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Fabrication of Novel Janus Membrane by Nonsolvent Thermally Induced Phase Separation (NTIPS) for Enhanced Performance in Membrane Distillation

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Abstract

This study proposed to use the nonsolvent thermally induced phase separation (NTIPS) method to fabricate a novel Janus membrane for MD applications. The as-prepared dual-layer membrane consisted of a thin hydrophobic PVDF top-layer and a relatively thick hydrophilic PVDF-PVA sub-layer. By adopting a facile one-step co-casting technique and water soluble diluent ε-caprolactam (CPL), delamination-free dual-layer membrane was obtained. The SEM morphologies and FTIR crystalline analyses suggested the membrane formation mechanisms, where the hydrophobic top-layer was formed via NTIPS process, resulting in an ultra-thin dense skin with finger-like pores formed beneath; while the hydrophilic sub-layer was induced by TIPS, producing highly porous cellular structure with high degree pore interconnectivity. Combining the structural observation and MD performance results, suitable fabrication parameters were identified as a PVDF concentration of 15 wt% for the hydrophobic layer and coagulation temperature between 20-40 $^{\circ}$C. The total membrane thickness was optimized as 100-150 μm, given the thickness of hydrophobic layer kept within an optimal range of 30-60 μm to ensure minimal mass transfer resistance. The Janus membrane exhibited stable salt rejection above 99.5% over continuous MD runs and superior permeation flux up to 165.3 kg$\cdot$m$^{-2}\cdot$h^{-1} at 80 $^{\circ}$C, which was remarkably higher than reported MD membranes.

1. Introduction

Membrane distillation (MD), an emerging membrane technology for seawater desalination, wastewater treatment and resource recovery applications, is driven by a vapor pressure difference resulted from the temperature difference across a hydrophobic membrane [1, 2]. Compared to traditional separation processes such as thermal distillation or reverse osmosis, membrane distillation is potentially cost effective due to its ability to incorporate low-grade waste heat and/or renewable energy. However, MD has achieved limited commercialization mainly due to the challenges associated with inadequate membranes and process control. These include the trade-off relationship between low permeability and unavoidably high conductive heat loss, and liquid intrusion into membrane pores (wetting) which will completely terminate the operation. To avoid pore wetting, the membrane needs hydrophobic properties and high liquid entry pressure (LEP) to maintain vapor-filled pores. Amongst the commonly used polymer materials for making MD membranes, poly (vinylidene fluoride) (PVDF) is most versatile with its hydrophobic properties and could be used as either bulk membrane or substrate via various fabrication methods, such as conventional nonsolvent induced phase separation (NIPS) [3] and thermally induced phase separation (TIPS) [4], as well as the recently proposed nonsolvent-thermally induced phase separation (NTIPS, also referred to as combined NIPS and TIPS) [5, 6]. The requirements to suitable structural characteristics for MD applications have driven the developments of specialized membranes [7, 8].

In direct contact membrane distillation (DCMD), high mass transfer and low heat transfer are preferred to enhance the vapour permeation flux and maintain the driving force arising from the temperature difference [9]. Therefore, effective mass transport coefficients require relatively porous and thin membranes to achieve high permeability; while high thermal efficiency and physical robustness come from thick membranes. To address this issue, it is preferable to reduce the vapour transport distance via a possibly thin hydrophobic layer; while maintain the overall membrane thickness via a thick hydrophilic layer to reduce conductive heat loss and temperature polarization effect [8,10,11]. A membrane with hydrophobic/ hydrophilic dual-layer structure can be considered as a Janus membrane, whose key feature is the opposing properties of both surfaces such as hydrophobicity and hydrophilicity, or positive and negative charges [12].Since 1982 the concept of Janus

membrane was first introduced to MD by Cheng and Wiersma [13], there is a surge of interest on developing membranes with asymmetric wettability for MD [9,12], *i.e.,* hydrophobic/ hydrophilic dual-layers. Hydrophobicity is a surface property influenced by many factors such as surface chemistry, roughness and porosity. The characterization of hydrophobicity is commonly through measuring the contact angle of water (CAw), where 65° has been defined as the boundary between hydrophilicity (CAw < 65°) and hydrophobicity (CAw > 65°) based on the difference in the structure of interfacial water [14,15]. Khayet et al. [16] reported a series of Janus composite membranes using polyetherimide (PEI) substrate modified by fluorinated surface modifying macromolecules (SMM). These membranes were fabricated by conventional phase inversion method using solvent N,N- dimethylacetamide and non-solvent γ-butyrolactone (GBL) and exhibited the characteristics of hydrophobic/hydrophilic structure. The membranes were tested [8,17] and showed 2 times higher membrane flux in DCMD at 45 °C compared to commercial PTFE membranes. Based on the experimental work, Qtaishat et al. [11] proposed the guidelines for preparing high flux dual-layer MD membranes through mathematical modeling. Figoli et al. [18] developed a hydrophobically coated membrane through dip-coating method, consisting of a top thin hydrophobic layer casted on the commercial hydrophilic membrane. Bonyadi et al.[19] first applied a co-extrusion method to fabricate hydrophobic/hydrophilic composite hollow fibers, which obtained a flux as high as 55 $kg \cdot m^{-2} \cdot h^{-1}$ at 90 °C in DCMD. Edwie et al. [20] also developed hydrophobic/hydrophilic dual-layer hollow fiber using methanol as a non-solvent additive with the dry-jet wet phase inversion method, obtaining flux up to 83.4 $kg \cdot m^{-2} \cdot h^{-1}$ in DCMD. Su et al. [21] embedded graphite particles and multiwall carbon nanotubes (MWNT) into the dual-layer hollow fiber to improve its thermal conductivity for DCMD by the dry-jet wet-spinning approach, achieving a significant increase in vapor flux from 41.2 to 66.9 $kg \cdot m^{-2} \cdot h^{-1}$. Yet, a simpler fabrication method should be sought after to produce robust and high flux Janus membranes for MD applications.

Until now, how to effectively avoid delamination is a crucial question in the fabrication of high performance dual-layer membranes. In particular, the mechanism of the adhesion/delamination phenomenon between layers is not well-understood [22]. It was report that two of the main factors causing layer delamination include variation in phase inversion rates during phase inversion process and uneven shrinkage rates of

different layering materials during membrane formation [23]. Hence, various methods have been adopted to resolve this issue, such as choice of compatible/miscible polymer types for the two layers [24], co-extrusion (of hollow fibers) or co-coating techniques [25], choice of additive (non-solvent) or diluent [26]. However, the above-mentioned work was mainly focused on hydrophilic/hydrophilic dual-layer membranes. Only a handful of literature reported on the integration of Janus type of membranes, i.e., hydrophobic/hydrophilic [27]. For example, due to the hydrophobic nature of the PVDF material, its use as the bulk membrane material has posed challenges in hydrophilic modification via conventional coating or blending methods, most of which may lead to delamination or leaching of hydrophilic moieties over long-term operation [28]. On the other hand, some of the modification methods may alter the hydrophilicity of the bulk membranes [22]. Currently, hydrophilic modifications of PVDF membranes were mainly applied in ultrafiltration (UF) and microfiltration (MF) processes. For instance, Vanangamudi et al. [28] fabricated Janus UF membrane by adopting an unconventional two-step process of electrospinning and subsequent casting, which successfully overcame the integration problem between the PVDF and chitosan/nylon layers. It was only recently reported in MD literature [29] that robust and delamination-free dual-layer hollow fibers could be prepared by manipulating the composition of dope solution to homogenize the shrinkage rate, such as fabrication conditions and the addition of Al_2O_3 nanoparticles into the inner layer dope. However, there is still lack of studies and understanding on the integration mechanism of hydrophobic and hydrophilic layers and how it will affect MD performance.

This study adopts the NTIPS method for the first time to fabricate a novel Janus composite membrane for enhanced MD performance. The prepared composite membrane consists of a hydrophobic PVDF top-layer and a hydrophilic PVDF/PVA sublayer. Delamination-free integration between the two layers is obtained mainly due to the use of water soluble diluent ε-caprolactam (CPL) and a facile one-step co-casting technique during membrane fabrication. The formation mechanisms of the PVDF top-layer and PVDF/PVA sub-layer were studied via morphological and crystalline analyses. The membrane pore structure was optimized by manipulating various fabrication parameters including casting thickness, PVDF concentration and coagulation temperature. The as-prepared membranes were tested in direct contact MD (DCMD) mode to investigate the optimal characteristics of Janus MD membranes.

2. Experimental

2.1. Material and chemicals

The commercial polymer poly(vinylidene fluoride) (PVDF, Model: 1015) was supplied by Solvay Co. The polyvinyl alcohol (PVA, Model: 1788) obtained from Aladdin Industrial was used as the hydrophilic copolymer. The ε-Caprolactam (CPL) and sodium chloride (NaCl, 99.5%) purchased from Sinopharm Reagent Inc. China. The CPL was used as the diluent for the dope solution and NaCl was the model salt for synthetic seawater.

2.2. Preparation of PVDF/PVDF-PVA Janus membranes

2.2.1. Preparation of dope solutions

Dope solution for hydrophobic top-layer: A series of PVDF polymer dope solutions with various concentrations C_d ranging from 12 wt% to 20 wt% were prepared by dissolving PVDF into CPL at 150 °C under nitrogen protection for 1h, then the mixtures were stirred mechanically for 3h to form homogeneous solutions. The dope solutions were degassed at the same temperatures to avoid bubbles before casting.

Dope solution for hydrophilic sub-layer: based on a previous study on PVDF/PVA membranes [30], in this study a dope solution containing PVDF, PVA and CPL in a fixed weight ratio of 12.8: 3.2: 84 was prepared. The PVDF and PVA were dissolved into CPL at 150 °C under nitrogen protection and mechanical stirring for 2h to become homogeneous. The solution was then degassed before use.

2.2.2. Co-casting of composite membrane

By maintaining the predetermined temperature (150 °C), the two dope solutions were casted simultaneously via a co-casting technique [31] by an automated high-temperature casting machine with two separate casting knives/scrapers which can control the total thickness δ_d of the dual-layer PVDF/PVDF-PVA membrane (Model: FM-7, Ningbo Gaotong Membrane Apparatus Factory, China), as shown in Figure 1. There are four steps involved in the co-casting of the proposed Janus composite membrane: (1) adjust the gap height between the casting knives and glass plate (0 to 400 μm) by the two scrapers to control the respective thickness of each casting layer; (2) place the two dope solutions in the respective position of the machine; (3) switch on the machine to start scraper movement in the same pace to cast both dope solutions

178   simultaneously; (4) immerse the casted dual-layer membrane in the coagulant bath at a

179   predetermined temperature T_c (5 -60 ℃) to complete the casting step. Finally, the wet

180   membranes were immersed in deionized (DI) water at room temperature for 24 hours,

181   allowing complete solvent exchange to remove residual CPL. The obtained membranes

182   were then frozen in a refrigerator for 12 hours and dried in a freeze drier (SCIENTZ-

183   10N, Ningbo Scientz Biotechnology Co., Ltd) for an additional 12 hours before MD

184   testing. To ensure reproducibility of experimental data, the same co-casting conditions

185   were repeated three times to obtain each membrane.
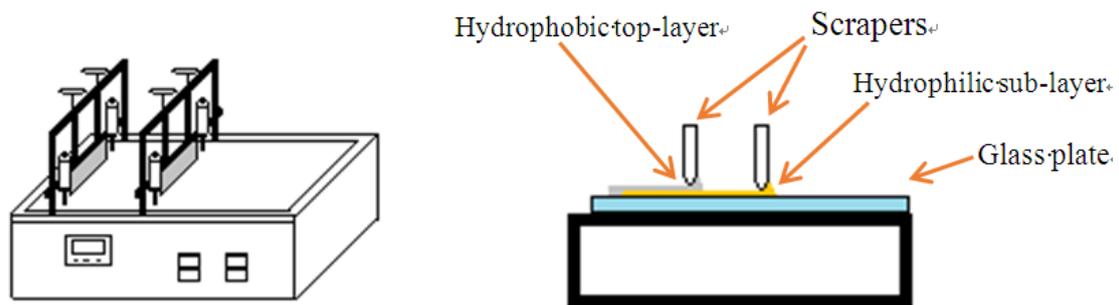
186

187   Figure 1. Schematic diagram for automatic casting machine and co-casting procedure

188

189   2.3. Preparation of single-layer PVDF membrane

190   The single-layer PVDF membrane was also prepared by NTIPS to compare against

191   the structure and performance of the Janus membrane. A series of PVDF polymer dope

192   solutions with various concentrations C_p ranging from 12 wt% to 20 wt% were prepared

193   by dissolving PVDF into CPL at 150 ℃ into 20 ℃ coagulation bath. The membrane

194   thickness δ_p of the single-layer PVDF membrane can be controlled through casting. The

195   details of single-layer PVDF membrane preparation can be found in the previous work

196   [5].

197

198   2.4. Membrane Characterization

199   The top/bottom surface and cross-sections of dual-layer flat sheet membrane were

200   observed using a scanning electron microscope (SEM, NOVA NANOSEM 450, FEI,

201   Hillsboro, USA). Prior to the scan, membrane samples were immersed in liquid

202   nitrogen, fractured and then coated with platinum using a coater (VACUUM DEVICE

203   MSP-1S). ATR-FTIR (Agilent Cary 660) was used to analyze the functional groups in

204   the top and bottom skin layers of the membrane. The penetration depth of the ATR-

205   FTIR is a few microns and hence can obtain the crystalline structural information of the

206 membrane [32].

207   The overall membrane porosity (ε) was calculated from the ratio of the pore

208 volume to the total volume of the membrane. The membrane pore volume was

209 determined by measuring the dry and wet weights of membrane using IPA as a wetting

210 agent [5, 33]. The measurement of liquid entry pressure of water (LEP_w) of the

211 membranes was conducted using a customized setup with synthetic seawater (i.e., 3.5

212 wt% NaCl solution, conductivity ~60 ms·cm^{-1}) as the testing liquid on the feed side and

213 DI water (conductivity <10 µs·cm^{-1}) as the reference at the permeate side to detect the

214 occurrence of pore wetting. During testing, the pressure of the NaCl solution side was

215 increased steadily using compressed N_2 gas, by 0.01 MPa increments in every 15 min.

216 The pressure at which a drastic initial increase on the conductivity of the permeate side

217 and a continuous conductivity increase was taken as the LEP. The conductivity of the

218 solution was monitored by a conductivity meter (DDSJ-308A, INESA Instrument). The

219 mean pore size (r_m) was determined and calculated based on the DI water filtration

220 velocity method [34]. The tensile properties (σ_m) of the membranes were measured via

221 tensile strength using a tensiometer (Model: 5542, Instron Corp., Boston, MA, USA).

222 Five membrane samples under same condition were tested to ensure reproducibility.

223 The contact angles of water (CA_w) of both surfaces of the as-prepared membranes were

224 measured by a Goniometer (model: Kruss DSA100, Hamburg, Germany). Five spots of

225 each membrane were tested and the average of measured values is reported.

226

227 2.5. Direct contact membrane distillation (DCMD) performance testing

228   To evaluate the performance of the as-prepared PVDF/PVDF-PVA Janus

229 membranes, DCMD experiments were conducted through a laboratory setup, as

230 illustrated in Figure 2. The effective membrane area was 10×10^{-4} m^2 and the

231 hydrophobic top-layer of the membrane was in contact with the hot feed solution

232 (synthetic seawater: 3.5 wt% NaCl); while the hydrophilic sub-layer faced towards the

233 permeate side with DI water. The feed solution was heated in the range of 50 ~ 80 °C

234 and recirculated with a flow rate of 110 L/h by a magnetic drive pump; while the

235 permeate was cooled to 17.5 °C with a flow rate of 110 L/h by a centrifugal pump. The

236 linear velocities of both feed and permeate sides were identical as 0.61 m/s and the

237 corresponding Reynolds number (Re) is approximately 4000. The feed and permeate

238 were recirculated through both sides of the modules in counter-current mode. The

239 continuous weight gain of the collected distillate was measured using a digital balance

(EK-2000i, A&D Co. Ltd.). The electrical conductivity of the permeate stream was monitored by the conductivity meter to calculate salt rejection. For each membrane, DCMD experiments were repeated three times to ensure reproducibility.
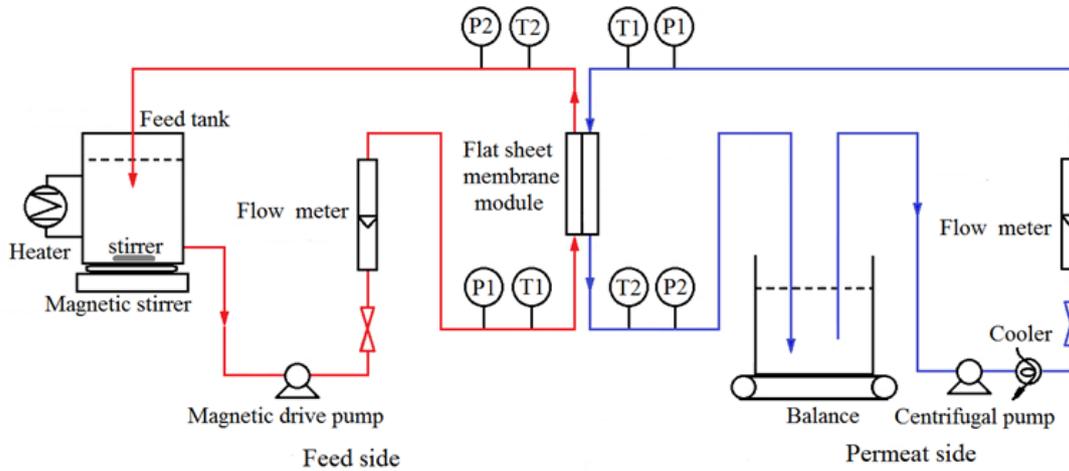
Figure 2 Schematic diagram for direct contact membrane distillation (DCMD) experimental setup

The MD permeation flux for each feed temperature was calculated using Eq. (1):

$$J = \frac{\Delta W}{A \cdot t} \tag{1}$$

where J is the permeation flux in $kg \cdot m^{-2} \cdot h^{-1}$, ΔW is the permeation weight automatically collected over a pre-determined period of time, in kg, t in hour, and A is the effective permeation area, in m^2.

The rejection R was calculated according to the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \tag{2}$$

where C_f and C_p are the concentration of the feed and permeate, respectively.

3. Results and Discussion

3.1 NTIPS membrane morphology and phase separation mechanism

Figure 3 illustrates the typical morphologies of the top/bottom surface and cross-section of the as-prepared Janus PVDF/PVDF-PVA membrane with 15wt% PVDF concentration in the hydrophobic layer. As shown in Figure 3(a)-(b), the surface

morphologies of the hydrophobic top-layer and hydrophilic sub-layer of the membrane are significantly different, i.e., the top surface is smooth and dense with no macropores (10,000×); while the bottom surface exhibits highly porous structure (10,000×). In Figure 3(c)-(f) the cross-section SEM images of membrane clearly show that the asymmetric structure consists of two layers with distinct interface between the hydrophobic top-layer and hydrophilic sub-layer (Figure 3(c) (800×)). In the enlarged images of Figure 3(d) (2500×) &(e) (10,000×), the hydrophobic top-layer (thickness of 40±10 μm) exhibits an ultra-thin dense skin (0.5 μm) with finger-like macrovoids and bicontinuous network formed beneath, which is similar to the asymmetric structure of the NTIPS membranes prepared in our previous work [5]. On the contrary, the PVDF-PVA hydrophilic sub-layer shows a relatively homogenous and highly porous cellular-like pore structure with large pore size in the range of 1-3 μm, as shown in Figure 3(f) (10,000×). The pores are highly connected forming a bicontinuous network. Overall, although a distinct interface is observed between the hydrophobic and hydrophilic layers, no delamination occurs due to the high degree of interconnectivity of pores in the transitional region, as shown in Figure 3(e). This can be mainly explained by the minimal interfacial resistance between the two layers due to use of same diluent CPL. Also, the two layers (PVDF and PVDF-PVA (8:2)) show strong adhesiveness due to the use of same bulk polymer.

The morphological results can be explained by the combined NIPS and TIPS mechanisms governing the formation of such dual-layer structure of the PVDF/PVDF-PVA membrane. In the hydrophobic layer the asymmetric structure, i.e., ultra-thin dense skin and finger-like pores, is mainly formed through the NIPS mechanism, and the bicontinuous network beneath the skin is created via TIPS. This is because that the dense skin is formed due to the rapid quenching into the coagulation bath; while the finger-like microvoids underneath is generated attributed to the relatively rapid exchange of water (non-solvent) and CPL diluent, mainly following the NIPS mechanism. On the other hand, the bicontinuous network pore of the hydrophobic layer is a typical structure formed by TIPS. Hence, the characteristic structure and morphology of the hydrophobic top-layer are consistent with the NTIPS membranes

developed previously [5]. The homogeneous cellular-like pore structure of the hydrophilic layer can be attributed to the TIPS formation mechanism. This is due to the generally much faster heat transfer rate (dominant in TIPS) in the dope leading to the phase separation and crystallization in the polymer-rich phase, and eventually the formation of the cellular-like pores, which is similar to the typical bulk structure of hydrophilically modified PVDF/PVA membrane fabricated via TIPS process in the previous work [30].
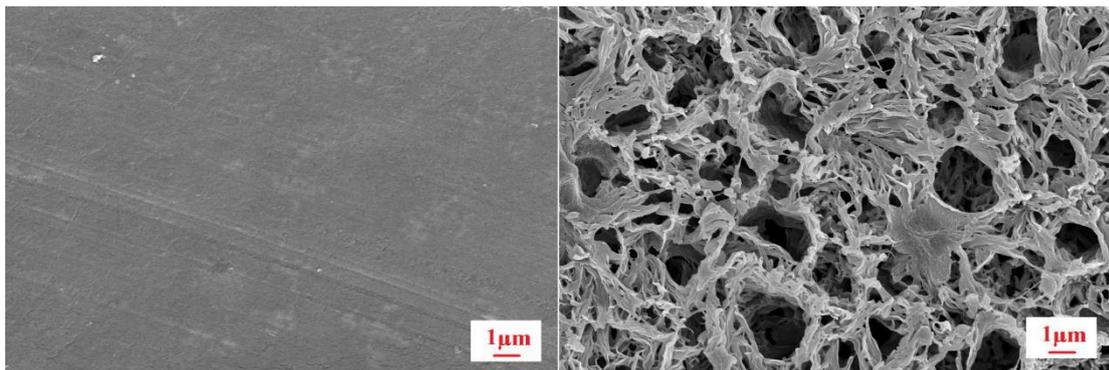
(a) Top surface (10,000×)   (b) Bottom surface (10,000×)
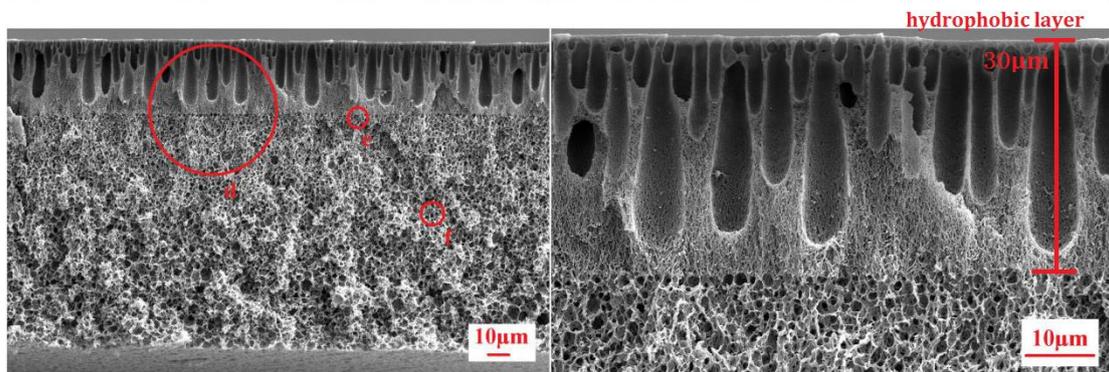
(c) Whole cross-section (800×)   (d) Cross section of hydrophobic layer (2500×)
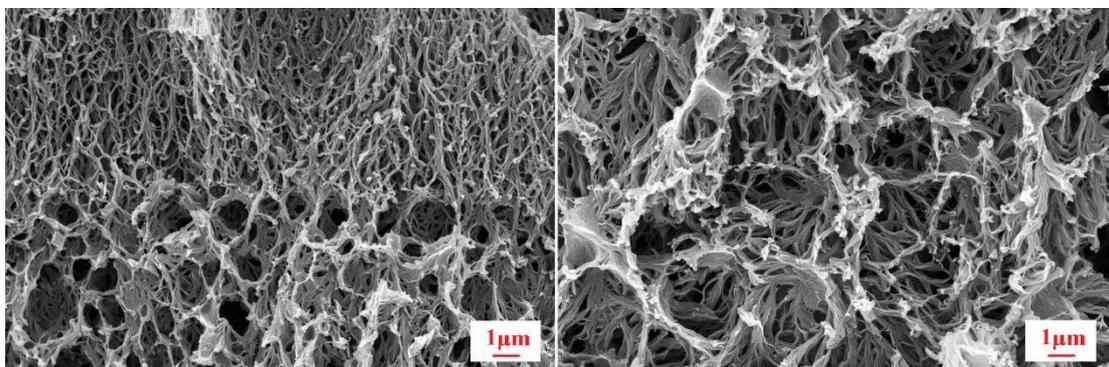
(e) Cross section of interface (10,000×)   (f) Cross section of hydrophilic layer (10,000×)

Figure 3 Surface and cross-section morphology of hydrophobic/hydrophilic dual-layer PVDF/PVDF-PVA membranes (membrane fabrication parameters: C_d=15 wt%, δ_d

305 $=150$ μm, $T_c =20$ ℃.)

306

307   To further investigate the phase separation mechanism during the formation of the

308 PVDF/PVDF-PVA Janus membrane, the PVDF crystalline structural information in the

309 top/bottom skin layers was obtained via ATR-FTIR. The resulting spectrum are shown

310 in Figure 4, in which the left figures shows the full spectra of the hydrophilic and

311 hydrophobic layers in comparison to the reference peaks of pure single-layer PVDF

312 membrane prepared by NTIPS. The scan of the pure PVA powder was to ensure that its

313 characteristic peaks would not interfere with that of the PVDF crystalline. While the

314 right figure in Figure 4 gives the enlarged window between wave length of 1300 and

315 700 cm^{-1}.

316   Generally, the IR absorption bands at approximately 1211, 1149, 1069, 975, 854,

317 794, and 763 cm^{-1} represent the characteristic spectrum of an α phase PVDF crystal

318 [35]; whereas the absorption bands at 1275 and 840 cm^{-1} represent the characteristic

319 spectrum of β phase PVDF[36, 37]. Based on the previous study [5] and discussion for

320 Figure 3, in the NTIPS process the $α$ phase crystallization of PVDF is induced by TIPS

321 and the $β$ phase is induced by NIPS. It is observed in Figure 4 that similar to the pure

322 single-layer PVDF membrane, the hydrophobic top-layer of the composite membrane

323 exhibit IR absorption bands at 840cm^{-1} (CH_2 rocking) and 1275 cm^{-1} (CF_2 group

324 symmetrical stretching vibration), as well as 763 cm^{-1} (CF_2 bending and skeletal

325 bending) and 1069 cm^{-1} (deformation vibration of C-F) [38-40], indicating the

326 occurrence of both $α$ and $β$ phase crystallization induced by the NTIPS mechanism.

327 While the hydrophilic sub-layer of the composite membrane only shows peaks at 763

328 cm^{-1} and 1069 cm^{-1}, indicating the occurrence of $α$ phase crystallization induced by

329 TIPS.
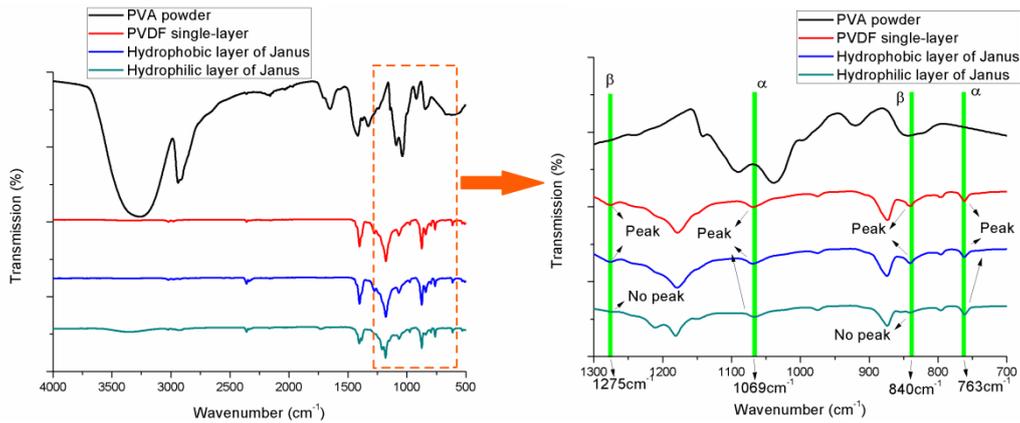
Figure 4. FTIR spectra of the different type of membranes, including pure PVA powder, pure single-layer PVDF membrane (top-surface), hydrophobic top-layer and hydrophilic sub-layer of dual-layer PVDF/PVDF-PVA membrane

3.2 Effect of fabrication parameters on membrane structure

3.2.1 PVDF concentration of hydrophobic top-layer

The effect of dope composition on the membrane structure was investigated via varying the PVDF concentration of the hydrophobic layer in the range of 12-20 wt%; while maintaining constant dope composition of the hydrophilic layer and constant overall thickness of 150 μm. Figure 5 displays the cross sectional morphologies of the Janus membrane with 12, 15 and 20 wt% PVDF in the hydrophobic layer. Similar to the typical morphology shown in Figure 3, all the membranes exhibit an ultra-thin dense skin with finger-like macrovoids and bicontinuous network formed underneath. However, the finger-like pores in the hydrophobic layer becomes shorter and the interface between the hydrophobic and hydrophilic layers is less distinct with the increase of PVDF concentration. This is mainly attributed to the increased dope solution viscosity, which reduced the CPL/water exchange rate and suppressed the instantaneous phase separation beneath the top surface regions. Also, 12 wt% PVDF dope was too dilute and may easily lead to defected pore structure; while the 20 wt% PVDF dope was too thick to cast smoothly in the co-casting process.
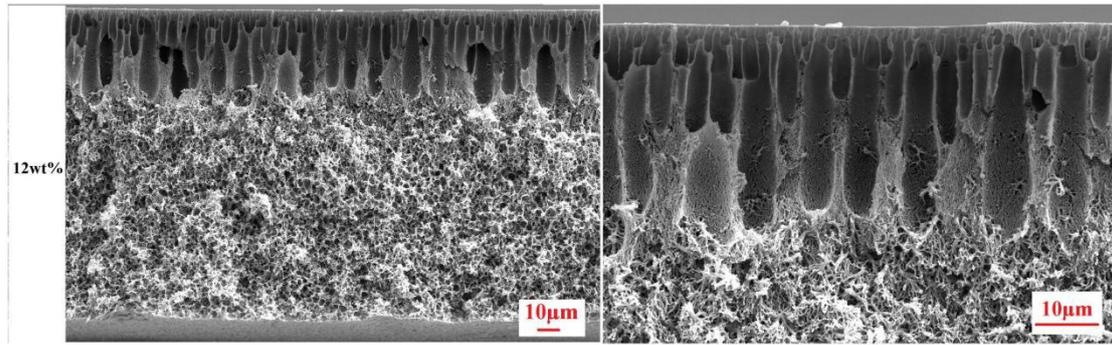
351

352   Whole cross-section (800×)   Cross section of hydrophobic layer (2000×)
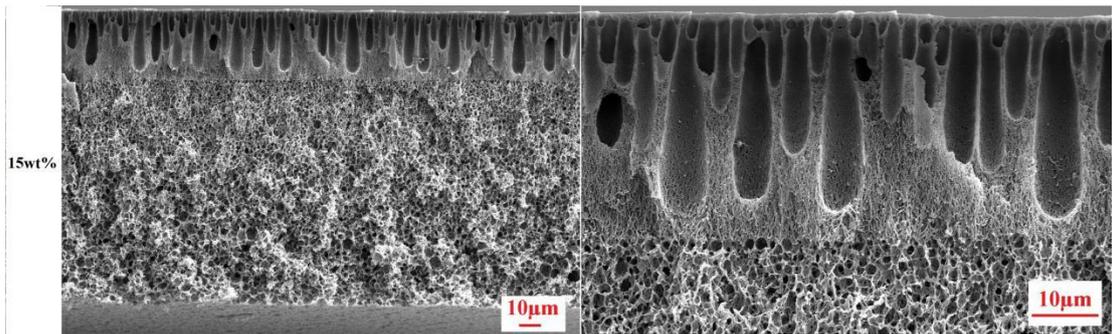
353

354   Whole cross-section (800×)   Cross section of hydrophobic layer (2500×)
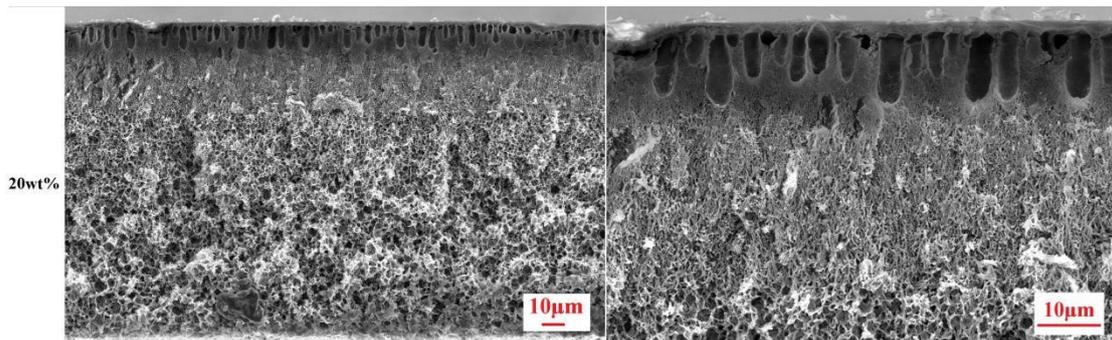
355

356   Whole cross-section (800×)   Cross section of hydrophobic layer (2500×)

357   Figure 5. Effect of different PVDF concentration of the hydrophobic top-layer on the

358   cross section structures of hydrophobic/ hydrophilic dual-layer PVDF/PVDF-PVA flat

359   sheet membrane (membrane fabrication parameters: δ_d =150 μm, T_c = 20 ℃)

360

361   3.2.2 Coagulation temperature

362   The effect of the temperature of water coagulant bath on membrane structure was

363   investigated. Figure 6 (a)-(d) shows that SEM image of the top and bottom surfaces,

364   and cross section morphologies of the membranes at coagulation temperatures of 5 ℃,

365   20 ℃, 40 ℃ and 50 ℃, respectively. The thickness of the hydrophobic top-layer is

366   marked in the SEM images of Figure 6. It is clear that the partial thickness of the top

367   layer K is within the range of 40±10 μm at coagulation temperature below 50 °C. The

368   respective layer thickness of the Janus membrane was mainly controlled by adjusting

14

the gap height during the membrane co-casting process. However, the resultant membrane structure could be influenced by other factors such as the coagulation temperature, as shown in Figure 6. The top surface becomes rougher as temperature increases. The cross section images show that the finger-like pores grow longer and the pore interconnectivity weakens as the coagulation temperature increases. This is because with the coagulant temperature increases from 5 to 50 $^\circ$C, the temperature difference between the casted film (150 $^\circ$C) and the coagulation bath decreased from 145 $^\circ$C to 100 $^\circ$C, causing the TIPS mechanism to weaken while NIPS is enhanced. In the hydrophobic top-layer, the higher coagulation temperature accelerates the diffusion rate between solvent and non-solvent in the nascent membrane [41], resulting in the formation of longer finger-like pores. Meanwhile, in the hydrophilic sub-layer the degree of pore interconnectivity has decreased due to the weakened TIPS mechanism. Overall, the change of coagulation temperature has an important role in the membrane formation mechanisms. Thus, it is important to choose a suitable range of coagulation temperature in preparing the NTIPS Janus membranes.

Top surface (10,000×)   Bottom surface (10,000×)   Cross-section (800×)

(a) 5 $^\circ$C

Top surface (10,000×)   Bottom surface (10,000×)   Cross-section (800×)

(b) 20 $^\circ$C

Top surface (10,000×)   Bottom surface (10,000×)   Cross-section (900×)

(c) 40 °C

Top surface (10,000×)   Bottom surface (10,000×)   Cross-section (900×)

(d) 50 °C

Figure 6. SEM image of the morphology of dual-layer PVDF/PVDF-PVA membranes obtained at various coagulation temperature (membrane fabrication parameters: C_d=15 wt%, δ_d=150 μm)

3.3 Evaluation of DCMD Performance

3.3.1 Effect of fabrication parameters on MD performance

With the PVDF concentration of the hydrophobic layer varied between 12 to 20 wt% and respective total membrane thickness fixed at δ_d=150 μm (un-optimized) and δ_p=110 μm, the DCMD performance of the dual-layer Janus and single-layer PVDF membranes was compared in Figure 7. It was found that membrane fluxes of the dual-layer membranes are much higher than that of the single-layer ones, reaching up to 149.5 kg·m^{-2}·h^{-1} at feed temperature of T_f=80 °C and permeate temperature of T_p=17.5 °C. This is because that the partial thickness of the hydrophobic layer of the dual-layer membrane is only about 40±10 μm (Figure 5), even though the total thickness of the dual-layer membrane is larger than that of the single-layer one, i.e., δ_d of 150 μm vs. δ_p of 110 μm. For the single-layer membrane, the flux decreases drastically from 124 to 80 kg·m^{-2}·h^{-1} as the PVDF concentration increases from 12 to 20 wt%. This is corresponding to the decreasing porosity of the membrane from 88 % to 82.4 %. On the contrary, for the dual-layer membrane, the flux remains relatively constant regardless of PVDF concentration at such total membrane thickness of 150 μm. This is

also related to the very thin hydrophobic layer, which is consistent with the optimal thickness range (30-60 μm) of the hydrophobic layer reported in MD literature [42]. Thus the significant advantage of the dual-layer membrane for MD application is easily justified. However, taking into account the influence of viscosity of the dope solution on membrane fabrication as discussed in Figure 5, an intermediate concentration of 15 wt% PVDF was chosen as a suitable operating condition. It is noted that the salt rejection for all membranes compared in Figure 7 remained above 99.5 %.
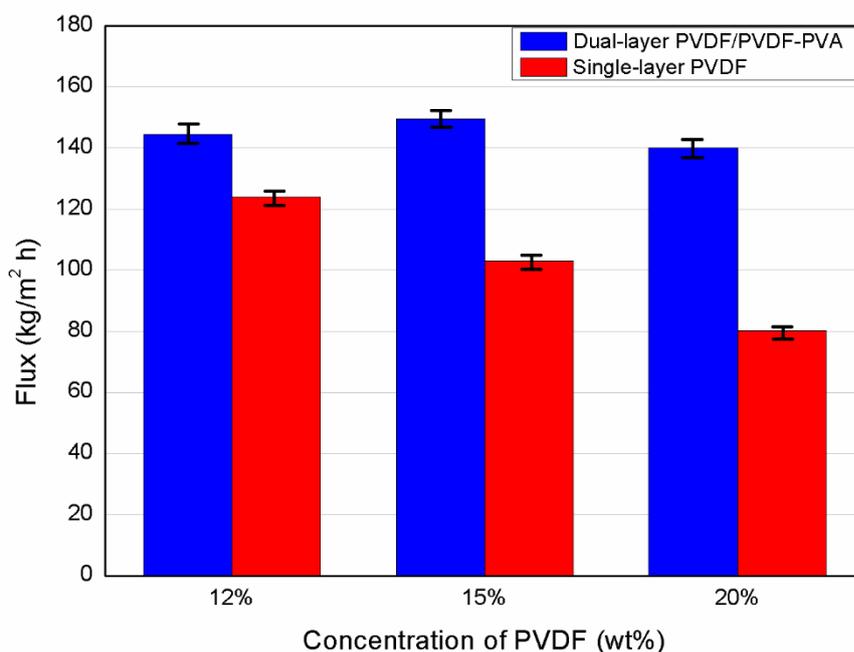
Figure 7. Comparison of DCMD performance of Janus and single-layer NTIPS membranes at varying PVDF concentration (DCMD parameters: T_f =80 °C, T_p = 17.5 °C; fabrication parameters: C_d=12-20 wt%, C_p=12-20 wt%, T_c = 20 °C, δ_d=150 μm, δ_p=110 μm)

As indicated by the morphological analysis in Figure 6, the variation of coagulation temperature T_c has a significant impact on the membrane structure. Hence, the effect of coagulation temperature of the as-prepared Janus membranes was investigated in terms of DCMD performance. The results are shown in Figure 8, in which an initial increase of membrane flux from 132 to 154 kg·m^{-2}·h^{-1} as T_c increases from 5 to 40 °C and subsequently a dramatic decrease, i.e., from 154 to 89 kg·m^{-2}·h^{-1} as T_c increases from 40 to 50 °C, is observed. Meanwhile, the salt rejection maintained above 99.7% for the membranes prepared under coagulation temperatures from 5 to 40

^{o}C; while slightly dropped to 99.3% at 50 ^{o}C. As explained in Section 3.2.2, the change in membrane formation mechanism from TIPS dominant to NIPS dominant as the temperature difference between the casted membrane and coagulant bath became smaller, causing the membrane to have much longer finger-like pores and denser structure in overall. Hence, the membrane permeability has been greatly sacrificed. Therefore, a suitable range of coagulation temperature of 20 ^{o}C to 40 ^{o}C was chosen in this work for the fabrication of Janus MD membrane, which is consistent to the morphological observations in Figure 6. In addition, considering the minor difference in membrane flux between membranes prepared at coagulation temperature of 20 and 40 °C, 20 °C was chosen as the preferred fabrication condition as it is closer to room temperature and thus requires minimal thermal input.
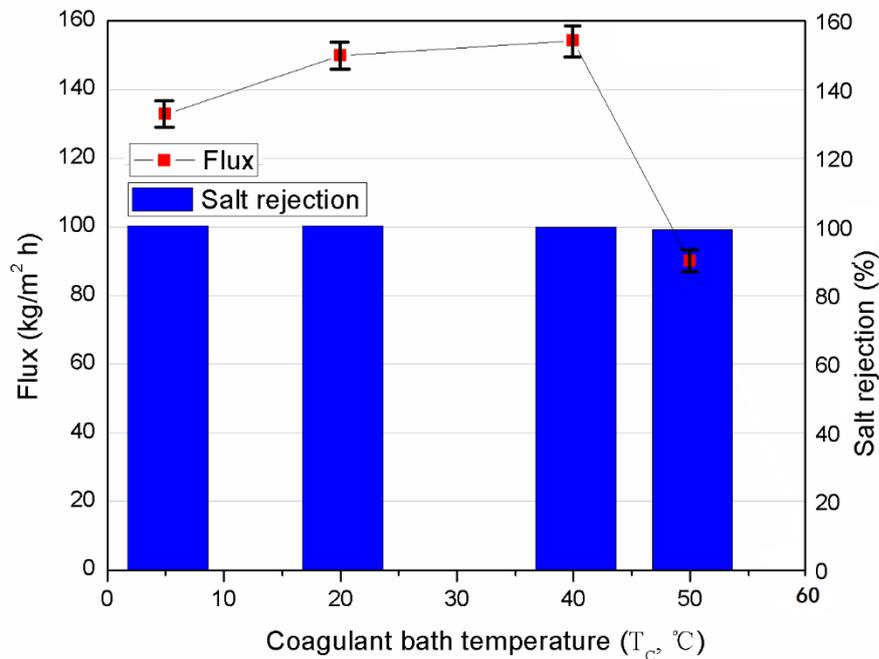
Figure 8. Effect of coagulation temperature on DCMD membrane flux of PVDF/ PVDF-PVA Janus membrane (DCMD parameters: T_f =80 °C, T_p =17.5 °C; fabrication parameters: T_c=5 °C to 50 °C, C_d = 15 wt%, δ_d = 150 μm)

The optimization of total membrane thickness of the Janus membrane was conducted. With the partial thickness of the hydrophobic top-layer kept within 40±10 μm, the total membrane thickness δ_d was tuned between 100 to 200 μm during membrane fabrication at a chosen coagulation temperature of 20 °C. The effect of membrane thickness on the DCMD performance was investigated and the results are

458   shown in Figure 9. It was found that the permeation flux is up to 165.3 kg·m^{-2}·h^{-1} at δ_d

459   of 120 μm. However, it decreases gradually to 70 kg·m^{-2}·h^{-1} as the δ_d continues to

460   increase to 200 μm. The decreasing trend of flux can be explained by the vapor transport

461   mechanism and temperature profiles through the hydrophobic/hydrophilic dual layer

462   structure proposed by M. Qtaishat et al [11], the hydrophobic layer is vapor-filled space

463   while the hydrophilic layer is filled with water in DCMD. The water vapor transports

464   through the hydrophobic layer of the membrane and condenses at the

465   hydrophobic/hydrophilic interface. The temperature gradient across the hydrophobic

466   layer serves as the driving force in MD. With the thickness of the hydrophobic layer

467   kept constant, the increasing thickness of hydrophilic layer (thus the total membrane

468   thickness) will lead to an increase of the temperature at the membrane vapor-liquid

469   interface due to the temperature polarization effect in the hydrophilic layer across the

470   bulk permeate. Therefore, it will result in a decrease of the MD driving force leading to

471   decrease in membrane flux. However, the trend of membrane flux vs total thickness

472   does not follow a linear relationship based on Figure 9. Hence, the ideal membrane

473   thickness of the Janus membrane can be chosen within the range of 100 to 150 μm to

474   simultaneously obtain high flux while maintain a reasonable total membrane thickness

475   to ensure mechanical robustness, given the partial thickness of the hydrophobic layer is

476   controlled within the range of 30-60 μm to minimize the mass transfer resistance.

477   Overall the Janus membrane still exhibited high flux of 110 kg·m^{-2}·h^{-1} even at a large

478   δ_d of 180 μm (Figure 9), which is higher than compared to its counterpart single-layer

479   PVDF membrane with a smaller δ_p of 110 μm, *i.e.,* 103.2 kg·m^{-2}·h^{-1} (Figure 7). It is

480   noted that the salt rejection for all membranes discussed in Figure 9 maintained above

481   99.5 %.
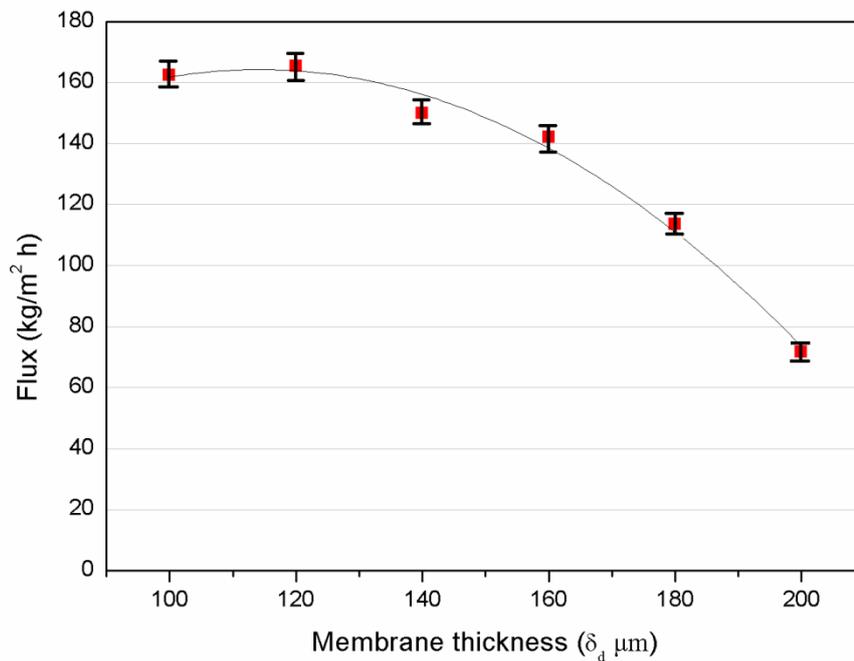
Figure 9. Optimization of total membrane thickness δ_d of dual-layer PVDF/ PVDF-PVA membrane in terms of DCMD performance (DCMD parameters: T_f =80 $^{\circ}$C, T_p =17.5 $^{\circ}$C; fabrication parameters: δ_d =100-200 μm, C_d=15 wt%, T_c = 20 $^{\circ}$C)

To prove the stability of the membrane in MD, a selected PVDF/PVDF-PVA Janus membrane was evaluated in a 22-hour continuous run at a feed temperature of 70 $^{\circ}$C. The membrane flux and salt rejection are presented in Figure 10. Overall, a stable flux of 118kg·m^{-2}·h^{-1} and high salt rejection above 99.5% were obtained during the continuous testing, which is a preliminary proof of the membrane stability. It is noted that there is a slight fluctuation (within a reasonable error range of 5%) of the membrane flux in the initial stage of operation, which is mainly due to the gradual stabilization of the operating conditions in DCMD such as the feed and permeate temperatures, as well as the hydrodynamics, i.e., flowrates / velocities. When the key parameters of the system were established, the flux remained relatively stable during the rest of the MD operation as shown in Figure 10.
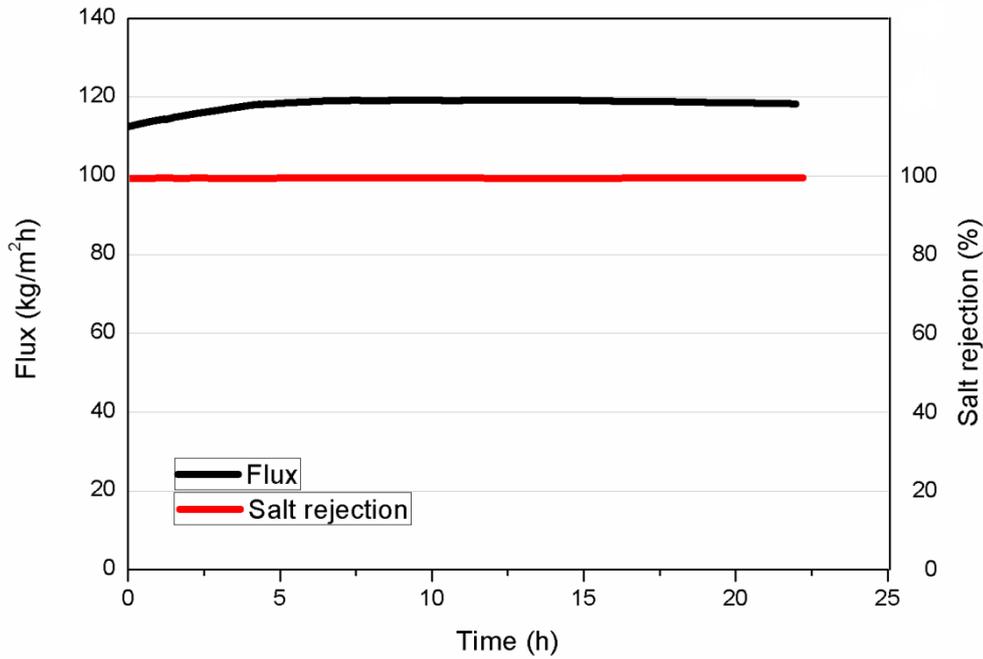
Figure 10. Continuous DCMD testing of selected Janus PVDF/PVDF-PVA membrane

(DCMD parameters: T_f=70 °C, T_p=17.5 °C; fabrication parameters: C_d=15 wt%,

δ_d=130 μm, T_c = 20 °C)

3.3.2 Characterization of optimal Janus membrane

With 15wt% PVDF concentration chosen as the dope composition of the hydrophobic layer, coagulation temperature of 20 °C and total thickness of 120 μm, the optimal Janus membrane was fabricated by NTIPS method with the one-step co-casting technique.

Table 1 shows the basic characteristics of the optimal Janus membrane in comparison to the single-layer PVDF membrane also prepared by NTIPS, including the porosity (ε), contact angle of water (θ), LEP of water (LEP_w), mean pore size (r_m), total membrane thickness (δ_d for Janus and δ_p for single-layer), partial thickness of the hydrophobic layer K and tensile strength (σ_m). With an overall membrane thickness (δ_d) of 120 μm, the as-prepared Janus membrane has a high porosity of 85%. The contact angle of water (CA_w) of the hydrophilic PVDF-PVA bottom-layer of the Janus membrane rapidly decreased to 0°, indicating complete penetration of water into the hydrophilic layer of the membrane; while that of the hydrophobic PVDF top-layer was

21

517 measured stably at 74±4°, which was similar to the CA_w of the single-layer counterpart

518 as shown in Table 1. Thus due to the opposing wettability of the top and bottom surfaces,

519 the membrane can then be classified as Janus-type membrane. The relatively low CA_w

520 of the hydrophobic layer is due to the smooth surface morphology as shown in Figure

521 3. Similar CA_w values of the PVDF membranes designed for MD can be found in the

522 literature exhibiting stable performance [43]. To measure the anti-wetting properties of

523 the membrane in MD, LEP_w is an important parameter and was measured as high as

524 3.6 bar for the Janus membranes prepared in this study, which is higher than most

525 reported data in the literature [44,45] indicating its superior ability to resist pore wetting

526 and sustain stable long-term performance. The single-layer counterpart exhibits similar

527 porosity and LEP_w but larger pore size of 34 nm and relatively weaker mechanical

528 strength. Although the overall thickness (δ_d) of the Janus membrane is slightly larger,

529 the proportion of the hydrophobic layer is very small, i.e., 30 μm, which is much thinner

530 than that of the single-layer membrane (110 μm). Therefore, Janus type membrane has

531 great potential in MD applications, as it could achieve very thin hydrophobic layer and

532 thus high permeability; while the addition of thick hydrophilic layer can maintain the

533 mechanical strength and potentially reduce the conductive heat loss through the

534 membrane [8,10,11].

535

536 Table 1 Comparison of characterization data of the optimal PVDF/PVDF-PVA dual-

537 layer and single-layer PVDF membranes (C_d =15 wt%, T_c=20 °C)

Membrane type	Porosity (ε, %)	Contact angle of water, (θ,°)		LEP_w (bar)	Mean pore size (r_m, nm)	Total thickness (δ_d, δ_p, μm)	K* (μm)	Tensile strength (σ_m, MPa)
		Top layer	Bottom layer					
Dual-layer	85±1	74±4	0	3.6±0.1	24±2	120±10	30	1.3±0.1
Single-layer	86± 1	73±2	/	3.5±0.1	34±3	110±5	110	0.9±0.1

538 * K is partial thickness of the hydrophobic layer.

539

540 3.3.3 Comparison with other MD membranes

A comparison of the as-prepared Janus membrane with other MD flat sheet membranes reported in the literature is presented in Table 2 and Figure 11. It was found that under similar operating conditions, the dual-layer PVDF/PVDF-PVA membrane exhibited superior permeability at optimized thickness of 120 µm, e.g., the flux reached 165.3 kg·m^{-2}·h^{-1} with 3.5 wt% NaCl solution and respective feed and permeate temperatures of 80 and 17.5 °C. It was plotted in Figure 11 to compare the membrane fluxes listed in Table 2 at varying feed temperature from 50 to 80 °C. It is encouraging that the as-prepared Janus membrane showed the highest flux, which was at least 60 % higher than its single-layer counterpart PVDF membrane also prepared in this work as well as other membranes listed. The superior fluxes (>120 kg·m^{-2}.h^{-1} at Tf=70 °C and Tp=17.5 °C, and >160 kg·m^{-2}.h^{-1} at Tf=80 °C and Tp=17.5 °C) obtained with the PVDF-PVDF-PVA dual layer membrane is mainly due to the unique asymmetric hydrophobic/hydrophilic structure that results in low mass transfer resistance through the thin hydrophobic layer. Also, the mechanism of water vapor permeating through the hydrophobic layer is considered as Knudsen flow, where the water vapor molecule - pore wall collision plays a dominant role in the mass transfer. This is because of the small mean pore size of 24 nm, which is below the mean free path of water vapor (λ_w >139.9 nm) [8, 46]. This is consistent with the literature that reported the theoretical DCMD flux considering the Knudsen mechanism was generally higher than the flux obtained based on the combined Knudsen/molecular diffusion mechanism, where the membrane pore size is larger than the mean free path of water vapor [46].

Table 2 Comparison of DCMD permeation flux (J) between as prepared PVDF/PVDF-PVA Janus membrane and other MD membranes reported in literature

Membrane code/material	J (kg·m^{-2}.h^{-1})*	Operating parameters	Ref.
PVDF HSV 900 modified	83.4	3.5wt.% NaCl; Tf=80 °C; Tp=17 °C.	[20]
GO-NBA incorporated membrane	61.9	3.5wt.% NaCl; Tf=80 °C; Tp=16 °C.	[47]
PTFE(Carbon	69	3.4wt.% NaCl; Tf=70 °C; Tp=20 °C	[48]

nanotube)

Membrane	Flux	Conditions	Ref.
PFPE- polyamide (commercial)	22	3.5wt.% NaCl; Tf=60 °C; Tp=14 °C.	[18]
PFPE- polyamide (commercial)	16.6	3.5wt.% NaCl; Tf=50 °C; Tp=14 °C.	[18]
PH-TiO$_2$	38.7	3.5wt.% NaCl; Tf=60 °C; Tp=20 °C	[49]
PVDF/nonwoven fabric composite membrane	12.5	3.5wt.% NaCl; Tf=50 °C; Tp=20 °C	[43]
Single-layer PVDF	103.2	3.5wt.% NaCl; Tf=80 °C; Tp=17.5 °C	This work**
Dual-layer PVDF/PVDF-PVA	55.2	3.5wt.% NaCl; Tf=50 °C; Tp=17.5 °C.	
	85.1	3.5wt.% NaCl; Tf=60 °C; Tp=17.5 °C.	This
	122.2	3.5wt.% NaCl; Tf=70 °C; Tp=17.5 °C.	work***
	165.3	3.5wt.% NaCl; Tf=80 °C; Tp=17.5 °C.	

564   * Permeate flux data report in the literature with unit conversion if necessary.

565   ** Parameters for single layer membrane: C_p=15wt%，δ_p=110μm，T_c = 20 °C

566   *** Parameters for dual layer membrane: C_d=15wt%，δ_d=120μm，T_c = 20 °C
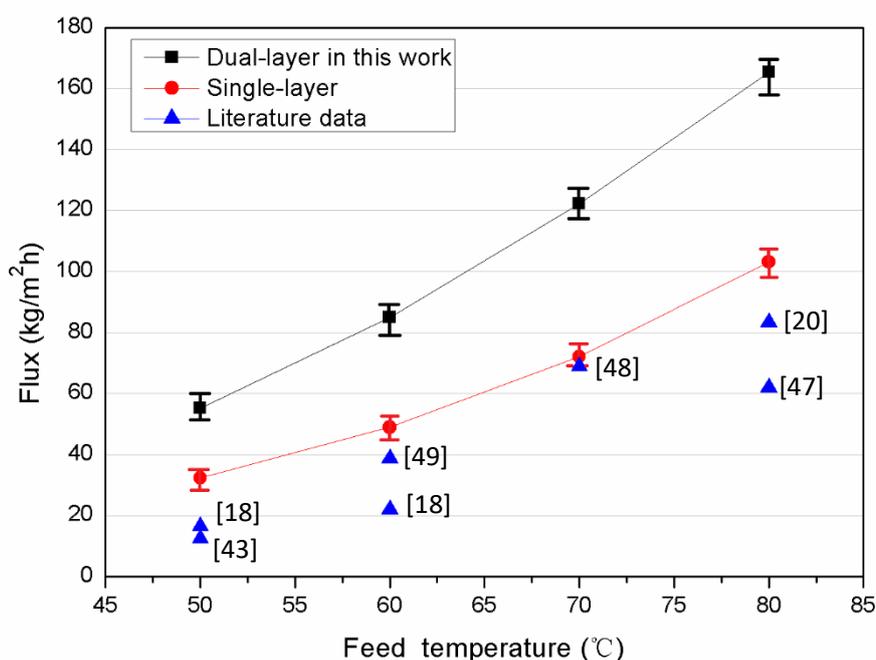
Figure 11. Comparison of DCMD flux as a function of feed temperature of as-prepared PVDF-PVDF/PVA Janus, single-layer PVDF and MD membranes reported in literature

4. **Conclusions**

In membrane distillation (MD), the trade-off relationship between the low membrane permeability and high conductive heat loss has been recognized as the main hurdle for achieving high performance. This study aimed to address this issue by fabricating a novel PVDF/PVDF-PVA Janus type membrane via a nonsolvent thermally induced phase separation (NTIPS) method.

Firstly, delamination-free dual-layer membrane was successfully obtained using a one-step co-casting technique and ε-caprolactam (CPL) as water soluble diluent. Combining the SEM morphological analysis and ATR-FTIR crystalline examination, the formation mechanism of the membrane was identified: the hydrophobic PVDF top-layer was induced mainly by the combined NTIPS process; while the hydrophilic PVDF-PVA sub-layer was formed via TIPS. The ultra-thin dense skin of the top-layer led to high LEP_w that ensured high salt rejection and long-term stability of the membrane; while the hydrophilic layer exhibited high degree of pore interconnectivity

25

586 and highly porous structure.

587   Secondly, the membrane structure was influenced by both the PVDF concentration

588 and coagulation temperature. The increase of PVDF concentration of the hydrophobic

589 top-layer led to the formation of shorter finger-like pores and lower membrane porosity.

590 While the increase of coagulation temperature affected both surface and pore structure

591 of the Janus membrane due to the weakened TIPS but enhanced NIPS mechanism.

592   Thirdly, the Janus membrane demonstrated superior permeability via the DCMD

593 performance testing. The flux remained relatively constant regardless of the PVDF

594 concentration of the hydrophobic layer at fixed total membrane thickness, as compared

595 to its single-layer PVDF counterpart that showed drastic reduction in flux. This was

596 mainly due to the low mass transfer resistance induced by the thin hydrophobic layer

597 (40±10 μm) and high porosity. Also, optimal coagulation temperature and overall

598 membrane thickness were also identified through MD testing. Based on the comparison

599 with literature data, the Janus membrane showed the highest flux thus far at various

600 temperature conditions.

601   Overall, the proposed membrane exhibited the desirable robustness and strong

602 potential in achieving high performance in MD attributing to its unique asymmetric

603 pore structure and Janus properties.

604

605

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