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**Towards improved separation performance using porous FO membranes:  
The critical roles of membrane properties and draw solution selection**

*Saren QI<sup>1,2</sup>, Ye LI<sup>1,2</sup>, Rong WANG<sup>1,2</sup>, Chuyang Y. TANG<sup>3</sup>*

*1. School of Civil and Environmental Engineering, Nanyang Technological University,  
Singapore 639798*

*2. Singapore Membrane Technology Centre, Nanyang Technological University, Singapore  
639798*

*3. Department of Civil Engineering, The University of Hong Kong*

\* To whom correspondence should be sent, [tangc@hku.hk](mailto:tangc@hku.hk)

## **Abstract**

The use of porous membranes for forward osmosis (FO) applications has been recently reported in the literature. In the current study, a series of porous-FO membranes were fabricated to systematically study the role of membrane separation properties on the FO performance of porous membranes. In addition, two types of draw solutes, a polyelectrolyte poly(sodium 4-styrene-sulfonate) (PSS) and a neutral linear polymer polyethylene glycols (PEGs), were evaluated as the draw solutes. The effect of draw solution properties (type of draw solutes, their molecular weight, and concentration) on the FO performance was investigated. Membrane post-treatment at higher annealing temperature was found to increase solute rejection and decrease water permeability. As a result, reverse solute diffusion (RDS) became less severe at higher annealing temperature. The FO water flux of the porous membranes was affected by RDS in addition to the water permeability of the porous FO membranes, [which also has a relationship with the annealing temperature](#). Compared to neutral PEG, the polyelectrolyte PSS was a much better choice for draw solutes with higher FO water flux and lower RDS. The better performance of PSS can be attributed to its higher rejection by the porous FO membranes and its high osmotic pressure compared to PEG at same weight concentration. Implications for the design of porous FO membranes and draw solution are discussed.

**Keywords:** Porous forward osmosis membranes; FO water flux; reverse solute diffusion; Internal concentration polarization (ICP); Polyelectrolyte draw solution

## 1. Introduction

Forward osmosis (FO) is an engineered osmosis process that utilizes an osmotic pressure difference across an FO membrane to drive water flux from a low concentration stream to a high concentration stream [1, 2]. FO has many applications ranging from desalination, water and wastewater treatment, and food processing [2-8]. As a core element in the FO process, FO membrane development has received major attentions in recent years. In existing literature, FO membranes are classified into two main groups based on the rejection properties of their selective layers: reverse osmosis (RO)-like FO membranes and nanofiltration (NF)-like FO membranes [9]. RO-like FO membranes have rejection layers closely resemble that of pressure-driven RO membranes in that they have high rejection towards monovalent ions and low molecular weight compounds. Representatives of RO-like FO membranes include cellulose triacetate (CTA) membranes prepared by phase inversion [10-13] and thin film composite (TFC) membranes made by interfacial polymerization [14-17]. Compared to RO-like counterparts, NF-like FO membranes have relatively low rejection towards monovalent ions but are able to adequately retain divalent and multivalent ions. Although they are generally not compatible with monovalent based draw solutions (DSs) such as NaCl or seawater, NF-like FO membranes tend to achieve higher FO water flux when a suitable DS (such as  $MgCl_2$ ) is used, thanks to their relatively high water permeability [9]. These membranes are prepared by interfacial polymerization with specific monomers [9], layer-by-layer assembly (LbL) or its variations [18-21], and other chemical modifications [22, 23]. For both RO-like and NF-like FO membranes, their rejection layer is non-porous, reflecting the traditional wisdom that a non-porous skin is always needed to maintain an

effective osmotic pressure difference for driving the FO process.

In a recent study, we demonstrated for the first time that FO can be realized with a porous membrane as long as a compatible DS is chosen (i.e., a DS large enough to be retained by the given membrane) [24]. In that study, an ultrafiltration (UF)-like FO membrane was developed and tested for FO performance using a polyelectrolyte [poly(sodium 4-styrene-sulfonate) (PSS)] as the DS. Since the permeability of the UF-like FO membrane was several orders of magnitude greater compared to those of traditional NF-like and RO-like FO membranes, this membrane shows a relatively high water flux in FO operation (approximately 7.6 L/m<sup>2</sup>.h) at a low osmotic pressure driving force of 0.11 bar. The use of low osmotic-pressure-DS may facilitate an easier regeneration of DS. The membrane was further demonstrated to be highly effective for oil-water separation, showing lower fouling tendency compared to UF operation [24]. Other potential applications of porous FO membranes may include wastewater treatment (e.g., porous-FO osmotic bioreactor) and valuable product recovery (such as protein concentration), among a wide range of possibilities, [although various operation conditions and membranes optimization will be further determined](#). Nevertheless, the effects of membrane and DS properties and the operating conditions on the performance of porous FO membranes are yet to be systematically investigated.

The objective of the current study is to systematically evaluate the role of membrane and DS on the separation performance of porous-FO based processes. A series of UF-like FO membranes with systematic changes in their separation properties were prepared. Two

families of DSs, polyelectrolytes represented by PSSs and neutral macromolecules represented by polyethylene glycols (PEGs) over a range of different molecular weights (MWs), were evaluated. The current study provides important insights and implications for the design of membranes and DSs for porous-FO based processes.

## **2 Experimental Details**

### **2.1 Chemicals and reagents**

The polymer dope solution was composed by polyacrylonitrile (PAN, average MW ~ 150 KDa, Sigma-Aldrich), N,N-dimethylformamide (DMF,  $\geq 99.8\%$ , Sigma-Aldrich) and lithium chloride (LiCl, Sinopharm), respectively. Feed solution was prepared by deionized (DI) water (Millipore Integral 10 water purification system, Singapore). Draw solutions were prepared with a series PSS solutions of different MWs ( $M_w \sim 70$  KDa, 200 KDa, and 1,000 KDa, received as 25-30% water solution from Sigma-Aldrich) or PEG solutions ( $M_w \sim 2$  KDa and  $\sim 10$  KDa from Merck). 0.1 M hydrochloric acid (HCl, Sigma-Aldrich) or sodium hydroxide (NaOH, Sigma-Aldrich) was used to adjust the pH of draw solution to around 5.5 to 6. A wide range of DS concentrations were evaluated. Unless stated otherwise, the DI water and analytical grade chemicals were used to prepare all solutions.

### **2.2 Membrane materials**

A base UF-like FO membrane was prepared according to our previous work [24]. Additional membranes with varied separation properties were systematically prepared by varying the annealing conditions in a post-fabrication treatment. Briefly, a casting knife (gate height of

150  $\mu\text{m}$ , Elcometer Pte Ltd, Asia) was used to spread the polymer solution (18% PAN, 2% LiCl and 80 % DMF) onto a clean glass plate. The plate was coagulated in a tap water bath at room temperature ( $23 \pm 1$  °C) to form the PAN membranes. These nascent membranes were then annealed in DI water at different temperatures (23 (i.e., no annealing), 45, 55, 65, 75 and 85 °C) for 2 mins. This annealing step was used to modify the membrane pore structure by tightening the pore size [25]. Accordingly, the UF-like FO membranes prepared in the current study are named as UF-T $n$ , where  $n$  is the annealing temperature (see [Table 1](#)). After cooling down to room temperature, all the membranes were soaked in 1.5 M sodium hydroxide (NaOH, Sigma-Aldrich) at 45 °C for 1.5 h to partially hydrolyzed PAN. This NaOH treatment step makes the surface more negatively charged and more hydrophilic by creating more carboxylic groups ( $-\text{COO}^-$ ) to the membrane surface [18]. The NaOH treated membranes were washed by tap water until the pH of the water became neutral.

### 2.3 Membrane intrinsic separation properties

A pressurized cross flow filtration setup was used to evaluate the intrinsic separation properties (pure water permeability ( $A$ ) and solute rejection) of FO membranes [26]. Briefly, DI water was used as feed water when the  $A$  was determined. [The  \$A\$  was determined by weighting the permeate water samples under the predetermined time and applied pressure.](#) When determining the NaCl rejection ( $Rej_{NaCl}$ ) and PSS rejection ( $Rej_{PSS}$ ), 10 mM NaCl and 0.05 % PSS (70 KDa) were used as feed solution, respectively. The rejection results were calculated based on measuring conductivity (Ultrameter II, Myron L Company, Carlsbad, CA) of feed and permeate water [18]. PEG rejection ( $Rej_{PEG}$ ) was evaluated by measuring the

organic carbon content using a total organic carbon analyzer (TOC-Vcsh, SHIMADZU, see Appendix Fig.A1) of permeate and feed water using feed water containing 0.005 % PEG (2 KDa).

## 2.4 Evaluation of FO performance

A cross flow FO setup was used to evaluate FO performance, which is described elsewhere [18, 27]. A cross flow velocity of 18.75 cm/s was set for both feed and draw solutions during all the FO tests at room temperature. Unless stated otherwise, the feed solution was used DI water. A new FO membrane was placed in the FO cell with an active filtration area  $\sim 42 \text{ cm}^2$  for each test. Polyelectrolyte solutions containing 0.05 %, 0.1 %, 0.5 %, 1 % and 5 % PSS ( $M_w \sim 70 \text{ KDa}$ ), 0.1 % PSS ( $M_w \sim 200 \text{ KDa}$ ) or 0.1 % PSS ( $M_w \sim 1,000 \text{ KDa}$ ) were used as DS, respectively. In addition, PEG solutions containing 1 %, 5 %, 15 % and 45 % PEG ( $M_w \sim 2 \text{ KDa}$ ) or 1 % PEG ( $M_w \sim 10 \text{ KDa}$ ) were also evaluated as DS, respectively. The viscosity and osmotic pressure of the PEG and PSS solutions are presented in Appendix (Fig.A2 and Fig.A3). Both active layer facing draw solution (AL-DS) and active layer facing feed solution (AL-FS) orientations were tested. At predetermined time intervals, we measured the weight changes of the FS to determine the FO water flux ( $J_v$ ). The rate of reverse diffusion of PSS was determined by monitoring the change of the FS conductivity, and that of PEG was determined by measuring the organic carbon content using a total organic carbon analyzer (TOC-Vcsh, SHIMADZU, see Fig.A1).

## 3 Results and Discussion

### 3.1 Intrinsic membrane separation property

The water permeability ( $A$ ), NaCl rejection ( $Rej.NaCl$ ), PSS rejection ( $Rej.PSS$ ) and PEG rejection ( $Rej.PEG$ ) of various UF-like FO membranes are presented in [Table 1](#). In general, the water permeability of the UF-like FO membranes decreased at increasing annealing temperature ( $T_a$ ), suggesting that membrane pore size was significantly reduced at higher  $T_a$ . [In addition, the FESEM images of cross-section of FO membranes with different annealing temperature were shown in Fig. A4](#). In all cases, the water permeability values in the current study were considerably higher compared to RO-like and NF-like FO membranes reported in the literature. Consistently, the membrane rejection of macromolecules (PSS and PEG in this case) also increased at higher  $T_a$ . Although NaCl rejection of UF-like FO membranes was typically  $\sim 0\%$ , the membrane annealed at  $85\text{ }^\circ\text{C}$  (UF-T85) showed a small but detectable NaCl rejection of  $8\%$ . The finite NaCl rejection of UF-T85 can be attributed to the electrostatic interaction between the solutes and membrane (i.e., the Donnan effect [18]) in addition to its small pore size. The NaOH treated PAN membrane had a negatively charged surface (zeta potential  $\sim -32\text{ mV}$  [18]), which helps to repel the anions ( $\text{Cl}^-$ ) while cations are retained to maintain the overall charge neutrality in the feed solution.

Table 1. Intrinsic separation properties of UF-like FO, NF-like FO and RO-like FO membranes.

Membrane type		Annealing temperature ( $^\circ\text{C}$ )	$A^1$ L/m <sup>2</sup> h bar	$Rej.NaCl^2$ %	$Rej.PSS^3$ %	$Rej.PEG^4$ %
RO-like <sup>7</sup>	CTA	N.A.	1.19±0.19	78.5	N.A.	N.A.
	TFC	N.A.	1.7±0.3	97±1	N.A.	N.A.
NF-like <sup>7</sup>		N.A.	3.4±0.4	60±3	N.A.	N.A.

UF-T23 (UF-like)	N.A.	87.5±5.6	0	80.5±5.2	2.1±0.5
UF-T45 (UF-like)	45	84.7±6.7	0	80.6±6.4	2.6±1.8
UF-T55 (UF-like)	55	78.8±7.2 <sup>5</sup>	0 <sup>5</sup>	82.3±4.4 (97.5±1.0 TOC) <sup>6</sup>	4.3±0.9
UF-T65 (UF-like)	65	56.0±12.6	0	85.8±1.3	4.3±0.1
UF-T75 (UF-like)	75	43.0±7.9	0	91.7±2.6	25.5±0.7
UF-T85 (UF-like)	85	17.5±6.7	8	94.1±2.1	42.2±1.0

#### Note

<sup>1</sup>: DI water as feed solution and compacted under 5 bars at least 2 hours.

<sup>2</sup>: 10 mM NaCl as feed solution and compacted under 5 bar at least 2 hours.

<sup>3</sup>: 0.05 % PSS (70 KDa) as feed solution and compacted under 5 bar at least 2 hours. The rejections were based on the conductivity measurements between feed and permeate.

<sup>4</sup>: 0.005 % PEG (2 KDa) as feed solution and compacted under 5 bar at least 2 hours.

<sup>5</sup>: data *A* and *Rej<sub>.NaCl</sub>* were got from ref. [24].

<sup>6</sup>: *Rej<sub>.PSS</sub>* for UF-T55 was 97.5±1.0 based on the TOC measurements between feed and permeate [24].

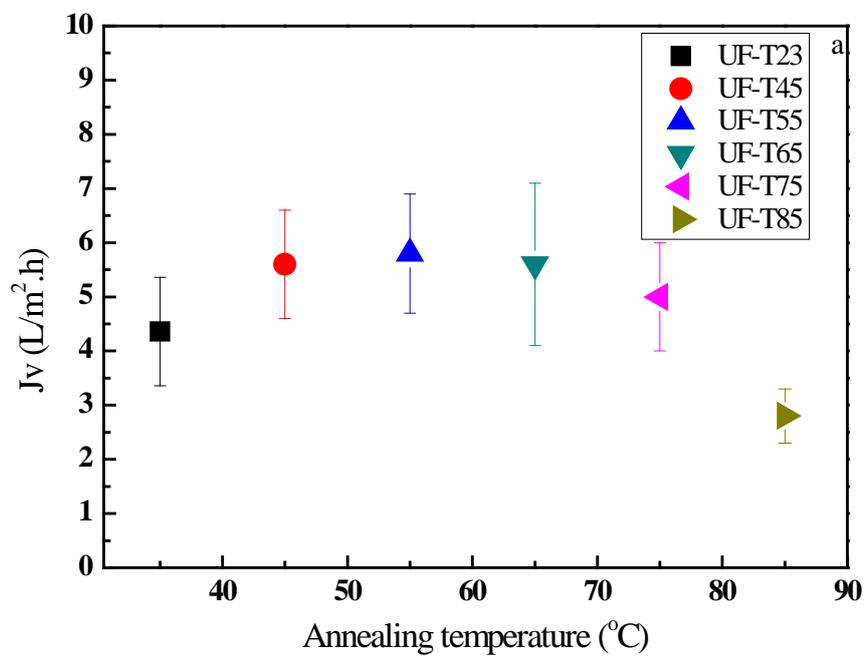
<sup>7</sup>: Data were cited from the Ref.[24].

## 3.2 FO performance

### 3.2.1 Effect of membrane properties on the FO performance of UF-like FO membranes

FO water flux ( $J_V$ ) and the ratio of solute and water flux ( $J_S/J_V$ ) against annealing temperature of UF-like FO membranes were drawn in **Fig. 1a** and **1b**, respectively, using a 5 % PEG (2 KDa) DS. The osmotic pressure of the DS was approximately 1.6 bar (**Fig. A3**). At high annealing temperature (i.e., 65 ~ 85 °C),  $J_V$  decreased at higher  $T_a$  as a result of lower membrane water permeability ( $A$ ) (see **Table 1**). Nevertheless, an opposite trend was observed over the low annealing temperature range (i.e., room temperature to 55 °C). In this range, decreasing  $T_a$  was accompanied with greatly increased  $J_S/J_V$  (**Fig.1b**). The  $J_S/J_V$  represents the effective solute concentration reverse diffused through an FO membrane [18]. Such high  $J_S/J_V$  tends to enhance the internal concentration polarization (ICP) in the membrane, which in turn negatively affects the FO water flux [10, 18, 28]. Thus, it was the

looser membrane pore structure and poor membrane rejection caused the reduced flux efficiency.  $J_s/J_v$  decreased as increasing the annealing temperature due to the higher rejection against PEG (Table 1). In general, the solute reverse diffusion appeared to be quite severe ( $J_s/J_v \sim$  or  $> 5$  mM, see Fig.1b) when the 2-KDa PEG was used as DS, which can be readily explained by the membranes relatively low rejection of PEG. Further discussion of the role of DS type and its MW on FO performance will be presented in Section 3.2.3.



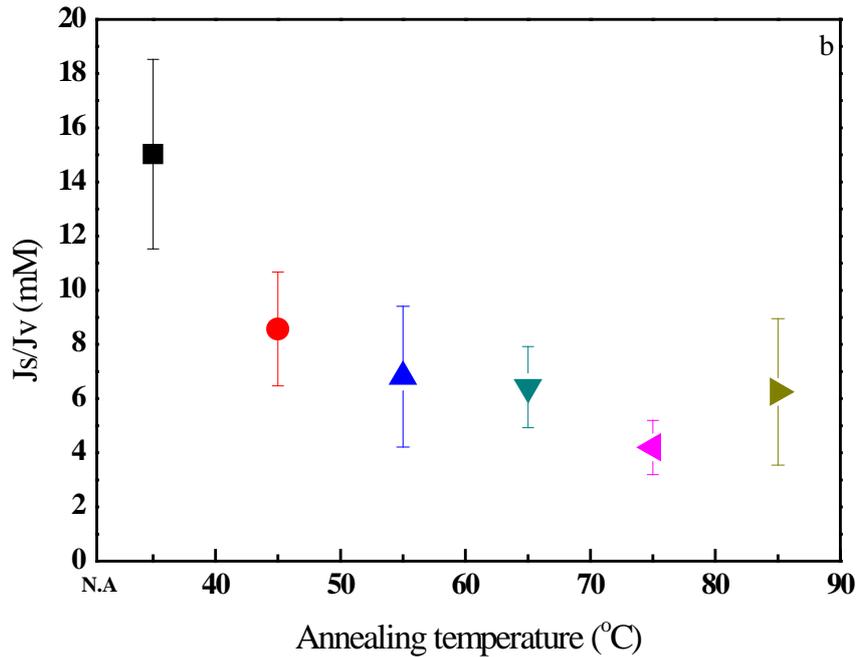
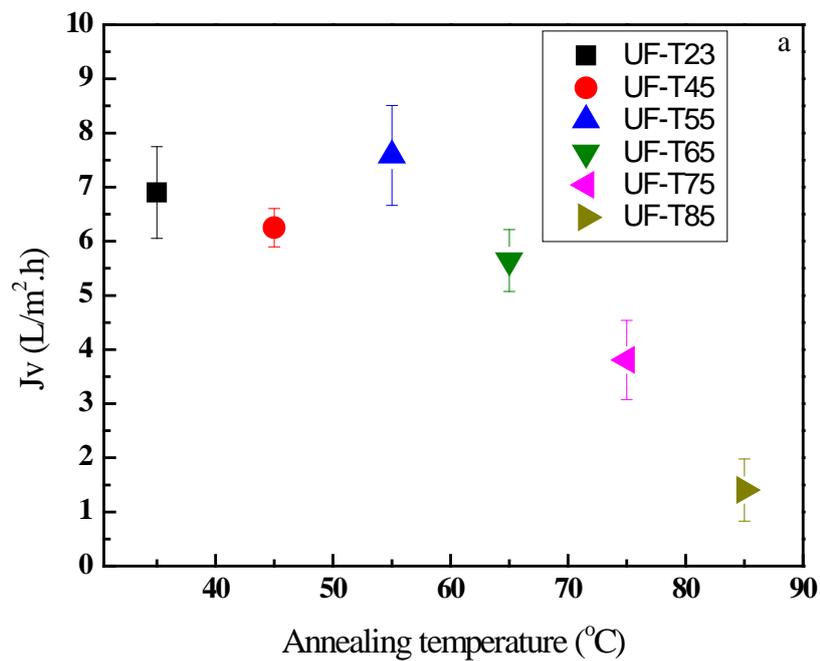


Fig.1. (a) Effect of annealing temperature on the FO water flux ( $J_V$ ) and (b) the ratio of solute flux and water flux ( $J_S/J_V$ ) against  $J_V$  for UF-like FO membranes with different annealing temperature. Testing conditions: 5 % PEG (2 KDa) as DS at AL-FS orientation.  $23 \pm 1$  ° C. Error bar was based the standard deviation of 3 replicate measurements.

**Fig.2** shows the  $J_V$  and  $J_S/J_V$  results against annealing temperature by using a 0.1% 70-KDa PSS solution as DS. Although the osmotic pressure of this DS ( $\sim 0.11$  bar, see **Fig.A3**) was an order of magnitude lower compared to the 5% 2-KDa PEG solution, slightly higher or comparative FO water flux was obtained for the PSS DS expected at the highest annealing temperature. Once again, the better FO water flux performance for the PSS DS can be attributed to its better rejection by the FO membranes (**Table 1**). Correspondingly, the solute reverse diffusion of PSS ( $J_S/J_V$  ranging from 0.001 – 0.004 mM, see **Fig. 2b**) was orders of magnitude lower compared to that of PEG (**Fig. 1b**). The lower  $J_S/J_V$  is preferred since it reduces the cost of DS replenishment and avoids the interference to feed water chemistry [18, 29, 30].

On the basis of both  $J_V$  and  $J_S/J_V$ , UF-T55 was chosen for further tests to evaluate the effect of DS types, MW, and concentration on the performance of porous-FO membranes. It should be noted that annealing treatment is only one of commonly used modification methods to vary separation performance of UF membranes [31]. Other modifications or synthesis methods, such as plasma [32], photochemical modification [33] and chemical treatment [34], can be similarly applied to prepared porous UF-like FO membranes with varied separation properties. Future studies are needed to further investigate the optimization of porous-FO membrane synthesis and modification.



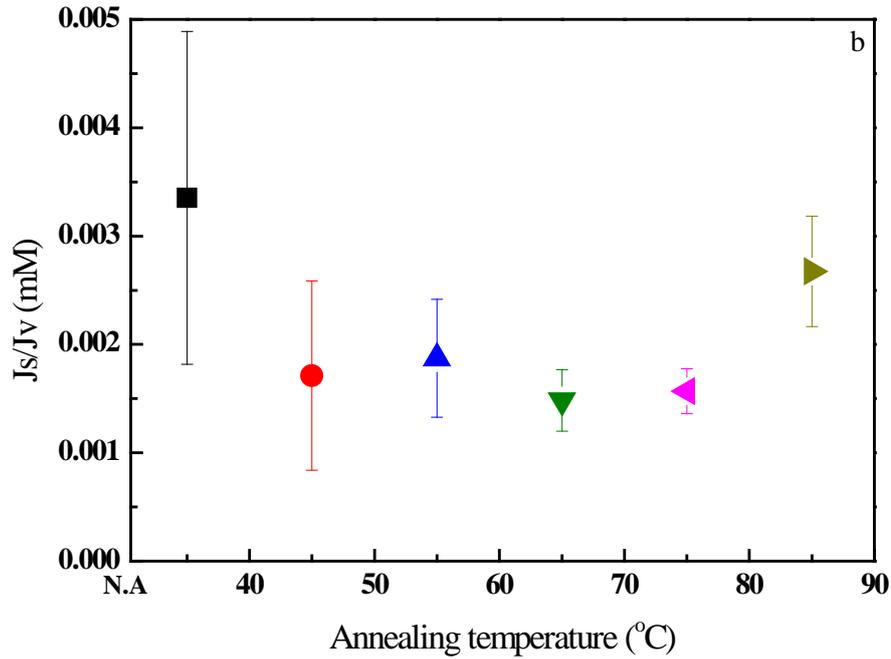


Fig.2. (a) Effect of annealing temperature on the FO water flux ( $J_V$ ) and (b) the ratio of solute flux and water flux ( $J_S/J_V$ ) against  $J_V$  for UF-like FO membranes with different annealing temperature. Testing conditions: 0.1 % PSS (70 KDa) as DS at AL-FS orientation.  $23 \pm 1$  ° C. Error bar was based the standard deviation of 3 replicate measurements.

### 3.2.2 Effect of DS concentration on the FO performance of UF-like FO membranes

The FO water flux ( $J_V$ ) and the ratio of solute and water flux ( $J_S/J_V$ ) of UF-T55 were studied by using PSS ( $M_w \sim 70$  KDa) or PEG ( $M_w \sim 2$  KDa) as DS over a wide concentration range (0.05% ~ 5% for PSS and 1% ~ 45% for PEG, see Fig. 3a and 3b). Both AL-DS and AL-FS orientations were tested. In general, little difference of the two membrane orientations were obtained, which agreed reasonably well with our prior study on porous FO [24]. For each DS type (PSS or PEG), the FO water flux generally increased at higher DS concentration of DS (Fig. 3a) as a result of increased osmotic pressure driving force (see Fig. A3 and [10]). The enhancement of water flux appeared to be more effective at low concentration range (i.e., PSS, 0.05 - 0.5 %), which can be explained by the relatively mild ICP under the lower water

flux levels. Comparing PSS with PEG, the former appeared to be a much more effective DS - much higher  $J_V$  was obtained at an identical weight concentration. The better water flux for PSS can be partially attributed to its more effective osmotic pressure generation mechanism. PSS is a polyelectrolyte and it releases its counter ions (such as  $\text{Na}^+$ ) when it is solubilized in water. Due to the overwhelming quantities of counter ions compared to the polymer macromolecules, the osmotic pressure of PSS is mainly contributed by its counter ions (Fig. A3). In the current study, the osmotic pressure of PSS solution was significantly higher than that of PEG solution at identical concentration (i.e., osmotic pressure =  $\sim 1.06$  bar for 1% PSS and 0.6 bar for 1 % PEG; and  $\sim 4.4$  bar for 5 % PSS and 1.6 bar for 5 % PEG). However, the difference in osmotic pressure alone is not adequate to explain the high efficiency of PSS. For example, even though the 5% PEG had higher osmotic pressure compared to the 1% PSS, the latter still had much higher water flux due to its low rejection of PEG. With PEG, even at a concentration of 45% (corresponding to an osmotic pressure of 60 bar), the water flux was only merely above 10  $\text{L}/\text{m}^2\cdot\text{h}$ . In comparison, fluxes of 20-30  $\text{L}/\text{m}^2\cdot\text{h}$  can be achieved by using 0.5 – 5% PSS as DS. As discussed earlier in Section 3.2.1, the use of PSS provides the advantage of greatly reduced reverse solute flux as a result of its much better rejection (Fig. 3b and Table 1). Accordingly, the reverse solute flux induced ICP was much mild for PSS compared to PEG [9].

The ratio of  $J_S/J_V$  is shown in Fig. 3b for both PSS and PEG. The value for PEG was relatively constant over the entire concentration range. Indeed, such independence of DS concentration and membrane orientations have been predicted by classical FO models

assuming that membrane solute permeability is independent of DS concentration [10, 30]. For the case of PSS, however, we observed a significant increase of the  $J_s/J_v$  ratio at higher PSS concentration (particularly for the 5% PSS solution), which indicate a weakened membrane rejection. It is worthwhile to note that both PSS and the PAN membrane are negatively charged, such as the Donnan exclusion effect [18] is expected to play an important role in the PSS rejection. With increased PSS concentration, the electrostatic repulsion between PSS molecules and the PAN membrane can be significantly weakened due to the increased ionic strength (i.e., the electrical double layer compression effect), leading to a comprised solute rejection. Similar concentration dependent reverse solute diffusion has been previously reported for a loose NF-like FO membrane using  $MgCl_2$  as DS [18]. In contrast, PEG is neutral and thus it is not affected by the Donnan effect.

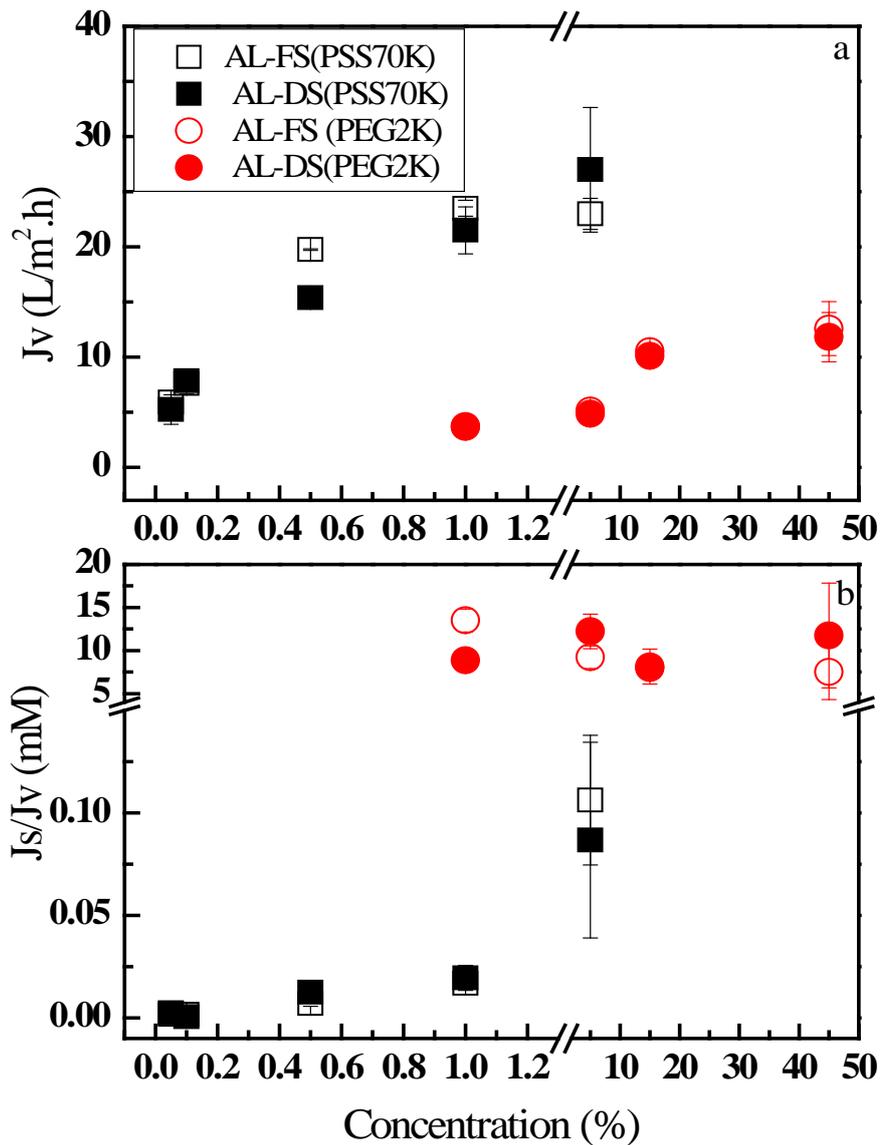


Fig.3. Effect of DS concentration of PSS (Mw: 70 KDa) or PEG (Mw: 2KDa) on the (a)  $J_V$  and (b)  $J_S/J_V$  of UF-T55 (UF-like) FO at both AL-FS and AL-DS orientation. Testing conditions: 0.05 %, 0.1 %, 0.5 %, 1 % and 5 % PSS or 1 %, 5 %, 15 % and 45 % PEG as DS at  $23 \pm 1$  ° C. UF-T55 (UF-like) FO membranes were used. Error bar was based the standard deviation of 3 replicate measurements. The  $J_V$  values which were measured using 0.05, 0.1, 0.5, and 1% of PSS as DS and DI water as FS in AL-FS orientation are according to the ref. [24].

### 3.2.3 Effect of MW of draw solutes on the FO performance of UF-like FO membranes

The FO water flux ( $J_V$ ) and the ratio of solute and water flux ( $J_S/J_V$ ) of UF-T55 were

evaluated by using DS of 0.1% PSS or 1% PEG with various  $M_w$  for the AL-FS orientation, respectively (Fig. 4a and 4b). Considering PEG, the FO water flux decreased insignificantly when the MW was increased from 2K to 10K of PEG (Fig. 4a). This reduction was likely caused by the significantly lower osmotic pressure of PEG-10K (i.e., ~ 0.19 bar compared to ~ 0.60 bar for PEG-2K, refer to the Fig.A3b). For PEG, the increase in MW results in reduced molar concentration at any fixed weight concentration and hence lower osmotic pressure driving force. As expected,  $J_s/J_v$  for PEG decreased at higher MW due to size exclusion (Fig.4b).

Additional experiments were performed by using PSS with various MW (70 KDa, 200 KDa and 1000 KDa) as DS at a fixed weight concentration of 0.1% (Fig. 4a). In contrast to the severely reduced water flux for the case of PEG, we observed relatively constant water flux for PSS regardless of its MW. As discussed in Section 3.2.2, the osmotic pressure of PSS is mainly contributed by its counterions [35]. Regardless of the MW, the 0.1% PSS solutions had nearly identical osmotic pressure of 0.11 bar in the current study (Fig. A3a). On the other hand, the adoption of a high MW is advantageous for PSS – the membrane retains the high-MW PSS effectively and small counter ions like  $\text{Na}^+$  are rejected based on the electro-neutrality constraint. This beneficial effect is reflected by the reduced  $J_s/J_v$  as shown in Fig. 4b.

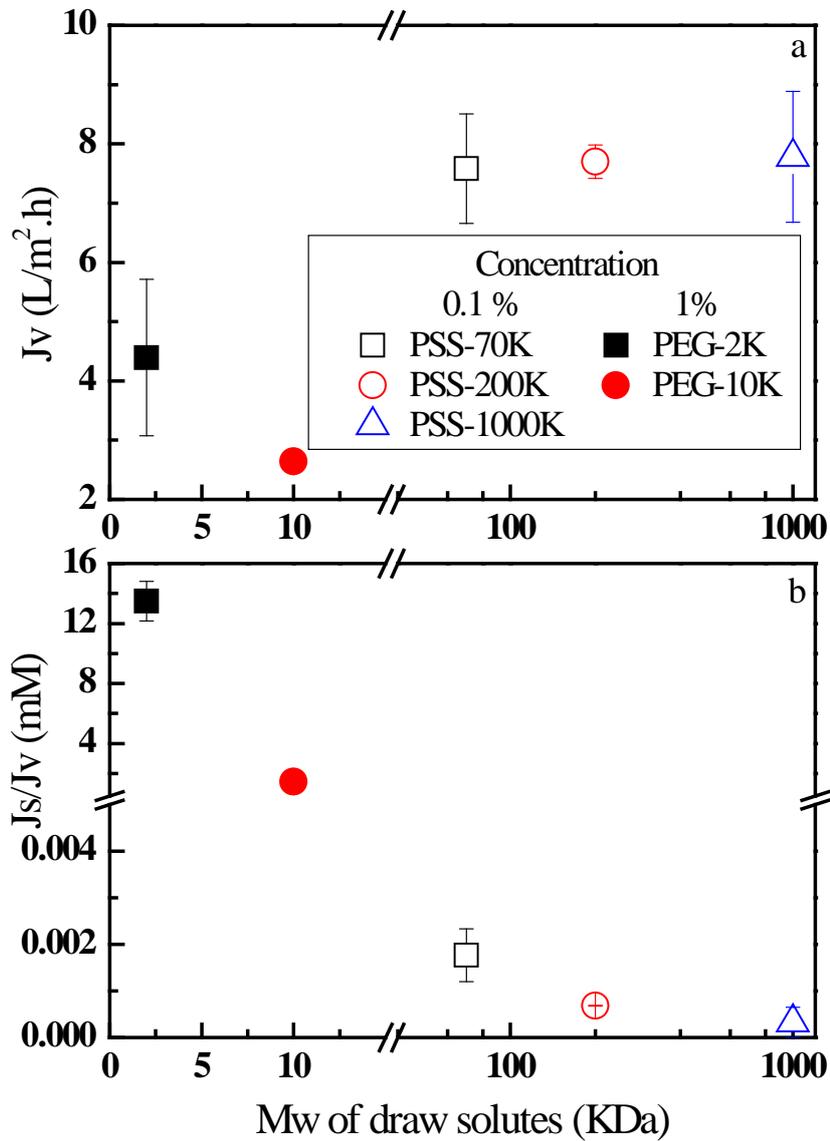


Fig. 4. Effect of Mw of draw solutes on the (a)  $J_v$  and (b)  $J_s/J_v$  for UF-T55 (UF-like) FO membranes at AL-FS orientation. Testing conditions: DS: 0.1 % PSS (Mw:70 KDa; 200 KDa and 1000 KDa); or 1 % PEG (Mw:2 KDa); or PEG (Mw:10 KDa) as DS at  $23 \pm 1$  ° C. Error bar was based the standard deviation of 3 replicate measurements.

#### 4. Implications

Using UF-like FO membranes have several advantages compared with traditional dense RO-like or NF-like FO membranes: 1) a wider range of membrane synthesis and modification techniques [25, 32, 34, 36] are available to prepare UF-like FO membranes with

tailored separation properties (e.g., pore size, surface charge, hydrophilicity, etc.); 2) reasonable water flux can be obtained using extremely low concentration of draw solution (in current study, only 0.1 % PSS was used as DS); and 3) macromolecules or nanoparticles can be potentially regeneration by a low-pressure UF process with relatively low energy demand. Such low-energy FO system can be potentially applied for food processing, biomedical applications, oil water separation, and membrane bioreactors, just to name a few.

The importance of matching the draw solutes and FO membranes should be adequately addressed. In the current study, we observed significantly better FO performance (higher water flux and lower reverse solute flux) for the porous FO membrane using PSS compared to PEG as the DS. The use of PEG as DS had limited scope due to its poor rejection by the PAN membrane. On the other hand, relatively high FO water flux for practical use (e.g., > 20 L/m<sup>2</sup>.h) can be achieved for the PSS at moderate concentration (e.g., 0.5-5%). The use of PSS is beneficial in the sense that relatively higher osmotic pressure can be generated by its counter ions. Furthermore, the use of higher MW PSS is possible without scarifying its osmotic pressure as a result of its unique mechanism of osmotic pressure generation, which allows high rejection of draw solutes to be achieved. This was not possible for the case of PEG, which an increase of MW generally means lower osmotic pressure (since molar concentration decreased with increased MW at any fixed weight concentration).

The UF-like FO membranes in the current study were far from being optimized. Other modifying technologies, such as plasma, UV and chemical treatment can be further applied.

Additionally, draw solutes are not limited in the range of polyelectrolytes. In literature, there are a lot of novel draw solutes in literature, which exhibited good osmotic pressure and easy recovery compared with traditional salt draw solutes. Examples include polyelectrolytes [37-39], dendrimers [40], novel temperature-sensitive micellar solutions [41], hydrogels [42], and magnetic nanoparticles [43]. However, those draw solutes presented relatively low water fluxes when using conventional dense FO membranes (for instances, only  $\sim 1.5 \text{ L/m}^2\cdot\text{h}$  achieved by using polymer hydrogels as DS [42] and  $\sim 13 \text{ LMH}$  water flux by using  $0.065 \text{ mol/L}$  magnetic nanoparticles with an osmotic pressure of as high as  $55 \text{ atm}$  as DS [43]). A key limitation of these examples was the relatively low water permeability of conventional dense FO membranes. By adopting porous FO membranes with far more permeable separation layers, the full potential of novel draw solutes may be unleashed. A carefully balanced combination of high permeability membrane, selectivity towards feed solutes, and selectivity against draw solutes deserves further investigation in such context.

## **5. Conclusions**

A series of porous-FO membranes were fabricated with different annealing temperature in the current study, and their water permeability and solute rejection (NaCl, PSS and PEG) were evaluated. The effect of draw solution properties (type of draw solutes, molecular weight of draw solutes, and concentration) on the FO performance was systematically investigated. The major findings are:

1. The higher annealing temperature during membrane post-treatment led to higher PSS

and PEG rejection but reduced water permeability of the porous-FO membranes.

2. The FO water flux  $J_V$  of the porous membranes was affected by both the membrane water permeability and reverse solute diffusion, with lower water permeability tends to reduce  $J_V$  while lower reverse solute diffusion tends to increase  $J_V$ .
3. Compared to neutral PEG, the polyelectrolyte PSS was a much better choice for draw solutes with higher  $J_V$  and lower reverse solute diffusion. The better performance of PSS can be explained by its better rejection by the porous FO membranes (thanks to the larger MW and Donnan exclusion effect) and its high osmotic pressure compared to PEG at same weight concentration. Higher FO water flux was obtained at higher concentrations of draw solution for both types of draw solutes.
4. When PEG was used as DS, increasing its MW led to a reduction in  $J_V$  due to the reduced osmotic pressure at fixed weight concentration. MW of PSS did not play a significant role on  $J_V$  since its osmotic pressure was mainly contributed by the counter ions (i.e.,  $\text{Na}^+$ ). For both PEG and PSS, the reverse solute diffusion was significantly reduced at higher MWs.

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Appendix:

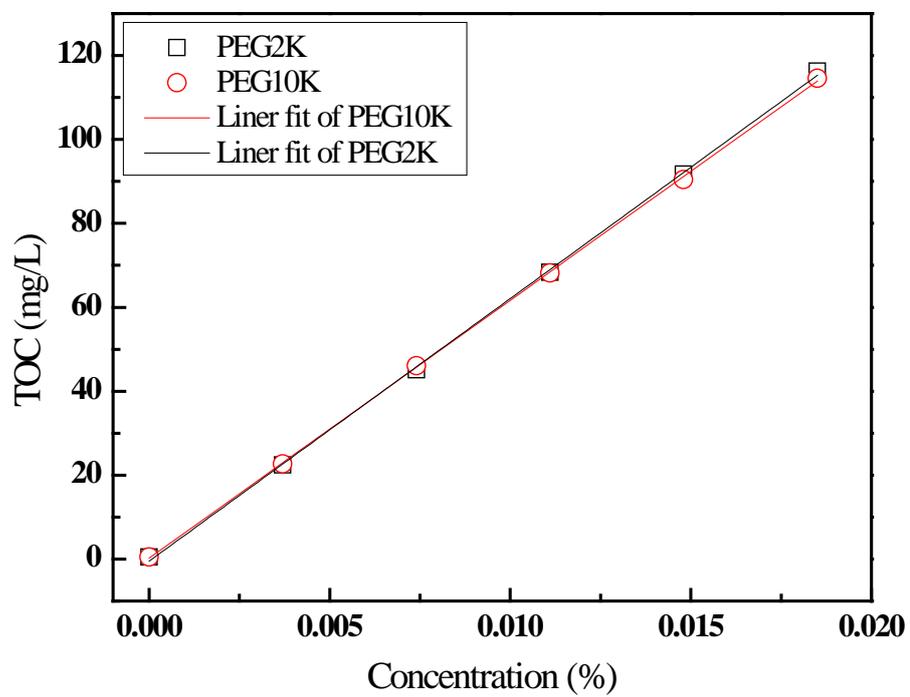


Fig.A 1. The TOC of different concentration of PEG with Mw 2 KDa and 10 KDa.

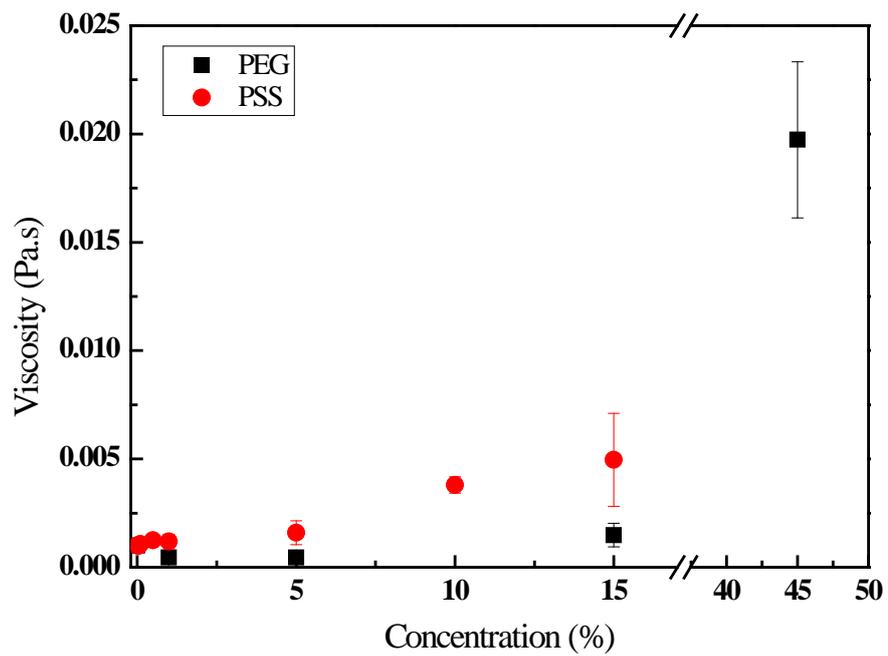


Fig.A2. The viscosity of different concentration of PSS (Mw ~ 70 KDa) solution and PEG (Mw ~ 2 KDa) solution.

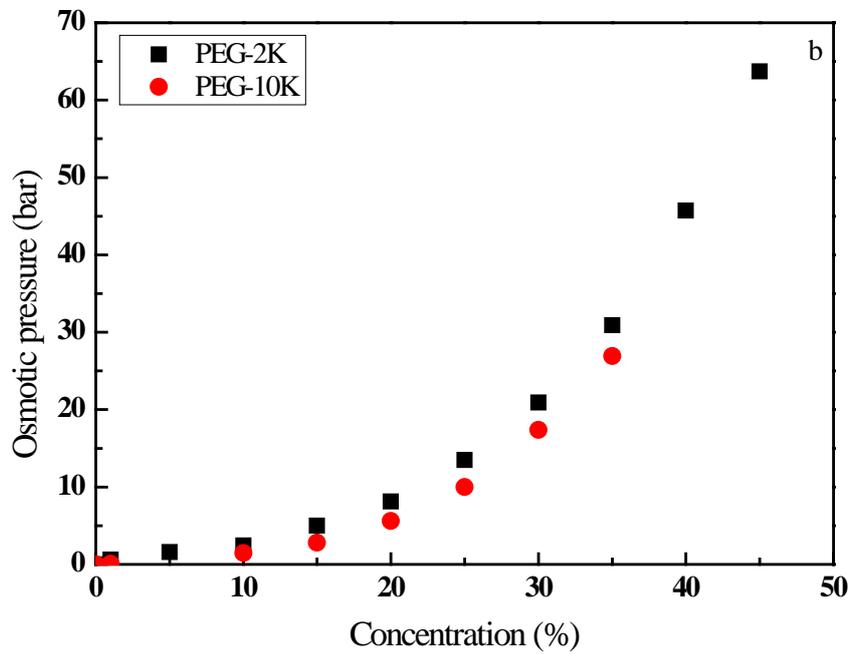
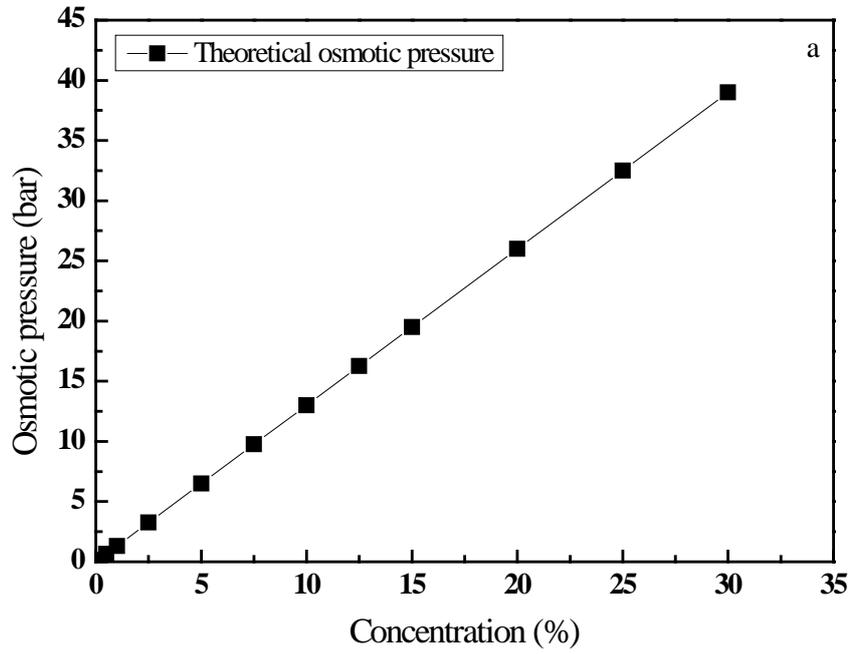


Fig.A3. The theoretical osmotic pressure of different concentration of PSS based on the  $\text{Na}^+$  concentration (assuming that all  $\text{Na}^+$  ionized in the solution) and (b) of PEG ( $M_w \sim 2$  KDa and  $M_w \sim 10$  KDa) solution. The osmotic pressure of PEG was according to the ref. [44].

Fig. A4. The FESEM images of cross-section of FO membranes with different annealing temperature.