested under 1 bar using 500 ppm NaCl). Adding lithium chloride to the polymer dope also led to a support with smaller pores and lower porosity, but increased surface pore number density. The resulting TFC membranes had a substantially higher water permeability and slightly higher salt rejection. In both arrays of membranes, all membranes shared similar thickness of polyamide leaf but a more crumpled film was found on a less porous support, suggesting that the surface porosity of the support affected the effective surface area of films. However, the TFC membrane with a higher effective surface area did not necessarily possess a higher permeability. Rather, a TFC membrane having a support with a higher surface porosity or a higher pore number density exhibited a higher water permeability, demonstrating that the lateral transport path of water through films had a significant impact on the water permeability of TFC membranes. Interestingly, in both cases, the selectivity of the TFC membranes was maintained when the water permeability increased. This study clarifies longstanding misunderstandings concerning the effects of the support on TFC membrane performance and provides insight into fabricating highly permeable and selective TFC membranes.

Keywords: Thin-film composite membrane; Support; Surface porosity; Pore number density; Hollow fiber membranes

1. Introduction

Thin-film composite (TFC) membranes are now dominant in broad applications including reverse osmosis (RO) [1, 2], forward osmosis (FO) [3, 4] and nanofiltration (NF) [5, 6] due to their excellent selectivity, acceptable permeability and easy fabrication process. A TFC membrane has a thin selective film integrated with a porous and mechanically robust support [7]. This unique structure not only minimizes the transport resistance of fluids through the membrane, but also allows tailoring both the film and the support to achieve the desired performance [8]. Interfacial polymerization is the most widely employed approach to fabricate TFC membranes. This process typically involves impregnating a support with an aqueous solution containing monomer **A** that is subsequently placed in contact with an immiscible organic phase containing monomer **B**. Usually, the solubility of monomer **A** in the organic solvent is much higher than that of monomer **B** in the aqueous solution [9, 10]. Thus, the asymmetric solubility makes the polymerization reaction take place primarily on the organic side [10, 11]. Yet, the interfacial polymerization is abruptly slowed down upon the formation of a cross-linked polymer film that impedes the contact between the monomers [10]. Therefore, the interfacial polymerization reaction is a self-limiting and self-terminating process [7, 10], which accounts for the formation of a polymer film with a finite thickness.

TFC membranes generally possess a high selectivity, but typically have a low water permeability [12]. Developing highly permeable and selective TFC membranes is of great interest for improving the separation efficiency and reducing energy consumption [5, 12]. It has long been recognized that the support of TFC membranes is more than a mechanically robust substructure; its physicochemical properties also have a significant impact on the formation of the polyamide film and the performance of the TFC membrane [13-17]. Note that the terminology “support” and

“substrate” have been used interchangeably in the literature. However, since “support” is used more commonly, it will be used throughout this paper. A reliable way to link the TFC membrane performance to the properties of the support has proved to be challenging. Some conclusions from independent studies are still being debated. For instance, Singh *et al.* [18] proposed that a support membrane with smaller pores was favourable for reducing the intrusion of polyamide into the support and therefore resulted in a thinner polyamide film with a higher water permeability. However, in contrast, Ghosh *et al.* [14] studied a series of TFC membranes fabricated on different polysulfone supports and found that a support with larger pores and higher hydrophobicity produced a more permeable TFC membrane. Further studies [19, 20] reached a similar conclusion that TFC membranes prepared on supports with a larger pore size had a higher water permeability. A recent study of the authors [8] also found that surface pores of hollow fiber supports that were elongated and narrowed when the take-up speed was elevated, resulted in TFC membranes with a lower water permeability.

Despite the contradictory conclusions drawn from independent studies, most investigators attribute a higher water permeability to a thinner polyamide film resulting from less penetration of polyamide into the support. However, a mathematical model [10] and direct microscopic observations [11, 21, 22] of polyamide formation demonstrated that the reaction primarily occurs on the organic phase side (particularly when low-molecular-weight monomers are used [21]); therefore, the penetration of the polyamide films into the support should be insignificant even if the support has a large pore size.

Scanning electron microscopy (SEM) has been the most commonly used technique to investigate the morphology of TFC membranes and to examine the thickness and structure of polyamide films. However, it is tricky to use the apparent thickness to reflect the actual thickness of a crumpled film

1 that is composed of numerous globular features. The recent development of high-resolution SEM
2 provided more proofs supporting that the observed globular features of fully-aromatic polyamide
3 films were voids that were filled with water when fully hydrated [23, 24]. As such, it was
4 postulated that the skin layer of TFC membranes is a dense base film at the interface of support
5 overlain by a crumpled film surrounding hollow protuberance (leaf-like morphology) [25, 26]
6 rather than an entirely dense polyamide film. It has been proposed to use the film thickness of
7 hollow protuberance or the base film, rather than the apparent thickness, to represent the actual
8 thickness of film and evaluate the transport resistance [23, 27]. To avoid any misunderstanding,
9 we consistently used the term of “polyamide film” instead of “polyamide layer” to describe the
10 selective layer of TFC membranes throughout the paper. We also found that the dehydration
11 approach of membrane samples prior to microscopic inspection has a substantial influence on the
12 structure and morphology of polyamide films due to the water-filled voids, as shown in Fig.1. The
13 hydrated polyamide film was about 0.97 μm thick (Fig. 1A), whereas the same membrane
14 desiccated in an oven was much thinner, approximately 0.25 μm thick (Fig. 1B). However, the
15 polyamide film could maintain nearly its original thickness if the sample was dehydrated by
16 freezing-drying (1.11 μm , shown in Fig. 1C) because this prevented the collapse of the water-filled
17 voids in the polyamide film [23]. To obtain a more accurate determination of the polyamide film
18 structure, the TFC membrane samples in the present study were dehydrated by freeze-drying prior
19 to SEM analysis.

Fig. 1. Cross-sectional SEM images of TFC membranes: (A) hydrated TFC membrane, (B) TFC membrane dehydrated in an oven with desiccants at room temperature and (C) TFC membrane dehydrated in a freeze-dryer. The apparent thickness of polyamide films is indicated in each image.

The water-transport resistance of a polyamide film is much larger than that of the support due to its intrinsically dense nature. Application of a classical transport-resistance model [7] indicates that the permeability of a TFC membrane is approximately equal to that of the polyamide film. However, the support of a TFC membrane has a limited surface porosity, which means that only those regions with open pores allow the transport of fluids, while the impermeable regions restrict the transport. Lonsdale *et al.* [13] contended that these additional restrictions increased the path length for fluid transport and made the transport of molecules at the pore openings in the support proceed at a higher rate (the “funnel” effect). The impact of this is that the resistance of water transport through a TFC membrane becomes much larger than the intrinsic resistance of an isolated polyamide film. Ramon *et al.* [15] applied a numerical model to simulate the restrictive effect of the support on water transport through a TFC membrane and predicted that a support having smaller pores and higher surface porosity would form a more permeable TFC membrane. An improved-expanded model [16] further elucidated that the pore-size distribution and distribution pattern also had a significant impact on the transport resistance. A schematic illustration (shown in Fig. 2) demonstrates the impacts of tuning surface pore structures of supports on the permeance of TFC membranes. Improving the pore size distribution (illustrated in Fig. 2D and 2B), increasing

pore size (illustrated in Fig. 2B and 2C) or increasing the surface pore number density (illustrated in Fig. 2B and 2A) can shorten the transport path of water and mitigate the “funnel” effect. Experimental results showed that the water permeability of a free-standing polyamide film in the absence of a support could reach $10 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ [21], far higher than that of a supported polyamide film. Direct experimental evidences for this come from recent studies of Karan. *et al* [5] and Jiang. *et al* [28] whereby the isolated polyamide film was integrated with different supports and the composite membranes exhibited very different permeabilities, which strongly supports the hypothesis of a restrictive effect arising from the support.

Fig. 2. Schematic illustration of the impacts of tuning the surface pore structure of supports (blue parts) on the transport of water through the polyamide films (orange parts). The distorted transport path can be shortened by increasing pore number density (the transition from B to A) or increasing pore size (the transition from B to C). Improving the pore size distribution can also shorten the transport path (the transition from D to B).

Although much effort has been made to elucidate how the support affects the performance of TFC membranes, a fundamental understanding is still lacking; moreover, some conclusions from

independent studies are diametrically opposed. More reliable experimental results are necessary to enhance our understanding of the support effect, resolve the conflicting studies, and validate the theoretical predictions. One of primary challenges is preparing a series of support membranes with finely tuned structures as specified in the simulation models. Owing to limitations in the fabrication technique, the preparation of flat sheet supports is confined to allowing only a few variables to be adjusted to obtain the desired surface properties such as pore size, porosity and hydrophobicity. However, hollow fiber fabrication allows adjusting several spinning conditions such as the bore fluid, bore-fluid rate and take-up speed that cannot be adjusted in the fabrication of flat sheet membranes. By tuning the fabrication conditions, a hollow fiber support can be readily manipulated to achieve desired structures that subsequently can be linked to the physicochemical properties of the TFC membranes. This study involved the fabrication of two arrays of polyetherimide (PEI) hollow fibers as supports that had a similar structural evolution tendency, but produced TFC membranes with markedly different water permeabilities. PEI was selected to fabricate hollow fiber supports for TFC membranes due to its excellent chemical and mechanical stability as well as its hydrophilic nature [29]. The goal of this study was to identify the critical properties of the TFC support that significantly influence the performance of TFC membranes. The results of this study clarify how the support plays a vital role in affecting the permselectivity of the resultant TFC membranes.

2. Materials and Methods

2.1. Materials

Polyetherimide (PEI, ULTEM 1100) was purchased from Sabic for support fabrication. N-methyl-2-pyrrolidone (NMP, Merck Chemicals) was used as the solvent for preparing the polymer dope. The monomers m-phenylenediamine (MPD, Sigma-Aldrich) and trimesoyl chloride (TMC,

Sigma-Aldrich) were chosen for fabricating a polyamide films via interfacial polymerization on the supports. All other chemicals or materials were purchased from Merck (Singapore) unless otherwise stated and were used as received.

2.2. Fabrication of supports and interfacial polymerization of thin films

Prior to dope preparation, the PEI polymer resin was dried at 50°C for at least 24 hours and then dissolved into NMP and was stirred at 60°C for 2 days until the mixture became a homogenous solution. All PEI hollow fiber supports were fabricated by the dry-jet wet spinning method. Details of the spinning process can be found in a previous paper of the authors [8]. The detailed spinning conditions and dimensions for all supports are summarized in Table S1 in the supplementary material.

The same formulation protocol was adopted for the interfacial polymerization for all TFC membranes fabricated in this study. The MPD aqueous solution (1.2 wt%) was pumped into the lumen side of the hollow fibers and held there for 20 min. The excess aqueous solution on the lumen side of the hollow fibers was gently removed before TMC dissolved in cyclohexane (1 g/L) was pumped via a peristaltic pump for 3 min into the lumen side of the hollow fibers to complete the interfacial polymerization reaction. After the reaction, the hollow fibers were dried in air for 10 min to evaporate the residual organic solvent and then kept in deionized water until testing.

2.3. Characterization of supports and TFC membranes

Five hollow fibers with an effective length of 25 cm were assembled into a module. The pure water permeability of the hollow fiber supports was determined via a cross-flow membrane filtration set-

up using an applied hydraulic pressure of 1 bar. The molecular weight cut-off (MWCO) of the supports was measured with a 2000 ppm dextran solution having a broad distribution of molecular weights ranging from 6000 Da to 500 kDa, which was circulated through the lumen side of the hollow fiber supports under a pressure of 1 bar. The MWCO of the supports was determined by examining the rejection of different molecular weight dextrans using gel-permeation chromatography (GPC) [3]. For the supports with a molecular weight cut-off (MWCO) significantly higher than 500 kDa, the mean pore size and pore-size distribution were determined using a gas-liquid capillary flow porometer (CFP-1500A, PMI Inc., USA). All the supports were pre-wet in Galwick (PMI Inc., USA) for 1 hour before measurement.

The scanning electronic microscopy (SEM) images of the membranes were obtained using a field-emission scanning electronic microscope (JSM-7600F, JEOL). For the high-vacuum operation mode ($\sim 10^{-4}$ Pa), all samples were pre-dried in a freeze drier for at least 12 hours and then coated with platinum before conducting the SEM characterization. For the low-vacuum operation mode (50 Pa), the hydrated samples were gently purged with nitrogen gas to remove any liquid droplets on the membrane surface and subsequently mounted onto a membrane holder for SEM investigation.

The surface porosity and pore number density of the inner surface of the supports were estimated by calculating the fraction of pore area in the SEM images (X 50,000 magnification) using ImageJ[®] software. Three replicate images were analyzed and averaged. The inner surface roughness of the hollow fiber supports was measured using an atomic force microscope (AFM, NX 10, Park system). The dried hollow fiber samples were sectioned lengthwise and glued onto a sample holder. Three $5 \times 5 \mu\text{m}^2$ areas were scanned using the non-contact mode in air. The average root-mean-square (RMS) roughness then was determined.

The surface wettability of the supports was determined by measuring the pure water contact angles using a contact angle goniometer (OCA 15EC, dataphysics). Ten hollow fiber samples were sectioned lengthwise and fixed onto a glass cover slip. Ten equilibrium contact angles (averaged by left and right plateau contact angles) were measured and averaged. The surface element information of polyamide films was acquired by X-ray photoelectron spectrometer (Kratos Axis Supra spectrophotometer with a dual anode monochromatic K α excitation source, Shimadzu). The binding energy of each element was corrected with respect to the adventitious carbon C 1s core level at 284.8 eV.

2.4. Evaluation of TFC membrane performance

The water flux (J_w) and salt rejection (R) of the TFC membranes were determined by a cross-flow membrane setup at 23 °C for which the applied pressure was 1 bar and the feed was an aqueous solution containing 500 ppm of sodium chloride. A relatively low pressure and low salt concentration were used to minimize the effect of concentration polarization and thus ensure a more accurate evaluation of water permeability (A) and salt permeability (B). The flow velocity in the hollow fiber modules was ~0.15 m/s. The effective length of the hollow fiber membranes was 25 cm; each module contained 5 hollow fibers. Permeate was collected in a beaker on an electronic balance and the mass change was monitored in real-time by a LabVIEW program. The water permeate flux (J_w) was calculated as follows:

$$J_w = \frac{\Delta m}{\rho_w A_m \Delta t} \quad (1)$$

where Δm is the mass of water permeate collected within a time period of Δt , ρ_w is water density, and A_m is the effective membrane area. The water permeability (denoted as A) of the TFC membranes was calculated from the following equation

$$J_w = A(\Delta P - \Delta \pi) \quad (2)$$

where ΔP is the applied pressure and $\Delta \pi$ is the osmotic pressure difference between the feed and the permeate. The salt rejection (R) was obtained by measuring the conductivity difference between the feed and the permeate. The salt permeability (denoted as B) was obtained from the following equation:

$$\frac{1-R}{R} = \frac{B}{A(\Delta P - \Delta \pi)} \quad (3)$$

Each module was pressurized for at least one hour to ensure the stabilization of water flux and salt rejection. For each sample, at least three independent modules were fabricated and tested to acquire replicate data.

3. Results and Discussion

3.1. Properties of supports fabricated with different bore fluid compositions

The first array of supports included three PEI hollow fiber membranes (S-1, S-2 and S-3) that were fabricated with the same polymer dope, but with different bore fluid compositions. SEM images (shown in Fig. 3) indicate that the surface pore size of the supports decreased dramatically when

the NMP content in the bore fluid was decreased, thereby making the inner surface of the fiber much denser.

Fig. 13. SEM images of the inner surfaces of PEI supports: (A) S-1 (bore fluid: 80 wt% NMP in water), (B) S-2 (bore fluid: 65 wt% NMP in water) and (C) S-3 (bore fluid: 25 wt% NMP in water). The inserted figure in each image shows the pore size distribution of the support.

The observations from the SEM images are in good agreement with the results from the MWCO tests and porosity measurements as summarized in Table 1. However, decreasing the content of the NMP in the bore fluid had a minor effect on the surface pore number density (i.e., number of pores per unit surface area). The denser support also had a significantly lower pure water permeability (PWP). The difference in the support structure was mainly due to an accelerated phase separation induced by the increased nonsolvent (i.e., water) concentration in the bore fluid. A faster demixing process is known to produce a skin layer with smaller pore size [7].

Table 1. Characteristics of S-1, S-2 and S-3 supports.

Support s	Bore fluid compositio n (NMP wt% in water)	PWP ^b (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	MWC O (kDa) ^a	Surface contact angle (deg.)	Surface porosity (%)	Roughness (RMS, nm)	Surface pore number density (pores/μm ²)
S-1	80%	518.5 ± 6.2	>500	85.9 ± 3.2	17.5 ± 0.6	27.2 ± 3.8	66 ± 4
S-2	65%	272.8 ± 8.4	>500	72.6 ± 1.0	7.8 ± 1.2	4.6 ± 0.8	67 ± 9
S-3	25%	162.4 ± 4.2	51	61.1 ± 3.3	1.2 ± 0.1	4.0 ± 0.1	48 ± 5

a. GPC measurement results showed that the S-1 support had a rejection of 12.5% and the S-2 support had a rejection of 75.4% for a 500 kDa dextran.

b. PWP indicates pure water permeability

The membrane surface wettability also was affected by the bore fluid composition. As shown in Table 1, adding less NMP into the bore fluid made the support more hydrophilic. In contrast to the intrinsic contact angle (θ_Y) of a material, the surface contact angle obtained via the static sessile drop method for a rough and porous surface such as a membrane, which is referred to as the apparent contact angle (θ^*), was affected by the surface roughness and surface porosity as indicated by the Cassie-Baxter model [30]:

$$\cos\theta^* = (1 - f)\psi\cos\theta_Y - f \quad (4)$$

where ψ is the roughness ratio defined as the actual solid surface area divided by the projected solid surface area; f is the surface porosity defined as the liquid-air contact area divided by the projected area of the entire interface. The Cassie-Baxter model indicates that if the surface is naturally hydrophilic (or hydrophobic), surface roughness will make it more hydrophilic (or more hydrophobic). Increasing the surface porosity f will make the surface less hydrophilic, irrespective of its original wettability. Since the PEI used for fabricating the supports was naturally hydrophilic

($\theta_Y < 90^\circ$), the decreased surface roughness would reduce the wettability whereas the decreased surface porosity would enhance the wettability of the support. Apparently, the surface porosity effect dominates the results shown in Table 1, thereby resulting in a smaller apparent contact angle and enhanced hydrophilicity.

3.2. Impacts of the supports fabricated with different bore fluid compositions on the characteristics and separation performance of TFC membranes

3.2.1. Characteristics of polyamide films and separation performance of TFC membranes

The cross-sectional SEM images in Fig. 4 showed that the majority of polyamide films was mainly contributed by leaf-like protuberances, and some fractures evidenced that the protuberance had a hollow structure (i.e. voids), as reported by other studies [23, 26, 27]. From the high-resolution images of the fractures we could estimate that the actual thickness of polyamide leaf on TFC-1 was ranging from 20 to 30 nm, as indicated in Fig. 4A. Also, TFC-2 and TFC-3 had similar thickness of polyamide leaf to TFC-1, as shown in Fig. 4B and Fig. 4C. The thickness of polyamide leaf observed had a good agreement with other reported values [23, 31].

Fig. 4. Cross-sectional SEM images of TFC membranes: (A) TFC-1, (B) TFC-2 and (C) TFC-3. The actual thicknesses of polyamide leafs are indicated in each image. The scale bar is 100 nm.

By examining the element information of polyamide film using XPS, we are able to analyse the cross-linking degree of polyamide film based on the O/N ratio since the cross-linking degree also affected the permselectivity. Typically, the O/N ratio of a cross-linked polyamide film ranges from 1 to 2 and the O/N ratio equal to 1 or 2 indicates a fully cross-linked structure and a fully linear structure, respectively [5]. The survey spectra of TFC membranes (Fig. 5A) showed three major characteristic peaks of carbon, nitrogen and oxygen. To quantify the chemical species of polyamide films, the C 1s peak was deconvoluted into five peaks representing different functional groups as indicated in Figs. 5B, 5C and 5D. The narrow scan results of XPS shown in Fig. 5 and Table 2 demonstrated that the carbon atomic concentration in O-C=O (288.8 eV) increased dramatically in the order of TFC-1 < TFC-2 < TFC-3 while the carbon atomic concentration in N-

1 C=O (288.2 eV) decreased simultaneously, validating the presence of a high density of pendant
2 carboxylic acid groups at the surface of polyamide films. Additionally, all TFC membranes had
3 O/N ratios higher than 2 (shown in Table 2), indicating that the periphery of polyamide film was
4 far from a cross-linked structure and its surface instead was occupied by a large portion of TMC
5 functional groups. Interfacial polymerization is a typical self-limiting reaction [10] where the
6 diffusion of MPD across reaction zone was impeded upon the formation of incipient film and thus
7 less MPD could diffuse into the organic phase to react with the abundant TMC, which might
8 eventually result in more pendant carboxylic acid groups than expected at the end of polymer
9 chains, giving rise to a high O/N ratio at the frontier of reaction zone [32].

Fig. 5. (A) XPS survey spectra of the polyamide films of TFC-1, TFC-2 and TFC-3. Deconvolution of C 1s core level XPS spectra of the polyamide films of TFC membranes: (B) TFC-1, (C) TFC-2 and (D) TFC-3.

Table 2. XPS results from the polyamide films of TFC-1, TFC-2 and TFC-3 membranes.

Membranes	C 1s (%)	O 1s (%)	N 1s (%)	COOH (%)	O/N
TFC-1	78.09 ± 0.16	16.40 ± 0.41	5.51 ± 0.53	5.6 ± 1.3	2.97 ± 0.35
TFC-2	78.89 ± 0.16	16.83 ± 0.05	4.28 ± 0.19	8.7 ± 0.6	3.94 ± 0.18
TFC-3	78.90 ± 0.28	16.61 ± 0.62	4.54 ± 0.83	9.8 ± 0.5	3.73 ± 0.82

However, all TFC membranes had fairly low salt permeability ($< 0.35 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, shown in Table 3), which meant that the surface cross-linking information revealed by XPS might not reflect the actual structural properties of polyamide films since the detection depth ($\sim 10 \text{ nm}$) of XPS was far lower than the apparent thickness ($> 700 \text{ nm}$) of the polyamide film. The polyamide film having good selectivity and low cross-linking degree at the top implied that there was a continuous base film (or a dense core) embedded in a loose film periphery while the base film served as a selective barrier [10, 25].

Table 3. Characteristics and separation performance of TFC-1, TFC-2 and TFC-3

TFC membranes	Apparent thickness of polyamide films (nm)	Actual thickness of polyamide leaf (nm)	Surface roughness (nm), RMS	Water permeability, A ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Salt permeability, B ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	B/A (bar)	Rejection (1 bar, 500 ppm NaCl)
TFC-1	742 ± 38	23.1 ± 3.3	46.0 ± 4.4	4.05 ± 0.56	0.33 ± 0.02	0.08 ± 0.01	0.879 ± 0.008

TFC-2	1070 ± 107	25.5 ± 2.4	40.8 ± 1.9	2.85 ± 0.16	0.24 ± 0.01	0.09 ± 0.01	0.876 ± 0.011
TFC-3	1482 ± 86	23.7 ± 3.1	111.7 ± 26.3	1.01 ± 0.14	0.22 ± 0.03	0.22 ± 0.05	0.729 ± 0.041

3.2.2. Characteristics of polyamide films and separation performance of TFC membranes fabricated with a reduced IP time

To further verify our speculation, the support S-1 was selected for fabricate a TFC membrane with a much shorter IP reaction time (i.e. 30 s) and the TFC membrane was denoted as TFC-1-30s. The SEM images (Figs. 6A and 6B) showed that the apparent thickness of polyamide film in TFC-1-30s (568 ± 30 nm) was much lower than that of film in TFC-1 (742 ± 38 nm), implying much less developed protuberances on TFC-1-30s which primarily shaped the morphology of polyamide films [24]. The O/N ratio and relative atomic content of C 1s contributed by COOH of TFC-1-30s (shown in Fig. 6C) were also lower than those of TFC-1, suggesting that the top surface of TFC-1-30s had a higher cross-linking degree than TFC-1. In addition, Fig. 6D showed that the water permeability of TFC-1-30s was slightly higher than that of TFC-1 while its salt rejection was only slightly lower. The results indicated that a relatively dense film had formed within 30 s upon reaction and further prolonging reaction time had minor effects on the permselectivity while it simultaneously promoted the growth of protuberance [21, 33]. Obviously, the developed protuberance after 30 s had little impact on separation performance of TFC although the growth of protuberance could increase the effective membrane surface area [33]. Our findings also agreed with one scenario of simulation work reported by Wong *et al.*[25] that varying void fraction in the polyamide film had little impact on permeability when the base film set the transport limit. In conclusion, our results strongly supported the existence of a continuous base film in a structurally heterogeneous polyamide film. Theoretically, the base film is typically adherent to the support as an incipient film forms immediately when two phases contacts owing to the rapid reaction kinetics

of MPD/TMC polymerization system [31]. Also, the thickness of the base film is supposed to be similar to the actual thickness of the polyamide leaf observed [34], meaning that the base films of TFC membranes in the first array had similar effective thickness, which was ranging from 20 nm to 30 nm.

Fig. 6. Cross-sectional SEM images of TFC membranes: (A) TFC-1-30s and (B) TFC-1; the apparent thickness of the polyamide film is indicated in each image, the scale bar is 200 nm. (C) The carbon content contributed by COOH and O/N ratio of polyamide films acquired by XPS for TFC-1-30s and TFC-1 membranes. (D) Water permeability and salt rejection of TFC-1-30s and TFC-1 membranes.

Based on the analytical results above, it was obvious that the effective surface area reflected by surface roughness was not the one of the critical factors determining the water permeability of TFC membranes owing to the presence of a loose periphery. As such, the effective area of the base

film, instead of the effective surface area of the entire film, essentially determines the permeability of TFC membranes. However, it is challenging to directly measure or estimate the effective area of the base film since the base film was entirely embedded in the loose periphery. Nevertheless, recent studies reported that a well-controlled interfacial polymerization condition could produce an ultrathin base film and simultaneously prevent the formation of the loose periphery [5, 28]. The film possessed a decent permeability and selectivity comparable to conventional TFC membranes. Further studies showed that the heat released by the interfacial polymerization had significant impacts on the morphology and structure of the polyamide film [35, 36] and a more porous support having more water entrapped (or absence of supports) could enable a more rapid heat dissipation generated by the cross-linking reaction, which otherwise would induce a crumpled film [28]. Our results also showed that TFC-3 fabricated on a denser support had a significantly higher apparent thickness and surface roughness than TFC-1. In addition, it had been showed that the film (primarily the protuberance) would grow continuously given a sufficient time, which agreed well with findings from other studies [21]. As such, it was reasonable to speculate that the effective areas of the base film and the entire film were positively correlated, given the same fabrication conditions.

Nonetheless, we did not observe a positive correlation between water permeability and the surface roughness, as summarized in Table 3. Contrarily, TFC-1, which had the lower surface roughness and was supposed to have a less effective area of the base film, had a substantially higher water permeability ($4.05 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) than TFC-3 ($1.01 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$). As salt rejection is subject to the testing conditions and a low hydraulic pressure was applied in our current study to evaluate the separation performance of TFC membrane, the salt rejection was relatively low in comparison with other reported values of TFC membranes tested under high pressures. However, the values of B/A , which are relatively independent of testing conditions, suggested that TFC- 1 and TFC-2 had very high selectivity because of their low B/A values (lower than 0.1 bar), comparable to those of

our previously reported highly selective TFC-FO membranes [8]. The salt rejection of TFC-1 was also the highest in the array of TFC membranes, indicating that the high water permeability of TFC-1 was not contributed by a trade-off of permselectivity. Also, since the pure water permeability of supports S-2 ($272.8 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) and S-3 ($162.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) was nearly two orders-of-magnitude higher than the water permeability of the corresponding TFC membranes ($2.85 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for TFC-2 and $1.01 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for TFC-3), it was very unlikely based on the well-established resistance-in-series model that the low water permeability of TFC-2 or TFC-3 was caused by the transport resistance across the entire support [28]. Rather, those experimental results evidenced that the only factor determining the water permeability was the surface porosity of supports and a more porous support produced a more permeable TFC membrane. Our results of the first array of supports and membranes apparently supported those predictions that the porosity of supports had a significant impact on the performance of TFC membranes due to its effects on the lateral transport distance for water permance, although a less porous support may produce a more crumpled film having a higher permeable area. To further validate the preliminary conclusions, a second array of supports was fabricated by altering the surface pores with varying additives rather than by changing the bore fluid composition.

3.3. Characteristics of PEI supports fabricated by adding lithium chloride (LiCl) into PEI dope

LiCl is a commonly-used pore-former additive in membrane fabrication. An earlier study of the authors [8] found that the addition of LiCl into the PEI dope could reduce the pore size of the resulting membranes. Hence, a second array of supports was fabricated by introducing different amounts of LiCl into the polymer dope, but with the same bore fluid composition (80 wt % NMP in water). The support S-1 (and TFC-1) was selected as the benchmark for bridging the two arrays of supports (and TFC membranes). The pore size and pore-size distribution of the supports were

1 first examined by SEM and at the same time, verified by flow porosimetry characterization. Since
2 the dehydration by freeze-drying may affect the pore size of support before SEM examination, the
3 largest pore size visualized by SEM was somewhat larger than the one acquire from flow
4 porosimetry. Nevertheless, both results showed an obvious similar evolution trend that, as shown
5 in Fig. 7, adding LiCl into the PEI dope made the pore size on the inner surface of the hollow
6 fibers significantly smaller by delaying the kinetics of the phase-separation process [8]. SEM
7 images (Figs. 7A, 7B and 7C) also showed that adding LiCl simultaneously creating more small
8 pores. This led to a higher pore number density, largely due to the pore-forming effect of LiCl.
9 Moreover, the introduction of LiCl also made the pore-size distribution of the inner surface of the
10 hollow fibers much narrower (shown in Figs. 7a, 7b and 7c).

11

12 Fig. 7. SEM images of the inner surfaces of PEI supports: (A) S-1, (B) S-4 and (C) S-5. Pore-size
13 distributions of PEI supports measured by gas-liquid capillary flow porometer: (a) S-1, (b) S-4 and (c) S-5.

14

15 However, despite the increased pore number density, the surface porosity of the hollow fibers
16 decreased significantly with the decrease in pore size after adding LiCl into the dope solutions, as

shown in Table 4. Consequently S-4 and S-5 became more hydrophilic than S-1 because of their decreased surface porosity.

Table 14. Characteristics of S-1, S-4 and S-5 supports

Supports	LiCl added (wt%)	PWP ($\text{L} \cdot \text{m}^{-2} \cdot \text{hour}^{-1} \cdot \text{bar}^{-1}$)	Mean pore size (nm)	Inner surface contact angle (deg.)	Surface porosity (%)	Roughness (RMS, nm)	Surface pore number density (pores/ μm^2)
S-1	0	518.5 ± 6.2	50.7	85.9 ± 3.2	17.5 ± 0.6	27.2 ± 3.8	66 ± 4
S-4	2%	898 ± 24.2	37.8	75.0 ± 1.1	10.2 ± 0.7	4.9 ± 0.5	97 ± 8
S-5	4%	1059.3 ± 30.6	24.7	73.6 ± 0.5	6.6 ± 1.2	3.4 ± 0.5	132 ± 9

3.4. Impacts of the supports fabricated by adding LiCl on the characteristics and separation performance of TFC membranes

The cross-sectional SEM images (Fig.8) showed that the second array of TFC membranes also had similar actual thickness of polyamide leaves, ranging from 20 to 30 nm. The length scale of effective thickness was nearly the same as that of TFC membranes in the first array, implying that our fabrication protocols had little effect on the actual thickness of polyamide leaves (or the actual thickness of base films) on different supports. The elemental analysis of polyamide films from XPS also showed that the surface of films also had an O/N ratio higher than 2 (Table S2 in supplementary material), indicating the presence of a highly non-crosslinked structure. The surface roughness results summarized in Table 5 also suggested that the polyamide film on a less porous support had a more crumpled structure, which agreed well with the findings from the first array of TFC membranes.

Fig. 8. Cross-sectional SEM images of TFC membranes: (A) TFC-1, (B) TFC-4 and (C) TFC-5. The actual thicknesses of polyamide leafs are indicated in each image.

In the second array of TFC membranes, the water permeability of TFC membranes increased in the order of TFC-1 < TFC-4 < TFC-5 and TFC-5 had a remarkably high water permeability ($5.51 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) in comparison with TFC-1 ($4.05 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$), as shown in Table 5, although TFC-5 had a support with the smallest pore size and the lowest surface porosity. Also, all TFC membranes had very low B/A values (lower than 0.09 bar), demonstrating an excellent selectivity. We observed a slight increase rather than a drop of salt rejection with the increased water permeability for the second array of TFC membranes, indicating that the enhanced water permeability was not induced by the trade-off of permselectivity. It was previously concluded that

a more porous support was favourable to producing a more permeable TFC membrane based on the results from the first array of membranes. However, the impact of the pore size and surface porosity of the support on the performance of TFC membranes was clearly in contrast to the first array of TFC membranes and also in disagreement with the conclusions drawn from prior studies [14, 20].

Table 5. Characteristics and separation performance of TFC-1, TFC-4 and TFC-5

TFC membranes	Apparent thickness of polyamide films (nm)	Actual thickness of polyamide leaf (nm)	Surface roughness, RMS (nm)	Water permeability, A ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	Salt permeability, B ($L \cdot m^{-2} \cdot h^{-1}$)	B/A (bar)	Rejection (1 bar, 500 ppm NaCl)
TFC-1	742 ± 38	23.1 ± 3.3	46.0 ± 4.4	4.05 ± 0.56	0.33 ± 0.02	0.08 ± 0.01	0.879 ± 0.008
TFC-4	867 ± 47	29.7 ± 2.0	145.9 ± 12.6	4.81 ± 0.53	0.36 ± 0.08	0.08 ± 0.03	0.887 ± 0.032
TFC-5	965 ± 37	25.9 ± 2.3	146.4 ± 10.6	5.51 ± 0.33	0.37 ± 0.04	0.07 ± 0.01	0.900 ± 0.008

By examining the two arrays of supports, in comparison with S-1, not only did S-3 have a smaller pore size, but also a lower pore number density. In contrast, S-5 possessed a smaller pore size, but a much higher pore number density than S-1. The increased pore number density, as predicted by previous simulation work [15], reduced the impermeable area of the “dead zone” in the support and thereby shortens the water transport path through polyamide film and mitigates the restrictive effects of channelling the water from the polyamide film into the distributed pores in the support. That explained why the second array of TFC membranes, different from the first array, had an increased water flux when reducing the surface porosity of supports. In addition, since it had been speculated that the effective area of the base film was strongly associated with that of the entire film, we cannot exclude the possibility that higher effective membrane area might account for the increased water permeability of TFC membranes (i.e. TFC-4 and TFC-5) on the less porous

1 supports. As such, the higher effective membrane area plus a shortened lateral transport path could
2 well explain the exceptionally high water permeability of TFC-5. Although it was previously
3 reported [37] that a support made of polyethersulfone with a large pore size (> 300 kDa MWCO)
4 may result in a defective polyamide film, this was not observed in our cases, probably due to the
5 more hydrophilic nature of polyetherimide than polyethersulfone. However, further enlarging the
6 pore size of supports may considerably change the wettability of supports (as discussed above) or
7 disturb the interface between two phases [31], which would affect the formation of polyamide
8 films. In comparison, increasing the pore number density of supports is a better alternative to
9 fabricate a more permeable TFC membrane.

10 Despite the aforementioned differences, both arrays of TFC membranes shared a similar trend,
11 that is, the salt rejection was maintained or slightly improved simultaneously with an enhancement
12 in the water permeability. The trade-off relationship between the permeability and selectivity has
13 been reported in studies of TFC membranes [38, 39], which had long been considered as an
14 intrinsic property of the polyamide film based on the solution-diffusion mechanism [38]. However,
15 the results in the present study demonstrate that a more porous support can enhance the water
16 permeability, and simultaneously maintain the salt rejection, which is different from the widely
17 reported trade-off correlation between permeability and selectivity for TFC membranes. Our
18 experimental results showed that an increased salt permeability was always coupled with the
19 increase of water permeability for both arrays of TFC membranes, which apparently corroborated
20 one conclusion of simulation work [15, 16] that altering supports had similar effects on water
21 permance and salt permance. However, the increment of salt permeability was completely offset
22 by the increment of water permeability and thereby a maintained salt rejection was observed [5].
23 Similar findings have been found in a number of recent studies, as summarized in Table 6, most
24 of which show that finely-tuned supports could enhance water permeability while maintaining salt
25 rejection of TFC membranes. In our present study, TFC-2 was selected as the control because

1 TFC-3 had a poor selectivity and a low permeability, which was apparently not applicable for
2 water purification applications. Although the conclusions drawn from these studies might vary,
3 the comparisons summarized in Table 6 suggested that the surface pore structure such as surface
4 porosity and pore number density were strongly associated with the separation performance of
5 TFC membranes. Our present study provided more solid experimental results to validate the
6 important roles that the surface pore structure of supports plays in the TFC membranes. On the
7 other hand, as we had shown that increasing the surface porosity or pore number density of
8 supports had a marked impact on the structure and morphology of polyamide films, it might also
9 result in an improved intrinsic selectivity of base films that accounted for the enhanced selectivity
10 observed in the two arrays of TFC membranes. A deeper investigation is highly desirable to guide
11 fabricating a more permeable and selective TFC membrane.

1

Table 6. A summary of recent studies on the impacts of tuning supports on characteristics and desalination performance of TFC membranes

N o.	Protocol of tuning supports	Surface porosity of supports	Surface pore number density of supports	Support hydrophilicity	Roughness of TFC membrane	Increment of water permeability in comparison with the control (Values of enhanced <i>A</i>)	Increment of salt rejection in comparison with the control	Ref. (Year published)
1	Increasing the content of NMP in coagulants (e.g. TFC-2 vs TFC-1)	Increased	Slightly Increased	Decreased	Decreased	42.1% (4.05 LMH/bar)	Maintained	Present work
	Adding LiCl into PEI dope (e.g. TFC-1 vs TFC-5)	Decreased	Increased	Increased	Increased	36.0% (5.51 LMH/bar)	2.4%	Present work
	Increasing the content of NMP in coagulants and adding LiCl into PEI dope (e.g. TFC-2 vs TFC-5)	Increased	Increased	Decreased	Increased	93.3% (5.51 LMH/bar)	2.7%	Present work
2	Reconstructing the surface of polysulfone (PSf) supports with organic solvent	Increased	Increased	Maintained	Increased	50.5% (~ 4.7 LMH/bar)	Maintained	[40] (2017)
3	Adding carbon nanotubes into PSf dope	Increased	N.A.	Maintained	Increased	35% (3.03 LMH/bar)	Maintained	[41] (2017)
4	Removing the silica nanoparticles mixed in PSf supports by alkali treatment	Increased	Increased	Maintained	N.A.	58.5% (3.55 LMH/bar)	0.4%	[17] (2015)
5	Adding polyaniline into polyethersulfone (PES)	Increased	Increased	Slightly increased	Slightly increased	101% (15.7 LMH/bar)	5.1% (MgSO ₄)	[42] (2015)
6	Decreasing PSf concentration in dope	Increased	N.A.	N.A.	Decreased	~ 270% (~ 10 LMH/bar)	Decreased (MgSO ₄)	[43] (2014)
7	Decreasing PSf concentration in dope	Increased	N.A.	Slightly increased	Decreased	~ 67% (~ 5.4 LMH/bar)	Maintained (Na ₂ SO ₄ and MgSO ₄)	[20] (2013)

2

4. Conclusions

Two arrays of hollow fiber PEI supports were fabricated whose structures were finely tuned by adjusting the fabrication conditions. The polyamide films were characterized by SEM, AFM and XPS to evaluate the actual thickness of polyamide film, the effective membrane area and surface element information. The polyamide films and separation performance of the resulting TFC membranes were found to be strongly affected by support properties, mainly surface porosity and surface pore number density. Several conclusions emanate from this study:

- There exists a base polyamide film embedded in a loose periphery and the base film determines the permselectivity of the entire polyamide film.
- The base film forms rapidly upon the contact of two monomers and further prolonging reaction time has little effect on water permeability though it promotes the growth of protuberances.
- A more crumpled film typically forms on a less porous support, probably due to the less heat dissipation that is induced by trapped water in supports.
- The selection of supports has little impact on the actual thickness of polyamide leaf (or base films) given the same fabrication conditions.
- A support with a higher surface porosity or higher pore number density is favourable to forming a more permeable TFC membrane as it could shorten the lateral transport path for water molecules through the films.
- A finely-tuned support can dramatically enhance the water permeability while maintaining the salt rejection.

It is suggested that a finely-tuned support is a promising way to address the trade-off between permeability and rejection widely reported for TFC membranes. By keeping the same thin film formation protocol and manipulating the structure of the supports, the water permeability of TFC

membranes can be increased significantly. Due to the self-supported structure, the applications of hollow-fiber TFC membranes have been confined to low-pressure processes such as FO, NF and low pressure RO. The high water permeability reported in the present study might not be achievable for the TFC membranes used for high-pressure applications such as seawater reverse osmosis (SWRO) because of the impacts of the operation pressure on TFC membranes [44]. Nevertheless, the findings from our studies have shed light on how to enhance the permeability of TFC membranes by manipulating the structure of supports, which is particularly more beneficial for the low-pressure RO and NF membranes [45].

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Appendix A.

Supplementary material

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