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Membranes and Processes for Forward Osmosis-based Desalination: Recent Advances and Future Prospects

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Abstract

Forward osmosis (FO) is an increasingly important technology that has been deemed promising for addressing the global issue of water scarcity. Rapid progress over the past decade has been marked by significant innovations in the membrane development and process design. The key idea is to develop next-generation membranes through advanced membrane fabrication methods as well as hybrid systems where the FO process can really value-add. As such, this article provides an overview of the various FO membrane designs, in particular the thin-film composite, surface-modified, and mixed matrix and biomimetic membranes. The pros and cons of each type of membranes are discussed together with the strategies used to optimize membrane properties such as structural parameter (S), water permeability (A) and salt permeability (B) to achieve enhanced FO performances. Furthermore, we also discuss the roles of FO in the various hybrid systems and evaluate the potential of these hybrid systems for desalination. Lastly, we provide our perspectives, especially in the area of membrane fabrications and FO hybrid systems, to shed light on the future research directions for harnessing the true potential of FO for desalination.

Key words: Forward osmosis; Membrane design and fabrication; Hybrid FO systems; Desalination; Future prospects.

Highlights:

- We present a critical review of the current state of FO membrane fabrication and FO based desalination processes.
- We evaluate different membrane fabrication methods for fabricating high performance FO membranes.
- We analyze the key parameters of FO membranes in desalination applications.
- The pros and cons of each FO based hybrid systems for desalination are highlighted.

1 Introduction

Global water scarcity is an escalating problem that is driven by increasing population, emerging economies and compounding effects from climate changes [1, 2]. Addressing this problem requires innovative technologies that provide energy-efficient and cost-effective solutions to recover potable water from unconventional water sources such as seawater, brackish groundwater and wastewater [2]. Today, the most robust and widely used desalination technology is the reverse osmosis (RO) process [3]. RO is a membrane-based process that utilizes a semi-permeable membrane to oppose and surpass the osmotic pressure of the saline solution to produce clean water. It is a thermodynamically non-spontaneous process, where a transmembrane pressure (TMP) is essential to provide the driving force for mass transport across the membrane [4]. The large intrinsic osmotic pressure of the seawater implies a high hydraulic pressure is necessary for the RO process. To this end, RO is still considered an energy- and cost-intensive process despite the fact that the low energy consumption has already been realized by advances in the technology [5, 6].

Forward osmosis (FO) for desalination emerges with the promise of overcoming the challenges of pressure-driven membrane processes [7]. In FO, spontaneous water permeation across a semi-permeable membrane occurs, which is driven by a chemical potential difference (osmotic gradient) arising from a concentrated draw solution (DS) and a diluted feed solution (FS). Since an external hydraulic pressure is not necessary, FO offers the advantages of lower energy demand (i.e., reduced capital and operational costs) as well as less irreversible membrane fouling as compared to the RO process [8, 9]. Due to these reasons, FO has attracted immense attention within the membrane community which sees research efforts intensifying over the past decade, especially within the last 5 years (Fig. 1).

Fig. 1. Number of citations, patents and publications on forward osmosis over the past ten years. The number of citations and publications are based on data from Web of Science, while data for the number patents are obtained from SciFinder.

Over this period, significant progress has been made in the FO technology [10]. Herein, we aim to cover this progress from two main aspects namely, membrane design and hybrid FO system. Our arguments for these two aspects are as follows. First, the key to a successful FO technology depends largely on the membrane itself [11]. Suitable membranes were once thought to be lacking as conventional asymmetric RO membranes turned out inappropriate for FO application given their lower than expected fluxes [12]. However, the success of the HTI (Hydration Technologies Inc.) membranes had inspired a burgeoning growth in FO membrane design given a better understanding of the desired characteristics of FO membranes. There are now more focused research efforts in the direction of thin film composite (TFC) membranes to develop membrane substrates with optimized parameters to mitigate internal concentration polarization (ICP) [13] and thin and robust selective layers for high FO performance and fouling control [14, 15]. Meanwhile, the emerging novel materials which have high capacities to create synthetic nanochannels are utilized in membrane design to further boost membrane performance [16, 17]. Polymeric membranes, in particular, play an instrumental role and act as

a versatile platform to facilitate all these efforts [11]. Second, hybrid FO system has become a topic of discussion recently as water treatment and desalination cannot be **achieved** with a standalone FO process [18], but it is possible to pair the FO process with another separation process to regenerate the diluted DS and/or employ FO as a pre-treatment for desalination [19]. Correspondingly, many studies have demonstrated the potential to lower the energy demand of desalination as compared to conventional desalination processes, or the increased capacity of the desalination process to handle feed water of high concentration with hostile trace contaminants [18]. To create an even larger impact, a good draw solute is crucial in facilitating easy recovery of the product water. Conventional inorganic draw solutes, whose main purpose is to create a DS with a higher osmotic pressure than FS, are non-responsive in nature [20]. The use of ammonia and carbon dioxide solution as an easily re-generable DS has sparked great interest in the research of responsive draw solutes [21, 22]. In recent years, ‘smart’ draw solutes that are responsive towards temperature, pH, electro-magnetic field or light have been vigorously pursued, motivated by the desire to regenerate diluted DS and recover the product water in an energy-saving and cost-effective way [23].

Therefore, in this review, we commence by first highlighting the basic principles and identifying the main challenges pertaining to the FO process. By drawing on our expertise in membrane fabrication and engineering, we then shortlist the key progress in FO membrane developments since 2010. Particularly, our discussions center around the various types of FO polymeric membrane fabrication and modification methods with a strong emphasis in tuning the structural parameters of membrane substrates, engineering flat sheet and hollow fiber membrane configurations as well as designing and optimizing TFC and mixed matrix membranes to achieve enhanced FO performances. Next, recent advancements in hybrid FO systems for desalination are provided. Notably, the design strategies on developing hybrid

systems are put into the perspective of finding the right fit for FO to harness its full potential for desalination. Lastly, we discuss the future prospects of membrane innovations and hybrid systems as well as how crucial they are in shaping the position of FO for desalination.

2 Basic principles and challenges of FO

Since FO utilizes the osmotic pressure difference across the membrane active layer as the driving force to draw the water flow from the FS (low concentration) side to the DS (high concentration) side, the hydraulic pressure difference across the membrane (ΔP) is almost equal to zero as described in Fig. 2. In addition to FO, the figure also shows the flux-pressure relationship of reverse (RO), pressure retarded osmosis (PRO) and pressure assisted osmosis (PAO), where ΔP is above zero. When hydraulic pressure is applied on the more concentrated solution side, the process becomes PRO ($\Delta P < \text{osmotic pressure difference } (\Delta\pi)$) or RO ($\Delta P > \Delta\pi$). In contrast, PAO is operated by applying hydraulic pressure on the lower concentrated solution side. Compared with the conventional RO separation, FO/PRO/PAO do not separate fresh water during the process. Instead, the permeated water flows to the DS side and a further process is required to separate the water from the dissolved solutes if clean water as the end product is desired.

Fig. 2. Water flux J_v (upper) and energy production W (lower) as a function of hydraulic pressure ΔP for PAO/FO/PRO/RO processes.

The DS, formed by homogeneously dissolving or dispersing draw solutes in water, plays a key role in an FO process. By capitalizing on the osmotic pressure difference generated by a concentrated DS and a dilute FS, the water is driven out from the FS to the DS to realize the separation. Hence, one of the most critical characteristics required of the DS is to have a high osmotic pressure, in addition to other desired qualities including high diffusion coefficient to reduce ICP, low reverse diffusion to the FS, low/no toxicity, chemically stable and cost-effectiveness [23]. More importantly, the DS must be easily regenerated/concentrated (when purified water extraction from the DS or draw solute regeneration is required) as it is strategic towards the design of the FO applications and the hybrid systems eventually adopted [23, 24]. Further discussion on the draw solutes can be found in Section 4.

On the other hand, the membrane is the key to a highly efficient FO system. During an FO process, the actual driving force (real osmotic pressure gradient across the membrane active layer) is significantly lower than the osmotic pressure difference between the bulk FS and the bulk DS, primarily due to the presence of ICP effect in the membrane support layer [7] (illustrated in Fig. 3), i.e., either through dilution of DS on the DS side (Fig. 3a) or accumulation of solutes on the FS side (Fig. 3b). The former is called the dilutive ICP, which generally occurs in the active layer-facing-feed solution (AL-FS) orientation (referred to as the FO mode); while the latter is the concentrative ICP in the active layer-facing-draw solution (AL-DS) orientation (i.e., the PRO mode (in which PRO process is generally operated)). ICP is different from the external concentration polarization (ECP) in the sense that ECP occurs at the membrane surface and can be alleviated by increasing the cross-flow velocity (CFV) across the surface. On the other hand, ICP can **only** be marginally minimized by an increased CFV as it occurs within the membrane support layer [7]. Hence, ICP is more closely related to the characteristics of the substrate, which can be described by a structural parameter (S value):

$$S = \frac{\tau \cdot l}{\varepsilon} \quad (1)$$

where τ is tortuosity, l is the substrate thickness and ε is the substrate porosity. A thin and porous substrate with interconnected pores (less tortuous) generally results in less severe ICP [15, 25] and thus higher FO water flux. In addition, such a substrate also suffers from less internal fouling as a result of less severe ICP of foulants/scalants when the membrane is operated in the AL-DS orientation [26, 27], especially in the case of fouling induced by saturated foulants. The property of the active layer is also critical for **the** FO membrane performance. In general, membrane with low hydraulic resistance (high water permeability, A value) and high solute rejection (low solute permeability, B value) is favourable because this combination not only gives rise to a higher FO water flux, it also results in less cross-

contamination of the FS and DS due to a reduction in the reverse solute diffusion and forward solute diffusion. For the application of desalination, it is highly desirable that FO membrane **has** high rejection to small solutes such as NaCl. In this regard, a RO-like skin layer is preferred.

Fig. 3. Schematic of internal concentration polarization (ICP) in membrane cross-section. (a) AL-FS orientation; and (b) AL-DS orientation.

To have a better understanding of the interplay between these parameters, the relationship between FO water flux, J_v (AL-FS orientation), S and A values **is reviewed by** using the following equation [25] and **as** illustrated in Fig. 4:

$$J_v = K_m \ln\left(\frac{A\pi_d + B}{A\pi_f + J_v + B}\right) \quad (2)$$

where K_m is mass transfer coefficient ($K_m = D/S$, and D is the diffusion coefficient), π_d and π_f are the osmotic pressure of draw solution and feed solution, respectively. It can be seen that the effect of increasing A value is more significant for the substrate with a small S value and for the dilute FS (Fig. 4a). By comparison, when FS contains 0.5 M NaCl, increasing A value only contributes to a minimal flux increment, especially when S value is larger than 500 μm (Fig. 4b). Therefore, increasing A value is beneficial on the basis that the S value is sufficiently

small. The benefit of large A value diminishes with increasing feed concentration. Similar result was reported in a prior study **where** the FO water flux did not increase when the A value was increased to a value beyond ~ 2 L/m²h/bar (LMH/bar) under the condition of 1.5 M NaCl feed and 4.0 M NaCl DS [28]. For a highly concentrated FS, the intrinsic water permeability of the membrane may not be a critical factor as compared to the S value and DS concentration (Fig. 4c). On the other hand, it is interesting to note that increasing B/A from 15 to 150 kPa does not result in a significant change in the water flux (Fig. 4d). However, in real operation, low B/A value is **still** preferred to achieve low reverse solute flux, considering its adverse effect on fouling [29] and draw solute replenishment [28, 30].

Fig. 4. Estimated FO water flux as a function of membrane structural parameter, showing the effect of A value (a-c) and B/A value (d). Modelling conditions are 10 mM NaCl FS and 0.5 M NaCl DS (a, blue symbols in d); (b) 0.5 M NaCl FS and 1.0 M NaCl DS (b, black symbols in d); and 0.5 M NaCl FS and 2.0 M NaCl DS (c, red symbols in d). Other conditions: AL-FS

orientation (FO mode) is applied, $B/A = 15$ kPa for (a-c), $A = 3$ L/m²h for (d). Osmotic pressure is calculated using OLI software (1 atm, 25 °C).

FO membrane fouling in the AL-FS orientation is similar to RO fouling. The foulants may adsorb or deposit on the membrane surface due to a flux drag towards the membrane surface [31, 32]. Important factors **influencing fouling** include membrane surface property, hydrodynamics and solution chemistry [33, 34]. These factors which **have impacts on RO** fouling can likewise play an important role in the FO fouling [27, 32, 35-37]. However, different from RO, the lack of high hydraulic pressure in FO usually leads to a less compact fouling layer that can be easily removed by physical cleaning [36, 38]. It has been reported that the membranes after gypsum scaling in the FO mode can be cleaned by hydraulic flushing and the flux was almost completely recovered, in contrast to the 90% flux recovery for scaled membranes in the RO mode [36]. Similar results were also obtained for the fouled membranes by organic foulant (**e.g.**, alginate) [39]. In addition, the unique ICP self-compensation effect during FO fouling may cause a marginal decrease in the water flux [25, 38]. It is known that increasing DS concentration **fails to** generate an expected water flux increase due to a greater ICP effect at higher water flux; hence, when the water flux is decreased due to fouling, the ICP effect is reduced which compensates for the water flux [25].

On the contrary, in the AL-DS orientation, i.e., the PRO mode, the membrane fouling is dominated by the foulant deposition/growth in the membrane support layer. The foulants that enter the porous substrate can result in a high internal foulant concentration to induce a concentrative ICP effect, which subsequently promotes gel or scale formation in the support layer [26, 27]. The extent of foulant ICP is correlated (positively) to the substrate structural parameter; an FO membrane with **a** larger S value usually suffers from more severe fouling in

the AL-DS orientation [26, 40]. Foulants with larger particle sizes are also likely to be trapped within the microporous structure. The internal fouling usually causes very severe flux decline, **which is** mainly **attributed** to the clogging of micropores in the substrate, causing reduced porosity and increased tortuosity (i.e., increased S value) [25]. Unlike the AL-FS orientation, the ICP self-compensation effect is less significant in the AL-DS orientation due to a milder ICP effect [25].

3 FO membrane developments

3.1 Conventional cellulose based membranes

The first commercial FO membrane developed by Hydration Technologies, Inc. (HTI) was made of cellulose triacetate (CTA) supported by polyester mesh [7, 41]. This successful commercial product sparked a number of studies on the cellulose acetate (CA)/CTA asymmetric FO membrane development, as shown in Table 1. The CA/CTA FO membrane **is** obtained simply by immersing casted or spun polymer dope into coagulants where phase inversion takes place and generates an asymmetric membrane structure featured with a skin layer integrally supported by a porous substrate [42, 43]. The solvent for preparing the polymer dope has to be volatile enough (e.g., with added acetone) to allow a fast solvent evaporation for ensuring a dense selective layer formation. This CA/CTA membrane has a lower fouling propensity due to its hydrophilic nature and a stronger chlorine resistance than conventional TFC membranes [42]. However, the asymmetric membrane also has a relatively low rejection to salt. A common practice for reducing pore size and enhancing selectivity through an annealing post-treatment is therefore necessary [42, 44, 45]. However, a major drawback is the low intrinsic water permeability given by the thick skin layer [41, 46], which is worsened during the annealing process (making the skin layer denser and less permeable) [44]. Although many efforts have been attempted to enhance the water flux and salt rejection of the CA/CTA

asymmetric FO membrane through exploring new materials [47], adjusting dope composition [42, 46], tuning fabrication conditions [44] and introducing new additives [45], little progress has been achieved in acquiring a high-performance CA/CTA asymmetric FO membrane. It is observed in Table 1 that the water flux of CA/CTA membranes is still well below 20 L/m²h (LMH) in the AL-FS orientation even with a concentrated DS. Also, the reverse solute flux is relatively higher in comparison with the TFC membranes. Generally, these observations draw out the disadvantages of the integrally asymmetric FO membranes. First, unlike TFC membrane, the integrally asymmetric FO membrane is fabricated in an integrated mass, which does not allow separate tailoring of the skin layer and substrate. Second, in general, the high polymer concentration used and the annealing process afford denser substrate with lower porosity, resulting in a larger structural parameter of the membrane [45]. Notably, the polymer concentration for fabricating CA/CTA asymmetric FO membrane is typically higher than 18% [42-44, 46], but the concentration of CA dope used for fabricating TFC FO support can be as low as 10% [48]. As such, these challenges continue to restrain the advancement and widespread applications of CA/CTA membranes in FO desalination.

Table 1. Summary of CTA/CA asymmetric FO membranes.

Membrane	thickness (μm)	Structure	<i>S</i> value (μm)	<i>A</i> (LMH/b ar)	<i>B</i> (LMH) (NaCl)	<i>J_v</i> (Lmh)	<i>J_s</i> (gmh)	<i>J_s/J_v</i> (g/L)	Orientation, area(cm^2)	DS	FS	Ref /year
HTI FO membrane	~50	Asymmetric single-skin with woven support	575	1.13	0.46	~10/~15.5	~6/~9	0.6/0.58	ALFS/ALDS	1.0M NaCl	DI	[49, 50]/2006
CA-NF hollow fiber	~100	Asymmetric single-skin	-	0.47	~0.05	5.0/7.3	-/0.53	-/0.073	ALFS/ALDS, 50	2.0M MgCl_2	DI	[43]/2010
CA flat sheet	35		54	0.17	0.07	10.3/17.3	0.8/1.2	0.08/0.07	ALFS/ALDS	2.0M MgCl_2	DI	[46]/2010
CA-NF flat sheet	~30	Double-skin	-	0.72	0.46	~17/~26	~3/~5	0.17/0.19	ALFS/ALDS, 16	2.0M MgCl_2	DI	[51]/2010
CTA-NF flat sheet	20-30	Asymmetric single-skin	-	-	-	9.0/12.8	6.2/6.8	0.69/0.53	ALFS/ALDS, 16	2.0M NaCl	DI	[52]/2012
CA flat sheet	17	Asymmetric single-skin	-	-	-	~10/~13	~3/~5.5	0.3/0.42	ALFS/ALDS	2.0M NaCl	DI	[53]/2011
CA- hollow fiber	118	Asymmetric single-skin	-	0.97	0.22	~8/~36	~1/~1	0.13/0.03	ALFS/ALDS, 80	2.0M MgCl_2	DI	[54]/2011
CA flat sheet	-	Asymmetric single-skin	-	0.51	0.40	12/21.6	5.1/10.6	0.42/0.49	ALFS/ALDS	2.0M NaCl	DI	[42]/2012
CA- hollow fiber	46.3	Double-skin	-	0.76	0.38	17.1	2.5	0.15	ALDS, 65	2.0M MgCl_2	DI	[55]/2012
CA propionate hollow fiber	65	Dual-layer	-	0.80	0.22	~8.0/17.5	~1.3/2.5	0.16/0.14	ALFS/ALDS, 80	2.0M NaCl	DI	[47]/2013
CTA/CA flat sheet membrane	~50	Asymmetric single-skin with support	-	-	-	10.39	4.91	0.47	ALFS, 27	1.0M NaCl	DI	[44]/2013
CA flat sheet membrane	~80	Asymmetric single-skin	740-832	1.23-1.31	0.12-0.14	11.6-12.7	-	-	ALFS, 57.4	2.0M Glucose	0.1M NaCl	[45]/2016

3.2 TFC membranes with RO-like rejection layers

The research and development of the TFC FO membrane started in the year 2010, pioneered by Yip and Wang for TFC FO membrane in flat sheet and hollow fiber configurations, respectively [56, 57]. HTI TFC membrane was the first commercially available TFC FO membrane. Recently, there were another two companies producing TFC FO membranes, i.e., Porifera Inc. and Oasys Water Inc. [58]. Today, TFC FO membranes have become one of the most competitive membranes owing to the high versatility of tuning the characteristics of membrane substrate and its active layer independently. Nevertheless, the FO performances of these commercial membranes **remain** inadequate with both membranes from Porifera and Oasys Water Inc. showing a moderate water flux of only ~17.5 LMH in the AL-FS orientation using 0.5 M NaCl as DS [59, 60]. This motivates a great amount of work in optimizing TFC membranes for FO application. In particular, efforts are focused mainly on making the support layer more interconnected and porous as well as thinner and less tortuous. Furthermore, a highly water permeable and selective active layer is also vigorously pursued by the membrane community. To deliver a clear overview of the progress achieved thus far, Table 2 provides key performances data of representative TFC FO membranes and their membrane parameters.

Table 2. Summary of the performance of TFC FO membranes.

	Membrane	Substrate thickness (μm)	Substrate porosity (%)	Substrate pore size/PWP	Fabric mesh	<i>S</i> value (μm)	<i>A</i> (LMH/bar)	<i>B</i> (LMH)	<i>J_v</i> (LMH)	<i>J_s/J_v</i> (g/L)	Orientation, area (cm ²)	NaCl DS	FS	Ref /year
TFC/phase inversion substrate	TFC-PSf	95.9			PET	492±38	1.16	0.47	18.16		AL-FS, 20.02	1.5 M	DI	[56]/2010
	TFC-PSf		82	190 LMH/bar	no	670±170 ^a	1.78	0.34	13.5/20	0.41/0.29	ALFS/ALDS, 60	0.5 M	10 mM	[15]/2011
	PSf	92.3		39.6nm	PET	312±72	1.90±0.3	0.33±0.19	25.0±4.1		AL-FS, 20.02	1.0 M	DI	[61]/2011
	PSf/SPEK	~20	77.2	10.7nm/152.7 LMH/bar	no	107	0.75	0.068	35/50	0.2/0.18	ALFS/ALDS, 4	2.0 M	DI	[62]/2012
	sPPSU	~25	83.41	10.72nm/846.4 LMH/bar	no	652	3.23	1.05	30/32	0.18/0.14	ALFS/ALDS, 4	0.5 M	DI	[63]/2013
	PAN	160			no	389	0.91	0.57	9.25/13.88	0.11/0.11	ALFS/ALDS, 8.25	0.5 M	DI	[64]/2013
	CAP	~25	91.5	13.5nm/1456 LMH/bar	no	31.9	2.85	0.345	45/58	0.14/0.13	ALFS/ALDS, 4	0.5 M	DI	[48]/2013
	polyketone 70(25/75)		80.6	83nm	no	287	2.5		24.4/	0.14/	ALFS/ALDS, 42	0.6 M	DI	[65]/2015
	polyketone 80(35/65)		84.5	210nm	no	NA	NA	NA	29.3/41.5	0.13/0.12	ALFS/ALDS, 42	0.6 M	DI	
	SPES	65	79		no	245	2.9	0.18	17/22	0.38/0.32	ALFS/ALDS	0.5 M	DI	[66]/2016
	HF-PES	175	75	12.7nm/278 LMH/bar	-	595	2.22	0.2	14/32.2	0.13/0.11	ALFS/ALDS, 78.5	0.5 M	DI	[57]/2010
	HF-PES	205	82	9.6nm/278 LMH/bar	-	550	3.5	0.22	42.6	0.1	ALDS	0.5 M	DI	[14]/2011
	HF-PES	180	75	12.7nm/275 LMH/bar	-	520	3.07	0.12	16.7/49.4	0.072/0.079	ALFS/ALDS	0.5 M	DI	[67]/2011
	HF-PES _{water/NMP/P}	~130	80.9	17nm/1021 LMH/bar	-	219	1.18	0.135	34.5/65.1	0.29/0.19	ALFS/ALDS, 18.8	2.0 M	DI	[68]/2012
	EG HF-PES _{water}	~170	80	15nm/835 LMH/bar	-	261	1.83	0.348	22.5/25.6	0.12/0.13	ALFS/ALDS, 15.1	0.5 M	DI	[69]/2013

TFC/nanofiber substrate	HF-sPPSU	180		6.3nm/213 LMH/bar	-	163	1.99	0.04	22.5/49.4	0.24/0.22	ALFS/ALDS, 20	0.5 M	DI	
	HF-PEI	110	82.3	71nm/1167 LMH/bar		172	3.66	0.31	38.5		ALFS, 38	1.0 M	DI	[70]/2017
	PVDF/2D freezing	92	74	5-15 µm	no	100	4.7	0.66	46/62	0.12/0.09	ALFS/ALDS, 4.9	0.5 M	DI	[71]/2017
	PES nanofiber	50	83	1139 LMH/bar		80	1.7	1.1	37.8		ALFS	0.5 M	DI	[72]/2011
	PAN/CA nanofiber	10-15 w/o PET			PET	311	1.80	0.58	27.6/43	0.14/0.04	ALFS/ALDS	1.5 M.	DI	[73]/2013
	PAN nanofiber	10-15 w/o PET			PET	290	2.04	1.57	29/50	0.28/0.06	ALFS/ALDS	1.5 M.	DI	[74]/2013
	PVDF nanofiber	63.8	67	280nm/1267 LMH/bar		812	1.21	0.33	11.6/30.4	0.3/0.21	ALFS/ALDS	1.0 M	DI	
	PET nanofiber - PSf	~130			No	651	1.13	0.23	12.9		ALFS, 20.02	1.0 M	DI	[75]/2013
	PET/PVA nanofiber	57							47.2	0.2	ALDS	0.5 M	DI	[76]/2014
	PVA nanofiber	51 w/o PET	93			66	1.69	0.24	27.2		ALFS, 64.7	0.5 M	DI	[77]/2014
	Nylon 6,6 nanofiber	8-10 w/o PET		7632 LMH/bar	PET	190	1.66	0.54	21/27	0.24/0.44	ALFS/ALDS	1.0 M	DI	[78]/2014
	Hydrophilized PVDF nanofiber	15.2 w/o PET			PET	193	1.28	0.25	15/20	0.15/0.35	ALFS/ALDS	0.5 M	DI	[79]/2016
	PAN nanofiber	80			no	168	1.47	0.28	17.5	0.23	ALFS, 40	0.5 M	DI	[80]/2017
	PSf/Zelite	66.3	79.8	461 LMH/bar	no	340	3.3	1.3	21/42.5	0.52/0.47	ALFS/ALDS, 60	0.5 M	DI	[81]/2013
	PSf/TiO ₂	68	75	165 LMH/bar	no	420	1.96	0.38	17.1/31.2	0.17/0.21	ALFS/ALDS, 14.62	0.5 M	10 mM	[82]/2014
Nanoparticles in	PEI nanofiber/CNT	96	81	2045 LMH/bar		310	2.5	0.6	26/48	0.11/0.06	ALFS/ALDS, 42	0.5 M	DI	[83]/2015
	PSf/GO	50	75	28 nm/ 700 LMH/bar	no	191	1.76	0.19	20/40	0.18/0.16	ALFS/ALDS	0.5 M	DI	[84]/2015

Nanoparticles in active layer	PSf /silica NP/ co-casting	97.2		36.4 nm/ 3134 LMH/bar	PET	169	1.64	0.29	31/61	0.24/0.26	ALFS/ALDS , 60	1.0 M	DI	[85]/2015
	PEI nanofiber/ silica NP	93.7	83	1280 nm	PET	174	2.99	0.41	40/70	0.12/0.1	ALFS/ALDS , 42	1.0 M	DI	[86]/2017
	Zeolite-PSf	70			no	782	2.57	1.57	13.5/25	0.43/0.39	ALFS/ALDS , 60	0.5 M	DI	[87]/2012
	SiO ₂ -PSf					376	3.4	2.8	22/36			2.0 M	10 mM	[88]/2014
	CNT-PSf		71		no	380	3.6	0.10	30/73	0.08/0.06	ALFS/ALDS , 30	2.0 M	10 mM	[89]/2013
	Halloysite nanotube						1.86	0.63	21/34	0.29/0.26	ALFS/ALDS , 20.02	2.0 M	10 mM	[90]/2015
	HNT-PSf						2.39	0.37	17.82	0.12	ALFS	0.5 M	10 mM	[91]/2015
	NH ₂ -TNT-PSf													
	AQP-HF-PES	~150			-		8	0.8	55.2	0.08	ALDS, 34.2	0.5 M	DI	[92]/2015
	GO-PAN		81.1	12.7 nm	no	85	2.04	0.83	22/25	0.15/0.16	ALFS/ALDS , 3.87	0.5 M	DI	[93]/2016
	AQP-HF-PEI	110	82.3	71nm/1167 LMH/bar	-	172	7.6	0.52	35/65	0.11/0.12	ALFS/ALDS , 38	0.5 M	DI	[70]/2017

3.2.1 Substrates made via phase inversion

Similar to the RO membrane fabrication, phase inversion still remains the most widely accepted and practiced technique for making the substrates of FO membranes. In most studies, a non-solvent induced phase separation (NIPS) method is utilized to form an ultrafiltration (UF) membrane as the FO substrate [94]. Both flat-sheet membranes and hollow fiber membranes can be realized using this method (Fig. 5). Since a substrate with faster mass transfer coefficient (i.e., thin, porous and low tortuosity) is the primary requirement for a high performance FO membrane, extensive work has been performed to understand the effect of the composition of polymer solution and casting/spinning conditions on the membrane structure formation [94].

Fig. 5. SEM micrographs of the cross-section of TFC-FO membranes. (a) PSf flat-sheet membrane including PET nonwoven fabric and (b) its magnified view of the dense, sponge-like morphology near the active layer [56]; (c) PES hollow fiber membrane from [57].

In general, factors, which have a major effect on the membrane structure, include choice of polymer, choice of solvent and nonsolvent, composition of polymer dope and composition of coagulation bath [95]. For porous membranes obtained by instantaneous demixing, the separation properties are mainly determined by the choice of solvent/nonsolvent. Indeed, this type of membrane structure appears to be independent of the choice of polymer [95]. However, other desired membrane properties such as thermal and chemical stability, hydrophilicity etc. are critically dependent on the nature of the polymer. Table 3 lists the various commonly used polymeric materials, which include polysulfone (PSf)/ polyethersulfone (PES), polyetherimide (PEI), polyacrylonitrile (PAN), and CA/CTA. PSf/PES are the most popular polymers for fabricating MF, UF membranes and the substrates for non-porous membranes [96-98], owing to **their** good chemical and thermal **stabilities**. For this reason, PES/PSf membranes have a relatively wide pH tolerance range (pH 2-13) and the absence of active functional groups makes them chemically robust. Nevertheless, PSf/PES are relatively hydrophobic, which is of concern especially if insufficient wetting of the support layer or strong fouling in the substrate (in the AL-DS orientation) occurs. The CA/CTA polymers are a group of hydrophilic materials that **is** more resistant towards fouling [99]. However, their poor **stabilities** to acids, bases, organic solvents and bio-organisms attack can limit their applications in niche areas [99]. Some other polymeric materials such as PAN [100, 101], PEI [70], polybenzimidazole (PBI) [102], polyphenylenesulfone [69] and polyketone [103] have also garnered much attention for their use in substrate fabrications for FO membranes. As an alternative of polymeric materials, inorganic materials show a clearer advantage in terms of outstanding chemical and thermal stability, as well as membrane lifespan. However, its complex preparation procedure and high cost of production have hampered the scalability potential of the inorganic membranes. In

addition, fabricating a highly selective layer on an inorganic support with relatively large pore sizes is still challenging to date.

Table 3. Summary of commonly used materials for FO substrates.

Materials	Advantages	Disadvantages	Ref.
PES/PSf	<ul style="list-style-type: none"> • Good chemical resistance and mechanical stability 	<ul style="list-style-type: none"> • Relatively hydrophobic (prone to fouling) 	[14, 57, 67]
CA/CTA	<ul style="list-style-type: none"> • Very hydrophilic, resistant to fouling 	<ul style="list-style-type: none"> • Very narrow pH tolerance range (pH 3~8) 	[48]
Polyetherimide (PEI)	<ul style="list-style-type: none"> • Low cost • Good durability • Excellent solvent resistance 	<ul style="list-style-type: none"> • Poor chemical resistance • Reactive with amine-containing chemicals at elevated temperature 	[70]
Polyacrylonitrile (PAN)	<ul style="list-style-type: none"> • Hydrophilic 	<ul style="list-style-type: none"> • Nitrile group is sensitive to alkaline 	[100]
Inorganic materials	<ul style="list-style-type: none"> • Outstanding thermal and chemical stability (e.g., strong tolerance to extreme pHs, physical or chemical cleaning) 	<ul style="list-style-type: none"> • High cost • Complex preparation process 	[104]

According to the literature, varying the polymer composition is the most commonly adopted method for obtaining an optimized porous FO substrate [94]. This can be achieved by decreasing the polymer concentration and varying the choice of additives and solvents along with their concentrations. More specifically, the objective is to increase the substrate porosity and reduce the membrane thickness, leading to a lower S value of the substrate [61]. Tiraferri, et al. reported that the S value of the FO membrane **was** decreased from $>2000\ \mu\text{m}$ to $389\ \mu\text{m}$ by reducing the PSf concentration from 18% to 9%. Meanwhile, the intrinsic water permeability increased by ~50% (from 1.09 at 18% to 1.63 LMH/bar at 9%) with minimal increase in the B/A ratio. These changes resulted in **an increased** FO water flux from 7.5 (18% PSf) to 21 LMH (9% PSf) using 1 M NaCl as DS and DI water as FS. Similar results have also been observed for PAN supported TFC membranes [101]. Nevertheless, decreasing polymer

concentration, in general, increases substrate surface pore size, which can affect the intrinsic property of the selective layer. Although a few studies have demonstrated that MF membrane supports can be also used for FO membrane fabrications [65], the substrates can potentially have surface pores that are too large to support the selective layer under a high hydraulic pressure [105]. While FO uses low or zero hydraulic pressure, sufficient mechanical strength is still needed for the membranes to endure the cross-flow hydrodynamics in a large module for a sufficiently long operating lifetime.

Apart from the polymers, additives such as LiCl, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are commonly used as pore formers [15, 70, 106] in membrane fabrication. The concentration of the additive in the dope solution can affect the FO membrane structure. For instance, Wu et al. observed that increasing PEG concentration from 0 to 6% helped to decrease the S value from 434 to 182 μm , and the A value was increased from 1 to 1.55 LMH/bar as a result. The resulting FO water flux was almost doubled when the DS concentration increased from 0.5 to 1.5 M (NaCl) [106]. Furthermore, additives of different molecular weights also affected the membrane structure [107]. Interestingly, beyond conventional additives, noteworthy compounds such as lignin [108] and diethylene glycol [109] have also been investigated as pore formers for improving the FO substrate properties. Another important factor impacting the membrane formation is the choice of solvent and nonsolvent [95]. It was reported that the PSf-based membrane substrate possessed a very different structure if the solvent was changed from NMP to DMF, and substrates prepared by poorer solvents such as DMF exhibited smaller S values [61, 110]. Considering the cost of solvent in addition to the nonsolvent, water is still the most preferred nonsolvent coagulant despite the fact that few studies have reported coagulation agents with a solvent at relatively low concentration [56].

The use of co-casting technique (simultaneous casting of two layers of polymer solutions using a double-blade) can produce favorable structured supports to reduce the ICP effect [85, 111-113]. It was demonstrated by Ng et al. that co-casting with two polymer solutions of different concentrations was able to produce permeable substrate, yet retaining a suitable surface morphology for the active layer fabrication [85, 111]. As discussed earlier and in section 3.2.3, a substrate with too large surface pores may not be able to support the selective layer effectively, resulting in poor formation of the rejection layer and relatively low membrane selectivity (high solute flux). A dual layered substrate produced with double-blade can resolve such a problem. In addition, co-casting has also been used to fabricate substrate with straight finger-like pores and open bottom surface morphology using a sacrificial-layer approach [112]. In the reported study [112], the PEI sacrificial layer was co-casted beneath the top PSf layer. The resultant PSf substrate with open bottom structure had an S value of as low as 167 μm , in contrast to the single layer casted substrate with an S value of 241 μm . The ICP effect was greatly reduced for the co-casted membrane especially at high DS concentration. A recent work examined a substrate with vertically oriented pores [71] that was prepared via a bidirectional freezing process. This superior structure corresponded to a perfectly low tortuosity (S value as low as ~ 100 μm) and produced a considerably high FO water flux. Although many prior studies advocated a substrate structure with finger-like/needle-like pores due to the potentially lower tortuosity as compared to that of a sponge-like substrate, such perception has been recently revised following new experimental evidences. Chung et al. fabricated a sponge-like substrate with a small S value (220-260 μm) to give a high performance FO membrane [114]. Besides, Li et al. found that incorporating an additive into the dope lowered the S value, although it kinetically slowed down the demixing process and induced a more sponge-like structure [70]. In principle, pore-forming additive not only helps to inhibit the formation of macrovoids, it

also creates more interconnected pores, suggesting that a sponge-like structure is not always equivalent to a dense structure with a large S value.

Unlike RO membranes, in-house fabricated flat-sheet membranes may not necessarily require fabric mesh supports, due to the relative lower hydraulic pressure used in a lab-scale FO system. The embedment of fabric mesh in the support layer generally decreases the mass transfer in the membrane and creates a larger S value. Although undesirable, membranes without the fabric mesh may not have sufficient mechanical stability to handle industrial-scale FO operation. Contrastingly, the self-supported hollow fiber membranes do not face such challenge and the S value of the FO hollow fiber membranes are generally smaller than that of the flat-sheet membranes. In addition, compared to lab-scale flat-sheet membrane fabrications, the production of hollow fiber membranes normally involves more control parameters such as bore fluid, air gap and take-up speed, thereby a more precise tuning of the membrane structures is viable. Again, water is the most popular non-solvent coagulant for membrane fabrication and adding solvents into the water coagulant can lead to a dramatic change in the membrane structure [114, 115]. The latter approach is not suitable for use in flat-sheet membrane fabrication because of the high consumption of solvents. In the spinning process, however, the amount of solvents added into the bore fluid or extruded from dual-channel spinneret [114] is much smaller. It was reported that adding solvents into coagulants delayed the phase separation process, giving rise to a larger surface pore size and a more porous structure [115]. This kind of structure is favorable to give a more permeable TFC membrane [116] with a smaller structural parameter. The effect of air gap on the structure of the hollow fiber membrane is more complex. Basically, an air gap is a deliberate distance left between the spinneret and the coagulant bath so as to help the polymer to relax after coming out of the spinneret and before the start of phase inversion. It also assists in the release of stress and reorientation of the

polymer chains [117, 118]. The minimal take-up speed in spinning is equal to the free-fall speed of the hollow fiber in the coagulant bath. Elevating take-up speed leads to the elongation of hollow fibers and the reduction in cross-section dimensions (i.e. outer and inner diameters). A smaller dimension may enhance the burst pressure of hollow fiber membranes given the same wall thickness [70]. However, an overly elevated take-up speed can also generate an undesirably high elongation stress that is detrimental to the mechanical strength of the hollow fibers [118]. It is also found that the surface pores can become elongated and narrow with an increase in the take-up speed [70], resulting in increased tortuosity and structural parameter together with a decreased intrinsic water permeability of the TFC membrane. Hence, a free-fall speed is usually chosen for fabricating hollow fiber supports for FO membranes [70].

3.2.2 Nanofiber substrates by electrospinning

The work by Song et al. reported an electrospinning-formed nanofibrous support for FO membrane fabrication [72]. The scaffold-like nanofibers can be tailored to be highly porous with interconnected pores **that contribute towards** a largely reduced tortuosity (Fig. 6). It is believed that the interconnected pores can be more easily achieved by electrospinning than by a phase inversion technique [73, 83, 119]. Apart from the relatively smaller S value, nanofibrous support provides another key advantage, i.e., the ability to tailor the substrate using different structured layers [120, 121]. For example, Tian et al. reported a tiered support that was made by a fine (top) and a coarse (bottom) PEI nanofiber layers [121]. The fine and thin nanofibers at the top are suitable for forming a rejection layer, while the bottom layer consisting of coarser fibers can provide robust mechanical support while improving the mass transfer within the substrate [121]. This approach is similar to the co-casting method (phase inversion), but offers more precise control of the substrate structure through electrospinning. In addition, the tiered structure can expand the pressure tolerance limit, making these membranes suitable

for the PRO process [120, 121]. Rather than two distinct layers of different structures, future work can explore multi-layered support layer to further optimize the substrate performance for the FO process [120].

Fig. 6. PES nanofiber supported TFC FO membrane [72].

3.2.3 Interfacial polymerization

In the literature, the rejection layers of most TFC FO membranes are prepared by interfacial polymerization (IP) between monomers of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) at the surface of a microporous support. The resulting polyamide layer should ideally exhibit both high water permeability and high permselectivity. This can be achieved by varying the composition of monomers [122], reaction time, the additives in the MPD/TMC solutions and the method for removing excess MPD, etc. [95]. As discussed in the previous section, the substrate characteristics may also affect the properties of the polyamide layer. Both experimental [116] and simulation [123] studies suggest that a support with a larger pore size or porosity is highly favorable to form a more permeable TFC membrane. Therefore, making more porous substrate (but not overly porous) can create a synergistic effect of minimizing the

structural parameter and enhancing the water permeability of TFC membranes. On the other hand, hydrophilic materials are often selected to enhance mass transfer within the support layer and reduce membrane fouling [124], but this type of substrate may result in the formation of a polyamide layer with lower permeability as compared to **that of** a hydrophobic substrate [116]. In addition, the hydrophilic surface may exhibit a poorer adhesion to the polyamide layer, presumably due to the difference in the swelling characteristics [94].

3.3 Surface-modified membranes with NF-like rejection layers

In addition to IP, surface-modification using layer-by-layer (LbL) assembly and chemical cross-linking with polyelectrolytes on a microporous substrate can also be used to prepare FO membranes [125]. These membranes usually have nanofiltration (NF)-like rejection layers, and larger draw solutes such as divalent salts, polyelectrolytes or micromolecules have to be used for the FO process. For LbL assembly, the first polyelectrolyte layer is typically deposited on the microporous substrate by electrostatic attraction [125] or hydrophobic interaction [126, 127]. The former requires an initial charged membrane surface **to commence the LBL assembly**. **In this way**, the first LbL FO membrane was made, where a PAN substrate was prepared and treated with NaOH to obtain negatively charged surface and followed by alternate poly(allylamine hydrochloride) (PAH)/ poly(sodium 4-styrene-sulfonate) (PSS) bilayer depositions [125]. Inspired by this study, hollow fiber LbL FO membrane was successfully prepared with a significant enhancement in the water permeability [127]. This membrane had a PES hollow fiber substrate with PSS/PAH deposited skin layer in the lumen side. It was reckoned that the first PSS deposition took place over the PES surface based on a hydrophobic interaction [128]. The LbL FO membranes was further optimized to achieve very high water permeability (A value >10 LMH/bar) and high rejection towards divalent ions [126]. However, these membranes could not perform well at a high ionic concentration (i.e., high draw solution

concentration), due to a drop in the solute rejection given an electrical double layer compression at a high ionic strength [125]. In spite of the efforts in improving the membrane stability by crosslinking the bilayers [100, 129], the application of such LbL FO membranes is still limited only to those using low DS concentration and neutral draw solutes for long-term operation.

Chemical cross-linking with polyelectrolytes is a more straightforward approach to obtain NF-like rejection layers for FO application. To this end, polyelectrolytes utilized include PAH [130], polyethyleneimine [131], glutaldehyde [132], p-xylylene dichloride [102], etc. with the objectives of furnishing charges to the rejection layers [133] as well as tuning the mean pore size and its distribution of the membranes [134]. For instance, Setiawan et al. developed a positively charged poly(amide-imide) (PAI) hollow fiber FO membranes by cross-linking with polyethylenimine under mild conditions [133]. These membranes exhibited good water flux and low back diffusion of divalent salts in the FO process, owing to a tight pore size, narrow pore size distribution and, notably, ions repulsion from the Donnan exclusion effect [135]. More importantly, because chemical cross-linking is facile to implement, it is also more versatile for modifying hollow fiber membranes. This has been exemplified by surface modifications made to the shell side of the hollow fibers in addition to the combination of chemical cross-linking with other approaches such as polyelectrolytes deposition and nanomaterials immobilization to further enhance FO performances and anti-fouling properties [136, 137]. The key drawback of the chemical cross-linking approach, however, is the loss in the mechanical properties of the membranes with excessive cross-linking [134]. Therefore, optimizing the degree of cross-linking is critical.

3.4 Mixed matrix and biomimetic membranes

Research interests in thin film nanocomposite (TFN) membranes have increased since the pioneering study from Hoek's group [138], who reported the fabrication of RO membrane via an IP process with immobilized zeolite NaA nanoparticles (NPs) of loading 0.004-0.4% (w/v) within the polyamide layer. Inspired by the zeolite TFN RO membranes, a similar approach was used to fabricate FO membranes by Tang and co-workers [81]. The water flux of the TFN membrane with 0.1 w/v% zeolite loading (in TMC/hexane) was about 50% higher than that of the neat TFC membrane in both the AL-FS and AL-DS orientations. The specific solute flux J_s/J_v (NaCl), however, remained almost unchanged as compared to the neat TFC membrane, suggesting no formation of defects in the polyamide selective layer. Further increase in zeolite loading significantly increased the solute flux without the benefit of gaining additional water flux [81]. In addition to zeolite, many other nanofillers have been investigated to form TFN membranes, such as carbon nanotubes (CNTs) [89], silica NPs [88], titanate nanotubes NH₂-TNTs [91], graphene oxide (GO) [93], etc. (Table 2). The increase in FO water flux is mainly attributed to the increase in intrinsic water permeability, and optimal loading of NPs is critical to the membrane design due to the concern of defect formation, which causes a high reverse solute flux at an excessive loading [139]. Apart from these emerging nanomaterials, aquaporin (AQP) incorporated vesicles exhibit excellent water permeability and high salt rejection, owing to the superior intrinsic characteristics of the AQPs as water channels [140]. Embedding AQP laden vesicles to the polyamide layer of RO membrane had been successfully demonstrated by Zhao et al. [141], and the vesicle embedded biomimetic membrane showed a 25% increase in water flux without compromising the NaCl rejection. The recent work by Li et al. [70] showed an improved membrane permeability from 3.7 to 7.6 LMH/bar by incorporating AQP laden vesicles to the polyamide selective layer of hollow fiber membranes. The FO performance of the optimized biomimetic membrane exhibited a high water flux of 35 and 63 LMH in AL-FS

and AL-DS orientation, respectively, even at a low osmotic gradient using 0.5 M NaCl as DS and DI water as FS (Fig. 7).

Fig. 7. Biomimetic hollow fiber FO membrane [70]. (a) cross-section of hollow fiber membrane; (b) aquaporin incorporated vesicles in rejection layer; (c) FO performance in AL-FS orientation; and (d) FO performance in AL-DS orientation.

Instead of adding nanomaterials into the polyamide rejection layer, researchers have also tried incorporating nanofillers into the membrane substrate via a direct blending method [142]. This method generally helps to decrease the substrate structural parameter by increasing porosity and/or reducing tortuosity, thereby reducing the ICP effect and increasing the water flux. Tang and co-workers demonstrated that embedding 0.5% zeolite to the PSf substrate can decrease the substrate S value from 960 to 340 μm [81], as a result of increased substrate surface porosity

and hydrophilicity as well as reduced tortuosity [81]. The intrinsic water permeability of the rejection skin layer was increased by 80%, which could be attributed to a reduced substrate hydraulic resistance. In addition, the resulting FO water flux performance was almost doubled in the AL-DS orientation. Similarly, the work on adding TiO₂ NPs into the substrate of FO membrane also reported a drop in the S value (from 980 to 420 μm upon 0.5 wt% TiO₂ loading), increased A value and higher FO water flux. The loading is generally optimized to avoid significantly increased salt permeability. Hydrophilic NPs such as silica and GO have also been proved to be beneficial in reducing the S value of the FO substrates [84-86]. Furthermore, embedment of NPs into the membrane substrate may also help to improve the mechanical property. CNTs are well-known for its high strength and its incorporation into FO/PRO membrane substrate can result in a higher mechanical strength along with a lower S value [83, 121]. Beyond structural and mechanical properties, the anti-fouling functionality of the NPs is also valuable for the FO membranes. For example, membranes with embedded silver NPs had been found to mitigate biofouling during a PRO mode operation [143].

3.5 Other FO membranes

In addition to the typical TFC membranes, surface-modified membranes and TFN membranes, other types of FO membranes have also been fabricated for various purposes. Since the water flux is normally higher in the AL-DS orientation than the AL-FS, the AL-DS orientation is more competitive if reliable methods are available to control the membrane fouling [144]. To overcome the internal fouling problem, double-skinned FO membranes have been proposed [145-150]. This concept utilizes a second skin layer formed at the bottom surface of the substrate in addition to a dense rejection layer on the top surface. Thus far, polydopamine (PDA) deposition [149], IP [150], LbL polyelectrolyte deposition [146, 148], etc. have been adopted to produce double-skinned FO membranes. With the second skin layer, membrane fouling in

the AL-DS orientation can be effectively reduced, despite a reduction in the water flux of the membrane as compared to its single-skinned counterpart. Moreover, a few studies adopted surface modification approach to improve the anti-fouling property of the rejection layer [151-154], through chemical grafting of PEG, GO, or amine-terminated sulfonated poly(arylene ether sulfone).

A novel thin film inorganic FO membrane was developed by You et al. [104]. It was made of microporous silica xerogels immobilized onto a stainless steel mesh substrate, i.e., a typical sol-gel method for preparing inorganic membranes [104, 155]. The advantages of such inorganic FO membrane are the extremely low S value (38 μm) and high mechanical strength [104]. The substrate with a small S value makes the membrane highly suitable for the AL-FS orientation as both orientations demonstrated similar water fluxes [104].

3.6 Summary of FO membrane fabrication methods and FO performances

All the FO membrane fabrication methods discussed so far are summarized in Table 4. TFC FO membranes (including TFC mixed matrix membranes) remain the most promising membranes for potential desalination applications, owing to their high rejection capabilities. By optimizing the various control parameters for membrane casting, spinning and/or embedding NPs into the substrates, FO membranes with desirably small structural parameter (e.g., $< 200 \mu\text{m}$) can be obtained. On the aspect of rejection layer, water permeability can be increased by adopting a good recipe for the skin layer formation, utilizing of a relatively permeable (porous) substrate and/or incorporating NPs into the skin. Presently, the best FO membrane with RO-like skin layer is demonstrated by the AQP incorporated hollow fiber FO membrane (A value of $\sim 8 \text{ LMH/bar}$ with a B/A ratio $< 10 \text{ kPa}$). On a different note, the use of commercial TFC FO membrane modules showed higher water flux and lower reverse solute

flux than commercial CTA membrane modules in pilot-scale desalination plants [156, 157], consisting with the intrinsic properties of these two types of membranes summarized in Tables 1 and 2. However, most existing membrane fabrication studies choose to focus on the membrane characterization, rather than the separation performance in real applications or pilot hybrid systems. As such, to close this gap, future investigations on membrane fabrications should pay special attention on the real applications of these high performance FO membranes so as to attest their performance in realistic desalination processes.

Table 4. Summary of FO membrane fabrication methods.

FO membrane fabrication methods	Advantages	Disadvantages
Asymmetric cellulose based membrane	- One-step formation	- Relatively low intrinsic permeability and selectivity - Low chemical and biological stability
TFC/phase inversion	- High water permeability and low salt permeability - Substrate with low structural parameter	- Subject to chlorine attack
TFC/nanofiber	- Porous substrate with low tortuosity; - Substrate with different layered properties can be easily tailored	- Large substrate surface pores may result in a rejection layer of relatively low selectivity and mechanical stability - Subject to chlorine attack
Layer-by-layer assembly	- High water permeability (NF-like skin)	- NF-like skin has low rejection to monovalent ions - Rejection layer may not function well under high ionic strength
Mixed matrix membranes	- NP embedded substrate has reduced S value - Increased water permeability if NPs are added in the rejection layer - Added function/improved properties	- Dispersion of NPs in dope solution is challenging - Unsure about the long-term stability and toxicity - Increased cost

4 Hybrid FO systems for desalination

Standalone FO, as an energy-efficient option for desalination, is now considered overly idealistic and has turned out to be realistically impractical in the continued absence of a competitive process to easily regenerate the diluted DS and recover the product water [18]. As such, FO can only find **desalination** applications in niche areas (**FO concentration application is not discussed here**), such as fertilizer drawn desalination **where the diluted fertilizer is directly used for irrigation** [158, 159], **sugar/dehydrated food drawn desalination for nutrient food preparations** [160], and waste products (e.g., sodium lignin sulfonate) drawn desalination for desert restoration [161]. The similarity among these applications is that the water extracted from the saline FS eventually ends up in the diluted DS which can serve as ready-to-use products without the need to carry out draw solute regeneration or water extraction. However, the use of independent FO to generate portable water remains a challenge. For this reason, the recent concept of coupling FO with another process to realize hybrid FO-based systems for desalination has been proposed to capitalize FO in a more advantageous way. In this section, we aim to review the different types of hybrid systems and the roles played by the FO process. Generally, when the seawater or the water to be desalted is used as feed water for the FO process, we seemingly refer to it as direct desalination. Conversely, indirect desalination refers to a system **where** the seawater or the water to be desalted is used as a DS instead. Based on these classifications, sections 4.1 to 4.3 **focus on** direct desalination hybrid systems (FO–distillation, FO–RO, and FO–non-RO), while indirect desalination systems are presented in sections 4.4 to **4.6** (FO–RO (osmotic dilution), PRO–RO, **and FO–microbial desalination cell (MDC)**).

4.1 FO–distillation

The concept of FO desalination using thermolytic draw solute ammonia carbon dioxide was first introduced in 2005 by Elimelech and co-workers [21]. The schematic of this process is

illustrated in Fig. 8. After the water is drawn into the concentrated ammonia carbon dioxide DS, the product water can be recovered by utilizing low-grade thermal energy to vaporize and decompose the ammonium salts into ammonia and carbon dioxide gases, which can then be reconstituted into the DS [21, 162]. This process mainly consumes thermal energy instead of electrical energy. Wherever a source of low-grade heat is available, this process can potentially lead to energy saving as compared to SWRO desalination and other conventional thermal desalination processes such as multi-stage flash (MSF) and multi-effect distillation (MED) [163]. Oasys Water Inc. had demonstrated the use of a hybrid FO system integrated with distillation column for desalination of high-salinity shale gas produced water [164]. It was reported that the specific energy consumption of this hybrid system was lower than other thermal distillation methods [164]. Nevertheless, the biggest drawback of this concept is the presence of lingering ammonia in the product water [19]. As recommended by the world health organization (WHO), the drinking water standard for ammonia content should be <1.5 mg/L, but **this standard** cannot be met by the thermal distillation of ammonia-carbon dioxide solution at present.

Fig. 8. The NH₃/CO₂ forward osmosis desalination process [162].

Similarly, FO-MSF and FO-MED are hybrid processes that utilize thermal energy (Fig. 9). Standalone MSF and MED are thermal distillation technologies commonly employed in the middle eastern countries for desalinating feed waters with high salinity, high temperature and high impurity [19]. Scaling, which is caused by dissolved inorganic compounds, is a major issue for these thermal processes [18]. The deposited and accumulated scales on the heat exchanger surface decrease the heat transfer efficiency and reduce the system temperature and overall system recovery [165]. However, this scaling problem can be overcome by integrating with a FO process. The FO process plays the role of pre-treatment in the hybrid system, where the scale precursors in the high salinity water can be removed together with the organic matters. This system may outperform the NF-MSF/ NF-MED systems, due to the potentially lower energy demand, higher rejection and lower fouling propensity of the FO process [18]. Prior modeling studies on FO-MSF and FO-MED systems for seawater desalination had demonstrated that FO pre-treatment could reduce the scaling effect on the heat exchangers and enable the thermal processes to operate at higher temperatures and water recovery rates [166-168]. Besides seawater, these hybrid systems can also be used for more challenging feed waters of higher salinities, such as the seawater RO brine (concentrate from seawater RO), oil and gas produced water [169], or waters that need to be treated to very high recoveries (e.g., zero-liquid discharge scheme) [18]. Since the maximum operating pressure of RO is approximately 70 bar, feed water with osmotic pressure exceeding this limit cannot be treated using the RO process. Thus, the FO-MED/FO-MSF systems can be considered for this type of application, especially if waste heat is readily available.

Fig. 9. Schematic of FO pretreatment for conventional RO/NF or thermal (MED or MSF) desalination process [18]. Feedwater foulants and scalants are excluded from the draw solution, enabling the conventional desalination process to operate at high recovery for draw solution reconcentration.

Alternatively, FO coupled with membrane distillation (FO-MD) can desalinate waters that are challenging to a standalone MD process [169], providing another way to leverage on low-grade thermal sources. It has been demonstrated that the MD process has many advantages over pressure driven processes, such as higher salt rejections than RO and NF, the absence of high pressure operation, less sensitive (flux) to the osmotic pressure of the feed and less membrane fouling problems [170]. Despite this, fouling and scaling in MD remain a problem as they not only decrease the water flux, but also cause membrane pore wetting which results in contamination of the product water. In the FO-MD system, FO can function as a pre-treatment process to separate multivalent/divalent ions and organic matters as well as to reduce inorganic scaling and organic fouling in the MD process [171]. A PRO-MD hybrid system has also been studied from both the theoretical and experimental aspects. These studies concluded with

promising results [172-174], but acknowledged the robustness of PRO membrane and the issue of PRO fouling as crucial limitations waiting to be resolved [173, 174].

4.2 FO–RO

FO desalination coupled with RO appeared unfeasible initially. Shaffer et al. pointed out that a FO-RO hybrid system actually consumed more electric energy than a standalone RO process [18]. This is because the diluted DS has a higher osmotic pressure than the feed water going into the FO process. As such, this results in the need for more energy to drive a higher hydraulic pressure in the hybrid system so as to maintain the same water flux and recovery achieved in the standalone RO process [18]. In addition, the energy demand for seawater desalination by current state-of-the-art RO is already within a factor of 2 of the theoretical minimum energy for desalination. This means that present energy demand is only 25% higher than the practical minimum energy for desalination using an ideal RO stage [2]. The room for improvement for other desalination processes is actually very limited. However, the FO-RO hybrid process can still value-add in some ways. As shown in Fig. 9, FO working as a pre-treatment can serve two main purposes for RO: 1) the organic matters and scaling precursors in the feed water are separated by the FO process; and 2) FO works as a first barrier to partially remove trace contaminants and boron that are generally poorly separated by the RO process [18, 30]. Technically, the pre-treatment of seawater by FO is aimed at removing most of the dissolved constituents from the feed water so that the diluted DS going into the downstream RO process has minimal fouling/scaling propensity. This can potentially enhance the quality of the RO product water. By comparing the FO fouling and the fouling of conventional RO desalination, the latter is more severe due to the greater extent of irreversible fouling and lower flux recovery after membrane cleaning [36, 39]. Many prior studies have also reported higher trace contaminant rejection in FO than in RO [175-177], which can be attributed to the retarded

forward solute diffusion as a result of the reverse diffusion of the draw solutes. Thus, these results suggest that the hybrid FO-RO system can be more advantageous than a double-pass RO system (i.e., the water permeate from the first-stage RO undergoes further treatment in a second-stage RO). A modeling study also presented a lower specific energy consumption in an FO-RO seawater desalination process than a two-pass RO process [177].

4.3 FO–non-RO

Apart from the RO process, FO can be coupled with a UF (i.e., FO-UF) or NF (i.e., FO-NF) process for desalination. In these systems, the pressure-driven processes utilize membranes with a more porous rejection layer than that of the RO skin. Therefore, using DS with solutes of much larger size is necessary. For example, Tan and Ng evaluated the performance of a hybrid FO-NF system as an alternative to the conventional RO (standalone) desalination process [178]. By using Na_2SO_4 as the draw solute (rejection by NF was 97.9%), an FO process integrated with a double-pass NF process was able to provide product water that met the requirement of drinking water quality (single-pass NF was not sufficient due to the high DS concentration). A similar study by Zhao et al. [179] proposed a FO-NF system using a divalent draw solute (e.g. Na_2SO_4 or MgSO_4) for brackish water desalination. Results highlighted the competitive advantage of using a lower pressure NF operation as compared to the RO system (less than 10 bar for NF against 30 bar for RO) [179]. Besides, it was found that inorganic salts and micro-organic molecules such as EDTA sodium salts [180, 181], sodium lignin sulfonate (NaLS) [182] and poly (aspartic acid sodium salt) (PAspNa, Mw ~1313 g/mol) [183] were deemed as good candidates for draw solutes to be used in the FO-NF system. To stretch this concept and further lower the operating pressure, draw solutes of even larger sizes can be considered should a FO-UF hybrid system be adopted. This is exemplified by Ge and co-workers who employed a UF process to successfully regenerate the draw solute sodium

polyacrylate (PAA-Na, MW ~1200 g/mol) [184]. Essentially, by utilizing larger draw solutes, NF and UF downstream processes can be leveraged upon to regenerate the DS and recover the product water with the advantage of lower membrane resistances, in spite of the same DS osmotic pressure that **needs to** be overcome by the pressure-drive process (regardless of RO, NF and UF) [18]. In addition, a larger draw solute size normally leads to **a** higher rejection by FO as reverse solute diffusion can be impeded to a greater extent [183]. However, larger draw solutes tend to have smaller diffusion coefficients, which increase the ICP effect in the membrane support layer, resulting in a lower FO water flux [18]. Hence, selecting a draw solute with an appropriate size is essential to balance its back diffusion and mass transfer coefficient.

Beyond the membrane method for draw solute regeneration, FO can be also integrated with other processes, depending on the functionality of the draw solutes. Water soluble magnetic nanoparticles (MNPs) are attractive as a novel draw solute due to their superparamagnetic properties, which allow regeneration by applying a simple magnetic field system [23]. For instance, Chung and co-workers applied this FO-magnetic field system to attest its relevance to desalination. Despite a lower reverse solute diffusion as compared to that of inorganic solutes, only low to moderate FO water flux (up to only 18 LMH) was achieved even with DI water as FS [185, 186]. Another issue is the difficulty in recovering the MNPs, as it is highly dependent on the strength of magnetic field and the particle size. High-strength magnetic field can increase separation efficiency but has a tendency to cause irreversible agglomeration of MNPs, which decreases significantly the effectiveness of the DS in subsequent use. This problem persists even after intense ultrasonication [23]. Furthermore, the separation efficiency of the diluted DS depends on the particle size of the MNPs. There is a likelihood that small MNPs do not respond readily to the magnetic field, resulting in residual MNPs in the product water and a need to further process this water (e.g. using NF) so as to meet the drinking water

standard [187]. Other responsive draw solutes with easy regeneration feature include the hydrogel-based materials, which are able to extract and release water in response to environmental stimuli (e.g., temperature, pressure or light) [19, 50, 124]. Different from traditional draw solutes that dissolve or disperse in water to form the DS, hydrogels serve as semi-solid draw agents which transform from de-swollen to swollen mode during the FO process [23]. The key advantage of hydrogels is their intrinsically zero reverse solute diffusion. However, they also face many drawbacks such as difficulties in balancing between the water drawing ability of the hydrogels and their water recovery upon stimuli as well as the small contact area between the hydrogel surface and the membrane support layer, causing the FO water flux to be generally low (highest water flux demonstrated to date is ~20 LMH by emulsion polymerized microgel particles [188]). A more comprehensive review on the draw solutes can be found in [23].

4.4 FO–RO (osmotic dilution)

Contrary to the hybrid systems discussed so far, the FO-RO (osmotic dilution) hybrid system is an indirect desalination process. In this system, a FO osmotic dilution concept, which utilizes the salinity difference between two solutions to drive the water towards the concentrated DS without the recovery of the DS, is introduced to carry out a pre-dilution of the seawater or high salinity water before it enters the downstream RO process [18]. By coupling the FO osmotic dilution process in this way, seawater RO desalination with lower energy demand and/or water augmentation can be achieved. Moreover, no particular requirement on draw solutes or recovery methods is necessary using this system. Fig. 10 shows a two-stage FO dilution **process** integrated with a SWRO system for seawater desalination [189]. In the first FO unit, seawater/pretreated seawater is osmotically diluted by an impaired water stream. Although seawater as a DS does not cause fouling to the FO process, pre-treatment may still be needed

to reduce the fouling potential in RO system [18]. Prior to discharge, the concentrated SWRO brine is diluted by the concentrated impaired water from the first unit. As such, the FO units not only serve to osmotically dilute the seawater/SWRO brine, they also help to reduce the volume of impaired water and lessen the environmental impacts by lowering the electricity requirement of the process and avoiding discharging brines of lower salinity to the aquatic system [18, 190, 191]. However, the economic sustainability of such hybrid FO-RO remains questionable as additional investment cost for integrating the FO units is incurred, and there is no clear advantage as compared to performing the same task using two distinct and simpler established water treatment processes, i.e., water reuse and desalination [192]. Blandin et al. suggested that an improvement in the water permeation flux, typically above 30 LMH for classical water recoveries (e.g., impaired feed water against seawater DS), was a prerequisite to lower the investment cost to an economically acceptable level. They also indicated the need to have membranes with high water permeability ($A > 5$ LMH/bar) and low S value ($S < 100$ μm) to drive the processes [192]. In this regard, several aforementioned FO membranes seem promising, especially the AQP incorporated hollow fiber TFC membranes [70] and the flat-sheet TFC membrane with vertically oriented pores prepared via a bidirectional freezing process [71]. Greater research efforts to develop superior performance FO membranes are definitely a key direction for strengthening the economic viability of such hybrid FO-RO process. In fact, low membrane flux is one of the most critical issues for direct FO desalination processes (section 4.1 to 4.3) because seawater or concentrated solution is used as the feed water. Such a feed normally requires DS of a much higher osmotic pressure to produce a reasonably high water flux. Coupled with the need to subsequently process the DS for water recovery and regeneration of the draw solute, higher energy consumptions inevitably bring about a less cost-competitive direct FO desalination.

Fig. 10. Schematic of hybrid FO-SWRO process where FO serves osmotic dilution purpose (adapted from [189]).

4.5 PRO-RO

On the other hand, osmotic dilution can also be achieved using the PRO process; the advantage of which lies in its ability to produce energy (by harnessing osmotic power) concurrently [193]. Prior analysis on PRO input energy and cost suggested that the minimum power density needed from the PRO process **was** 5 W/m^2 in order for the PRO concept to be economically viable [194, 195]. Besides, due to the membrane orientation in the PRO operation (AL-DS to withstand the high hydraulic pressure at the DS side), membrane fouling/scaling in the support layer tends to be a major issue for PRO applications [26, 27]. One study [196], which examined the hybrid PRO-RO system for simultaneous treatment of seawater and wastewater, showed that inorganic scaling played a dominant role in the decline of the membrane flux. The use of anti-scalant was reported to be effective in maintaining a relatively stable water flux. Nevertheless, the effect of anti-scalant diminished when the scaling precursors in the feed water were present in a large amount [26]. In this case, pre-treatment of the feed water prior to entering the PRO unit is necessary. On the aspect of membranes for the PRO process, a substrate with a relatively small S value (but maintaining the capacity to withstand high

pressure) is useful in reducing the concentrative ICP effect of foulants and thereby lowering the fouling propensity [26, 197]. To gain a higher power density, the SWRO brine instead of seawater can be used as a DS to increase the osmotic pressure gradient across the membrane. However, the initial water flux is of particular concern because a high water flux tends to significantly increase the ICP and fouling potential, causing fast flux reduction during the PRO operation. Recently, a PRO study using real wastewater (wastewater RO brine) as feed and 1 M NaCl DS demonstrated a power density of 13.4 W/m² with the aid of an anti-scalant and periodical cleaning. This result was promising, despite ~40% reduction in flux as compared to the unfouled membrane [198]. We believe that future work should focus on reducing PRO membrane fouling and realizing long-term performance stability.

4.6 FO-MDC

In addition to the osmotic dilution hybrid systems coupling with RO, microbial desalination cell (MDC) is another option to obtain desalted water after the FO process [199, 200]. Similar to the FO-RO (osmotic dilution) system, FO in a FO-MDC system also plays a role of concentrating the feed water (treated organic solution from MDC) while diluting a highly concentrated DS (e.g., seawater). The diluted DS is further desalinated in a MDC process to achieve desalination purpose. It was reported that the FO-MDC system could reduce wastewater volume by 64% and enhance salt removal in saline water by two times, as compared to a standalone MDC [200]. Another similar hybrid system with alternative use of FO membrane has also been proposed for desalination application, such as osmotic membrane fuel cell – MDC (OsMFC-MDC) [201, 202]. In this approach, OsMFC aims to degrade organic compounds and dilute concentrated seawater, in addition to generating electricity. With the use of an FO membrane in between the anode and cathode, it was found the OsMFC produced more electricity than a conventional MDC under both batch and continuous operating

conditions. The higher performance and efficiency are attributed to the better proton transport with water flux through the FO membrane. After being diluted in the OsMFC cathode, the saline water is being treated in the MDC process to further remove ions. Although these systems show promise for desalination, they are still under development and only lab-scale studies have been performed to date.

5 Conclusions and perspectives

Initially, when FO first gained attention a decade ago, there was a lack of optimized membranes for the process. Today, as driven by a remarkable advancement in membrane fabrications, we have now better control over many membrane properties including the thickness, porosity, and pore structure of the membrane substrates and the water permeability, selectivity and physicochemical characteristics of rejection layers. In this review, we have discussed several recent advancements in FO membrane designs and how they have contributed to the FO performances. Moreover, there is now a stronger focus in finding more rationale and practical applications where the true potential of FO can be unlocked to value-add the desalination process. This can be observed from the various bench-scale hybrid systems developed thus far. Moving forward, we believe that the prospects in FO should build on existing research efforts and continue in the following directions.

First, apart from sustaining the efforts in optimizing FO membranes, leveraging on novel chemistries and emerging materials for next-generation FO desalination membranes is a key area of focus; the use of nanoparticles including zeolites, CNTs, graphene-based materials and AQPs **have** already produced promising results in engineering the FO water flux, selectivity, fouling-resistance and -release capacity as well as mechanical and chemical stability. We reckon that future efforts should gear **towards** large-scale membrane fabrications and pilot-

scale testings rather than a relentless effort in exploring new materials. Large-scale fabrications are important to demonstrate the feasibility of large-area, uniform and defect-free modifications which could otherwise lead to poor membrane performances. Therefore, to enhance the scalability of next-generation FO membranes, it is more practical to design membrane synthesis that stays aligned with existing techniques. For instance, the biomimetic hollow fiber membranes exhibited highly reproducible FO performances because a simple modified IP method was employed to immobilize the AQPs embedded vesicles uniformly in the polyamide layer [70, 72]. Pilot-scale testings, on the other hand, are necessary to anticipate any specific issues with large-scale membranes in realistic desalination implementations. These issues can range from long-term performance stability to long-run economic impact.

Second, the desire to further optimize the FO membrane can potentially see an acceleration in the uptake of the hollow fiber membrane configuration, especially with the recent success in fabricating TFC hollow fiber membranes. The hollow fiber configuration offers key advantages such as a self-supporting structure and high packing density in membrane modules. The construct of hollow fiber modules also facilitates the use of novel hydrodynamics as means to improve mass transfer and mitigate fouling. Besides, it can effectively support liquid flow on both sides of the membranes without the use of spacers, making hollow fibers highly relevant for osmotically driven membrane applications. More importantly, the fabric support-free hollow fiber fabrications allow greater control of the membrane structural parameters. Currently, many hollow fiber membranes possess S values lower than 200 μm (Table 2); such low S value can mitigate ICP when exploited as FO membrane substrates, hence resulting in better FO performances. However, the major challenge to a new generation of hollow fiber FO membranes is the technical difficulty in fabricating externally skinned TFC hollow fiber membranes. Until now, polyamide layers are mostly synthesized in the lumen side of the

membranes owing to a better control of the IP process. More work is therefore needed to develop uniform and defect-free polyamide layers on the shell side so as to capitalize on the advantages of hollow fiber membranes for FO desalination.

Third, FO still offers many compelling opportunities to achieve low carbon footprint desalination. Particularly, indirect desalination by using FO in combination with RO appears most promising. The idea stems from using FO as an energy-efficient approach to perform osmotic dilution of the seawater by low salinity impaired FS to give diluted DS as a feed stream for the subsequent downstream process. This is advantageous as the diluted DS contains lower salinity or more clean water can be obtained in the downstream RO process. Meanwhile, the volume of impaired FS can be reduced. On the **aspect** of FO direct desalination where the FS contains relatively high salinity, the energy consumption in the downstream processes (e.g., distillation, RO, etc.) remain **a** concern for its successful application. However, they may still find their niche applications such as extremely high salinity feed water and high water recovery (e.g., zero liquid discharge). PRO is another attractive option with the greatest selling point lying in its ability to extract power from concentrated saline water to partially compensate the energy requirement of desalination. However, the take-up rate of PRO is currently low due to the lack of high performance PRO **membranes**. The balance between low S value and high mechanical strength is critical. A possible solution is to adopt self-supporting hollow fiber configurations coupled with a mixed matrix approach to achieve the required mechanical strength. Moreover, the fouling control in PRO depends not only on membrane property, but also on the FS quality. A cost-effective way to minimize fouling is necessary for realizing PRO applications. In summary, whichever process that FO combines with in a hybrid system, the call for optimized membranes is an undisputable fact. Most of our conclusions on the hybrid FO systems **are** based on results using commercial flat-sheet CA and TFC membranes with

modest FO performances. Potentially, the development of a stable and high-performance prospective FO membrane may see a change in the competitive position of FO and cause a shift in the perspective on these FO hybrid systems.

Finally, the success of FO desalination relies closely on the availability of a better DS. To this end, simple dissolved inorganic and thermolytic salts remain the most widely-used and effective draw solutes given their ability to generate high osmotic pressures. Future direction in DS should therefore focus on low molecular weight draw solutes with capacity to mitigate ICP and induce high osmotic pressure in the DS. Most desirably, the DS should also be easily regenerable using an energy-efficient approach to recover the product water, chemically inert towards the membrane and possess low or no toxicity.

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Table 1. Summary of CTA/CA asymmetric FO membranes.

Membrane	thickness (μm)	Structure	<i>S</i> value (μm)	<i>A</i> (LMH/b ar)	<i>B</i> (LMH) (NaCl)	<i>J_v</i> (Lmh)	<i>J_s</i> (gmh)	<i>J_s/J_v</i> (g/L)	Orientation, area(cm^2)	DS	FS	Ref /year
HTI FO membrane	~50	Asymmetric single-skin with woven support	575	1.13	0.46	~10/~15.5	~6/~9	0.6/0.58	ALFS/ALDS	1.0M NaCl	DI	[49, 50]/2006
CA-NF hollow fiber	~100	Asymmetric single-skin	-	0.47	~0.05	5.0/7.3	-/0.53	-/0.073	ALFS/ALDS, 50	2.0M MgCl_2	DI	[43]/2010
CA flat sheet	35		54	0.17	0.07	10.3/17.3	0.8/1.2	0.08/0.07	ALFS/ALDS	2.0M MgCl_2	DI	[46]/2010
CA-NF flat sheet	~30	Double-skin	-	0.72	0.46	~17/~26	~3/~5	0.17/0.19	ALFS/ALDS, 16	2.0M MgCl_2	DI	[51]/2010
CTA-NF flat sheet	20-30	Asymmetric single-skin	-	-	-	9.0/12.8	6.2/6.8	0.69/0.53	ALFS/ALDS, 16	2.0M NaCl	DI	[52]/2012
CA flat sheet	17	Asymmetric single-skin	-	-	-	~10/~13	~3/~5.5	0.3/0.42	ALFS/ALDS	2.0M NaCl	DI	[53]/2011
CA- hollow fiber	118	Asymmetric single-skin	-	0.97	0.22	~8/~36	~1/~1	0.13/0.03	ALFS/ALDS, 80	2.0M MgCl_2	DI	[54]/2011
CA flat sheet	-	Asymmetric single-skin	-	0.51	0.40	12/21.6	5.1/10.6	0.42/0.49	ALFS/ALDS	2.0M NaCl	DI	[42]/2012
CA- hollow fiber	46.3	Double-skin	-	0.76	0.38	17.1	2.5	0.15	ALDS, 65	2.0M MgC_2	DI	[55]/2012
CA propionate hollow fiber	65	Dual-layer	-	0.80	0.22	~8.0/17.5	~1.3/2.5	0.16/0.14	ALFS/ALDS, 80	2.0M NaCl	DI	[47]/2013
CTA/CA flat sheet membrane	~50	Asymmetric single-skin with support	-	-	-	10.39	4.91	0.47	ALFS, 27	1.0M NaCl	DI	[44]/2013
CA flat sheet membrane	~80	Asymmetric single-skin	740-832	1.23-1.31	0.12-0.14	11.6-12.7	-	-	ALFS, 57.4	2.0M Glucose	0.1M NaCl	[45]/2016

Table 2. Summary of the performance of TFC FO membranes.

	Membrane	Substrate thickness (μm)	Substrate porosity (%)	Substrate pore size/PWP	Fabric mesh	S value (μm)	A (LMH/bar)	B (LMH)	J _v (LMH)	J _s /J _v (g/L)	Orientation, area (cm ²)	NaCl DS	FS	Ref /year
TFC/phase inversion substrate	TFC-PSf	95.9			PET	492±38	1.16	0.47	18.16		AL-FS, 20.02	1.5 M	DI	[56]/2010
	TFC-PSf		82	190 LMH/bar	no	670±170 ^a	1.78	0.34	13.5/20	0.41/0.29	ALFS/ALDS, 60	0.5 M	10 mM	[15]/2011
	PSf	92.3		39.6nm	PET	312±72	1.90±0.3	0.33±0.19	25.0±4.1		AL-FS, 20.02	1.0 M	DI	[61]/2011
	PSf/SPEK	~20	77.2	10.7nm/152.7 LMH/bar	no	107	0.75	0.068	35/50	0.2/0.18	ALFS/ALDS, 4	2.0 M	DI	[62]/2012
	sPPSU	~25	83.41	10.72nm/846.4 LMH/bar	no	652	3.23	1.05	30/32	0.18/0.14	ALFS/ALDS, 4	0.5 M	DI	[63]/2013
	PAN	160			no	389	0.91	0.57	9.25/13.88	0.11/0.11	ALFS/ALDS, 8.25	0.5 M	DI	[64]/2013
	CAP	~25	91.5	13.5nm/1456 LMH/bar	no	31.9	2.85	0.345	45/58	0.14/0.13	ALFS/ALDS, 4	0.5 M	DI	[48]/2013
	polyketone 70(25/75)		80.6	83nm	no	287	2.5		24.4/	0.14/	ALFS/ALDS, 42	0.6 M	DI	[65]/2015
	polyketone 80(35/65)		84.5	210nm	no	NA	NA	NA	29.3/41.5	0.13/0.12	ALFS/ALDS, 42	0.6 M	DI	
	SPES	65	79		no	245	2.9	0.18	17/22	0.38/0.32	ALFS/ALDS	0.5 M	DI	[66]/2016
	HF-PES	175	75	12.7nm/278 LMH/bar	-	595	2.22	0.2	14/32.2	0.13/0.11	ALFS/ALDS, 78.5	0.5 M	DI	[57]/2010
	HF-PES	205	82	9.6nm/278 LMH/bar	-	550	3.5	0.22	42.6	0.1	ALDS	0.5 M	DI	[14]/2011
	HF-PES	180	75	12.7nm/275 LMH/bar	-	520	3.07	0.12	16.7/49.4	0.072/0.079	ALFS/ALDS	0.5 M	DI	[67]/2011
	HF-PES _{water/NMP/P}	~130	80.9	17nm/1021 LMH/bar	-	219	1.18	0.135	34.5/65.1	0.29/0.19	ALFS/ALDS, 18.8	2.0 M	DI	[68]/2012
	EG HF-PES _{water}	~170	80	15nm/835 LMH/bar	-	261	1.83	0.348	22.5/25.6	0.12/0.13	ALFS/ALDS, 15.1	0.5 M	DI	[69]/2013

TFC/nanofiber substrate	HF-sPPSU	180		6.3nm/213 LMH/bar	-	163	1.99	0.04	22.5/49.4	0.24/0.22	ALFS/ALDS, 20	0.5 M	DI	
	HF-PEI	110	82.3	71nm/1167 LMH/bar		172	3.66	0.31	38.5		ALFS, 38	1.0 M	DI	[70]/2017
	PVDF/2D freezing	92	74	5-15 µm	no	100	4.7	0.66	46/62	0.12/0.09	ALFS/ALDS, 4.9	0.5 M	DI	[71]/2017
	PES nanofiber	50	83	1139 LMH/bar		80	1.7	1.1	37.8		ALFS	0.5 M	DI	[72]/2011
	PAN/CA nanofiber	10-15 w/o PET			PET	311	1.80	0.58	27.6/43	0.14/0.04	ALFS/ALDS	1.5 M.	DI	[73]/2013
	PAN nanofiber	10-15 w/o PET			PET	290	2.04	1.57	29/50	0.28/0.06	ALFS/ALDS	1.5 M.	DI	[74]/2013
	PVDF nanofiber	63.8	67	280nm/1267 LMH/bar		812	1.21	0.33	11.6/30.4	0.3/0.21	ALFS/ALDS	1.0 M	DI	
	PET nanofiber - PSf	~130			No	651	1.13	0.23	12.9		ALFS, 20.02	1.0 M	DI	[75]/2013
	PET/PVA nanofiber	57							47.2	0.2	ALDS	0.5 M	DI	[76]/2014
	PVA nanofiber	51 w/o PET	93			66	1.69	0.24	27.2		ALFS, 64.7	0.5 M	DI	[77]/2014
	Nylon 6,6 nanofiber	8-10 w/o PET		7632 LMH/bar	PET	190	1.66	0.54	21/27	0.24/0.44	ALFS/ALDS	1.0 M	DI	[78]/2014
	Hydrophilized PVDF nanofiber	15.2 w/o PET			PET	193	1.28	0.25	15/20	0.15/0.35	ALFS/ALDS	0.5 M	DI	[79]/2016
	PAN nanofiber	80			no	168	1.47	0.28	17.5	0.23	ALFS, 40	0.5 M	DI	[80]/2017
	PSf/Zelite	66.3	79.8	461 LMH/bar	no	340	3.3	1.3	21/42.5	0.52/0.47	ALFS/ALDS, 60	0.5 M	DI	[81]/2013
	PSf/TiO ₂	68	75	165 LMH/bar	no	420	1.96	0.38	17.1/31.2	0.17/0.21	ALFS/ALDS, 14.62	0.5 M	10 mM	[82]/2014
Nanoparticles in	PEI nanofiber/ CNT	96	81	2045 LMH/bar		310	2.5	0.6	26/48	0.11/0.06	ALFS/ALDS, 42	0.5 M	DI	[83]/2015
	PSf/GO	50	75	28 nm/ 700 LMH/bar	no	191	1.76	0.19	20/40	0.18/0.16	ALFS/ALDS	0.5 M	DI	[84]/2015

Nanoparticles in active layer	PSf /silica NP/ co-casting	97.2		36.4 nm/ 3134 LMH/bar	PET	169	1.64	0.29	31/61	0.24/0.26	ALFS/ALDS , 60	1.0 M	DI	[85]/2015
	PEI nanofiber/ silica NP	93.7	83	1280 nm	PET	174	2.99	0.41	40/70	0.12/0.1	ALFS/ALDS , 42	1.0 M	DI	[86]/2017
	Zeolite-PSf	70			no	782	2.57	1.57	13.5/25	0.43/0.39	ALFS/ALDS , 60	0.5 M	DI	[87]/2012
	SiO ₂ -PSf					376	3.4	2.8	22/36			2.0 M	10 mM	[88]/2014
	CNT-PSf		71		no	380	3.6	0.10	30/73	0.08/0.06	ALFS/ALDS , 30	2.0 M	10 mM	[89]/2013
	Halloysite nanotube						1.86	0.63	21/34	0.29/0.26	ALFS/ALDS , 20.02	2.0 M	10 mM	[90]/2015
	HNT-PSf						2.39	0.37	17.82	0.12	ALFS	0.5 M	10 mM	[91]/2015
	NH ₂ -TNT-PSf													
	AQP-HF-PES	~150			-		8	0.8	55.2	0.08	ALDS, 34.2	0.5 M	DI	[92]/2015
	GO-PAN		81.1	12.7 nm	no	85	2.04	0.83	22/25	0.15/0.16	ALFS/ALDS , 3.87	0.5 M	DI	[93]/2016
	AQP-HF-PEI	110	82.3	71nm/1167 LMH/bar	-	172	7.6	0.52	35/65	0.11/0.12	ALFS/ALDS , 38	0.5 M	DI	[70]/2017

Table 3. Summary of commonly used materials for FO substrates.

Materials	Advantages	Disadvantages	Ref.
PES/PSf	<ul style="list-style-type: none">• Good chemical resistance and mechanical stability	<ul style="list-style-type: none">• Relatively hydrophobic (prone to fouling)	[14, 57, 67]
CA/CTA	<ul style="list-style-type: none">• Very hydrophilic, resistant to fouling	<ul style="list-style-type: none">• Very narrow pH tolerance range (pH 3~8)	[48]
Polyetherimide (PEI)	<ul style="list-style-type: none">• Low cost• Good durability• Excellent solvent resistance	<ul style="list-style-type: none">• Poor chemical resistance• Reactive with amine-containing chemicals at elevated temperature	[70]
Polyacrylonitrile (PAN)	<ul style="list-style-type: none">• Hydrophilic	<ul style="list-style-type: none">• Nitrile group is sensitive to alkaline	[100]
Inorganic materials	<ul style="list-style-type: none">• Outstanding thermal and chemical stability (e.g., strong tolerance to extreme pHs, physical or chemical cleaning)	<ul style="list-style-type: none">• High cost• Complex preparation process	[104]

Table 4. Summary of FO membrane fabrication methods.

FO membrane fabrication methods	Advantages	Disadvantages
Asymmetric cellulose based membrane	- One-step formation	- Relatively low intrinsic permeability and selectivity - Low chemical and biological stability
TFC/phase inversion	- High water permeability and low salt permeability - Substrate with low structural parameter	- Subject to chlorine attack
TFC/nanofiber	- Porous substrate with low tortuosity; - Substrate with different layered properties can be easily tailored	- Large substrate surface pores may result in a rejection layer of relatively low selectivity and mechanical stability - Subject to chlorine attack
Layer-by-layer assembly	- High water permeability (NF-like skin)	- NF-like skin has low rejection to monovalent ions - Rejection layer may not function well under high ionic strength
Mixed matrix membranes	- NP embedded substrate has reduced S value - Increased water permeability if NPs are added in the rejection layer - Added function/improved properties	- Dispersion of NPs in dope solution is challenging - Unsure about the long-term stability and toxicity - Increased cost

Fig. 1. Number of citations, patents and publications on forward osmosis over the past ten years. The number of citations and publications are based on data from Web of Science, while data for the number patents are obtained from SciFinder.

Fig. 2. Water flux J_v (upper) and energy production W (lower) as a function of hydraulic pressure ΔP for PAO/FO/PRO/RO processes.

Fig. 3. Schematic of internal concentration polarization (ICP) in membrane cross-section. (a) AL-FS orientation; and (b) AL-DS orientation.

Fig. 4. Estimated FO water flux as a function of membrane structural parameter, showing the effect of A value (a-c) and B/A value (d). Modelling conditions are 10 mM NaCl FS and 0.5 M NaCl DS (a, blue symbols in d); (b) 0.5 M NaCl FS and 1.0 M NaCl DS (b, black symbols in d); and 0.5 M NaCl FS and 2.0 M NaCl DS (c, red symbols in d). Other conditions: AL-FS orientation (FO mode) is applied, $B/A = 15$ kPa for (a-c), $A = 3$ L/m²h for (d). Osmotic pressure is calculated using OLI software (1 atm, 25 °C).

Fig. 5. SEM micrographs of the cross-section of TFC-FO membranes. (a) PSf flat-sheet membrane including PET nonwoven fabric and (b) its magnified view of the dense, sponge-like morphology near the active layer [56]; (c) PES hollow fiber membrane from [57].

Fig. 6. PES nanofiber supported TFC FO membrane [72].

Fig. 7. Biomimetic hollow fiber FO membrane [70]. (a) cross-section of hollow fiber membrane; (b) aquaporin incorporated vesicles in rejection layer; (c) FO performance in AL-FS orientation; and (d) FO performance in AL-DS orientation.

Fig. 8. The NH_3/CO_2 forward osmosis desalination process [162].

Fig. 9. Schematic of FO pretreatment for conventional RO/NF or thermal (MED or MSF) desalination process [18]. Feedwater foulants and scalants are excluded from the draw solution, enabling the conventional desalination process to operate at high recovery for draw solution reconcentration.

Fig. 10. Schematic of hybrid FO-SWRO process where FO serves osmotic dilution purpose (adapted from [189]).